On the gasification of biomass in a steam-oxygen blown CFB gasifier with the focus on gas quality upgrading: technology background, experiments and mathematical modeling

Proefschrift

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door

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Daarom bad ik, en mij werd verstand gegeven; ik riep aan, en de geest der Wijsheid kwam tot mij. Ik hield meer van haar dan van scepters en tronen; en rijkdom acht ik niets in vergelijking met haar. Ik vergeleek geen edele steen bij haar, want al het goud ten aanzien van haar is als een weinig zand, en zilver is als slijk tegen haar te rekenen. Boven gezondheid en schone gestalte heb ik haar bemind, en heb haar verkoren om te hebben tot een licht; want de glans uit haar wordt niet uitgeblust. En allerlei goed kwam tot mij met haar, en ontelbare rijkdom door haar handen.

Boek der Wijsheid, 7:7-11

Therefore I prayed, and prudence was given me; I pleaded and the spirit of Wisdom came to me. I preferred her to scepter and throne, and deemed riches nothing in comparison with her, nor did I liken any priceless gem to her; because all gold, in view of her, is a little sand, and before her, silver is to be accounted mire. Beyond health and comeliness I loved her, and I chose to have her rather than the light, because the splendor of her never yields to sleep. Yet all good things together came to me in her company, and countless riches at her hands.

Book of Wisdom, 7:7-11

Dla mojego pradziadka Stanisława – człowieka technicznie utalentowanego

For my great-grandfather Stanisław – a technically-minded person

Summary

On the gasification of biomass in a steam-oxygen blown CFB gasifier with the focus on gas quality upgrading: technology background, experiments and mathematical modeling

Since the dawn of the Industrial Revolution the demand for energy is increasing continuously. Although the Earth is still able to meet this demand, the stored reserves of fossil fuels accumulated over past millions of years are shrinking very fast. The threat of shortages in fuel supply for future generations, accompanied by the side effects of massive utilization of fossil fuels (global warming, air pollution, increasing costs of energy) luckily lead to an increasing awareness of the need to search for other, renewable and sustainable, sources of energy. Considering the fact that biomass harvested in a sustainable way and at competitive prices could cover 50–55% of the world's primary energy demand, its use as an energy source gained significant interest over the last few decades. However, due to its physical appearance and properties raw biomass cannot be used directly in the same conversion plants as the fossil fuels. Solid and relatively dry biomass (moisture content lower than 30–40% by mass) can be converted via mechanical extraction or thermochemical conversion routes, while wet biomass can be processed biologically or in a supercritial water gasification process. The product of the conversion step can be heat or combined heat and power (CHP) applications - these solutions are mainly suitable for decentralized, stationary applications. By converting the biomass into a stable (liquid) secondary energy carrier also mobile applications like heavy transport can benefit from this renewable energy source. This can be realized via thermochemical conversion (gasification) and synthesis route, with the final products being, e.g., methanol, DME or Fischer-Tropsch diesel. Depending on the technology applied, gasification produces either syngas (a mixture of CO, H₂, CO₂ possibly containing also nitrogen and water vapor) or product gas - syngas with methane and other light and (poly-)aromatic hydrocarbons (tar), nitrogen and sulfur containing impurities and particles. With the intention to produce secondary transportation fuels from biomass on the industrial scale the fluidized bed technology shows the best balance between the advantages and disadvantages. This technology is very flexible regarding the fuel input in terms of fuel quality and kind, it is very well scalable between a few and hundreds of megawatts thermal throughput, but it generates product gas, which subsequently needs upgrading for any advanced synthesis application.

In this work the process of steam-oxygen blown gasification of biomass in a circulating fluidized bed (CFB) was investigated experimentally using a 100 kW thermal fuel input test rig. The investigations were focused on tar conversion and the gas quality optimization in terms of syngas components tailored to the production of synthetic biomass-based transportation fuels. Four different kinds of biomass representing clean and demolition wood, an energy crop (miscanthus) and an agricultural residue (straw) were tested in combination with three different bed materials: quartz sand, magnesite and olivine. Fuels containing high amounts of alkali metals in the ash were expected to cause bed agglomeration when gasified on a silica-based bed material; this was successfully counteracted by using kaolin as in-bed additive. The use of magnesite not only showed excellent resistance to agglomeration but also a catalytic effect on the water-gas shift and tar conversion reactions was proven. The measured concentration of poly-aromatic and phenolic tar compounds was reduced below 2 g m⁻³ on raw gas basis, while the H₂:CO ratio increased from ca. 0.6 to above 2.0 compared to the tests where sand was used as bed material. Although also measurable catalytic activity on tar conversion was expected from olivine, this effect was not observed disregarding whether fresh or thermally pre-treated olivine was used. This lack of activity was attributed to the different origin of the mineral compared to ones studied in the literature.

For better understanding of the gasification process and in order to reduce the amount of necessary experiments, a biomass gasifier model was developed based on an existing CFB coal combustor model. This model divides the riser of a CFB into a core and annulus structure in the radial direction and a finite number of cells in the axial direction. The model is able to calculate the drying and pyrolysis times and gas composition, it takes into account the hydrodynamics and reaction kinetics (of both homogeneous and heterogeneous reactions) and the heat exchanging equipment. The biomass pyrolysis model is a newly implemented feature, just as the gasification reactions kinetics including the conversion of tar. The model equations are solved in mass and energy balance iteration loops. First the working of the model was assessed by simulating an experimental case using the kinetic parameters derived from the literature. To match the simulation results with the experimental values the pre-exponential factors of the Arrhenius equations were adjusted. This investigation revealed that the char combustion, the water-gas shift reaction and the wet methane reforming reaction appear to proceed in the gasifier at (significantly) lower rates than indicated in the literature. A sensitivity analysis study of three model parameters was carried out on the tuned model: particle size distribution of the fuel, stoichiometric oxygen-to-fuel ratio (lambda) and biomass char density. All parameters gave expected response in the simulation results upon their perturbation, but the increase of lambda with more than 5% relatively to the base case, and the increase of char density lead to convergence problems. The convergence problems also occurred during the simulation of some other experimental cases. The comparison of measured axial gas composition profile with the calculated one showed the best agreement for oxygen and methane (maximum absolute deviation of 4.1%-point); the main discrepancy was observed for the nitrogen and it was attributed to the way of introducing the nitrogen purge flows, that in reality are distributed over the length of the riser but are taken as a fraction of primary fluidization flow in the model. Finally, the performance of the developed model was compared to the commercial modeling software CSFMB[®] / CeSFaMBTM. Despite a much more extensive user interface, a large number of simulation options and an already long development process, also this simulator suffers from the sensitivity to certain process variables, which leads to instable solution of the calculations. However, the lack of access to the source code makes the investigation of such problems very complicated if not impossible – this being a very important argument to further develop an own model of the gasifier.

Overall it was concluded that the steam-oxygen blown circulating fluidized bed biomass gasifier is a powerful technology able to produce hydrogen-rich product gas from solid biomass. For future research it is recommended to test the observed positive influence of magnesite on the gas composition together with catalytic hot gas filtration in order to produce syngas in a more integrated gas cleaning and upgrading process. Also further development of the mathematical model is recommended in order to be able to simulate the effects of the changes made to the process and operational parameters, including the presence of catalytic bed materials, on the reactor performance.

Marcin Siedlecki, September 2011

Samenvatting

Over het vergassen van biomassa in een met stoom en zuurstof bedreven circulerend wervelbed gericht op het verbeteren van de kwaliteit van het gas: achtergrond van de technologie, experimenteel onderzoek en mathematische modellering

Sinds het aanbreken van de Industriële Revolutie is de vraag naar energie gestaag gestegen. Hoewel de Aarde nog steeds in staat is om aan deze vraag te voldoen, zijn de reserves fossiele brandstoffen, die gedurende afgelopen miljoenen jaren zijn opgebouwd, in een rap tempo aan het afnemen. De dreiging van een tekort aan brandstoffen voor de toekomstige generaties, vergezeld met de bijverschijnselen van grootschalig gebruik van fossiele brandstoffen (opwarming van de Aarde, luchtverontreiniging, toename van brandstofprijzen) hebben gelukkig geleid tot een toenemende bewustwording van de noodzaak om naar andere, vernieuwbare en duurzame bronnen van energie te zoeken. Gezien het feit dat biomassa die op een duurzame manier en tegen concurrerende prijs beschikbaar is wel 50 tot 55% van de wereldwijde vraag naar primaire energie zou kunnen dekken, is de interesse in haar aanwending als een energiebron in de afgelopen decennia sterk toegenomen. Echter door haar fysische vorm en eigenschappen kan de biomassa niet zonder meer in de installaties die voor de fossiele brandstoffen zijn ontworpen worden gebruikt. Vaste en relatief droge biomassa (met een vochtgehalte lager dan 30-40% op massabasis) kan via mechanische extractie (persen) of thermochemische weg worden omgezet, terwijl natte biomassa biologisch of in een superkritisch watervergassingsproces verwerkt kan worden. Het omzettingsproces kan zijn afgestemd op de productie van warmte, of op de warmte-kracht koppeling (WKK); deze systemen zijn voornamelijk geschikt voor decentrale, stationaire toepassingen. Door biomassa in een stabiele (vloeibare) secundaire energiedrager om te zetten zouden ook mobiele toepassingen, zoals wegtransport, van deze vernieuwbare energiebron kunnen profiteren. Dit is mogelijk door het toepassen van een thermochemische omzettingsstap (vergassing) gevolgd door een synthesestap, met als eindproduct bijv. methanol, DME of Fischer-Tropsch diesel. Afhankelijk van de toegepaste technologie levert vergassing of syngas (een mengsel van koolmonoxide, waterstof, kooldioxide, mogelijk met stikstof en waterdamp), of productgas – syngas met methaan en andere lichte en (poly-)aromatische koolwaterstoffen (teer), stikstof- en zwavelhoudende verontreinigingen, alsmede vaste deeltjes. Indien de productie van transportbrandstoffen uit biomassa op industriële schaal beoogd wordt, dan biedt de wervelbedtechnologie de beste balans tussen de voor- en nadelen van de omzettingsmethode. Deze technologie is geschikt voor diverse brandstofstromen met betrekking tot de soort en de kwaliteit, het is goed schaalbaar tussen enkele en honderden megawatt thermisch doorzet vermogen, maar het genereert productgas, welke naderhand opgewaardeerd moet worden tot syngas voordat het voor enige geavanceerde synthesetoepassing kan worden gebruikt.

In dit werk is experimenteel onderzoek uitgevoerd naar de vergassing van biomassa in een met stoom en zuurstof bedreven circulerend wervelbed, middels een testopstelling van 100 kW thermisch brandstoftoevoerequivalent. Het onderzoek was toegespitst op de omzetting van teer en de optimalisatie van productgassamenstelling richting de syngascomponenten voor best mogelijke aansluiting op het productieproces van synthetische transportbrandstoffen uit biomassa. Vier soorten biomassa, namelijk schoon en afvalhout, een energiegewas (miscanthus), en agrarisch afval (stro), zijn getest in combinatie met drie verschillende soorten bedmateriaal: kwartszand, magnesiet en olivijnzand. Brandstoffen met een grote hoeveelheid alkalimetalen in de as vormen een risico voor het ontstaan van bedagglomeratie indien vergast met gebruikmaking van een silicarijk bedmateriaal; dit werd met succes tegengegaan door het gebruik van kaolin als in-situ additief. Magnesiet vertoonde niet alleen een uitstekende agglomeratiebestendigheid, maar ook een katalytische invloed op de water-gas shift reactie en teeromzetting is aangetoond. De gemeten concentratie van polvaromatische en fenolachtige teercomponenten was lager dan 2 g m⁻³ op ruwe gas basis, terwijl de H₂:CO ratio gestegen is van ongeveer 0.6 tot meer dan 2.0 ten opzichte van de tests waar kwartszand als bed materiaal gebruikt werd. Hoewel er op basis van de literatuurstudie ook van olivijnzand een meetbaar katalytisch effect werd verwacht, werd dit niet waargenomen ongeacht of er onbehandeld of thermisch voorbehandeld olivijnzand gebruikt werd. Dit gebrek aan activiteit werd toegewezen aan een andere herkomst van het mineraal dan van die, welke in de literatuur werd bestudeerd.

Om het vergassingsproces beter te kunnen begrijpen en om de hoeveelheid experimenten in de toekomst te kunnen reduceren, werd er een mathematisch model van de biomassavergasser opgezet, uitgaande van een bestaand model van een CFB bestemd voor de verbranding van steenkool. Dat model deelt de riser van de CFB in de radiale richting op in een *core-annulus* structuur, en in de axiale richting in een eindig aantal cellen. Het model beschouwt de hydrodynamica van het bed, het droog- en ontvluchtigingsproces van de brand-

stofdeelties, de reactiekinetiek zowel van homogene als heterogene reacties, en de apparatuur voor warmteoverdracht. Het biomassapyrolysemodel is een nieuwe uitbreiding, zo ook de kinetiek van vergassingsreacties inclusief het omzetten van teer. Het stelsel vergelijkingen wordt middels een iteratieproces opgelost in massa- en energiebalans lussen. Eerst werd de werking van het model beoordeeld door een experiment te modelleren met gebruikmaking van kinetische parameters uit de literatuur. Om simulatieresultaten in overeenstemming te krijgen met de meetgegevens werden de pre-exponentiële factoren in de Arrheniusvergelijkingen aangepast. Hierdoor werd duidelijk dat de houtskoolverbrandingsreactie, de water-gas shift reactie en natte methaanreforming in de vergasser (aanzienlijk) langzamer verlopen dan de afzonderlijke reacties, zoals ze in de literatuur werden bestudeerd. Een gevoeligheidsanalyse van drie modelparameters, namelijk deeltjesgrootteverdeling van de brandstof, stoichiometrische zuurstof-brandstofverhouding (lambda) en de dichtheid van houtskool, werd met het afgeregelde model uitgevoerd. Alle parameters gaven een verwachte respons aan in de simulatieresultaten bij hun verandering, maar een toename van lambda met meer dan 5% ten opzichte van het uitgangspunt en ook de toename van de dichtheid van het houtskool leidden tot convergentieproblemen. De vergelijking tussen de gemeten en berekende axiale gassamenstellingsprofiel liet de beste overeenkomst zien voor zuurstof en methaan (maximale absolute afwijking van 4.1%-punt); de grootste afwijking werd waargenomen voor stikstof en toegeschreven aan de kleine reinigingsstromen die in het model in het geheel als een fractie van de ingaande gasstroom worden beschouwd. Tot slot zijn de simulatieresultaten van het ontwikkelde model vergeleken met de resultaten verkregen met een commercieel programma CSFMB[®] / CeSFaMBTM. Ondanks een veel uitgebreidere gebruikersinterface, een groot aantal simulatieopties en een jarenlang ontwikkeltraject is ook deze simulator gevoelig voor bepaalde procesvariablelen, hetgeen tot de instabiliteit van het rekenproces leidt. Echter door het gebrek van de toegang tot de broncode is het vaststellen van de oorzaken van zulke problemen zeer lastig – een belangrijke reden om de ontwikkeling van eigen model voort te zetten.

In het algemeen kan worden geconcludeerd, dat een met stoom en zuurstof bedreven circulerend wervelbed biomassavergasser een krachtige technologie is, die in staat is om uit biomassa een waterstofrijk productgas te maken. Het testen van de waargenomen positieve invloed van magnesiet op de samenstelling van het gas in combinatie met katalytische gasfiltratie op hoge temperatuur, teneinde syngas te kunnen maken met een meer geïntegreerd gasreinigings- en opwaarderingssysteem, wordt voor verder onderzoek aanbevolen. Ook wordt aanbevolen om het mathematische model verder te ontwikkelen, zodat de effecten van de wijzigingen in het proces en in de operationele parameters, inclusief de aanwezigheid van katalytische bedmaterialen, op de prestaties van de vergasser gesimuleerd kunnen worden.

Marcin Siedlecki, september 2011

Streszczenie O zgazowaniu biomasy w cyrkulacyjnym złożu fluidalnym napędzanym tlenem i parą wodną z ukierunkowaniem na poprawę jakości gazu: podstawy technologii, doświadczenia badawcze oraz modelowanie matematyczne

Od początków Rewolucji Przemyslowej nieustannie rośnie popyt na energię. Mimo, że Ziemia ciągle jest w stanie sprostać temu popytowi, to jednak zapasy paliw kopalnianych nagromadzone przez miliony lat maleją bardzo szybko. Niebezpieczeństwo braku dostępu do paliw dla przyszłych generacji, oraz skutki uboczne zmasowanej utylizacji paliw kopalnianych (ocieplenie klimatu, zanieczyszczenie powietrza, rosnące koszty energii) na szczęście doprowadziły do zwiększonej świadomości o konieczności poszukania innych, odnawialnych i zarazem trwałych źrodeł energii. Ze względu na fakt, iż biomasa zbierana w sposób ekologiczny oraz dostępna po konkurencyjnych cenach mogłaby pokryć od 50 do 55% światowego zapotrzebowania na energię pierwotną, zainteresowanie jej zastosowaniem jako źródła energii znacznie wzrosło na przestrzeni poprzednich kilku dekad. Jednak z powodu postaci pod jaką występuje oraz właściwości fizycznych biomasa nie może być bezpośrednio stosowana w zakładach obecnie przetważających paliwa kopalniane. Względnie sucha biomasa (zawartość wilgoci poniżej 30-40% wagowych) w postaci stałej może być przetwarzana drogą ekstrakcji mechanicznej (tłoczenie) lub drogą termo-chemiczną, podczas gdy mokra biomasa może zostać poddana procesom biologicznym lub zgazowania w procesie stosującym wode w stanie nadkrytycznym. Produktem procesu przetwarzania może być ciepło lub ciepło oraz energia elektryczna rozwiązania te są głownie przewidziane dla zdecentralizowanych zastosowań stacjonarnych. Przetwarzając biomasę na chemicznie stabilny (ciekły) nośnik energii również sektory takie, jak transport drogowy mogłyby korzystać z tego odnawialnego źródła energii. Założenie to może być zrealizowane przez zastosowanie konwersji termo-chemicznej (zgazowania) oraz procesu syntezy,

gdzie ostatecznym produktem są np. metanol, DME lub substytut oleju napędowego uzyskany przy pomocy procesu Fischer-Tropsch'a. W zależności od zastosowanej technologii gazyfikacja wytwarza albo tzw. gaz syntezowy (*ang: syngas*), czyli mieszankę CO, H₂, CO₂, możliwie zawierającą również azot oraz parę wodną, albo tzw. gaz generatorowy (*ang: product gas*), czyli gaz syntezowy zawierający metan i inne węglowodory lekkie oraz (poli-)aromatyczne (substancje smoliste), zanieczyszczony związkami azotu i siarki, oraz cząsteczkami pyłu. Przystępując do produkcji wtórnych paliw płynnych z biomasy na skalę przemysłową można uznaç, że technologia oparta o złoże fluidalne wykazuje najkorzystniejszy bilans pomiędzy jej zaletami i wadami. Technologia ta jest bardzo elastyczna jeżeli chodzi o jakość oraz rodzaj przetwarzanego surowca, może być stosowana w skali od kilku do kilkuset megawatów przerobu termicznego, ale wytwarza ona gaz generatorowy, który wymaga uzdatnienia przed zastosowaniem w każdym zaawansowanym procesie syntezy.

W ramach niniejszej pracy zostały wykonane badania nad procesem gazyfikacji biomasy w cyrkulacyjnym złożu fluidalnym (ang: Circulating Fluidized Bed, CFB) zasilanym mieszanką tlenu i pary wodnej, przy pomocy stanowiska doświadczalnego o mocy przetwórczej 100 kW. Badania były skupione na konwersji substancji smolistych oraz optymalizacji jakości gazu w kierunku składników gazu syntezowego, zakładając zastosowanie gazu w produkcji syntetycznych paliw transportowych pochodzących z biomasy. Cztery różne rodzaje biomasy reprezentujące drewno czyste, drewno z odzysku, uprawy energetyczne (miskant) i odpady rolnicze (słoma) były poddane procesowi zgazowania w połaczeniu z trzema różnymi materiałami złoża: piaskiem kwarcowym, magnezytem palonym oraz oliwinem. Gazując surowce zawierające duże ilości metali alkalicznych w popiele, a stosując złoża bogate w kwarc spodziewano się zaistnienia zjawiska aglomeracji złoża; w takim przypadku skutecznym środkiem zapobiegawczym było zastosowanie kaolinitu jako dodatku do złoża. Złoże z magnezytu wykazało doskonała odporność na zjawisko aglomeracji. Ponadto zostało też udowodnione działanie katalityczne na reakcję konwersji gazu wodnego (ang: water-gas shift reaction) i na reakcje związane z konwersją substancji smolistych. Steżenie poli-aromatycznych oraz fenolowych substancji smolistych zostało zredukowane poniżej 2 g m $^{-3}$ w gazie surowym, podczas gdy stosunek stężenia H₂ do CO wzrósł z ok. 0.6 do powyżej 2.0 w porównaniu do doświadczeń, w których złoże składało sie z piasku kwarcowego. Mimo, że wymierna aktywność katalityczna była również oczekiwana od oliwinu, to efekt ten nie został zaobserwowany, niezależnie od tego czy użyty oliwin był poddany wstępnej obróbce termicznej, czy nie. Ten brak aktywności został przypisany innemu pochodzeniu minerału, w porównaniu do tego, który został opisany w literaturze.

W celu lepszego zrozumienia procesu gazyfikacji oraz w celu zmniejszenia ilości niezbędnych eksperymentów opracowany został matematyczny model gazogeneratora, w oparciu o istniejący już model kotła węglowego w technologii CFB. Model ten zakłada, że rura wznośna (*ang: riser*) złoża cyrkulacyjnego składa się ze struktury rdzeniowo-pierścieniowej (*ang: core-annulus structure*) w kie-

runku promiennym, oraz ze skończonej ilości komórek w kierunku osiowym. Model jest w stanie obliczyć skład gazu wraz z czasem trwania procesu suszenia i pirolizy, bierze pod uwagę hydrodynamikę złoża, kinetykę reakcji chemicznych (homogenicznych i heterogenicznych), jak również osprzęt do wymiany ciepła. Model procesu pirolizy biomasy oraz kinetyka reakcji związanych z gazyfikacją, łącznie z konwersją substancji smolistych, należą to nowej części modelu. Równania matematyczne sa rozwiazywane podczas procesu iteracji bilansu masy oraz ciepła. Na poczatku funkcjonowanie modelu zostało ocenione poprzez wykonanie symulacji jednego z eksperymentów przy użyciu parametrów kinetycznych pobranych z literatury. Aby uzyskać zgodność pomiedzy wynikami symulacji oraz pomiarami, wartości czynników przedwykładniczych równania Arrhenius' a zostały odpowiednio dostosowane. Wyniki wykazały, że reakcje spalania wegla drzewnego, reakcja konwersji gazu wodnego, oraz reforming parowy metanu są (znacznie) wolniejsze wewnatrz gazogeneratora niż opisywane w literaturze. Analiza wrażliwości została dokonana dla trzech zmiennych zoptymalizowanego modelu: rozkładu wielkości cząsteczek paliwa, stechiometrycznego współczynnika tlenu do paliwa (lambda) oraz ciężaru właściwego węgla drzewnego. Modyfikacja ww. parametrów dała oczekiwane wyniki, chociaż zwiększenie parametru lambda o więcej niż 5% względem scenariusza podstawowego oraz zwiekszenie cieżaru właściwego wegla drzewnego prowadziło do problemów ze zbieżnościa symulacji. Problemy ze zbieżnościa zajstniały również podczas symulowania innych eksperymentów. Porównanie osiowych profili składu chemicznego gazu wewnątrz reaktora obliczonych podczas symulacji i zmierzonych podczas doświadczeń wykazało najlepszą zgodność dla stężenia tlenu oraz metanu (maksymalne absolutne odchylenie 4.1 punktu procentowego); główna niezgodność była zaobserwowana dla azotu i została przypisana sposobowi podawania strumieni przedmuchujacych aparature pomiarowa (ang: purge flows): w rzeczywistości strumienie te sa równomiernie rozłożone wzdłuż długości reaktora, podczas gdy symulacja zakłada, że strumień azotu podany jest razem z pierwotnym strumieniem napędzającym proces fluidyzacji. Na zakończenie wyniki uzyskane przy pomocy opracowanego modelu zostały porównane do wyników uzyskanych przy pomocy komercyjnego pakietu CSFMB [®] / CeSFaMBTM. Mimo dużo bardziej zaawansowanego interfejsu użytkownika, dużej ilości opcji oraz dużo dłuższego procesu rozwoju, również ten symulator wykazał zwiększoną czułość co do niektórych zmiennych, co prowadzi do niestabilnych wyników obliczeń. Jednak brak dostępu do kodu źródłowego powoduje, że rozwiazywanie tego typu problemów jest bardzo trudne, lub nawet niemożliwe – jest to bardzo ważny argument aby kontynuować rozwój własnego modelu gazogeneratora.

Po przeprowadzeniu badań można wnioskować, że zgazowanie biomasy w cyrkulacyjnym złożu fluidalnym napędzanym tlenem i parą jest bardzo mocną technologią umożliwiającą produkcję gazu o wysokiej zawartości wodoru ze stałej biomasy. Dla dalszych badań zalecane jest testowanie pozytywnego wpływu magnezytu na skład gazu razem z wysokotemperaturowym katalitycznym odpylaniem gazu, w celu opracowania procesu produkcji gazu syntezowego w bardziej zintegrowanym procesie oczyszczania i uzdatniania. Także zalecany jest dalszy rozwój modelu matematycznego, aby móc symulować wpływ zmian wprowadzonych do procesu oraz jego parametrów operacyjnych, włączając obecność katalizatorów w złożu na osiągi reaktora.

Marcin Siedlecki, wrzesień 2011

Nomenclature

| Abbreviations | | |
|----------------------------|---|--|
| annu | in the mathematical model: related to the annulus | |
| | phase | |
| ar | as received | |
| BC | base case | |
| BFB | bubbling fluidized bed | |
| BTL | biomass to liquid | |
| BTX | benzene, toluene and xylenes | |
| bubb | in the mathematical model: related to the bubble | |
| | phase | |
| CC | carbon conversion efficiency | |
| CFB | circulating fluidized bed | |
| CFBG | circulating fluidized bed gasifier | |
| CGE | cold gas efficiency | |
| CHP | combined heat and power | |
| CI | cascade impactor | |
| daf | dry, ash-free | |
| DME | dimethyl ether, CH_3OCH_3 | |
| dnf | dry, nitrogen-free | |
| ECN | Energieonderzoek Centrum Nederland (Energy re- | |
| | search Centre of the Netherlands) | |
| EFR | entrained flow reactor | |
| EHE | external heat exchanger (ash cooler) | |
| FB | fluidized bed | |
| FCCC | fuel cell combined cycle | |
| FG-DVC | functional group – depolymerization vaporization | |
| FIGER | condensation | |
| FICFB | fast internally circulating fluidized bed | |
| FT | Fischer-Tropsch | |
| FTIR | Fourier transform infra-red spectrophotometer | |
| GA | gas analysis | |
| GC | gas chromatograph | |
| GT | gas turbine | |
| Continued on the next page | | |

| Continued | | | |
|-----------|--|--|--|
| Abbrevia | Abbreviations | | |
| GTCC | gas turbine combined cycle | | |
| GTL | gas to liquid | | |
| HG | heated grid reactor setup | | |
| HHV | higher heating value | | |
| LHV | lower heating value | | |
| MBD | mass balance discrepancy | | |
| NDIR | non-dispersive infra-red | | |
| n.m. | not measured | | |
| PAH | poly-aromatic hydrocarbons | | |
| P&ID | piping and instrumentation diagram | | |
| PM | paramagnetic | | |
| ppb(v) | parts per billion (by volume) | | |
| ppm(v) | parts per million (by volume) | | |
| PV | photovoltaic | | |
| R&D | research and development | | |
| SB | steam to biomass ratio (by weight) | | |
| SCWG | supercritical water gasification | | |
| SD | standard deviation | | |
| SNG | substitute natural gas | | |
| SOFC | solid oxide fuel cell | | |
| SPA | solid phase adsorption | | |
| STP | standard temperature and pressure: $0^{\circ}\mathrm{C}$, 101325 Pa | | |
| TC | thermocouple | | |
| TUD | Technische Universiteit Delft (Delft University of Technology) | | |
| WGS | water-gas shift | | |
| XRF | X-ray fluorescence | | |

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|-------------|----------|
| N11 | heerinte |
| 1 70 | |
| | 00011000 |

| annu | annulus phase |
|-----------|--|
| bubb | bubble phase |
| crit | critical |
| dwn | downward flow |
| е | electrical |
| ehe | external heat exchanger, ash cooler |
| feedgas | gas (oxidant) fed to the reactor |
| feedflue | flue- or product gas recirculated to the reactor |
| , fl | fluidization |
| g | gas |
| Continued | l on the next page |
| | xvi |
| | |

| Continued | | |
|------------|---|--|
| Subscripts | | |
| in | inlet, input | |
| j | in the mathematical model: gaseous component j in | |
| | the component matrix | |
| max | maximal | |
| mf | minimum fluidization | |
| n | at normal conditions (same as STP) | |
| out | outlet, output | |
| recy | recirculation | |
| R^{-1} | reactor | |
| S | solid | |
| th | thermal | |
| tr | transport | |
| ир | upward flow | |
| vol | by volume | |
| vola | volatiles | |
| wt | by weight | |
| x | in the mathematical model: (back)mixing flow of | |
| | solids between the two subsequent core cells | |

| Mathem | Mathematical symbols | | |
|---------|--|--|--|
| А | area | m^2 | |
| d | diameter | m | |
| i | in the mathematical model: particle size class identifier | _ | |
| j | in the mathematical model: gaseous component identifier | - | |
| k | in the mathematical model: cell number in the riser discretization | - | |
| m | in the mathematical model: solid mate- rial identifier | _ | |
| m | mass | kg | |
| ṁ | mass flow rate | $kg s^{-1}$ | |
| n | molar amount | mol | |
| Ż | volume flow rate | $\mathrm{m}^3\mathrm{s}^{-1}$ | |
| r | radius | m | |
| r | in the mathematical model: reaction rate | $ m mol~s^{-1}$ | |
| R | universal gas constant, 8.314 | $\mathrm{J}\mathrm{mol}^{-1}\mathrm{K}^{-1}$ | |
| u | velocity | ${ m m~s^{-1}}$ | |
| t | time | S | |
| Continu | ed on the next page | | |

| Contir | nned |
|--------|------|
| Contin | iucu |

| | Continued | |
|----------------------|---------------------------------------|---------------------------------|
| Mathematical symbols | | Units |
| Т | temperature | K |
| \mathbf{X}_S | mass fraction of solid component S | $\mathrm{kg}\mathrm{kg}^{-1}$ |
| y_G | molar fraction of gaseous component G | $\mathrm{mol}\mathrm{mol}^{-1}$ |
| Z | axial coordinate | m |
| η | efficiency | % |
| μ | viscosity | Pa s |
| ho | density | $ m kgm^{-3}$ |
| $\dot{\Phi}$ | mole flow rate | ${ m mol}{ m s}^{-1}$ |

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Hence, we deal with an essentially fixed storehouse of energy which we are drawing upon at a phenomenal rate. M.K. Hubbert – Shell Oil Company, Inc., 1949

Introduction

1.1 Background information

The annual energy consumption of a small apartment in Amstelveen, the Netherlands, is 3100 kWh (11.2 GJ) of electricity and 1426 m³ of Dutch natural gas [143]. A large detached house occupied by one family in Eastern Europe uses 6062 kWh (21.8 GJ) of electricity and 4329 m³ of natural gas per year [142]. Average energy consumption per capita in the United States of America, China, the Netherlands and Africa in 2010 is given in Table 1.1. Total worldwide energy consumption has been estimated at 490 EJ in 2005 [152], 503 EJ in 2010 [18]. Most of that energy (380 EJ) originates from fossil fuels.

| Region | Primary energy ^a [Mtoe] ^b | Primary energy [EJ] | Population [millions] ^c | Primary energy per capita [GJ] |
|-----------------|---|---------------------------|---------------------------------------|--------------------------------------|
| Africa | 372.6 | 15.6 | 1030 | 15.1 |
| China | 2432.2 | 101.8 | 1138 | 89.5 |
| the Netherlands | 100.1 | 4.2 | 16.6 | 252.5 |
| USA | 2285.7 | 95.7 | 309.6 | 309.1 |

Table 1.1: Primary energy consumption (total and per capita) in 2010 in four different regions of the world

^{*a*} 2010 data, retrieved from [18]

^b 1 toe (tonne of oil equivalent) = 41.868 GJ

^c 2010 data, retrieved from [128]

This human behavior has the following consequences:

- depletion of fossil fuel reserves: crude oil within 60 to 70 years from now, natural gas 130 to 140 years, assuming current rate of consumption and the availability of conventional resources. The availability of coal at current consumption rate is estimated at more than 800 years, but if coal should replace the depleted resources of oil and gas, then the conventional resources will last for ca. 200 years;
- prolonged net emission of large amounts of greenhouse gases into Earth's atmosphere in 2005 26 Gt of CO_2 was released and this value is increasing at about 1.5% per year [152, p. 261]. This already has led to an increase of CO_2 concentration in the atmosphere from 260–280 ppmv in pre-industrial times to more than 380 ppmv at present. Major climate changes are expected to follow, and the onset to these changes can be experienced already in present times (e.g., increase of the average temperature on Earth's surface, increasing sea level, extreme weather phenomena);

• increased air pollution due to incomplete combustion (carbon monoxide, volatile hydrocarbons, soot), oxidation of nitrogen during combustion (nitrogen oxides, nitrous oxide), trace elements (mostly heavy metals) and the emission of particles (soot, ash). Certain diseases and health effects (allergies, astma, certain tumors, etc.) are proven or are thought to be caused by the decreasing air quality over the last decades.

From the above it is clear, that if the human kind wishes to avoid self-destruction caused by a combination of the increasing shortage of fossil fuels and the environmental effects of their use, we should at first reduce the dependence on the availability of fossil fuels. Alternative energy sources started to gain attention already in the first half of the 20th century, which was also caused by a shortage of fossil fuels (mainly crude oil), but that was dictated rather by temporary factors like political isolation or conflicts and wars. When those factors were taken away, the interest in alternative energy sources decreased accordingly. The situation changed after the first oil crisis (1973) and the increasing general concern about the deteriorating state of the natural environment, which was pointed out by the issues of acid rains, ozone layer depletion ("ozone holes"), air pollution, smog formation and, more recently, global warming. Scientific studies, often supported by public funding, were started to explore the possibilities of (partial) replacement of established energy sources, mainly consisting of fossil fuels, by alternative resources. Being an umbrella term, "alternative energy" refers to all energy sources that could replace traditional energy sources taking away the undesired consequences of their use. It has to be mentioned, that nuclear energy, although not contributing to the three problematic issues listed at the beginning of this section, often causes a dispute whether it should be considered as an (true) alternative energy source. This is caused by the problems related to the treatment of nuclear waste, the general public concern about the safety of nuclear reactors and nuclear energy, and the potential use of nuclear fuel for the production of weapons of mass destruction. From the long-term point of view the optimal solution would be to fully switch to a subcategory of alternative energy sources – the renewable energy. "Renewable energy" indicates energy resources, that are "naturally replenished" on a short term, and include solar energy, wind energy, biomass, hydropower, geothermal energy, tidal energy and rain.

Currently the mostly exploited renewable energy resource is hydropower. From the estimated 62 EJ of hydropower available on a yearly basis (2005 data, [152]), nearly 26 EJ (42%) is being used. Looking at the availability of modern biomass (so including agricultural wastes and crops grown for energy purposes), which in 2005 was estimated at 250 EJ per year only 9 EJ (3.6%) has actually been used for energy generation. At the moment the largest share of renewable energy (37 EJ per year) originates from traditional biomass, which most often means burning of wood for cooking and heating. Although seemingly popular, this way of using biomass is not very efficient from energetic point of view (low process efficiency), and it can even lead to a locally increased air pollution – emissions of carbon monoxide, condensable hydrocarbons and particles ("smoke"). Of the three most abundant renewable energy resources (geothermal - 5000 EJ per year, solar 1600 EJ per year, wind 600 EJ per year) only 3.2 EJ are currently being employed. This is due to the high investment costs combined with often poor conversion efficiency (like in the case of solar energy). Summing up the total available hydropower and biomass resources, and taking into account the still limited use of other renewables it can be observed, that currently the supply of renewable energy could theoretically cover 65% of the yearly demand. Therefore an important extension of the use of other renewables should be achieved in order to totally abandon the consumption of fossil fuels. However, at this moment both statements done above (complete use of hydropower and biomass resources and hundredfold increase in the use of other renewables) are just theoretical, and in the current state of affairs their practical implementation and realization is still decades away.

The reduction of the dependence on the availability of fossil fuels was mentioned as the primary step towards the sustainable man kind. However, switching to renewable energy without the reduction of energy consumption may lead to the same issues as the use of fossil fuels – constantly increasing prices due to an continuously increasing demand and a limited supply. Also, just the switch to renewables is not a universal remedy to the environmental issues. For instance, burning biomass or the fuels derived from biomass can be just as polluting as burning fossil fuels. Therefore the energy transition process should be accompanied by two other activities:

- social and economic transition: we should be aware, that the real cause (and solution) to the energy problem is the human behavior: the individual claim on the Earth's natural resources. It is still difficult to accept that the solution will not be provided by the discoveries of new oil and gas fields, not in the exploration of shale gas or any other non-renewable resources. Neither is the panic search for another planets or civilizations that could be colonized so that the "ole Earth" could be left behind, drained from resources and devastated. A radical reduction of the energy consumption, especially in the "developed" countries is a prerequisite without fulfilling this condition most, if not all, of the efforts currently spent on the development of existing and novel energy conversion processes will be rather useless;
- technology development: it has already been indicated that just the use of a renewable source of energy is not per se renewable, not only because of the "established" emissions, but also because of the increased demand for other resources, e.g., rare metals (catalysts, batteries), semiconductor material (PV panels), etc. Therefore the need for better, cleaner and more efficient conversion technologies will persist.
Although the social aspects of energy production and consumption fall outside the scope of this work, they should in fact be considered every time when drawing the conclusions about some novel development or progress in the field of energy technology. Regarding the technology development, considerable research efforts are being undertaken worldwide to bring the energy transition closer and provide a long-term sustainable solution for the energy supply. A tiny contribution to these efforts is presented in this work.

Large part of the research presented in this book was also a contribution to the European Integrated Project "CHRISGAS" funded by the European Commission. In this project 19 partners from 8 EU member states joined with an objective to within a five year period develop and optimize an energy-efficient and cost-efficient method to produce hydrogen-rich gases from biomass.

1.2 Objectives

As stated in Section 1.1 the Earth provides us yearly with a substantial amount of biomass that forms a potential source of sustainable and renewable energy. So-far only a relatively small fraction of that potential is actually employed – mostly solid traditional biomass ¹. Also the current way of conversion into usable energy has many drawbacks. The key issue now is to develop a way of processing the biomass that has the following characteristics:

- being able to accept various kinds of biomass, preferably these now considered as "waste";
- showing high energy conversion efficiency;
- producing minimal amount of waste or harmful byproducts;
- applicable at different scales, depending on the availability of biomass;
- being attractive from commercial point of view (costs, return on investment, reliability).

As mentioned earlier, today's use of biomass mostly amounts to the generation of heat for space heating and cooking (traditional biomass). Industrial generation of heat, eventually for power generation, recently also has gained attention, but the applications are usually limited to the co-combustion of biomass with fossil fuels. Another possibility would be the production of secondary energy carriers. This means that biomass, which as such is not very convenient to use due to its solid appearance, varying composition and relatively low energy density would be converted into a gaseous or liquid energy carrier with energy density comparable to fossil fuels and with well-defined quality specifications.

¹From this point on "biomass" refers to solid, relatively dry biomass, unless noted otherwise

Such an energy carrier could act as a universal platform for the production of chemicals (e.g., hydrogen, ammonia, poly-ethylene), advanced liquid biomassderived fuels (e.g., FT diesel, DME, methanol), or could be fired directly in a CHP facility. One of such chemical platforms is syngas (synthesis gas) which is a mixture of carbon monoxide, hydrogen, carbon dioxide, water vapor and possibly nitrogen. Syngas can be obtained from a thermal gasification process, where the organic fuel is thermally decomposed in an oxygen-lean atmosphere. Among many solid fuel conversion routes the fluidized bed gasification technology is one that responds positively to the requirements presented above. Unfortunately, it is not free from problems or drawbacks. The main issues that are of importance for the processing of biomass are the facts that:

- the product of the gasifier is not of syngas quality due to the presence of particles (fly ash), inorganic impurities (e.g., sulfur- and nitrogen-containing species, trace elements), larger condensable hydrocarbons ("tar"). This makes the gas not directly suitable for the most of the aforementioned applications, and requires the use of gas cleaning and upgrading techniques;
- the presence of large amounts of alkali metals, chlorine and silica in the ashes of herbaceous biomass, together with the presence of silica in the bed material leads to an interaction between the alkali and the silica. Upon the interaction salts will be formed with a melting point below the process temperature, causing the formation of sticky layers on the ash and bed material particles, ultimately leading to their fusion (agglomeration). Chlorine accelerates this process. If no countermeasures are taken this will lead to large problems in the fluidized bed reactor ("defluidization) and downstream ("fouling").

Being aware of the potential and the challenges in the field of biomass gasification, the objective of this work was to investigate and propose solutions to the problems mentioned above, by studying the state-of-the-art, the process conditions and the process design. The investigations were focused on tar conversion and the gas quality optimization in terms of syngas components in a Circulating Fluidized Bed biomass gasifier, tailored to the production of synthetic biomassbased transportation fuels. Also the operability of the test rig was assessed when herbaceous biomass was gasified – both with and without the use of agglomeration countermeasures - aiming at the long-term stable operation. The experimental investigations have been carried out at the laboratory gasification pilot plant of the Process & Energy department at TU Delft consisting of a CFB gasifier (maximum 100 kW fuel power input) followed by a high-temperature filter unit operating at process temperature, and a catalytic reformer and water-gas shift reactor in the slip stream. This test rig was able to demonstrate the full process chain from raw biomass to hydrogen-rich syngas, and although the gas cleaning and upgrading steps are outside the scope of this work, some attention will be given to the process integration aspects.

1.3 Outline of the thesis

This book consists of three key parts. In Chapter 2 a theoretical background to the process of biomass gasification is given. This includes the motivation to use gasification for producing secondary fuels from biomass, and to employ a circulating fluidized bed technology for that purpose. Also a literature review and the state-of-the art of this technology will be presented there. Chapter 3 gives the description of the test facility at Delft University of Technology, the 100 kW thermal fuel input Circulating Fluidized Bed Gasifier (CFBG). The experimental procedures and the results from the gasification experiments performed within the scope of this work are presented in Chapter 4. Chapter 5 focuses on the discovered effect of the use of magnesite as the bed material in the CFBG on the composition of the product gas and the tar yield as compared to "standard" bed material (quartz sand). The focus is put on the direct comparison of the influence of the two bed materials *ceteris paribus*. To complete this work, a 1.5-dimensional mathematical steady-state model of the CFBG is presented in Chapter 6. The simulation results are validated using the experimental data from Chapter 4, and also a comparison is made with the results of the commercially available Comprehensive Simulator for Fluidized and Moving Beds (CSFMB[®]). In the last chapter the overall conclusions and recommendations arising from this work are given.

We're heading for a big worldwide traffic jam . . . Sailor, *Traffic Jam*, 1974

Thermochemical conversion of biomass into advanced secondary energy carriers - a literature and technology review

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Introduction

Biomass is the oldest fuel used by mankind and at the end of the fossil era it has been recognized as a renewable and potentially sustainable energy source for many applications varying from heat generation to the production of advanced secondary energy carriers. The latter option would allow mobile services like the transportation sector to reduce its dependency on the fossil fuel supply. This chapter reviews the state-of-the-art of the fluidization technology applied for the gasification of biomass aimed at the production of gas for subsequent synthesis of the liquid energy carriers via, e.g., the Fischer-Tropsch process. It discusses the advantages of the gasification technology over combustion, considers the size of the conversion plant in view of the local biomass availability, assesses the pros and cons of different gasifier types in view of the application of the product gas. Subsequently the chapter focusses on the fluidized bed technology to discuss the main process parameters and their influence on the product composition and the operability of the gasifier. Finally a synthesis process (FT) is introduced shortly to illustrate the necessary gas cleaning steps in view of the purity requirements for the FT feed gas.

2.1 Biomass – background information, properties, availability and conversion pathways

2.1.1 History of biomass use for energy generation

Biomass is the oldest fuel known by mankind and has been used for thousands of years for cooking and heating purposes. Fossil fuels were also known, for example coal was used by the Chinese probably as early as 1000 B.C., and by the Romans prior to A.D. 400 [23], however the first biblical references that indicate its use are approximately from the 13^{th} century onwards [83]. The use of coal was also initially limited as compared to biomass. However, since the beginning of the Industrial Revolution in the 18^{th} century, the demand for energy started to increase. This was initially due to industry and later also to households. Biomass could not compete with the "convenient" and seemingly inexhaustible fossil fuels that also had significantly higher energy density than biomass. At the end of the 19th century, due to the introduction of the automobile, petroleum gained wider use as a fuel. However, crisis situations worldwide exposed the first weakness of fossil fuels, namely their strictly distributed availability. After World War I and especially during World War II, shortage in petroleum supplies led to the re-introduction of biomass use as an energy source. However, in contrast to previously mentioned applications of biomass the process did not involve combustion (complete oxidation), but production of a secondary (gaseous) energy carrier via the gasification (partial oxidation) route. The German term "Holzgas" (woodgas) is still a widely recognized term for the vehicle

fuel produced in that way. Figure 2.1 shows the practical implementation of such a system. Next to this woodgas technology, a synthesis process of diesellike fuel, invented by F. Fischer and H. Tropsch successfully yielded substitute vehicle fuel, which ultimately covered 90% of German consumption at that time [105]. Although the Fischer-Tropsch process was based on (brown)coal, it initiated the interest in solid-to-liquid fuel technologies, also applicable for biomass. After World War II development in this area was abandoned due to lack of strate-



Figure 2.1: A WWII car with woodgas generator [81]

gic impetus and abundant availability of cheap fossil fuel. However, some countries (e.g., Sweden) continued to work on producer gas technology and included it in their strategic emergency plans [87].

Today's interest in biomass (and other renewable energy sources), and its related research & development, for the most part, dates from the 1973 oil crisis. The developing political situation made clear that the concentration of major fossil fuel resources in certain (often politically unstable) areas of the world threatened the energy security of the depending countries. Decreased supply and demand which is still increasing has led to an excessive rise in energy prices – this being the second weakness of fossil fuels. Around that time a third weakness was also exposed, being the negative environmental impact of the emissions related to the rapid consumption of carbonaceous resources stored under the Earth's crust. Phenomena like acid rain, smog, global warming, air pollution, etc. forced not only the improvements of existing conversion technologies in terms of efficiency and residue (exhaust) cleanup, but also the search for alternative, renewable and environmentally neutral sources of energy. Biomass is one of such – sustainable – energy sources.

For some applications the production of secondary (gaseous or liquid) fuels has remained the best option. Consequently high efforts, both financially and intellectually, are currently being put into the revival, expansion and improvement of the work initiated by Fischer and Tropsch, now coupled with biomass gasification.

2.1.2 Definition and the availability of biomass

Currently the mostly exploited renewable energy resource is hydropower. From the estimated 62 EJ of hydropower available on a yearly basis (2005 data [152]), nearly 26 EJ (42%) is being used. Looking at the availability of modern biomass (thereby including agricultural wastes and crops grown for energy purposes), which in 2005 was estimated at 250 EJ [152] per year only 9 EJ (3.6%) has actually been used for energy generation. Biomass has been mentioned to be the fourth largest energy resource in the world, after geothermal, solar and wind energy, currently contributing to about 15% of the world's total primary energy consumption, while fossil fuels contribute to about 81% [152]. The total estimated biomass resources amount to about 2900 EJ per year (of which 1700 EJ are from forests, 850 EJ from grasslands and 350 EJ from agricultural areas). However, only 270 EJ [139] (250 EJ in [152], see also Table 2.1) could be considered available on a sustainable basis and at competitive prices. The management of biomass resources and delivery of the energy, either in the original form (raw biomass) or as secondary fuel, to the end user are the key aspects that will decide whether a certain batch of biomass can be considered as being sustainable or not.

There are several definitions of biomass. The European Commission (EC) states, that biomass "shall mean the biodegradable fraction of products, waste and residues from agriculture (including vegetal and animal substances), forestry and related industries, as well as the biodegradable fraction of industrial and municipal waste" [58]. However, in general terms it can be described as "plant materials and animal waste used especially as a source of fuel" [112]. The renewability and sustainability aspects of biomass originate from the fact that the carbon dioxide from the atmosphere is stored by the plants during the photosynthesis process, and released again during biomass conversion to generate usable energy. In between those two processes the plant material is either harvested and it enters the conversion process directly or as a waste stream from, e.g., agriculture or forestry, or alternatively it enters the food chain (this is why animal waste is also considered as being biomass). Figure 2.2 shows the carbon cycle, together with photosynthesis and the main biomass conversion technologies. This figure clearly illustrates that biomass is a CO₂ neutral energy source (so no net CO_2 emission in the atmosphere). However it should be mentioned that this cycle shows the ideal situation and that the input of minerals/fertilizers whilst plants are growing, and emissions during biological degradation (CH₄ that has a significantly higher greenhouse gas potential than CO_2), transportation, drying and storage of biomass have not been taken into account. Therefore, the use of biomass can also have an adverse effect on the environment and care should be taken to minimize these negative effects in order to remain on the sustainability path. Life Cycle Analysis (LCA) can be a helpful assessment tool in this process (see, e.g., [25]).

| Renewable resource | Estimated availability [EJ] | Rate of use (2005) [EJ] |
|--------------------|-----------------------------|-------------------------|
| Hydro | 62 | 25.8 |
| Wind | 600 | 0.95 |
| Biomass | 250 | 46^a |
| Geothermal | 5,000 | 2 |
| Solar (PV) | 1,600 | 0.2 |
| Total | 7,512 | 75.0 |
| Current demand | 490 | |

Table 2.1: Energy demand and availability of main renewable resources on annual basis (adapted from [152])

 a including 37 EJ of traditional biomass use (heating and cooking)

2.1.3 Types and properties of raw biomass

From the definition given above it is quite evident that biomass may vary significantly in its physical and chemical properties. A typical composition of biomass comprises of cellulose, hemicelluloses, lignin, extractives, lipids, proteins, simple sugars, starches, water, inorganics (ash), and other compounds. As a result of different origins and variety of compositions, the classification of biomass is not an easy task. Many classification attempts can be found in literature. Demirbas [47] gives the following categorization:

- 1. forest products: wood, logging residues, trees, shrubs and wood residues, sawdust, bark, etc.;
- 2. bio-renewable residues: agricultural wastes, crop residues, mill wood wastes, urban wood wastes, urban organic wastes;
- 3. energy crops: short rotation woody crops, herbaceous woody crops, grasses, starch crops, sugar crops, forage crops, oilseed crops;
- 4. aquatic plants: algae, water weed, water hyacinth, reed and rushes;
- 5. food crops: grains, oil crops;
- 6. sugar crops: sugar cane, sugar beets, molasses, sorghum;
- 7. landfill;
- 8. industrial organic wastes;
- 9. algae, kelps, lichens and mosses.





Figure 2.2: Carbon cycle, photosynthesis and main steps in biomass technologies [47]

When considered as a primary energy carrier, each category will have its specific benefits and problems, depending on the conversion technique. The main issues are:

- the amount of ash. Ash refers to the inorganic part of a solid fuel, in analytical chemistry it refers to the remaining solid matter after complete oxidation of the combustible fraction, mostly consisting of metal oxides. A high amount of ash will lower the energy content of the fuel and may cause handling problems during and after the conversion process (solid residues);
- the composition and the structure of ash. The interaction of ash with the remaining species in the process will depend on its composition. Often ash will show an inert behavior, not leading to any chemical interaction with the process. Some metal oxides, like CaO, MgO, Fe_xO_y may act as catalysts for some chemical reactions during and after the conversion process (see Section 2.3.2 bed materials and additives part). This can be

beneficial (faster conversion of species) or problematic (smouldering of disposed off ashes). In addition it is well known, that the presence of alkali metals in the ash, promoted by the presence of chlorine, will lead to the formation of low-melting, "sticky" compounds that are likely to cause problems, in particular during high temperature conversion processes. Furthermore, the presence of heavy trace metals (e.g., lead, mercury) may cause environmental and health problems irrespective of the conversion process applied. The structure of the ash may have negative influence on the volatile release and the burn-out of a fuel particle, leading to higher emissions or lower conversion efficiencies (e.g., the case of pepper plant residue, PPR [93, 92]);

• the moisture content of raw biomass. Moisture, naturally present in raw biomass – just like ash – will lower the energy content of the fuel. However, for some conversion processes the presence of moisture is desired or even essential. The "classical" thermal conversion processes in particular, however, will not accept biomass of which the moisture content is too high (typically maximum 30% by weight [21]; Demirbas [47] quotes 10% moisture, which in practice would not be realistic, as drying to achieve such a low moisture content is expensive [73]; Hofbauer [80] indicates test runs with wood chips containing 20–30% moisture; the website of IEA Bioenergy Task 32 [84] reports commercial biomass gasifiers operating on fuels with 20–50% moisture, e.g., in Lahti). Therefore often some kind of drying process will be applied upstream. Additionally, high moisture content of raw biomass will significantly increase the transportation costs, unless the biomass is transported as a slurry using pipelines.

From the above it is clear, that the diversity of biomass will make the development of one universal conversion process very difficult. In Section 2.1.5 the most common biomass conversion processes will be introduced and their suitability to convert certain categories of biomass will be indicated. Figure 2.3 shows the main components of any organic fuel. It is obvious, that the calorific value is governed by the fraction of carbon (C), hydrogen (H) and sulphur (S), while moisture and ash basically act as "dilutants". The proximate analysis indicates the amount of volatile matter and fixed carbon in the fuel, which together with the oxygen (O) content gives an indication of the reactivity of a fuel. Highest rank coals consist of over 90% fixed carbon [170], making them not very reactive. Biomass, on the other hand, is mostly composed of volatile matter and a significant amount of oxygen (>20% by weight), which makes it much more reactive than coal. Table 2.2 shows the main composition of some representatives of different classes of biomass; an extensive overview can be found elsewhere [77, 55, 54]. In addition to the very diverse composition and presence of potentially problematic constituents, as explained above, there are further aspects which do not make raw biomass very convenient to use, and for some applications it may not even be directly suitable. These are that:



Figure 2.3: General composition and main chemical elements in typical solid organic fuels

- biomass is a solid and therefore can only be distributed as any other bulk material (except for slurries, but their very high water content needs to be considered);
- biomass has a relatively low volumetric energy density (typically 9 ± 5 MJ m⁻³, compared to 38 ± 5 MJ m⁻³, both on LHV-basis, for natural gas), which makes transport over long distances inefficient. Furthermore the energy density of biomass strongly depends on the appearance and densification methods applied (pelletized or "loose");
- conversion of a solid fuel is more complicated from a technical point of view than conversion of a gas or a liquid. In particular issues like pretreatment (size reduction), reactor feeding, ash removal (dedusting), etc. form main hurdles and make the processes more complicated compared to homogeneous gas processes or liquid/gas processes.

The (industrial) applications where raw biomass can be directly converted into the final product are basically limited to (co-)combustion. Over the last decades, many different technologies have been proposed to convert solid biomass into a more convenient secondary energy carrier. Figure 2.4 shows the currently known and investigated biomass conversion routes. It shows the three main groups of conversion technologies: mechanical extraction, biochemical conversion and thermochemical conversion. It also shows, that there are many possible pathways that essentially lead to three products: electricity, heat and fuels (secondary energy carriers). Most of the conversion routes presented in Figure 2.4 are well-known chemical processes, but the difficulty is that those

| Biomass | С | Н | 0 | Ν | S | Cl | Ash | Moisture |
|----------------------------|------|------|------|------|------|------|------|----------|
| Pine | 52.1 | 6.36 | 41.0 | 0.07 | 0.05 | 0.01 | 0.37 | |
| Oak | 49.9 | 5.98 | 42.6 | 0.21 | 0.05 | 0.01 | 1.29 | |
| Barley straw | 42.9 | 5.53 | 45.5 | 0.56 | 0.25 | 0.35 | 4.95 | |
| Hay | 45.5 | 6.1 | 39.2 | 1.14 | 0.16 | 0.31 | 5.70 | |
| Miscanthus | 47.5 | 6.2 | 40.7 | 0.73 | 0.15 | 0.22 | 3.90 | |
| Algae (micro) ^a | 52.7 | 7.22 | 28.9 | 8.01 | 0.49 | 0.18 | 2.5 | |
| Black liquor ^b | 35.5 | 3.15 | 0.79 | 0.27 | 5.30 | 0.08 | 57.5 | 9.61 |
| MSW | 47.6 | 6 | 32.9 | 1.2 | 0.3 | | 12 | |
| Sewage sludge | 32.6 | 4.5 | 18.9 | 4.38 | 1.69 | 0.12 | 37.5 | 85.0 |
| | | | | | | | | |
| Coal (bitum.) | 75 | 4 | 14 | | 2 | | 5 | |

Table 2.2: Main compositions of different kinds of biomass (mass percentages); coal listed for comparison [77]

^a retreived from [55]

^b adapted from [7]

processes have not (extensively) dealt with biomass as a feedstock yet. The research and practical experience obtained from small pilot projects have shown that the use of biomass as feedstock can cause unexpected problems that have to be solved before a certain conversion route will be mature for industrial introduction. Except the technological advancement and maturity, the choice of the conversion route will strongly depend on the scale on which the process will be applied. The order of the magnitude of the scale of the three process categories mentioned above, expressed in terms of fuel thermal power input are as follows:

- mechanical extraction: 500–50,000 tonnes product (oil) annually. Assuming a total biomass-to-oil efficiency of 42% and the heating value of biomass of 16 MJ kg⁻¹ it is approximately an equivalent of 0.6–60 MW fuel thermal power input ([140], pp. 143–172);
- biochemical conversion: up to 400 MW fuel thermal power input [74], or even >800 MW [154] for 1st generation ethanol production;
- thermochemical conversion: 1–1000 MW fuel thermal power input [77].

The above list shows that although the thermochemical conversion route gives the biggest scale-up possibilities, the biochemical conversion and the mechanical extraction can also be performed at significant scale. However, at present there is a serious concern related to the first two processes when applied to the production of secondary energy carriers, namely they compete directly with the food and fibre production (except possibly the ethanol production from sugar cane) [153]. Using ligno-cellulosic residue streams and energy crops (the 2^{nd} generation biofuels), that issue can be overcome. Nonetheless, both the mechanical extraction and biochemical conversion produce a solid waste stream that can only be utilized using a thermochemical conversion process. Currently the concept of a "biorefinery" is also receiveing substantial attention; here each constituent of biomass is extracted or utilized using a dedicated process. Such a concept can include biochemical and thermochemical conversion side-by-side. However, this topic falls outside the scope of this work.

2.1.4 Optimal scale of the biomass conversion plant

Notwithstanding having different conversion processes available in a broad capacity range, the optimal size of the plant will still need to match the available biomass resources. Power plants fired on fossil fuels easily reach hundreds of megawatts of electrical output (often meaning more than 1 GW thermal output). This is justified by the economy of scale and the relatively low transportation costs of fossil fuels due to their high specific energy content and often concentrated deposits. Contrarily, biomass is often distributed over a large area. In order to maintain the sustainability aspect of biomass use, and minimize the energy consumption and emissions related to the transport of biomass to the processing site, the size (in terms of fuel throughput) of the plant needs to match the local biomass resources. To illustrate this a simple comparison of the raw biomass resources and their demand was undertaken for three different regions of France, one of the largest countries within the European Union. In that comparison the annual primary energy consumption *per capita* was retrieved from three different sources and averaged. Then the availability of biomass within the radius of 100 km from three different French cities was calculated using BIO-RAISE, a tool for biomass resources assessment in Southern Europe [26]. With the known average population density in France (100.9 people per km^2 [57]), the match between the supply and demand can be assessed. The input and the results of that comparison are presented in Table 2.3. The assumed heating value of biomass was 16 MJ kg $^{-1}$, which is typical for relatively dry biomass: this value has been used throughout the comparison as the biomass resources are reported in "oven-dry tonnes" (o.d.t.). The primary energy requirement per capita is estimated from the following sources:

- 140 GJ, commercial & non-commercial, 1995 data for Western Europe [66];
- 4.5–6 toe (189–252 GJ, average 221 GJ), 2004 data for Western Europe [152];
- 6.5 kW (205 GJ per year), data for industrialized countries [138].

The average of the above will return 188.5 GJ per capita per year of primary energy demand. That figure and the average population density are used to

calculate the demand for raw biomass within a 100 km radius; for the French case this amounts to approximately 37 Mtonnes per year. From Table 2.3 it is clear that the current biomass *potential* covers 12–29% of the demand, whilst the *available* biomass would satisfy only 9–18% of the demand. These figures may seem discouraging at first glance and they might be quoted by people that are sceptical about the use of biomass as an energy resource. However, already in Section 2.1.2 it was indicated that the world's total biomass resource available on a sustainable basis and at competitive prices (250–270 EJ per year) would only be enough to cover approximately 50% of the primary energy needs (490 EJ per year). Therefore it is clear that to match the supply with the demand other renewable energy sources must also be used. In addition, it is unavoidable (but perhaps for many difficult to accept) that demand should also be reduced – meaning a global reduction of energy consumption. It should also be kept in mind, that the 188.5 GJ per capita represents the *total* primary energy requirement. Assuming that demand is equally split between the generation of electricity, spacial heating and cooking, transportation and industry (also accounted for in the total figure), then the biomass resources would be sufficient to cover one of the areas of partial demand. For example, the production of secondary fuels from biomass could cover the energy demand of the transportation sector; solar and wind energy assisted by small, decentralized (or even domestic) CHP units could contribute to the supply of heat and power. The industry should benefit from the synergetic effects of the existence of biomass conversion plants, such that their individual energy requirements could be partially covered by the "waste streams" from the biomass plant (e.g., steam, lowtemperature heat). It is thus clear that the final solution of the "energy issue" is to be a complex mixture of technology development, system studies, legislation. as well as information and education.

At this point it can be concluded that the size of a biomass conversion system should be chosen with care, and that probably more distributed units of smaller size may fit better to the fuel availability pattern. For Europe the suggested maximum size of a biomass processing plant was 30–80 MW generated electrical power in the short to medium term [22].

If the biomass is intended to be used in a process producing secondary energy carriers, and in particular liquid fuels for the transportation sector, then there is an obvious benefit from the economy of scale and therefore medium or large-size conversion plants come into consideration. From the list given at the end of Section 2.1.3, at present only the thermochemical conversion route allows scale-up possibilities into the tens or hundreds of megawatts scale. As the focus of this paper is on the production of liquid biofuels, henceforth this work deals with the thermochemical conversion of biomass.

| Region | Coord | inates ^a | Bion | nass | | Cos | sts | |
|-------------|------------|---------------------|--------------------|------------------------|------------------|-----------------|---------------------------------|---------------------|
|) | х | y | potential o.d.t | availability o.d.t. | collection k€ | transport k€ | total \in tonne ⁻¹ | ct GJ ⁻¹ |
| Bordeaux | 3512775 | 2435650 | 4,675,295 | 3,265,897 | 89,463 | 76,678 | 50.87 | 0.32 |
| Nancy | 4039916 | 2848642 | 5,858,141 | 3,794,951 | 108,898 | 74,213 | 48.25 | 0.30 |
| Paris | 3761197 | 2889300 | 10,942,994 | 6,757,463 | 120,784 | 134,547 | 37.79 | 0.24 |
| Est. averag | e demand j | per region | 37,344,9 | 95 o.d.t. | | | | |
| | | | | | | | | |

| fferent regions in France | |
|---------------------------|--|
| in three di | |
| of biomass | |
| Availability | |
| Table 2.3: | |

a BIORAISE input

| | Combustion | Gasification | Pyrolysis |
|---|--------------------------------------|--|---|
| Main products | heat, flue gas | combustible gas, heat | oil, (combustible) gas & char |
| Energy balance | exothermal | autothermal | allothermal |
| Carbon conversion | >99% | 80 - 95% | \approx 75% (oil yield) |
| Main product constituents (raw gas) | CO_2 , H_2O , N_2 | CO, H_2 , CH_4 , CO_2 , H_2 O, N_2^a , tar^b | oil, tar vapor, CO, H ₂ , CH ₄ , CO ₂ , H ₂ O, char |
| Oxygen stoichiometry (λ) | >1, typically 1.3 for solid fuels | $0 \leq \lambda < 1$ tvnicallv 0.2< $\lambda < 0.4$ | 0 |
| Chemical reactivity of the | inert | combustible, but stable | combustible, reactive |
| main product Physical appearance Heating value [MI kg ⁻¹] | gas 0 | gas tvnicallv 5–20 | solid, liquid & gas 16–19 (HHV) |
| ^a in case of air-blown gasification | | | |

Table 2.4: Main characteristics of the three thermochemical fuel conversion processes

 b amount strongly depending on the gasification process



2.1.5 Biomass conversion routes

Figure 2.4: Main biomass conversion routes [66]

Table 2.4 shows an overview of the main characteristics of the three thermochemical fuel conversion processes, as listed in Figure 2.4. The most wellknown and applied process is combustion. The product of that process is a hot, inert gas. As storage is not a viable option, heat is usually transferred to another medium, that often undergoes a thermodynamic cycle which delivers net work. A typical example of such an application is a power plant employing a steam cycle or an Organic Rankine Cycle to produce electricity. In fact, the functioning of the most countries relies on the electricity generated in a steam cycle, and its sudden absence has severe consequences (as, e.g., during blackouts in New York City in 1965 and 1977). However, the combustion process and the electricity production route are not free from drawbacks. To begin with, electricity is a very convenient energy carrier, but its application is so far limited to stationary applications (disregarding small personal portable devices and the rail roads, which require dedicated infrastructure). Considering the problems faced in the development of electric passenger cars related to the operational range of the vehicle, it is clear that heavy road transport will not run on electricity until significant improvements will be made in the field of electricity storage capacity. At this stage processes like pyrolysis or gasification come into consideration (see Table 2.4), as both yield a combustible product in a liquid and/or gaseous state. The pyrolysis process can even be tuned to produce high fractions of liquids (pyrolytic oils); unfortunately their chemical composition is highly variable and can not be controlled easily. Furthermore high content of oxygenated compounds and the acidity of the oil make it reactive and degradable, causing problems with storage [22, 39].

2.1.5.1 Motivation to apply gasification as biomass conversion step

In contrast to pyrolysis, the raw product of the gasification process, usually called "product gas" or "producer gas" consists of stable chemical species; the term "syngas" usually does not apply to the raw gas, as most gasification systems do not produce gas of such quality (syngas: a mixture of H_2 , CO, CO₂ and H_2 O) and the gas needs to be upgraded to be called "(bio-)syngas". Therefore (biomass) gasification produces a more versatile secondary energy carrier, which is suitable to use in more downstream processes, than solely the generation of electricity, as in the case of combustion. This also opens a new path for the application of solid renewables, as the production of liquid fuels from biomass via the syngas route could allow the transportation sector to benefit from the renewable energy resources. In addition to the aforementioned benefit, also in the process of producing electrical energy, gasification is favorable above combustion in terms of the conversion efficiency. Figure 2.5 shows the main steps involved in the conversion process and their respective energy conversion efficiencies. A biomass boiler with a steam cycle operating at supercritical steam conditions will at present yield a maximal electrical efficiency of approximately 47%. This is expected to increase to 52% in the future, when new materials become available, allowing further increase of the live steam temperature. On the other hand, a gasifier-gas cleaning combination with a gas turbine combined cycle (GTCC) can reach an electric efficiency of approximately 50%, while an even higher value (approximately 55%) can be achieved when a fuel cell combined cycle (FCCC) is employed. The combined heat & power (CHP) efficiencies exceed 90% for all the three cases mentioned above. Last biomass conversion route presented in Figure 2.5 utilizes the syngas to produce a liquid energy carrier using a synthesis step instead of combusting it in a gas turbine or a fuel cell. It is clear, that gasification not only shows a higher overall fuel-toelectricity conversion efficiency, but also extends the combined heat and power (CHP) principle with the possibility of producing secondary fuels or chemicals. The secondary fuels production route shows significantly lower total efficiency (42%) compared to the electricity production routes. However, as already indicated earlier, heavy road transport will not run on electricity on a short term, therefore synthetic liquid energy carriers from biomass are a viable option to provide fuels based on renewables to this important part of the economy.

The gasification of biomass has already been developed far enough to come into consideration as one of the contributors to the sustainable energy "well" during and after the energy transition. Nevertheless there are still some issues to be addressed before the successful large-scale commercial introduction of biomass

gasification. These issues, depending on the type of the gasifier, are related to:

- 1. technology scale-up;
- 2. size distribution of raw biomass;
- 3. operability of the gasifier with fuels containing large amounts of ash, especially if the fraction of alkali, chlorine and sulfur is high [64];
- 4. the formation of condensable higher hydrocarbons (tar);
- 5. cleaning and upgrading of the gas for dedicated downstream application.

The section below gives an overview of the available thermochemical gasification technologies, and discusses their characteristics in view of the issues mentioned above. Together with the requirements imposed on the gas quality for the synthesis of liquid secondary fuels, the current choice of the most appropriate gasification system is evaluated.

2.2 Thermochemical gasification of biomass

2.2.1 Overview of gasification processes

A wide range of reactors for thermochemical gasification of biomass is under investigation at different commercial companies and research institutes. The aspects that play a role in the decision of employing a certain reactor design for biomass gasification are:

- scale of operation;
- feedstock flexibility (size and composition);
- sensitivity to the amount of ash and its composition;
- tar yield.

Scale of operation will most likely be the primary criterion. Small, decentralized systems will benefit from a simple, easy to control and maintain, and cheap reactor. On the other hand, a Biomass-to-Liquid (BTL) plant, for example, or maybe even a biorefinery where the gasifier is only one of the units-of-operation will benefit from the larger scale of the reactor in terms of its thermal efficiency and the economy-of-scale.

The feed flexibility is also a point of attention. Biomass is very fibrous and will consequently be difficult to cut or pulverize. Therefore it is not desirable to reduce the biomass in size too much because of the adverse effect on the energy efficiency of the whole process. Additionally, raw biomass is not dry, but contains a varying amount of moisture. Taking the above into consideration the



Figure 2.5: Comparison of the solid fuel combustion and gasification processes in terms of overall conversion efficiency. Notes: ^{*a*} supercritical steam conditions; ^{*b*} values greater than approximately 40% apply to supercritical steam conditions [129], typical values of 35% and 39% are reported for subcritical steam conditions by respectively [152] and [155]; ^{*c*} from [152], page 284; ^{*d*} from [7]; ^{*e*} from [16]; ^{*f*} from [22]; ^{*g*} from [16], based on the chemical efficiency of the gasification process of 93%. Subscripts: *therm* – thermal; *unit* – of the single process unit (block); *CHP* – Combined Heat & Power; *chem* – in terms of the chemical energy in the product; *C-conv* – in terms of the carbon conversion; *e* – electrical; *FT* – Fischer-Tropsch process; *fuel* – in terms of the chemical energy in the produced fuel

gasification reactor should be able to cope with the changes in fuel supply characteristics, both physical and chemical.

As already mentioned in Section 2.1.3, in addition to the moisture and volatile fraction, each type of biomass also contains an amount of inorganic matter, usually referred to as ash. The main ash-related issues have already been high-lighted. While ash-related issues may lead to difficulties in gasifier operation and unscheduled maintenance stops, the downstream equipment may be af-

fected in a negative way by the tar produced in the gasifier. "Tar" is an umbrella term for various kinds of larger hydrocarbons produced during gasification. A clear and often used definition of tar is given in [118]: "A generic (unspecific) term for the entity of all organic compounds present in the producer gas excluding gaseous hydrocarbons (C1 through C6). Benzene is not included in tar". A similar, clear definition of tar found in literature [171] states that "tar" are "all organic compounds with a molecular weight larger than benzene (excluding soot and char)". Tar formation is a well-known problem in gasification processes [114, 171, 95, 34]. Although the main issues related to tar are condensation problems in the equipment downstream the gasifier that operates at lower temperatures (typically below 500°C), tar also significantly contributes to the heating value of the product gas. Therefore its physical "removal" from the gas will reduce the net carbon conversion efficiency of the process, and in fact a "conversion" route should be preferred, where tar is broken into smaller molecules (e.g., CO and H_2). In any case, the exact extent of the "tar problem" depends on the downstream application of the product gas. For combustion applications the tolerance for tar is higher (even up to several grams per cubic meter at STP, whereas for fuel cell applications, synthesis of chemicals, etc. it is essential to minimize the concentration of tar produced during gasification, not only to prevent the fouling of the downstream equipment, but also to make the chemical energy stored in the tar molecules available to the conversion process. Since the first (controlled) attempts do perform thermochemical gasification of biomass a number of reactor designs have evolved as being suitable for that process. These reactors are:

- fixed beds (sometimes referred to as "moving beds"): updraft, downdraft, crossdraft;
- fluidized beds: bubbling, circulating, dual;
- entrained flow reactors.

Although each of these reactors is capable of carrying out the gasification process, each of them is also a compromise between the quality of the produced gas, conversion efficiency, suitability for handling of the feedstock with varying physical and chemical properties, the complexity of the design, complexity of the operation, and the investment costs. The main characteristics of the reactors listed above are described below; also some attention is given to novel, innovative technologies that are currently under consideration. First, however, in the next section the fuel conversion in a gasifier will be explained for better understanding of the advantages and disadvantages of each gasification system.

2.2.2 Conversion steps inside the gasifier

When a solid (organic) fuel undergoes a process of thermochemical conversion it passes through a number of conversion steps. These steps are listed below and are illustrated by the prevailing physical and chemical reactions.

• drying: evaporation of the fuel moisture;

$$fuel_{raw} \longrightarrow fuel_{dry} + H_2O(g)$$
 (2.1)

• pyrolysis (devolatilization): the volatile fraction of fuel constituents (see Figure 2.3) is released into the gas phase; the remaining solid is called char, i.e., fixed carbon and ash;

$$fuel_{dry} \longrightarrow gases + vapors(tar) + char \tag{2.2}$$

• oxidation: the products of the pyrolysis step react with an externally supplied oxidant. The most common oxidant is the O₂ molecule itself, either from the (enriched) air or in the pure form, but also steam and CO_2 can act as oxidants:

$$C(s) + 1/2O_2 \longrightarrow CO \qquad \text{partial oxidation reaction}$$

$$CO + 1/2O_2 \longrightarrow CO_2 \qquad \text{combustion reaction}$$

$$(2.3)$$

$$O + 1/2O_2 \longrightarrow CO_2$$
 combustion reaction (2.4)

$$H_2 + 1/2O_2 \longrightarrow H_2O$$
 combustion reaction (2.5)

• gasification / reforming: this step will proceed only when there is (local) depletion of oxygen, therefore it does not apply to combustion processes with sufficient excess air. Opposite to the oxidation reactions, most gasification and reforming reactions are endothermic (the water-gas shift reaction, Equation 2.8, being an exception), therefore it is necessary to provide the required amount of heat to maintain the desired gasification temperature. In the "direct gasification" concept this is achieved by supplying more oxygen so the heat of combustion of the oxidation reactions will balance the heat required by the reduction reactions (plus the heat losses of the gasifier). In the "indirect gasification" concept, the heat from outside the gasification reactor is usually transferred by a circulating heat carrier.

| $CH_4 + CO_2 \longrightarrow 2CO + 2H_2$ | dry reforming reaction (2.6) |
|--|---|
| $CH_4 + H_2O \longrightarrow CO + 3H_2$ | wet reforming reaction (2.7) |
| $CO + H_2O \longrightarrow CO_2 + H_2$ | water-gas shift reaction (2.8) |
| $C(s) + H_2O \longrightarrow CO + H_2$ | water-gas reaction (2.9) |
| $C(s) + CO_2 \longrightarrow 2CO$ | Boudouard reaction (2.10) |
| $C(s) + 2H_2 \longrightarrow CH_4$ | methanation (hydrogasification) (2.11) |

As shown in Figure 2.6, in a Fixed Bed reactor (discussed in Section 2.2.3) the location of different fuel conversion zones described above can be identified quite clearly, as in that process the (back-)mixing effects are insignificant. However, in a Fluidized Bed (see Section 2.2.4), due to intense mixing causing high heat and mass transfer rates between the reactants, the locations of the reaction zones will depend on the geometry of the reactor and the distribution of the feed points. Typically the engineering will aim to realize the char combustion zone close to the oxidant feed point(s), in order to increase the carbon conversion efficiency and generate the heat to drive the gasification reactions, and also to minimize the negative impact of partial oxidation on the cold gas efficiency.

2.2.3 Fixed Bed reactor

The two major kinds of fixed bed gasifiers, also known as "moving bed gasifiers", are updraft and downdraft reactors. The names are based on the directions of the flows of the fuel and the oxidant (either co- or countercurrent).

2.2.3.1 Updraft gasifier

In the updraft (counter-current) gasifier the feedstock and the oxidant (e.g., air or steam) flow in opposite directions. Biomass enters from the top and gasifying agent from the bottom. In Figure 2.6 (top), typical zones of an updraft gasifier are shown. The biomass moves down through a drying zone (100 $^{\circ}$ C), followed by a pyrolysis zone (300° C) where char and gaseous species are produced. Char continues to move down to react in the gasification / reforming zone (900°C) and finally it is combusted in an oxidation zone (1400°C) at the bottom of the gasifier by the incoming gasification agent [21]. The gaseous pyrolysis products are carried upwards by the upflowing hot gas stream. As can be seen from the figure, the product gas consists mainly of these pyrolysis products and the products of char oxidation that pass over a relatively cold drying region. The tar in the vapor either condenses on the relatively cold descending fuel or is carried out of the reactor with the product gas; hence the high tar yield of this type of gasifier, even up to 100 g m^{-3} . The condensed tar is recycled back to the reaction zone, where it is further cracked to gas and soot. Most of the tar present in the product gas must be removed for any engine, turbine or synthesis application [122]. On the other hand, direct heat exchange with the entering feed and therefore the low gas exit temperature is beneficial for the thermal efficiency of the process. Another advantage of the updraft gasifier is its relatively low sensitivity to the amount of the ash in the fuel. This is caused by the fact, that the highest temperature is achieved at the bottom of the reactor, close to the ash discharge point. Therefore there is little risk of the fusion of soft, sticky ash or solidification of slag and subsequent blockage of the reactor when proceeding to the zone with a lower temperature, as it is the case in a downdraft fixed bed



Figure 2.6: Fixed Bed Updraft (top) and Downdraft (bottom) reactor schematics with the indication of the different reaction zones. Also the trends of the temperature profile and the concentration of pyrolysis products in the gas phase are shown. Adapted from [12] and [77]

reactor. Furthermore, the updraft gasifiers have simple construction and theoretically there is little scaling limitation, however, there have been no very large updraft biomass gasifiers built [21]. Probably the mostly well-known commercial application of the updraft gasifier is the Harboøre project where the produced tar from the updraft gasifier is stored for peak load CHP operation [158]. Nevertheless the process is not considered relevant for the production of liquid transportation fuels from biomass.

2.2.3.2 Downdraft gasifier

In the downdraft (co-current) gasifier, the fuel and the product gas flow in the same direction. This flow can be directed up or down, although, most co-current gasifiers are of the downward flow type [117]. As can be seen in Figure 2.6 there is a constriction (throat) where most of the gasification reactions occur. The reaction products are intimately mixed in the turbulent high-temperature region around the throat, which aids tar conversion. Some tar conversion also occurs below the throat on a residual charcoal bed, where the gasification process is completed [21]. This configuration produces a relatively clean gas – less than 500 mg m^{-3} (STP) of tar is feasible with a carefully designed throat [12, 77]. Due to the low tar content in the gas this technology is often applied for small scale electricity production with an internal combustion engine [117, 21]. The fraction of fines (here: particles smaller than ca. 1 cm) in the feedstock should be low for this type of gasifier. The upper limit of the feedstock size is related to the size of the throat, and values of 30 cm in the longest dimension have been reported [21]. The size of the throat also forms a limitation for the scale-up process, and therefore the downdraft gasifier is not suitable for the implementation in a large-scale plant. Finally, due to the arrangement of the reaction zones there will be a limit to the amount of the ash in the fuel. High local temperatures in the oxidation zone could cause the melting of some of the ash constituents and the subsequent fusion of the melt to bigger lumps upon cooling in the gasification zone. These lumps would then obstruct the overall flow of the solids and the discharge of the ashes at the bottom of the reactor.

2.2.4 Fluidized Bed reactor

The principle of fluidization is the foundation of the fluidized bed reactor. In such a reactor the fuel together with inert bed material behaves like a fluid. This behavior is obtained by forcing a gas (fluidization medium) through the solid inventory of the reactor [102, 11]. Air, steam, steam- O_2 mixtures are examples of commonly used fluidization media. Silica sand is the most commonly used bed material, but using other bulk solids, especially those that exhibit catalytic action in the process can be beneficial; see Section 2.3.2. Depending on the velocity of the fluidization medium in the reactor, the fluidized bed reactors are divided in bubbling fluidized beds (BFB) and circulating fluidized beds (CFB).

Bubbling beds operate at relatively low gas velocities (typically below 1 m s⁻¹). while the circulating fluidized beds operate at higher gas velocities (typically 3– 10 m s^{-1}), dragging the solid particles upwards with the gas flow. These particles are separated from the gas in the cyclone and recycled to the bottom of the fluidized bed. In both cases most of the reactions during the conversion of a fuel into a product gas take place within the dense bed region (bubbling bed); to a lesser extent they continue in the freeboard (tar conversion) [21]. The inert bed enhances the heat exchange between the fuel particles, and therefore a fluidized bed can operate under nearly isothermal conditions. The maximum operating temperature is limited by the melting point of the bed material and will typically lie between 800 and 900°C. At these relatively low operating temperatures and also relatively short gas residence times the (slow) gasification reactions do not reach their chemical equilibrium if no catalyst is applied. This is the reason for the presence of the hydrocarbons (tar, methane) in the product gas; the tar production falls between that of an updraft and downdraft fixed bed gasifier. The conversion rate of the feedstock is typically high.

Due to their geometry and excellent mixing properties fluidized beds are very suitable for scaling up. The energy throughput per unit of reactor cross-sectional area is higher for a CFB than for a BFB. Both configurations can be operated under pressurized conditions, which will further increase the throughput, and will also be beneficial when the downstream process requires a pressurized input stream, as for instance in the case of Fischer-Tropsch synthesis. Intense mixing also allows the reactor to accept a wider particle size distribution of the fuel feed, starting already from relatively fine particles. Furthermore, in contrast to other reactor systems presented here, the fluidized bed gives the possibility for the use of additives, e.g., for the in-situ removal of pollutants (like sulphur) or the primary measures to increase tar conversion.

The weakest point of the fluidized bed technology emerges when fuels with high content of ash, and alkali metals in particular, are applied. When the fraction of alkali metals in the fuel is high, those compounds can form eutectics with silica present either in the bed material, or in the fuel ash itself. The presence of chlorine amplifies this effect. Those eutectics have melting points that are considerably lower than that of pure silica. Therefore they will start to melt at process temperature, likely causing stickiness of the particles, that eventually will lead to the formation of bigger lumps ("agglomerates"). Their presence will dramatically change the hydrodynamics of the reactor, ultimately leading to "defluidization" and necessary shut-down of the reactor. Those phenomena are discussed further in Section 2.3. Nonetheless, by applying proper countermeasures, the fluidized bed will still be able to accept fuels with an ash content higher than those allowable for a fixed bed reactor [12]. Van der Drift et al. [168] tested ten residual biomass fuels (from demolition wood to sewage sludge and verge grass) in an air-blown CFB gasifier and concluded that this technology seems to be very suitable for the gasification of all types of different biomass materials.

Depending on the way that heat is supplied for the gasification reactions, the (circulating) fluidized beds can be divided into the directly heated and indirectly heated units. In the directly heated concept, a part of the product of the gasification process is burned directly in the gasification reactor. Obviously the designs should be optimized for the maximal interaction of the entering oxygen with the recirculated char, however, due to the intense mixing it is nearly inevitable to avoid the combustion of some fraction of the product gas as well. To overcome this, and to avoid the dilution of the product gas by nitrogen but without the use of pure oxygen instead of air, the indirectly heated gasifier concept has been developed. The principle of operation is based on two interconnected reactors: usually a steam-blown gasification reactor and an air-blown combustion reactor. The bed material and the char are transported from the gasification reactor to the combustion reactor where char is oxidized with air, generating the necessary heat for the gasification part. The heated bed material is recirculated back to the gasification reactor to complete the cycle. Several implementations of that concept exist. The most well-known are the Battelle's Silvagas[®] process, the Fast Internally Circulating Fluidized Bed (FICFB) developed by TU Vienna, and the Milena gasifier developed by ECN. The schematics of the classical directly heated CFB as well as of the three indirectly heated gasifier concepts are presented in Figure 2.7. At present it is difficult to state which process is better. Certainly, there is more practical experience with the classical CFB concept, and also with its operation under pressurized conditions. The gas produced using the indirectly heated CFB is richer in hydrogen and there is less CO₂ present, but the content of methane is also higher. Together with the relatively low product gas temperature (circa 650°C compared to 850°C in a directly heated gasifier) this process seems to be more suitable for tar removal by scrubbing and subsequently the production of substitute natural gas (SNG), while the directly heated concept is likely to be followed by methane and tar reforming and the production of secondary liquid energy carriers. Both reactor concepts and various combinations of downstream processes are now subject to intense investigations.

2.2.5 Entrained Flow reactor

The entrained flow reactor (EFR) is well-known in coal combustion processes. In this type of reactor no inert added solid material is present, like it is the case in a fluidized bed. The feedstock is fed co-currently with the oxidant agent by means of a burner and the flow velocity is high enough to establish a pneumatic transport regime. EFR gasifiers operate at much higher temperatures than the previously discussed reactors (1200–1500°C). This allows thermal conversion of tar and also of methane [21], so the composition of the product gas is very close to the chemical equilibrium composition, and therefore also close to syngas quality. However, when coal is used as a fuel it is crushed into a powder (\approx 50 μ m diameter) before feeding. This is immediately its biggest disadvantage



Figure 2.7: Different CFB gasification concepts: (a) classical, directly heated [121]; (b) indirectly heated dual CFB, Battelle [121]; (c) indirectly heated FICFB, TU Vienna [100]; (d) indirectly heated Milena, ECN [166]

with respect to a biomass application, as the size reduction of biomass is a very costly process in terms of energy, as stated earlier. In addition, due to the spread in particle size distribution some methane can still be expected when biomass is gasified [12]. This drawback can be partially overcome by pre-treating the biomass in the process of torrefaction [132]. However, this is a relatively novel technology and has only recently started to be demonstrated on a pilot scale [94]. In addition, in order to reach high gasification temperature more product gas needs to be oxidized, which will reduce the cold gas efficiency [96]. Finally, extreme reaction conditions pose problems to materials selection. Large quan-

tities of molten ash (slag) will be formed during the gasification of all kinds of biomass, except for relatively clean wood, and the presence of high amounts of potassium is a concern with respect to the life of the refractory lining [79].

2.2.6 Supercritical water gasifier, heat pipe reforming, chemical looping and other novel processes

The reactors described in the paragraphs above represent technologies that over the past decades gained an established place among the solid fuel conversion processes. Nonetheless, continuously new technologies are being developed, searching for the solution of the problems known from the state-of-the art. Below three of these novel technologies are highlighted.

2.2.6.1 Supercritical water gasification (SCWG)

As the name already suggests, this process is carried out under supercritical conditions of water, i.e., a temperature over 374° C and pressure higher than 221 bar. Under these conditions biomass is rapidly decomposed into syngas components at high conversion efficiency – values close to 100% are reported [111, 71]. The acceptance of very wet biomass (such as sewage sludge or cattle manure) and the fact, that the product contains relatively low concentrations of tar and char makes SCWG an interesting process for further development. For SCWG process to attain a reasonable thermal efficiency the system must recover enough heat to obtain the supercritical state. This is one of the challenges for the development of this process, as preheating of the slurry above 525 K will initiate its decomposition, which may cause plugging and/or fouling upstream the reactor [47, 62]. Furthermore, the issue of construction materials requires attention as extensive corrosion of the reactor walls have been reported when using nickel alloys [5]. Although extensive research efforts on SCWG have been undertaken in recent years, this process is currently still in a R&D stage.

2.2.6.2 Heatpipe reformer

The heatpipe reformer is a type of indirect gasifier where the heat necessary for the endothermal gasification reactions is transferred from the char oxidation zone by means of the heatpipes. A heatpipe is a modularly constructed pair of heat exchangers (a "pipe") using an internally circulating medium to transfer the heat from the input side to the utilization side, see Figure 2.8. It can be seen as an equivalent of an indirect fluidized bed gasifier presented earlier (see Section 2.2.4), but without the circulation of the bed material over the gasification and combustion part. As in that process, the gasification reactor (a fluidized bed) can be operated using steam only, while the necessary heat is provided from an "external" source (allothermal reactor principle). Also in the heatpipe reformer the heat is generated by the oxidation of char that has not been gasified in the gasification step [89]. An important advantage of the heatpipe reformer is the possibility of heat coupling with an SOFC that requires external cooling in order to maintain the operational temperature and consequently its conversion efficiency. However, the scale-up of this type of reactor to a megawatt-scale and larger is economically not justifiable (there being better alternatives in that plant size region), therefore its application is limited to decentralized CHP systems, and this makes it less relevant for BTL processes.



Figure 2.8: The operational principle of a heat pipe (from [89])

2.2.6.3 Other indirect gasification processes

In view of the potential benefits from the indirect gasification processes, of which the ability to use the air for oxygen supply without diluting the product gas with nitrogen is the most pronounced one, a number of alternative processes have been under investigation. Some of them turned out to be not attractive enough, due to various problems (design, technical, operational, etc.) and their development has been discontinued. Examples include the Agip-Italenergie process where the heat was transferred between the gasification and the oxidation zone through the reactor wall separating the two vessels, and the Lund University gasifier which was constructed of three concentric tubes, to separate the steam gasification zone and the char combustion zone [12].

An interesting development of the indirect gasification principle is the use of reactive heat carrier instead of an inert heat carrier, mostly being the bed material, or a system similar to a heatpipe as described in previous sections. Early developments of such process combined with gasification reported by Beenackers [12] include for example the EXXON Research Oxygen Donor Process, where the heat and the oxidant are carried to the gasification zone by means of calcium sulphate (CaSO₄); no steam being used in this process. Although no results or indications of the further development of this process have been found in the

literature, this kind of operation recently started to regain recognition, and is now being referred to as "Chemical Looping Combustion" (CLC). In this process the oxygen is being transferred from the air to the gaseous fuel via a metal oxide that is exothermic during its reduction (e.g., iron, copper or nickel). The advantage of CLC is the fact that, just like Solid Oxide Fuel Cell, it is a combustion technology with inherent CO_2 separation [28, 48, 98]. As this process is applied *after* the gasification step, it is not discussed here in more detail.

Another improvement proposed for the indirect gasification systems is the Adsorption Enhanced Reforming (AER) process. Here, again a solid is used to influence the gas composition, not in a catalytic way but through the adsorption of one of the gas constituents, for example CO_2 by CaO. The three main advantages of such a process are the shifting of the reaction coordinate of the water-gas shift reaction to the hydrogen side and therefore an increased hydrogen yield, the integration of the heat of adsorption and the heat of the water-gas shift reaction (both are exothermic), and the possibility for in-situ CO_2 capture [124, 125, 1, 176]. The process of CO_2 adsorption by CaO is of course not new [38], and although this application is very promising the fact that this process requires relatively mild gasification conditions (temperature of approximately 700°C, may lead to an increased tar yield or reduced carbon conversion and cold gas efficiency. This will need to be verified and eventually solved by further R&D efforts.

2.2.7 Optimal choice for industrial scale gasification process: Fluidized Bed technology

In the previous paragraphs several gasification technologies have been introduced. Some of them are still in the R&D phase, whilst others are already at a more advanced stage and therefore more viable for industrial application as intended in this review paper. Each of these technologies have certain characteristics, which make them more or less suitable for the generation of highquality product gas, or preferably even syngas. None of these technologies are free from drawbacks in that respect, and consequently the choice of the most suitable gasification system will be based on a compromise, depending on the application of the gas. Table 2.5 gives an overview of the main characteristics of the above-mentioned reactor types. Returning to the criteria listed at the beginning of this section and applied to the process of syngas production for the synthesis of liquid biofuels, the most suitable technology can be identified as presented in Table 2.6. Nonetheless, the numbers provided by the equipment manufacturers show that 75% of the gasifiers offered commercially were of the downdraft type, 20% of the (circulating) fluidized bed type and 2.5% were of the other types [22].

| ypes (adapted from [97]) | B EF | | 00 1300-1500 | am, O_2 air | itical very fine particles | ediate none | 100% 100% | 20 >100 | 2- | | gh high | ediate very complex | | |
|--------------------------|-------|-----------|-----------------------------|-------------------|----------------------------|--------------|-------------------|-------------------------|---------------------------------|---------------|------------|---------------------|--|--|
| reactor t | CF | | 6> | air, stea | less cr | interm | >9(| >2 | Ω I | | βid | interm | | |
| shed gasification | BFB | | <900 | air, steam, O_2 | less critical | intermediate | >90% | 10 - 100 | 1.2 - 1.6 | | moderate | intermediate | n [155] | |
| e five establis | Bed | updraft | 200-900 | air | critical | very high | near 100% | <20 | 1–2 | | low | very easy | wer input; ^c fror | |
| cteristics of th | Fixed | downdraft | 700-1200 | air | very critical | low | $93-96\%^{a}$ | \dot{c} | 1–2 | | low | easy | of fuel thermal po | |
| Table 2.5: Main chara | | | Process temperature [°C] | Oxidant | Feedstock size | Tar yield | Carbon conversion | Scale ^b [MW] | Thermal throughput ^c | $[MW m^{-z}]$ | Investment | Control | a from [27] page 8; b in terms | |

Table 2.6: Response of the main characteristics of the established conversion processes to application criteria related to the syngas production for the synthesis of liquid biofuels. Symbols used: + (suitable), 0 (less suitable), - (not suitable)

| | Suitability | y for BTL applic | ation | |
|---|----------------|------------------|-----------|----|
| Criterion | FB (downdraft) | FB (updraft) | BFB / CFB | EF |
| Scale of operation | - | 0 | + | + |
| Feed flexibility | - | 0 | + | - |
| Sensitivity to ash amount and composition | 0 | + | 0 | 0 |
| Tar yield | + | - | 0 | + |

The assessment of gas quality is, however, also very important, as the product gas will be used as a feed for certain downstream process. Evaluating the configuration of biomass gasification and production of liquid fuels, requirements for the intermediate gas cleaning will need to be set up to comply with the impurities. Table 2.11 shows an overview of such requirements for the production of FT-diesel and methanol (an intermediate for DME production).

On the basis of the information presented above it can be concluded, that at present the fluidized bed reactor complies the best with the requirements for the production of bio-syngas for the synthesis of liquid transportation fuels via thermochemical gasification route. Obviously, the state-of-the art is changing continuously and new technologies are emerging, nevertheless the amount of experience with the fluidized bed technology and its characteristics make it a mature and reliable technology. What is lacking is the final technology push to solve the remaining, but important problems, and a breakthrough in industry's hesitation to support the construction of large-scale fluidized bed gasification demonstration units.

2.3 Fluidized Bed biomass gasification process

In the previous section the motivation was presented to employ fluidized bed technology for the production of bio-syngas. Main characteristics of that and other possible thermochemical biomass conversion systems were presented and compared. In this section deeper background information on the fluidized beds is presented, including their principle of operation and the effect of various process parameters on the product gas quality. The presented information is based on a review of the relevant scientific publications supported by own experience and fact-findings.

2.3.1 Hydrodynamics and fluidization regimes

When a gas is blown upwards through a batch of bulk material, the behavior of the inventory will differ depending on gas velocity. Figure 2.9 shows the possible flow regimes, arranged by the increasing superficial gas velocity. The fluidization of particles is only possible, when the drag of the gas stream on the particles at least equals the gravitational force on those particles less their buoyancy. This is achieved when the gas reaches the so-called minimum fluidization velocity. The superficial gas velocity being higher than the minimum fluidization velocity is the basic and primary condition to achieve fluidization. The formation of gas bubbles in the bed, while the bed surface is still clearly visible will indicate the regime of bubbling fluidization; further increase of the fluidization velocity will lead to a turbulent bed, which is a highly expanded and violently active regime. Particles are thrown into the freeboard and the surface of the bed will still exist. but will be highly diffused [11]. Reaching of the so-called transport velocity is the condition to enter the fast fluidization regime. This regime can be described as a nonuniform suspension of slender particle clusters moving up and down in a dilute, upwardly flowing gas-solid continuum [11]. Circulating fluidized beds operate in the regime of fast fluidization, while the bubbling fluidized beds operate in the regime of bubbling fluidization. This difference has a number of consequences for the the gasification process, depending on which type of the fluidized bed reactor is being used. Some characteristics of the BFB and the CFB gasifiers have already been introduced in Table 2.5 to show the main differences between the reactor types that could possibly be used for gasification of biomass. A more detailed comparison between industrial-size bubbling and circulating fluidized beds is given in Table 2.7. From the table it is clear that the CFBs have slightly better characteristics (higher carbon conversion, less tar in the product gas, higher fuel flexibility, better scale-up potential) compared to the BFBs. Therefore for an advanced application like the large-scale production of secondary fuels from biomass a CFB will be the choice of the reactor, especially when a directly heated gasifier is to be designed. The indirectly heated gasifiers have also been designed as CFBs with BFB features (CFB-BFB hybrid), as shown in Figures 2.7c and 2.7d.

2.3.2 Main process parameters

Given a fluidized bed gasifier, the operator can alter a number of input variables or parameters to influence the process and the output variables. Table 2.8 shows the main input variables and the variables they affect. The definitions of the calculated process parameters reported in the table are given below, while the process variables indicated in bold face are discussed in more detail in the subsequent paragraphs. The symbol \dot{m}_i indicates the mass flow of a component denoted by the subscript.



Figure 2.9: Visualization of different vertical gas-solid flow regimes [102]

Stoichiometric oxygen ratio (λ):

$$\lambda = \frac{\text{external } O_2 \text{ supply / fuel supply } (d.a.f.)}{\text{stoichiometric } O_2 \text{ requirement / unit of fuel input } (d.a.f.)}$$
(2.12)

Steam-to-biomass ratio (SB):

$$SB = \frac{steam \ mass \ flow}{fuel \ feed \ flow}$$
(2.13)

Modified steam-to-biomass ratio (SB *):

$$SB^* = \frac{steam\ mass\ flow + fuel\ moisture\ mass\ flow}{dry,\ ash-free\ fuel\ feed\ flow}$$
(2.14)
| Property | BFB | CFB | References |
|-------------------------|---------------------|--------------------------|------------|
| Fluidization regime | bubbling bed | fast bed | [11] |
| Mixing | very good | excellent | [11] |
| Solids feed flexibility | fines not desirable | fine & coarse material | |
| (size) | | | |
| Tar yield | avg.: 12 (moderate) | avg.: 8 (lower than BFB) | [11, 155] |
| $[g m^{-3} (STP)]$ | | | |
| Carbon conversion | lower than CFB | typically 88–96 | [167] |
| [%] | | | |
| Carbon loss by en- | significant | low | [106] |
| trainment | | | |
| Particle concen- | average: 4 | average: 20 | [155] |
| tration in the gas | | | |
| $[g m^{-3} (STP)]$ | | | |
| Bed height / fuel | 1–2 | 10–30 | [11] |
| burning zone [m] | | | |
| Therm. throughput | 1.2-1.6 | 5–7 | [155] |
| $[MW m^{-2}]$ | | | |
| Process control | less complex | more complex | |
| Scale-up potential | good | very good | |

Table 2.7: Overview of the differences between a bubbling and a circulating fluidized bed gasifier, constructed on an industrial scale

Carbon conversion (CC):

$$CC = \left(1 - \frac{\dot{m}_{C,residue}}{\dot{m}_{C,feed}}\right) \cdot 100\%$$
(2.15)

Cold Gas Efficiency (CGE):

$$CGE = \frac{\sum \dot{m}_i \cdot LHV_i}{\dot{m}_{fuel} \cdot LHV_{fuel}}$$
(2.16)

Superficial fluidization velocity (u_{fl}) :

$$u_{fl}[m \ s^{-1}] = \frac{actual \ volumetric \ feed \ gas \ flow \ rate}{cross-sectional \ area \ of \ the \ bed}$$

$$= \frac{\dot{Q}_{gas} \ [m^3 \ s^{-1} \ (STP)] \cdot T_{process}[K] \cdot 1.013[bar]}{A_{bed}[m^2] \cdot P_{process,abs}[bar] \cdot 273.15[K]}$$
(2.17)

Table 2.8: Main process variables and parameters, and their interactions assuming only one variable changing (increasing) at a time. Variables in bold face are discussed in more detail in the text. Symbols used: + (increase), - (decrease), OPT (optimal range exists to maximize or minimize the desired effect), x (other effect, see footnote)

| | | Ι | nput | | | Output | |
|----------------------|-----------|----|---------------------------|------------------|------------------|------------------|------------------|
| Variable | λ | SB | \bar{u}_{fl} , τ^a | \mathbf{T}^{b} | CC | CGE | Tar yield |
| Biomass feed rate | _ | _ | | _ | _ | + | + |
| Oxygen feed rate | + | | + | + | + | - | + |
| Steam feed rate | | + | + | _ | OPT | OPT | OPT |
| Process pressure | | | _ | | _ | + | _ |
| Kind of bed material | | | \mathbf{X}^{c} | | \mathbf{x}^{e} | \mathbf{x}^{e} | $_d$ |
| Used additive | | | | | \mathbf{x}^{e} | \mathbf{x}^{e} | \mathbf{X}^{f} |

^a gas residence time

^b only if the temperature cannot be controlled independently using, e.g., external electrical heating

 c no direct influence, but can impose constraints on the minimum / maximum velocity applied

 d catalytic bed materials will have (large) influence; inert bed material will have no effect

 $^{e}\,$ possible influence, effect depending on the kind of solid used

^f catalytic additives will have (large) influence, agglomeration counteracting ones less or none

2.3.2.1 Fluidization media

The stoichiometric oxygen ratio is commonly used for the identification of different "oxidation regimes" during a thermochemical fuel conversion process. This parameter, also called "equivalence ratio", "air factor" or "air ratio", is represented by the symbol λ (lambda). From the formula given in the previous paragraph it is clear that $\lambda > 1$ refers to combustion processes, $\lambda = 0$ to pyrolvsis, and $0 < \lambda < 1$ to gasification, see also Table 2.4. With the aim to produce a gas suitable for transportation fuels synthesis application, high yields of H₂ and CO are required; this can be achieved in low lambda value regions. On the other hand, partial oxidation of the fuel is necessary to generate heat to drive the mostly endothermic gasification reactions and allow the reactor to work in the autothermal mode. The most common fluidization and oxidation medium used in gasification processes is air. Although air is cheap and abundant, the fact that the nitrogen present in air cannot be easily separated from the product gas is a significant drawback of that gasification medium. Air gasification produces gas of low calorific value, and approximately 50% of the volume of the product is the inert nitrogen. Therefore it would be better to use a combination of gases that will either react to form useful products or will be easily separated from the final product stream. The gasification agent will typically consist of a gas that provides the necessary oxygen for partial oxidation of the fuel and a gas that will act as a moderator / fluidization medium, unless the heat to drive the strongly endothermal reactions is supplied externally, e.g., from the combustion of char, as in a dual (or: indirect) gasifier – then gasification with pure steam is possible. For a direct gasifier a mixture of pure oxygen and steam fulfils the criteria mentioned above and both gases are very common in process industry. Besides acting as a fluidization medium steam is also a reactant in many gasification reactions, therefore its presence and amount have an influence on the product gas composition. The amount of steam supplied to the process is often related to the amount of biomass feed in a so-called steam-to-biomass ratio (SB). In the literature it is not often mentioned whether the fuel feed is given on an "as received" or "dry (and ash-free)" basis. However, in case of fuels with higher moisture and / or ash content, the difference in the calculated SB will be significant, depending on the choice of the denominator. Additionally, the moisture present in the fuel should not be neglected in the calculation of the SB, as the resulting steam will be the first to interact with the organic part of the fuel upon devolatilization in the reactor. Also in case of fuels with higher moisture content the amount of steam that originates from the fuel will not be negligible compared to the overall steam input. Considering the above, a modified steam-to-biomass ratio (SB*) is proposed. Regarding the effect of the fuel moisture van der Drift concluded that the water content of raw biomass will be one of the most dominant fuel characteristics influencing carbon conversion, cold gas efficiency and the heating value of the gas [168].

The effect of λ on the main output parameters is depicted in Figure 2.10. Higher availability of oxygen will lead to increased combustion of the product gas and char, and therefore to an increase of the reactor temperature and the carbon conversion. However, the yield of the combustible products and thus also the cold gas efficiency will decrease. Tar yield will decrease with increasing λ , partially due to oxidation reactions and partially due to enhanced tar cracking caused by the increased process temperature. Considering the above, the choice of λ will be a compromise; the typical values used in fluidized bed gasification processes vary between 0.2 and 0.4.

A similar consideration applies to the SB value. Here, however, a larger variation in the suggested optimal values has been found in the literature. Table 2.9 shows the results of the investigations on the effect of SB on the gasification process. Most researchers concluded that choosing the SB value between 0.3 and 1.0 will have a positive effect on carbon conversion, cold gas efficiency, hydrogen yield and tar reduction. However it has to be stated that all the investigations reported in Table 2.9 have been carried out using BFBs. CFBs operate at a higher fluidization velocity, and therefore a higher steam input may be needed to achieve this. Nonetheless, the higher the SB ratio the more energy is required to heat up the steam to process temperature, which at some point will cancel the positive effect on the CGE. In addition, higher values (SB >1) lead to a high



Figure 2.10: Effect of the variation of λ on the main process parameters

amount (>60% by volume) of unreacted H_2O in the product gas, which, even when the recycling via condensation/vaporization/reheat is applied, will cause a significant drop in the thermal efficiency of the whole process [33]. Also, the conversion of H_2O decreases with increasing SB ratio, and is typically limited to approximately 10% [33, 169].

The increase in the hydrogen yield due to steam addition cannot be explained solely by the water-gas shift reaction, as the changes in H_2 and CO concentrations do not match. It is highly probable that the added steam acts as an oxygen donor for the oxidation of CO, char and perhaps also tar. This could be confirmed by the results presented in [24], which show a slightly increased carbon conversion and a slightly decreased cold gas efficiency when comparing the extreme SB ratios investigated there.

Kinoshita et al. [95] performed some tests in an air-blown bench-scale FB gasifier to test the influence of process temperature, equivalence ratio and residence time on the formation of tar species. Tar yield, expressed in gram per kilogram of dry fuel showed a maximum at the temperature of ca. 750°C and decreases with increasing temperature ($\lambda = 0.22$, $\tau = 3.75$ s). Tar yield also decreased with increasing equivalence ratio (range: 0.22–0.32) at *constant* temperature, while the influence of the residence time in the studied interval (3.0–5.0 s) was negligible. Next to the total (measurable) tar, the yields of different tar classes were studied. The increase in temperature caused a large increase of the benzene fraction, while other monoaromatics decreased. At the same time naphthalene fraction increased, just as the fractions of 3 and 4-ring compounds, but the fraction of 2-ring compounds other than naphthalene decreased in the studied temperature range (700–900°C). The oxygenated compounds (e.g., phenol) were absent in the temperatures above 800°C. A very similar trend is observed for an increasing equivalence ratio at *constant* temperature, except the

fact that here also the 2-ring compounds other than naphthalene showed an increasing trend. The effect of the residence time on the tar composition is much less pronounced than that of the temperature or the equivalence ratio; mainly a linear decrease of monoaromatic compounds other than benzene, and an increase of 3- and 4-ring compounds at higher residence times (>4.5 s) were observed. It is very likely that the influence of the residence time would be much more pronounced at lower values ($\tau \approx 1$ s).

| Lit. reference | Test equip- ment | Range | Reported optimal range | Remarks |
|----------------|------------------------|----------|------------------------------|---|
| Corella [33] | BFB | 0.2–2.0 | 0.40-1.0 | values higher than 1.2–1.5 not rec- ommended |
| Campoy [24] | BFB | 0-0.63 | 0.3–0.4 | slight positive effect on CC and CGE |
| | | | | increased H ₂ yield from 8.7 to $13.3\%_{vol}$ and 17.8 to 27.7 $g kg_{biomass,daf}^{-1}$ decrease of the total yield of main combustibles from 555 to 507 $g kg_{biomass,daf}^{-1}$ |
| Franco [60] | BFB | 0.4–0.85 | 0.6–0.7 | maximum for CC, gas yield and H_2 concentration in the gas |
| Gil [63] | BFB | 0.3–1.3 | 0.50–0.75 | max. H_2 concentration of 29% _{vol,dry} very difficult to obtain tar concentration below 5–10 g m ⁻³ _{n,dry} |

Table 2.9: The results of several investigations related to SB

2.3.2.2 Temperature

Temperature is an important process parameter in thermochemical fuel conversion. The temperature range relevant for biomass gasification in a fluidized bed lies between approximately 650° C and 950° C. Higher temperature will increase the carbon conversion efficiency and reduce the amount of tar produced, however, in the case of a fluidized bed reactor the maximum operating temperature is limited by the melting point of ashes or of the bed material. Additionally reactor construction materials can become an issue. In practice the reaction temperature is directly linked to λ , as for a higher temperature more product gas needs to be oxidized, which in its turn reduces the cold gas efficiency, as explained earlier. However, in (small) laboratory test rigs temperature

can often be controlled by installed external heating elements, and therefore be independent of λ . This is not only interesting, but also necessary, as due to relatively larger heat losses in a small laboratory test rig it may be impossible to achieve the same temperature at a certain lambda value as in a big industrial unit solely by autothermal operation. As most gasification (equilibrium) reactions are endothermic their reaction coordinate will increase with higher gasification temperature. One of the important exceptions is the water-gas shift reaction, which being slightly exothermic will shift to the CO+H₂O side as the temperature increases. This effect is, however, often of lower importance than the high temperature necessary to reduce the amount of tar and to achieve high carbon conversion.

2.3.2.3 Pressure

Although pressurized operation puts significant additional requirements on the design and operation of a gasifier, it is often desirable. Firstly, higher pressures result in lower volumetric gas flow rates, which means smaller size of the reactor and downstream gas cleaning and upgrading equipment. Secondly, many downstream processes using the produced syngas require pressurized conditions (e.g., Fischer-Tropsch process, gas turbines), and the fact is that it is easier to pressurize the reactants separately (lock-hopper system for the solids, compressors for the gases) than to compress hot, combustible, hydrogen-rich product gas compensates the technical and operational complications [12]. Compressing the product gas will require removal of tar and moisture below their dew points to avoid condensation during compression. Also the cooling of the gas to approximately 90°C is required [7]. However, process improvements are still needed, for instance in the high-pressure feeding systems, although commercially available units exist [161].

Pressurized conditions will also influence the process of gasification. The equilibrium reactions that are not equimolar (reactions 2.6, 2.7, 2.10, 2.11) will be driven towards the condition with the lowest volume (Le Chatelier's principle). In the list of the main gasification reactions, three out of four non-equimolar reactions involve methane, therefore the methane yield from the pressurized gasification process will be higher than from an atmospheric process performed at otherwise similar conditions. The tar yield will, however, go down with increasing pressure; this is due to the fact that during the pyrolysis phase the recarbonisation of the tar precursors will be more pronounced as the pressure increases. Some of the carbon formed will subsequently react to methane, but generally the carbon conversion will also decrease with increasing pressure [41].

Additional benefits from the pressurized conditions could be achieved by operating the gasifier under pressure conditions that favor the recarbonization of CO_2 on earth-alkaline species, typically calcium. Under atmospheric gasification conditions the typical partial pressures of CO_2 would require a temperature well below 800°C to enter the thermodynamic region where $CaCO_3$ is formed.

However, such a low gasification temperature will result in lower carbon conversion and an increased tar yield. By increasing the operational pressure of the gasifier and thus also the partial pressure of CO_2 the typical fluidized bed gasification temperatures can be maintained while benefiting from the CO_2 capture by recarbonization. The enhanced hydrogen production by the adsorption of CO_2 was studied by several authors: enhanced high-temperature WGS [70], adsorption enhanced reforming [124, 125], HyPr-RING (Hydrogen Production by reaction-integrated novel gasification) [107], and also its application for postcombustion CO_2 removal has been investigated [15].

2.3.2.4 Bed materials & additives - catalytic activity on gasification reactions

The main purpose of the presence of the bed material in the fluidized bed is the heat storage and heat transfer between the particles undergoing exothermic processes (chemical reactions like oxidation and water-gas shift) and endothermic processes (drying, pyrolysis, and most gasification reactions). The heat produced during exothermic processes is "stored" (accumulated) in the bed material and due to intense mixing of the bed inventory (fluidization) it is transferred to the processes that require heat input. In this way large temperature peaks in the oxidation zone are avoided and a nearly uniform temperature distribution can be observed in the bubbling zone (BFB) or even throughout the reactor (CFB).

In principle the bed material is assumed to remain inert during the gasification process. To a large extent this is true for the bed material used most often – quartz sand. However, the choice of the bed material can have an important influence on the process if that bed material shows catalytic activity on some of the reactions involved, or its interaction with the fuel constituents results in a considerable change of its physical properties. The former effect is mostly desirable, as in the case of gasification it often leads to the increased conversion rate of tar, leading to an improved gas quality. In the latter case the most often observed effect is called bed agglomeration, which is highly undesirable – this will be discussed in the next section.

Using catalytically active bed materials can significantly influence the gas composition in terms of increased hydrogen yield, and reduced amounts of methane and tar, bringing the gas closer to syngas composition. These materials can also be applied as in-bed additives – an important feature of a fluidized bed. Regarding the tar decomposition, the ability to use metal oxides derived from natural rock minerals in the fluidized bed (as primary tar measures) appears to be more advantageous than the use of (commercial) Ni-based catalyst. This is due to the fact that the loss of solids, and of the fine fraction in particular, is often not negligible in these kind of reactors [29, 114, 40]. Dolomites (CaMg(CO₃)₂), calcites (CaCO₃), magnesites (MgCO₃) and olivines ((Mg,Fe)₂SiO₄) are potentially attractive in-bed additives or even bed materials because they are non-toxic and can be significantly active at high temperatures. The main problem of the minerals mentioned above, with the exception of olivine, is their low attrition resistance and the continuous deterioration of their mechanical strength over the reaction time. In addition, the costs of catalysts are usually high; this is especially true for metal-based catalysts, while the prices of natural rock minerals are often higher than quartz sand, but acceptable. Furthermore, most of the additives have been tested only on (laboratory-)pilot scale, although olivine [80] and magnesite [156] have also been tested in larger plants.

Delgado et al. [45] reported that of the three natural rock minerals applied in the downstream fixed bed reactor for the upgrading of the product gas, calcined dolomite (CaO-MgO) showed the highest catalytic activity on tar cracking, followed by pure calcined magnesite (MgO) and calcined calcite (CaO). Also relatively low deactivation was observed for tar concentrations below 48 g m⁻³ (STP) (which is even higher than the typical tar concentrations measured in reasonably operating (C)FB gasifiers), at temperatures above 800°C, when small particles are applied (d < 1.9 mm) [46]. An additional advantage was the simultaneous coke formation and its elimination by steam gasification, leading to the prolonged lifetime of the catalyst. The integration of the heats of CO₂ adsorption reaction and water-gas shift reaction into the complex network of (endothermal) gasification reactions will lead to the improvement of the product gas in terms of higher hydrogen yield and reduced amount of tar [29, 46, 45, 101, 124, 145]. Hanping et al. [76] performed air-blown biomass gasification tests in a small-scale (ca. 12 kW fuel thermal power input) CFB gasifer with the addition of dolomite, magnesite and olivine, and although they reported a significant reduction (>50%) of tar content in the gas, they did not report any values showing the change in the concentration of the permanent gases, except in the dolomite case where only the concentration of H₂ increased significantly. During the study presented in this book, magnesite used both as an additive and as the bed material in a steam-oxygen blown TUD CFB gasifier (see Chapter 3) showed a positive effect on the conversion of tar and methane, and an increase of H₂:CO ratio. This was presented in detail in [145]; see also Chapter 5.

Devi et al. [51] compared the effect of dolomite and fresh olivine on the conversion of tar, by using these minerals as additives to a sand bed in an air-blown BFB gasifier. Both additives showed a reduced tar concentration in the product gas, as compared to pure sand bed, but the highest tar conversion was achieved with dolomite. The effect of the pre-treatment (calcination at 900°C) of olivine was also investigated, using steam- and dry reforming of naphthalene as the model tar conversion component and reaction [50]. Pre-treated olivine proved to be a significantly more active catalyst under the mentioned conditions than the untreated one. Also the calcination time was observed to play a role with a 30% and 80% increase in naphthalene conversion for 1 hour and 10 hours treatment, respectively. However, under model syngas atmosphere the conversion was lower than only in the presence of steam and CO_2 . This can be attributed to the presence of H₂ and CO in the gas, as these species are known inhibitors

of tar reforming reactions (see also, e.g., [30]). Also the origin of olivine, and more precisely its mineral composition, will influence its activity related to the conversion of tar. Rauch et al. [134] compared the influence of two different kinds of olivine on the tar yield and the gas composition during the operation of the Güssing 8 MW fuel thermal power input CHP demo-plant supported by detailed characterization of the bed material. The researchers came to the conclusion that the presence of free iron oxide outside the olivine structure is very likely a possible requirement for the desired catalytic activity. Siedlecki and de Jong [144] observed the lack of the activity of a certain kind of olivine on tar vield, even despite the calcination pre-treatment at two different temperatures (900 and 1200° C, 10 hours); see also Chapter 4. On the other hand Corella [33] compared the use of different catalytically active bed materials, using the H₂ and tar concentration (both on dry gas basis) as a benchmark for gas composition and gas quality respectively. Based on those experiments it was concluded that olivine is a promising catalytic bed material resulting in a hydrogen concentration varying between 34-52% by volume, while the reported tar content varied between 0.25–1.5 g m $^{-3}$ (STP) [33, 134].

Char, although it is hard to call it an "additive", as it is always present in the bed except during startup, has also been recognized as an important catalyst for the conversion of hydrocarbons – both tar [3] and methane [53]. Detailed comparison of various catalysts for tar conversion showed that the activity of char for naphthalene conversion is even higher than dolomite at 900° C [2]. The high activity of char is partially attributed to the fact that it is continuously activated by steam and CO₂, and above that, there is a continuous supply of fresh char from biomass pyrolysis. However, in order to use char efficiently as an in-situ catalyst the fluidized bed should be designed in a way to allow long char-tar interaction times. In a standard (C)FB this is limited only to the devolatilization phase and the stochastic interaction between upflowing gas and fluidized char particles. Also Brage [20] claims that the holdup of char in the reactor results in the decreased amount of tar in the gas, being a proof of the catalytic activity of char on tar conversion mechanisms. In addition, he states that coal char is more active than biomass char, as higher coal char holdups can be achieved, due to lower reactivity of coal char.

2.3.2.5 Bed materials & additives – agglomeration resistance and counteractions

As already explained in the previous section, in principle the bed material is assumed to remain inert during the gasification process, but its interaction with the fuel constituents may result in a considerable change of its physical properties. This highly undesirable effect is called bed agglomeration. The research performed in this area indicates that bed agglomeration will occur upon the interaction between the silica-containing bed material and the inorganic part of the fuel (i.e., ash), especially if the latter contains high amounts of alkali metals and/or chlorine. During biomass conversion when alkali compounds are released, and also when silica is present either from the bed material or biomass ash itself, then the formation of alkali-silicates (K₂O-SiO₂) can be expected. Those compounds have an eutectic point of about 770°C, while the eutectic point of K₂O-CaO-SiO₂ structures is even lower [9]. Ergudenler [56] found that quartz sand will agglomerate in the presence of straw ash (with 1.2% by weight of K_2O in the dry fuel) at around 800°C, causing defluidization. This has also been observed and investigated by other researchers [65, 56, 108, 64, 175]. From the above it can be concluded that silica-containing bed materials should be avoided when operation with "difficult" biomass fuels is intended. Natural rock minerals, already introduced in the previous section as catalytically active bed materials or additives could be an option here, but their mechanical strength is often much lower than that of silica-based materials and therefore they are very prone to attrition. As an alternative synthetic bed materials (e.g., alumina) could be employed, but their high price - especially important when applied on a larger scale – will be an obstacle here. Therefore the choice of the bed material will be a compromise between mechanical stability, agglomeration resistance, catalytic activity and price.

In case a silica-rich bed material is to be used with alkali-rich fuels the agglomeration problem can be counteracted using in-bed additives. Known additives that are supposed to reduce the agglomeration phenomena are kaolin $(Al_2Si_2O_5(OH)_4)$, calcium oxide, calcium carbonate and bauxite [8]. Introduction of alumina-rich compounds, such as kaolin, may result in the formation of alkalialuminum silicates (K₂O-Al₂O₃-SiO₂), which have a much higher melting temperature than the alkali silicates (K₂O-SiO₂) formed otherwise [9]. In Chapter 4 the author reports a successful application of kaolin during the gasification of miscanthus and Dutch straw, both containing a high amount of alkaline elements in the ash, when silica-rich bed materials (sand and olivine) were used - no agglomeration occurred during the operation with the additive, while agglomeration was reported during the test when no additive was used. Also the gasification tests with demolition wood ("B-quality" wood), a fuel that judging from its ash amount and composition should not cause any agglomerationrelated problems, ended up with defluidization. There too the addition of kaolin proved to be a sufficient remedy.

2.3.3 Overview of industrial gasification pilot plants

Since the (re)gain of interest in gasification technology, now almost four decades ago, next to the small laboratory-sized units a number of industrial-size gasification plants based on fluidized bed technology have been constructed and operated. An overview of the industrial-size gasifier concepts based on the fluidized bed principle can be found in Table 2.10. Some of those concepts, like for example High Temperature Winkler process have been originally developed for coal gasification and the concept was applied for biomass gasification at a later

Table 2.10: Overview of the industrial-size gasifier concepts based on the fluidized bed principle and operated on biomass fuels. Names listed in boldface indicate plants that are currently in operation. Letters between brackets indicate the use of the product gas: ammonia synthesis (A), cement or lime kiln (C), gas engine (G), integrated gasification combined cycle (I), steam cycle – also in co-combustion mode (S) [21, 35, 137, 121, 176, 155, 104, 126, 99, 6, 123, 136, 84, 59]

| Technology identifier | HT Winkler | ONIM | $\operatorname{Renugas} \oplus$ | Lurgi | Pyroflow | Bioflow | Silvagas ® | FICFB |
|-----------------------|---------------------------------|---|--|------------------------------|--|--|--------------------------------|---------------------------------------|
| Related Companies | Rheinbraun ^a | Studsvik AB, | IGT^{b} , | Lurgi GmbH | FW ^c Energia Oy, | FW ^C Energia Oy | Battelle CL ^d | Babcock Borsig |
| / institutes | | TPS AB, | Tampella e , | | API^{f} | | Battelle ML^{g} | TU Vienna |
| | | Ansaldo h , | Enviropower, Carbona Inc. | | VIT | | FERCO | |
| Gasifier topology | CFB | CFB | BFB | CFB | CFB | CFB | dual CFB | FICFB ⁱ |
| Heat supply | direct | direct | direct | direct | direct | direct | indirect | indirect |
| Operational pressure | 10 bar | 20 bar (Mino), atm (TPS) | 30 bar (max.) | atm. | atm. | 20 bar | atm. | atm. |
| Fluidization medium | steam-O ₂ | steam- 0_2 , | air (+steam) | air | air | air | steam (gasif.), air (comh.) | steam (gasif.), air (comb.) |
| Operators (examples) | Oulu Kemira (A) 120 MW 4 b . | Studsvik 2.5 MW+1, (airblown). | PICHTR | Rüdersdorf (C) 100 MW4 E. | Norrsundet (C) 27 MW 44. | VVBGC (fr. Sydkraft) (C) Värnamo 18 MW 4 k. | Burlington (S) | Gitssing (G) 8 MW _{4 b} . |
| | | Grève-in-Chianti (S) | Tampere, | Geertruidenberg | Pietarsaari (C), | | | . 11 0 |
| | | 2 x 15 MW _{t h} , ARBRE (Aire Vallev) | (S) 20 MW _{t h} , Skive (G) | (S) 83 MW_{th} , | 35 MW _{th} , Kvmilärvi (Lahti) | | | |
| | | (C) 8 MW _e | $20 \mathrm{MW}_{th}$ | | (S) 40–70 $\overline{\text{MW}}_{th}$, Ruien (S) | | | |
| | | | | | 50-86 MW 4 L | | | |

a Rheinische Braunkohlenwerke AG, b Institute of Gas Technology, c Foster Wheeler, ^d Columbus Laboratories, e Tampella Power Inc., f Ahlstrom Pyropower, 9 Memorial Laboratory, $h\,$ Ansaldo Aerimpianti Spa
, $^{i}\,$ Fast Internally Circulating Fluidized Bed stage. From the table it could be concluded, that already a significant number of biomass gasification plants at relevant industrial scale have been built and have been or are at present being operated. This is certainly true, however, it has to be stated that most these plants are fueled with wood, wood waste or similar biomass type; only at the Värnamo gasifier some runs with agricultural fuels as, e.g., miscanthus have been performed. These woody fuels are not very demanding in terms of ash-properties and the related operational issues. Furthermore the produced gas is used for co-firing in an fossil-fueled boiler, or in a gas engine. Also that application, although beneficial in terms of reduced net CO₂ emission, does not pose very high requirements with respect to the gas cleaning. As with the aforementioned applications the gas needs to be cooled down (e.g., to 100-200°C for the gas engine application), consequently the particles can be efficiently removed using reliable low-temperature filtration techniques, alkali salts will be removed together with the particles, heaviest tar will condense in the gas cooler (a design issue!). The N and S-containing compounds are not directly problematic for the combustion application, although their amount needs to be controlled in order to meet the exhaust emission directives (NO_x, SO_x). Also, the produced gas does not need to meet the syngas composition requirements; next to the CO and H₂ all hydrocarbons including methane, volatile species (e.g., ethylene, acetylene, benzene) and tar (not condensed) will be accepted by the gas engine or the burners in a boiler.

As already mentioned at the end of Section 2.2, if the product gas is to be used for the production of advanced secondary fuels from biomass, it needs to comply with the far more stricter quality requirements. The following section touches upon one of the possible syngas applications, namely the production of biodiesel by means of Fischer-Tropsch synthesis. As this topic can be considered to be equally as broad as biomass gasification an extensive review is not presented here, merely a short summary to illustrate the present status of the technology and the potential challenges of biomass gasification and Fischer-Tropsch synthesis (BGFT) coupling.

2.4 Industrial application of bio-syngas: production of liquid transportation fuels

Production of Fischer-Tropsch diesel from fossil fuels is now a well-known industrial process. There are plants owned by large oil companies, like Sasol in South Africa (initially coal-to-liquid, CTL; now gas-to-liquid, GTL) and Qatar (GTL) and Shell in Malysia (GTL), producing over 200,000 bpd of synthesis products, including gasoline, diesel, naphtha, kerosene and other chemicals [105]. The composition of the products of FT-synthesis ("FT-syncrude") depends mostly on the type of catalyst and the reaction conditions:

• catalyst: iron- or cobalt-based;

• temperature: 210–260°C (Low Temperature FT, LTFT) or 310–340°C (High Temperature FT, HTFT).

The LTFT produces a higher fraction of the higher-boiling (above 360° C) hydrocarbons, and the total distillate yield is significantly higher than in the case of HTFT. However, the LTFT does not produce final fuels, but rather fuel blending stocks. On the other hand, the production facilities for HTFT are far more complex than those for the LTFT [105].

Regarding the FT catalyst, the advantage of the cobalt-based catalyst is its higher conversion rate and longer lifetime. Also less unsaturated hydrocarbons and alcohols are produced compared to the process employing an iron catalyst. On the other hand, iron catalysts do have a higher tolerance to sulphur and are cheaper. The Fischer-Tropsch synthesis can be represented by the following chemical reaction:

$$CO + 2H_2 \longrightarrow -(CH_2) - +H_2O \tag{2.18}$$

If the feed gas has a H_2 :CO ratio lower than 2, the iron catalyst can be used simultaneously to adjust it by means of the water-gas shift reaction; the activity of Co-catalyst on the water-gas shift reaction is negligible, hence the H_2 :CO ratio needs to be adjusted upstream [148].

Although the use of a product gas from an air-blown gasifier as feed gas for FT synthesis is theoretically possible, this will affect the synthesis process in a negative way. Firstly, high dilution by the nitrogen will cause the need for excessively large process equipment, leading to higher investment costs. Besides, high nitrogen partial pressures would make it act as an "inhibitor" on the catalytic processes, considerably reducing the reaction rates. Also, at certain elevated pressures the ammonia/nitrogen/hydrogen equilibrium may start shifting to the ammonia side. Consequently, the use of an air-blown gasifier upstream the FT process should be evaluated very carefully and processes producing a nitrogenfree gas, like steam-O₂ or indirect gasification, should be considered instead. As with most catalytic processes, as in the FT process, there is a potential risk of the deactivation of the active sites by pollutants or catalyst poisons. To avoid frequent replacement of the catalyst, which would not be acceptable mainly from an economical point of view, the feed gas needs to meet certain purity criteria. These criteria have been summarized in Table 2.11. Given a typical product gas from fluidized bed gasification of biomass and the gas requirements mentioned above, the typical gas cleaning train will consist of the following steps:

- hot gas filtration the particles need to be removed as they will otherwise pollute / foul the downstream equipment. This should preferably be done at the temperature close to the gasification temperature to reduce the thermodynamic losses before the next high-temperature upgrading step, namely
- methane and tar reforming although advanced tar removal technologies based on scrubbing do exist (e.g., OLGA technology [13, 17]), in the case of

gas upgrading for advanced synthesis processes there is a benefit of combined (catalytic) conversion of tar and methane. When tar is removed by means of a scrubbing process, the methane will remain in the gas, but not being a feedstock for the synthesis process it will lead to a decreased product yield. However, if a catalytic process is to be applied here it will pose additional requirements on the capture of particularly sulphur species in the gasifier, to avoid the premature deactivation of the catalyst;

- alkali and residual particle removal as the gas is cooled down after the high-temperature upgrading steps an additional filtration step may be necessary. This is due to the formation of solid alkali salts from their vapors, present at temperatures of around 800° C and above;
- removal of N- and S-compounds in this final upgrading step typical catalyst poisons are removed, if they have not already been removed before the catalytic hydrocarbon reforming.

Due to the relatively low temperature of the FT process compared to, e.g., Solid Oxide Fuel Cell application, the gas cleaning is slightly easier as not all the cleaning steps need to be carried out at elevated temperatures. Of course the application of a heat regenerator could enable the use of low temperature cleaning steps followed by the reheat of the gas, but the total energy efficiency of the process is reduced due to the losses associated with the Second Law of thermo-dynamics.

| Contaminant | FT synthesis | Methanol synthesis |
|--------------------------|---|---|
| Particles | 0 ppb a , 0.1 mg m $_n^{-3}$ e | low |
| Tar and BTX | below dewpoint b,e | |
| Hydrogen halides (HCl, | ${<}10{ m ppbv}^{b,e}$ | ${<}10~{ m ppbv}^e$ |
| HBr, HF) | | |
| Alkaline metals | $< \! 10 \mathrm{ppbv}^{b,e}$ | |
| N-compounds | $< 1 \text{ ppmv}^b$, $< 20 \text{ ppb}^{c,e}$ | 10 ppmv NH ₃ , 0.01 |
| - | | ppmv HCN ^e |
| S-compounds | < 1 ppmv ^b , $<$ 20 ppb ^c , | <1 ppm ^d , 0.1 ppmv ^e |
| - | 0.1 ppmv^e | |
| $Pressure^d$ | 20–30 bar | 140 bar |
| Temperature ^d | 200–400 °C | 100-200°C |
| - | | |

Table 2.11: Syngas quality requirements (allowable concentrations of impurities) for the synthesis of secondary fuels.

^{*a*} from [159]; ^{*b*} from [16]; ^{*c*} from [160]; ^{*d*} from [27]; ^{*e*} from [121].

Catalytic hot gas filtration (so a combined particle removal and hydrocarbon reforming step) was investigated by Simeone et al. [149] using model gas and tar compounds, and by Rapagna et al. [133] using a ceramic candle filter installed directly in the freeboard of a small laboratory-scale steam-blown bubbling fluidized bed. Both investigations showed promising results in terms of tar conversion. The removal of contaminants from the product gas downstream a steam-blown BFB and a particle filter was investigated, e.g., by Cui et al. [37] using columns containing different sorbents. Although CH₄, tar and NH₃ were successfully converted to permanent gases using a nickel catalyst, and H₂S was reduced below 1 ppmv using a commercial ZnO sorbent, the authors indicate that the application of catalysts and sorbents for product gas cleaning remains a challenging task. Boerrigter et al. [16] performed a demonstration campaign of 650 hours based on the gasification of clean wood followed by Shell FT process. Tar was removed in a high-temperature tar cracker, while NH₃ and H₂S were removed using wet scrubbing followed by active carbon and ZnO filters. Total removal of BTX (benzene, toluene, xylenes) is indicated as the design guideline for the FT process, as otherwise the BTX in the gas would cause rapid saturation of the active carbon filters. With this approach the tar problem is immediately solved as BTX are more difficult to remove / convert than tar. In a Finnish project "UltraClean Gas" the gas cleaning followed by FT synthesis is being tested in the slip-stream (5 MW) of the 12 MW fuel thermal power input atmospheric biomass gasifier in Varkaus [103], while the development of a pressurized unit and the construction of a first commercial scale BGFT-plant is currently scheduled for 2012-2014 as an industrial follow-up project [119].

2.5 Conclusions and outlook

This paper has reviewed the application of fluidized bed technology in the process of biomass gasification that produces a feed stream for the synthesis of advanced secondary energy carriers - Fischer-Tropsch products in particular. With the disadvantages of the extensive exploitation of the fossil fuel resources and its consequences being very evident now, alternative renewable and sustainable sources of primary energy are being sought. The current annual world's primary energy demand amounts to approximately 490 EJ, of which 250–270 EJ could be covered by biomass that is available on a sustainable basis and at competitive prices. However, raw biomass is not very convenient to use, mainly due to its solid appearance and low volumetric energy density. Out of combustion, pyrolysis or gasification routes the latter one proves to be very suitable, especially when production of advanced secondary energy carriers is opted for. If the process is to be carried out at large industrial scale (100 MW fuel thermal power input order of magnitude), then the fluidized bed technology shows the best balance between the advantages and disadvantages. The strong points are related to the already established acquaintance with fluidization engineering in thermochemical conversion processes, acceptance of a wide variety of the feedstock regarding the size and the chemical composition, good scalability of the reactor, moderate amount of the tar formed and the ability of using the *in-situ* additives to improve the conversion process. The main vulnerability is related to the fuel ash issues, and especially the presence of alkali metals together with silica in the reactor which can lead to the formation of bigger bed material lumps (agglomerates) and cause undesirable interruptions in the operation. However, by using appropriate additives (e.g., kaolin) this issue can be managed. The composition of the product gas and the process efficiency (usually expressed in terms of the carbon conversion and the cold gas efficiency) strongly depends on the operational parameters of the gasifier. The elimination of nitrogen is crucial for obtaining medium calorific value gas and is achieved either by using steam-O₂ blown gasifier or an indirect gasification concept. The choice of the bed material will be of utmost importance, due to a proven catalytic activity of minerals like dolomite, magnesite and olivine on the hydrocarbon conversion reactions and the water-gas shift reaction, which makes them more attractive than quartz sand. The bed materials with low silica content also show a significantly better agglomeration resistance. Additional benefits can be obtained from pressurized gasification, although the reactor design and operation are significantly more complicated than in the case of an atmospheric gasifier.

Gas produced in the fluidized bed gasification process is not yet of the syngas quality. The design of the gas cleaning and upgrading system, although less demanding than the one required, for instance, for an SOFC application, needs to be done carefully to benefit from the fact that some steps can be carried out at the temperature of the FT process, instead of at the elevated gasification temperature.

Nowadays only a few (C)FB biomass gasifiers are being operated at industrial scale using woody (thus "easy") fuels, and they produce gas for co-firing in a boiler. This application poses significantly lower requirements on the gas cleaning than the fuel cells or synthesis processes. Fischer-Tropsch production plants also exist, but they use fossil fuels as feedstock. The combination of biomass gasification and the production of advanced secondary fuels has not left the demo-scale yet, but this step is currently "work in progress".

Laat me, laat me, laat me mijn eigen gang maar gaan, laat me (...) ik heb het altijd zo gedaan Leave me, leave me, let me do it my own way, leave me (...) I've always done it this way Ramses Shaffy, *Laat me / Vivre*, 2005

TUD Circulating Fluidized Bed Gasifier test rig and experimental methodology

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Introduction

The previous chapter presented the motivation for the research in the field of biomass gasification; also the current state-of-the-art was indicated. To achieve an advancement in the state-of-the-art a proper mix of theoretical and applied research is required. Experimental work is an important part of this mix; after all even the best mathematic model, even if it would exist, will not produce any hydrogen. In the case of thermochemical conversion of solid fuels the experimental work is usually performed at a significantly smaller scale than the actual target process. This has to do with the practical considerations, mainly the investment and operation costs, availability of manpower to run the test rig, ease of the alteration and repair of the parts of the process. Since mid 90'ies section Energy Technology at Delft University of Technology has been developing a circulating fluidized bed (CFB) test rig. Over the years, this test rig has been functioning both as a gasifier and as a combustor; its maximal biomass feed rate in gasification mode is nearly 20 kg h^{-1} , which corresponds to an approximate thermal input of around 100 kW. This chapter contains a detailed description of the CFB test rig. Also the methods used during the experiments for the analysis of the gas composition are presented here.

3.1 Experimental facility: TUD Circulating Fluidized Bed Gasifier

3.1.1 Basic geometry, instrumentation and functionality

A schematic drawing of the working principle of a CFB is presented in Figure 3.1, while a piping and instrumentation diagram (P and ID) of the whole test rig is presented in Figure 3.2. The main characteristics of the rig are summarized below.

- Geometry and materials:
 - riser length: 5.5 m;
 - riser inner diameter: 83 mm; downcomer inner diameter: 54 mm;
 - cyclone inner diameter: 102 mm; total height (excl. flanges): 630 mm; inlet inner dimensions: 21 x 50 mm (width x height); gas outlet inner diameter: 54 mm; solids outlet inner diameter: 45 mm (initially 36 mm but later enlarged to 45 mm, due to the problems with the blockage during operation with solid fuel. Those problems will be described in Section 4.5);
 - material: stainless-steel AISI310, DIN 1.4845 for the parts exposed to nominal process temperature and to contact with the reactants and

 \prime or products; for other parts stainless-steel AISI316, DIN 1.4404 is used.

- Reactor heating system:
 - the riser (except the bend in the top part), downcomer and the cyclone were heated using modular, semi-cylindrical ceramic fiber radiant heaters supplied by ZMC Zamac (Poland). Length of each module was 40 cm, maximum heating power 2.4 kW at 230 V, maximum operating temperature 1200°C. In total 20 heaters have been installed on the riser and 20 on the downcomer, grouped in segments consisting of 4 heaters. To obtain adequate power rating within each segment, pairs of heaters have been connected in series, while all the pairs have been connected in parallel. This resulted in a heating power of 2.4 kW per segment. For the cyclone a custom sized pair of heaters was ordered, with different diameter and length, but the same power rating as the heaters described above;
 - top part of the riser and the gas ducts to the filters were heated using heating cables supplied by Tyco Thermal Controls, type KMIN, 200 W m^{-1} , length 10 m each, maximum operating temperature of 1000°C;
 - electrical circulation heater supplied by Watlow, heating power of 6 kW, was used to preheat the primary gaseous input stream (fluidization stream). Its maximum operating temperature was 400°C, nominal operating temperature 360°C.
- Gas and solids supply systems:
 - feeding system with a maximum feed rate of approximately 20 kg h^{-1} of biomass (corresponding to approximately 100 kW fuel thermal power input) with in addition the possibility of independent cofeeding of two other kinds of solids (e.g., additives). The feeding system is designed to be gas tight; during the operation it is continuously swept with a small flow of nitrogen (0.7 kg h^{-1}) to maintain inert conditions within the bunkers. The biomass and bed material bunkers are equipped with lock-hopper systems to allow refilling during operation;
 - two optional fuel admission ports on the riser: one directly above the gas distribution plate and one located 900 mm above the gas distribution plate. In all experiments described here the upper feeding port has been used;
 - gas distribution plate consisting of nine tuyeres (d_o = 6 mm, d_i = 4 mm) with two holes (d = 2 mm) each;
 - as primary (fluidization) flows nitrogen, air, steam and oxygen can be supplied independently, although restrictions are imposed on the

fraction of oxygen in the input stream (maximum of 50% on mass basis, due to safety considerations), and on the fraction of nitrogen and/or air in steam (to avoid cooling down of the steam and hence the condensation upstream the reactor).

- Gas cleaning systems:
 - high-temperature ceramic fibre tissue candle filter unit (BWF, Germany) operating at 450 $^{\circ}\mathrm{C}$; and
 - high-temperature Si-SiC ceramic candle filter (Pall Filtersystems GmbH, Germany) operating at a maximum temperature of approximately 800°C.
- Reactor control and measurement systems:
 - flow measurement of all primary gaseous input streams, using Endress & Hauser AT70 thermal flow meters for all primary flows, except for steam, where an Endress & Hauser Prowirl 72 vortex flow meter is used;
 - for the flow control of the primary flows Samson pneumatic control valves are used. Those valves are controlled by the signal from the PI-control loops in the PLC;
 - purge flows, L-valve control, and other small flows are controlled using mass flow controllers (M+W Mass-Stream) supplied by Bronkhorst High Tech B.V.;
 - the flow of the product gas is measured using a differential pressure flowmeter (McCrometer V-cone [®]);
 - eight thermocouples (K-type), of which seven are located on the riser and one on the downcomer. Initially two more thermocouples have been used in the downcomer, but they were removed as they were causing flow stagnations in the pipe;
 - nine differential pressure (dp) cells measuring the pressure drop over different parts of the installation;
 - in-house implemented Supervision, Control, And Data Acquisition (SCADA) package coupled to a Programmable Logical Controller (PLC, make ABB, type SattCon200) for test-rig control, which is operated from two PCs in the control room. Process data is logged with a frequency of 0.1 Hz (1 Hz is possible).

Figure 3.3 shows four pictures of the different parts of the test rig.



Figure 3.1: Schematic drawing of the Circulating Fluidized Bed Gasifier at TUD. Symbols 1-10: differential pressure sensors; T1-T8: thermocouples; P_R : absolute reactor pressure; T_{in} : gas temperature at the inlet of the reactor



Figure 3.2: P&ID of the gasification test rig: CFBG and high-temperature ceramic filters



Figure 3.3: CFB gasification test rig at the Process&Energy department at TUD: the bottom of the reactor with the main screw feeder (top left); top of the reactor with the gas duct towards the high-temperature filter unit (top right); the 2009 gasification team members (bottom left) – from left to right: Davide Barbera (visiting researcher from Bologna University, catalytic reforming), Alex Litinas (M.Sc student, gasification), Marcin Siedlecki (gasification), Eleonora Simeone (hot gas filtration), Yair Stokkermans (M.Sc student, hot gas filtration); two screen shots of the SCADA software showing the overview screen and the differential pressure trend lines (bottom right)

3.2 Analysis methods

During the operation a sample flow of the product gas is extracted continuously from the main stream just downstream of the gas outlet of the cyclone. The schematic drawing of the sampling line is presented in Figure 3.4. The gas analysis probe points into the direction of the flow to avoid the coarsest particles from penetrating the line. The gas sampling line was heated using a trace heating cable (resistance wire) from the company Horst (type HSS-450 $^{\circ}$ C). Additionally, the particle filter vessel was heated using a heating jacket (Tyco IJ-GL glass silk heating jacket). The temperature of both the sampling line and particle filter vessel is maintained at 300°C using temperature controllers. The Solid Phase Adsorption (SPA) tar sampling point is located immediately downstream of the filter outlet. An additional thermocouple is used to confirm the gas temperature in the line at the SPA sampling point. The gas is then led through a (primary) condenser to remove the condensables with the highest boiling point, predominately heavy tar and some water, before carrying the gas to the control room, where the gas analysis takes place. After passing through a secondary condensation vessel and two impinger bottles filled with silica gel beads, the dried gas is characterized with several analysis methods. For the analysis of the wet gas (Fourier Transform InfraRed spectrophotometer and gravimetric water content measurement) a second gas sampling probe was installed to allow permanent connection of the heated line (170°C), and simultaneous dry and wet measurements. The layout presented in Figure 3.4 depicts the final arrangement of the sampling lines directly downstream the gasifier. The complete overview of the analysis methods applied is presented in Table 3.1. As shown in Table 3.1, the FTIR analysis is applied to both dry and wet gas. Applying FTIR analysis to wet gas has a number of advantages. It allows for the quantification of water-soluble species, such as NH_{3} , and also water concentration can be measured directly, however, only up to approximately 20% by volume because of peak saturation. In the process considered in this work the water concentration in the gas can be expected to be between 40 and 70% by volume. Nevertheless it can still be determined from the dry and wet FTIR gas analysis data by comparing the respective concentrations of a compound, e.g., methane or ethylene. Then, the water concentration (volumetric fraction) can be calculated using the following simple formula:

$$y_{H_2O} = 1 - \frac{y_{i,wet}}{y_{i,dry}}$$
(3.1)

where the subscript *i* refers to a component measured both on a dry and wet basis. The approach applied here was to calculate the water concentration from methane and ethylene concentrations and take the average of those two values. Offline measurements of the tar by SPA, where tar is adsorbed on a solid aminophase porous block, in combination with gas chromatography (GC) analysis of the eluted tar were also performed. The complete analysis procedure of tar can



Figure 3.4: Main gas analysis line: schematic (top) and practical implementation (bottom)

be found in [19]. The results of the analysis are divided into two parts: the polyaromatic hydrocarbon (PAH) species and the phenolic species. As mentioned above the sampling point is located directly after the dust filter because the temperature needs to approach 300°C to avoid condensation of the higher tar components. A sample of 100 ml *dry* gas was drawn with a syringe and directly sealed to avoid interaction with air and stored in the refrigerator. After the experimental campaign the samples were sent for analysis to the Royal Institute of Technology (KTH, Stockholm, Sweden). The measured quantities were delivered in micrograms per sample, which can be recalculated to mg m⁻³ (STP) of tar in the dry gas. Of course, it is the *raw* gas that is drawn through the SPA cartridge during sampling; however, water is partially adsorbed on the column, and the fraction that breaks through condenses instantaneously. The volume of the droplets formed can be neglected in comparison to the volume of 100 ml of sample, and therefore, the tar sample is assumed to be taken on a *dry* basis.

The following PAH compounds have been quantitatively analyzed by KTH: benzene, toluene, m/p-xylene, o-xylene, indan, indene, naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, biphenyl, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene. The phenolic fraction consisted of phenol, o-cresol, m-cresol, p-cresol, 2,4-xylenol, 2,5/3,5xylenol, 2,6-xylenol, 2,3-xylenol, and 3,4-xylenol. Also, the non-identified peaks could be quantified using an internal standard. The sum of the unknowns was added to PAH and phenolic subtotals, respectively.

The concentrations of benzene, toluene and xylenes (BTX) analyzed with SPA were known to show a relatively high error value compared to other species analyzed with the same method. Due to their volatility these components tended to evaporate from the sample before analysis could take place. Therefore, the SPA results are not used for those components; instead, the micro-GC results are used for further evaluation. However, it has to be mentioned, that the concentration of the BTX compounds was greatly influenced by the type of adsorbent used in the gas sampling line (the impinger bottles). Initially no adsorbent was used at all, but that still led to too high moisture contents in the gas entering the analyzers. When phosphorus pentoxide (P_2O_5) was used for desiccation, it did not lead to BTX adsorption. However, its powdery form proved not to be very convenient for this application, so silica gel beads were used instead. Unfortunately, those adsorb BTX fully, until they become saturated – that is the reason why for some experiments no BTX results are reported, since they were considered not to be reliable.

| Technique | Specification | Components | A^a | P^b |
|---|---------------|---|----------------|----------------|
| Hartmann&Braun Uras10P (NDIR) | online | CO ₂ and CO | $98\%^c$ | 0.5% |
| Hartmann&Braun Magnos6G (PM) | online | 0_2 | 98% | 0.5% |
| Varian CP4900 micro-GC | semi-online | BTX (benzene, toluene, | n/a | 1% |
| module: CP-Sil 5 CB, 4m | | xylenes) | | |
| Varian CP4900 micro-GC | semi-online | N_2 , H_2 , CO, CO ₂ , CH ₄ | 98% | 1% |
| module: CP-COX, 1m | | | | |
| Fourier Transform Infrared (FTIR) | off-line, dry | CO_2 , CH_4 , C_2H_4 , CO , | 98% | 10% |
| ThermoElectron Nicolet 5700 | | C_2H_2 | | |
| heated gas cell (150°C), | off-line, wet | as above plus COS, HCN, | 98% | 10% |
| $2m$ optical length, resol. 0.125 cm^{-1} | | H_2O, NH_3 | | |
| Gravimetric water measurement | off-line | H_2O | n/a | n/a |
| Solid Phase Adsorption (SPA) | off-line | PAH, Phenolics | 94%[19] | 1.7% |
| ^a accuracy | | | | |

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 b precision or repeatability standard deviation (r.s.d.) c limited by the accuracy in the composition of the calibration gas mixture

3.3 Fuels, bed materials, additives

3.3.1 Fuels

Four solid biomass fuels have been used in this work. These fuels represent different categories of biomass:

- clean woody biomass: A-quality wood (further referred to as A-wood) delivered by the company Labee Group in Moerdijk (NL). The fuel is delivered in pelletized form (almost white colored), 6 mm in diameter. It represents the category of biomass which poses the least problems during thermal conversion due to its low ash content. Therefore this fuel has been used as a "Base Case" fuel in this study;
- recycled woody biomass: B-quality (demolition) wood (further referred to as B-wood) also delivered by Labee Group as 12 mm brown colored pellets. This category represents the more sustainable category of woody biomass, as it concerns a recycle stream. This type of biomass is characterized by a higher ash content than A-wood, and also the content of trace elements in the ash is higher. These characteristics are enough to cause operational problems during fluidized bed conversion (i.e., agglomeration), and also the emissions of trace elements with the product gas are an issue, although this topic falls outside the scope of this work;
- energy crops: Miscanthus Giganteus (further referred to as miscanthus) is a fast growing plant, highly suitable for cultivations as an energy crop. This biomass was delivered by the company Agromiscanthus in Ter Apel (NL) as 8 mm pellets. The ash content is significantly higher compared to B-wood. Also, the amount of alkali elements is a clear sign of potential for agglomerate formation when used in fluidized bed reactors. On the other hand, miscanthus ashes have been observed to be highly reactive, and they could also show some catalytic activity during the gasification process; and
- agricultural residues: 1997 Dutch straw (further referred to as straw), delivered as 8 mm pellets. This category, although highly sustainable, poses the most challenges with respect to thermal conversion processes when compared to the kinds of biomass listed above. Its very high ash content and ash composition form a severe threat for fluidized bed conversion (agglomeration) if no countermeasures are taken.

The chemical composition of the biomass fuels mentioned above had been analyzed by Forschungzentrum Jülich (DE); the results are summarized in Table 3.2. From Figure 3.5 it is clear that the content of carbon and hydrogen on a dry, ash-free basis is nearly equal for all four fuels. However, major differences can be observed in the ash amounts and compositions. Considering the amounts of

| Type of fuel: | A-wood | B-wood | Miscanthus | Straw '97 |
|--------------------------------|------------|-------------|-------------------|-----------|
| Provimate analysis as rec | eived raw | data mas | s fractions in % | <u></u> |
| Moisture | 8 10 | 6 20 | 6 80 ^a | 7 30a |
| Wolsture | 0.10 | 0.20 | 0.00 | 7.50 |
| Ultimate analysis, as rece | ived, norn | nalized, ma | ass fractions in | % |
| С | 47.0 | 47.9 | 45.7 | 40.7 |
| Н | 6.13 | 6.02 | 5.93 | 5.50 |
| Ν | 0.203 | 0.752 | 0.678 | 0.596 |
| S | 0.0203 | 0.0501 | 0.111 | 0.151 |
| 0 | 46.3 | 44.2 | 44.0 | 41.0 |
| | | | | |
| Cl | 0.0122 | 0.0421 | 0.225 | 0.368 |
| SiO ₂ | 0.0390 | 0.215 | 1.21 | 7.13 |
| Al_2O_3 | 0.00 | 0.0549 | 0.0975 | 0.0897 |
| Fe ₂ O ₃ | 0.00 | 0.0846 | 0.0463 | 0.0534 |
| CaO | 0.118 | 0.224 | 0.184 | 0.480 |
| MgO | 0.0151 | 0.0565 | 0.129 | 0.114 |
| Na ₂ O | 0.00 | 0.0216 | 0.0382 | 0.0313 |
| K ₂ O | 0.0354 | 0.0459 | 0.877 | 2.07 |
| P_2O_5 | 0.000 | 0.0138 | 0.179 | 0.118 |
| Total ash (analyzed) | 0.344 | 0.983 | 3.33 | 11.7 |
| Total fractions | 100.0 | 100.0 | 100.0 | 100.0 |
| | | | | |
| LHV (ar) $[MJ kg^{-1}]$ calc. | 15.7 | 16.7 | 15.6 | 14.0 |

Table 3.2: Composition of biomass fuels used in this work

^{*a*} these values were swapped by mistake in the publication [144]



Figure 3.5: CHNSO (top) and partial ash analysis (bottom) of the fuels used in this work

silica, potassium and chlorine in miscanthus and especially straw it is obvious that these fuels will cause agglomeration-related problems for the operation of the fluidized bed, if no measures will be taken to avoid them [56, 175, 9]. To allow a comparison between different fuels and to provide tools for the assessment of the risk of agglomeration various relationships between the ash constituents have been proposed in the literature. For example the following so called "agglomeration indicators" are proposed to assess the risk of agglomeration during fluidized bed operation using sand as bed material [172]:

agglomeration indicator
$$I = \frac{Na + K}{2S + Cl}$$
 (mass basis) (3.2)

agglomeration indicator
$$2 = \frac{Na + K + Si}{Ca + P + Mg}$$
 (mass basis) (3.3)

If both agglomeration indicators described above are larger than 1, then they predict a high potential of alkali induced agglomeration based on the fuel characteristics in combination with SiO_2 bed material at temperatures $800^{\circ}C$ [172]. Following the ash composition given in Table 3.2 (for the calculation elemental mass fractions are needed, instead of oxide mass fractions), both agglomeration indicators confirm expected agglomeration risk for miscanthus and straw, as stated earlier. However, it has to be stressed that those indicators are purely empirical, and thus the conclusions from their use should be drawn with care, as will become clear for the case of B-wood.

3.3.2 Bed materials

For the function as bed material in the CFB the selected bulk solids are listed below. Their chemical compositions and cumulative particle size distributions can be found in Table 3.3 and Figure 3.6, respectively.

- quartz sand: this is an abundant and cheap material, well-proven in various (C)FB applications. The possibility of purchasing a closely defined grain size range, its resistance to attrition and its availability make sand a very attractive basic bed material for a wide range of types and sizes of the reactors based on fluidization technology. However, silica easily forms low-melting eutectics with alkali compounds, which are often found in biomass, as shown in the section above. Those eutectics, when melting, form a sticky layer around bed material particles, causing them to form bigger lumps agglomerates. Therefore precautions need to be taken when sand bed is used during conversion of biomass that is rich in alkali;
- magnesite: this is a mineral consisting mainly of MgCO₃ (MgO in case of calcined magnesite), and of smaller fractions of CaO, Fe₂O₃ and silica. Its low silica content and acceptable price, being $\in t^{-1}$ (M-85, Integra Group, Slovakia) versus $\in t^{-1}$ for sand (Filcom B.V., The Netherlands) make it an

attractive bed material, as it should be more resistant to the formation of agglomerates. Its value as a bed material for a fluidized bed has been successfully demonstrated in the Värnamo plant in 1990s, where different difficult biomass feedstocks have been gasified with air without extensive defluidization / agglomeration issues. A high amount of metal oxides in magnesite and some similarity with dolomite make it also a potential catalyst in the gasification process. This has been observed and investigated at our institute during the CHRISGAS project, and some of the results have already been published [145], see also Chapter 5;

• olivine: magnesium iron silicate ((MgFe)₂SiO₄), one of the most common minerals on Earth. In its properties and chemical composition is can be regarded as an intermediate between quartz sand and magnesite. The attrition resistance of olivine is much better than that of magnesite and its silica content half of that of sand, though still high enough to cause agglomeration. Olivine is successfully used as bed material in the Güss-ing (FICFB) gasifier in Austria. Laboratory studies with model tar compounds carried out in the past had shown that thermal pre-treatment significantly enhances the activity of olivine as tar-cracking catalyst. During this project that approach has been tested in the gasifier under real gasification conditions. The olivine used in this work originates from the company Askania AB (Sweden), brand name "Olivin33".

| | Quartz sand | Magnesite | Olivine |
|-------------------------|----------------|-----------|---------|
| $d_{p,mean}$ (μ m) | 386 | 286 | 492 |
| Composition, | mass fractions | in % | |
| SiO ₂ | >99.5 | 4.44 | 43.2 |
| Al_2O_3 | - | 0.94 | 1.57 |
| CaO | 0.02 | 16.8 | 0.40 |
| Fe_2O_3 | 0.17 | 4.36 | 9.44 |
| K ₂ O | 0.04 | 0.09 | 0.05 |
| Na_2O | 0.01 | 0.27 | 0.07 |
| MgO | 0.01 | 72.2 | 44.2 |

Table 3.3: Mean particle size and chemical composition of quartz sand, magnesite and fresh olivine

3.3.3 Additives

One of the greatest advantages of the fluidized bed reactor is the possibility to use in-situ additives to enhance the process. Different additives are commonly



Figure 3.6: Comparison of cumulative Particle Size Distributions of sand, magnesite and olivine

used in gasification; sulphur getters, alkali getters, and tar conversion agents are the most well-known. For the research described in this report the following additives were used:

- kaolin (kaolinite): is a clay mineral with the chemical composition $Al_2Si_2O_5(OH)_4$. During the project it has been successfully shown, that it can be effectively used as an alkali getter to counteract agglomeration phenomena. When during biomass conversion alkali are released, and also silica is present either from the bed material or biomass ash itself, then the formation of alkali-silicates (K_2O-SiO_2) can be expected. Those compounds have an eutectic point of about 770°C, while the eutectic point of $K_2O-CaO-SiO_2$ structures is even lower. Introduction of alkalialuminum silicates ($K_2O-Al_2O_3-SiO_2$), which have a much higher melting temperature [9]. Therefore during most experiments with fuels rich in alkali kaolin was used to allow stable operation during the test;
- magnesite: mentioned in the above section as a possible bed material, it has been also tested as an additive. Addition of magnesite during gasification to a sand bed resulted in significant change in gas composition and tar concentration.

3.4 Reaction conditions

Process or reaction conditions are typically governed by a number of characteristic variables. These variables can in theory have very wide ranges, but from practical and scientific interest points of view mostly carefully predefined ranges have been investigated here [63, 116, 163]. A summary of those ranges can be found in Table 3.4.

Table 3.4: Summary of relevant process conditions

| Parameter | Raı | nge |
|------------------------------------|------|------|
| λ[-] | 0.20 | 0.40 |
| SB* [-] | 0.50 | 1.5 |
| Temperature [°C] | 800 | 850 |
| Fluidization velocity $[m s^{-1}]$ | 3.0 | 4.5 |

3.4.1 Stoichiometric oxygen ratio (λ)

The stoichiometric oxygen ratio is commonly used for the identification of different "oxidation regimes" during a thermochemical fuel conversion process. This parameter, also called "equivalence ratio", "air factor" or "air ratio", is represented by the symbol λ (lambda) and its formula is given below:

$$\lambda = \frac{\text{external } O_2 \text{ supply / fuel supply (daf)}}{\text{stoichiometric } O_2 \text{ requirement / unit of fuel input (daf)}}$$
(3.4)

Given the formula it is clear that $\lambda > 1$ refers to combustion processes, $\lambda = 0$ to pyrolysis, and $0 < \lambda < 1$ to gasification. With the aim to produce a gas suitable for transportation fuels synthesis application, high yields of H₂ and CO are required; this can be achieved in low lambda regions. On the other hand, partial oxidation of the fuel is necessary to generate heat to drive the mostly endothermic gasification reactions, and allow the reactor to work in the autothermal mode. Based upon own experience, literature data and practical considerations the lambda range to be studied in this work was chosen between 0.2 and 0.4, so the effect of that parameter on the process could be investigated. Later on, when other process variables were investigated, the lambda range was narrowed down to values between 0.30 and 0.35.

3.4.2 Temperature

Temperature is an important process parameter in thermochemical fuel conversion. The temperature range relevant for biomass gasification in a fluidized
bed lies between approximately 650° C and 950° C. Higher temperature will increase the carbon conversion efficiency and reduce the amount of tar produced. however, in the case of a fluidized bed reactor the maximum operating temperature is limited by the melting point of ashes or of the bed material. Also reactor construction materials can form an issue. In practice the reaction temperature is directly linked to λ , as for higher temperature more product gas needs to be oxidized, which in its turn reduces the cold gas efficiency (heating value of the product gas compared to the heating value of the original fuel). However, in (small) laboratory test rigs that temperature can be controlled by the heating elements installed, and therefore decoupled from λ . This is not only interesting, but also necessary, as due to relatively larger heat losses in a small laboratory test rig it might be impossible to achieve the same temperature at a certain lambda value as in a big industrial unit, solely by autothermal operation. Considering the above, and the fact that maximum operating temperature at TUD CFBG is limited to 900°C, the operational window has been set between 800 and 860° C. In addition, to allow a longer run time with alkali-rich fuels without using the additives some experiments were carried out at the temperature of around 750°C.

3.4.3 Pressure

Although pressurized operation puts significant additional requirements on the design and operation of a gasifier, it is often a desirable route. Firstly, higher pressures result in lower volumetric gas flow rates, which means smaller size of the reactor and downstream gas cleaning and upgrading equipment. Secondly, many downstream processes using the produced syngas require pressurized conditions for the reactions (e.g., Fischer-Tropsch), and the fact is that it is easier to pressurize the reactants separately (lock-hopper system for the solids, compressors for the gases), than to compress hot, combustible, hydrogen rich product gas. The CFB gasifier in our laboratory does not facilitate real pressurized operation, however. The maximum pressure at which the reactor can be operated is 1.5 bar(a). Such pressure increase in the system can only be caused by the back pressure of the hot gas filters present downstream the reactor, or some kind of a blockage in the pipeline downstream the reactor.

3.4.4 Steam-to-biomass ratio

The most common fluidization and oxidation medium used in gasification processes is air. Although air is cheap and abundant, the fact that the nitrogen present in air cannot be easily separated from the product gas is a significant drawback of that gasification medium. Air gasification produces gas of low calorific value, and approximately 50% of the volume of the product is the inert nitrogen. Therefore it would be better to use a combination of gases that either will react to form useful products or will be easily separated from the final product stream. That gasification agent will typically consist of a gas that provides the necessary oxygen for partial oxidation of the fuel (as explained in Section 3.4.1) and a gas that will act as a moderator / fluidization medium. A mixture of pure oxygen and steam fulfils the criteria mentioned above and both gases are very common in process industry. Besides acting as a fluidization medium steam is also a reactant in many gasification reactions, therefore its presence and amount have an influence on the product gas composition. The amount of steam supplied to the process is often related to the amount of biomass feed in a so-called steam-to-biomass ratio:

steam-to-biomass ratio (SB) =
$$\frac{\text{steam mass flow}}{\text{fuel feed flow}}$$
 (3.5)

In the literature it is not often mentioned whether the fuel feed is given on "as received" or "dry (and ash-free)" basis. However in case of fuels with higher moisture and / or ash content, the difference in the calculated SB will be significant, depending on the choice of the denominator. Besides, the moisture present in the fuel should not be neglected in the calculation of the SB, as the resulting steam will be the first to interact with the organic part of the fuel upon devolatilization in the reactor. Also in case of fuels with higher moisture content the amount of steam that originates from the fuel will not be negligible compared to the overall steam input. Considering the above, a modified steam-to-biomass ratio (SB*) is proposed:

steam-to-biomass ratio (SB*) =
$$\frac{\text{steam mass flow + fuel moisture mass flow}}{\text{dry, ash-free fuel feed flow}}$$
(3.6)

In practice as reported by the literature the range for SB varies between 0.5 and 2.0. In this work most experiments were carried out at SB^* between 0.9 and 1.5.

3.4.5 Fluidization velocity

During the operation of a fluidized bed reactor the superficial fluidization velocity (often shortly referred to as "fluidization velocity" or "velocity") is an important parameter that together with the information about the bed material used will reflect the fluidization mode of the reactor:

$$u_{fl}[m \, s^{-1}] = \frac{\dot{Q}_{gas} \, [m^3 \, s^{-1}(STP)] \cdot T_{process}[K] \cdot 1.013[bar]}{A_{riser}[m^2] \cdot P_{process,abs}[bar] \cdot 273.15[K]} \tag{3.7}$$

For bubbling bed mode the fluidization velocity has to exceed the minimum fluidization velocity, while for circulating fluidized bed the fluidization velocity has to exceed the transport velocity. An overview of minimum fluidization and transport velocities of the bed materials used in this research is given in Table 3.5. The gasifier was operated at fluidization velocities slightly exceeding the transport velocities given in Table 3.5 and above. The maximum fluidization velocity applied was below 5 m s⁻¹. Those ranges are well within the ranges applied in industrial circulating fluidized bed gasifiers.

Table 3.5: Overview of minimum fluidization and transport velocities for the bed materials used in this research

| | Sand | Magnesite | Olivine (untreated) | Olivine (treated) |
|-----------------------|------|-----------|---------------------|-------------------|
| $u_{mf} [m s^{-1}]$ | 0.05 | 0.03 | 0.12 | 0.1 |
| $u_{tr} [m s^{-1}]$ | 3.1 | 2.8 | 3.9 | 3.7 |

3.5 Experimental procedure

3.5.1 The course of the experiment

Gasification experiments have been run on the test rig described in the previous section. The operation of the gasifier was started by applying a nitrogen flow through the gas preheater allowing the primary flow to heat up to a temperature of about 300° C. The flow of the hot gases also caused heating-up of the parts downstream the filters, that were not heated electrically, so the risk of steam condensation was anticipated in that way. When the temperature in every part of the test rig exceeded 100° C, the fluidization agent was switched to steam and bed material circulation was initiated. The initial bed mass amounted to approximately 7 kg, to be fed into the riser using the feeding system. Alternatively, the bed material could be dumped into the downcomer through the top flange on the cyclone before the fluidization flow was started; that method, however, does not work for bed materials with a high fraction of fines. Biomass feed was started as soon as the average temperature in the reactor was above 500°C, and as soon as CO was detected by the gas analysis, confirming that biomass is actually entering the reactor, the oxygen flow was started. The strategy was to reach the operational temperature (i.e., $830-850^{\circ}$ C) as quickly as possible, ensuring that substoichiometric conditions were maintained at all times. Subsequently all the inlet flows were adjusted to the desired setpoint and after a stabilization time of 20-30 minutes the measurements could be started.

For the experiment to be designated "successful" the following measurements should be performed in a satisfactory way for each setpoint during operation. The measurements are listed in order of importance.

• CFB gasifier part:

- basic gas analysis downstream the CFBG: NDIR and GC;
- tar sampling (SPA) performed during steady-state operation; samples at least in duplo, preferably in triplo;
- gravimetric water concentration measurement: a well-quantifiable amount of condensate and the volume of the gas need to be sampled. This is done parallel to the wet FTIR analysis;
- dry FTIR analysis, at least five runs per analysis.
- High-temperature filter part:
 - at least first two measurement items from the CFBG part;
 - cascade impactor measurements both upstream and downstream the filter;
 - measurements as in the CFBG part, but performed downstream the filter.

Assuming stable operation of the gasifier in steady-state, the time required to perform the measurements downstream the CFBG was approximately 1.5 to 2 hours, with two people involved. In theory this would allow the testing of multiple setpoints during a single experimental day (8-10 hours of operation). In practice, however, this was done only few times, when no measurements around the filter were taking place. This is because the cascade impactor measurement downstream the filter takes 4 to 6 hours, and if also the measurement upstream the filter needs to be done (which is preferred, to have a complete set of data) another two hours must be added for the preparation and sampling. Besides, the filter requires longer steady-state periods, as only then conclusions can be drawn from the recorded pressure drop data. The results from the filtration tests are not a part of this work, but some of them can be found in the literature [149, 150, 151].

When all the necessary measurements had been taken, the reactor shut-down was initiated. First the oxidant flow was stopped, while maintaining the fluidization velocity. Subsequently all the solids feed flows were stopped, and then the circulation of the bed material was terminated (all solids would then be transported to the downcomer). Finally, the whole system was flushed with nitrogen for approximately 15 minutes to remove the product gas present in the rig. During a gasification campaign the test rig remained heated at about 550° C in between the experiments to reduce thermal stress on the reactor and heating elements. Furthermore a small purge (ca. 2 kg h⁻¹) of nitrogen was fed into the reactor all the time to avoid oxidizing conditions in the system. This is especially important for the hot gas filters as the carbon deposited on the filtration elements could spontaneously ignite in the presence of oxygen.

3.5.2 Data analysis and interpretation

As mentioned already in Section 3.1 the CFB gasification test rig described in this work is controlled using an industrial PLC unit. The PLC takes care of the control loops and input / output operations according to the commands given by the operator via the SCADA software. In this software also the data logging routine can be initiated, during which all the 172 analogue input and output signals are stored in a text file with an interval of 10 seconds (1 second is a selectable option). So during an 8-hours test run 2880 entries are stored for every signal, which makes an analysis "by hand" each time pretty cumbersome, especially when large number of experiments needs to be considered. Therefore a data post-processing tool was developed, to partially automate the process of data interpretation. Considering the portability of the application it has been chosen to use Microsoft Excel 2003 as the calculation environment as it is available on most office and home computers. In addition a custom-made executable interface was implemented in order to facilitate faster and partially automated post-processing of the large data files. The interface, called Energy technology Reactor Data Evaluator (ERDE) has been programmed using Microsoft Visual Basic 6.0 Professional and has been tested thoroughly to run under Microsoft Windows XP with previously mentioned spreadsheet application. The ERDE application allows the user to do the following:

- import the signals list as stored in the text file and display them in a selection window;
- open the data file in Excel for further processing;
- automatically plot five charts with most important process data: gas input flows, solids input, temperature profiles, gas analysis, and V-cone data;
- easily plot or add to an existing plot the time trends of any selected signals(s);
- put time markers in one or all plotted charts to allow for easier identification of the order of events;
- calculate slopes or average values of the signals selected from the list during the desired period of time, or calculate the slopes and / or average values for the signals from a predefined file, and store them in an indicated worksheet.

The advantage of using ERDE is a considerable reduction of time necessary to perform basic data analysis (plotting of the trend lines, steady-state period identification, and calculation of steady-state average values and slopes). The automation of some of those tasks also reduces the number of mistakes made during data processing. A screen-shot of the application window is given in Figure 3.7. The steady-state values calculated during data post-processing can be



Figure 3.7: Screen-shot of the data post-processing application ERDE

automatically stored in a data overview spreadsheet. From there each steadystate can be imported into a calculation spreadsheet, where:

- an overview of all the input flows and their steady-state values is presented;
- a post factum calculation of dimensionless process parameters (λ, SB) is carried out to verify if the a priori assumptions and settings were correct;
- total and elemental mass and mole balance calculations are performed;
- a simple data reconciliation can be carried out;
- a number of process benchmarks are calculated: carbon conversion (CC), cold gas efficiency (CGE), lower heating value of the product gas (LHV), and the total analyzed tar content of the gas.

The output of the calculation spreadsheet is stored together with the steadystate data in the overview spreadsheet. A schematic representing the steps described above is presented in Figure 3.8.



Figure 3.8: Overview of the data analysis steps, from the raw data file to the overview spreadsheet including mass balance results

I . . . have become comfortably numb Pink Floyd, Perfectly Numb, 1979

Experimental results and discussion

Parts of this chapter have been published in:

SIEDLECKI, M. and DE JONG, W. Biomass gasification as the first hot step in clean syngas production process – gas quality optimization and primary tar reduction measures in a 100 kW thermal input steam-oxygen blown CFB gasifier, *Biomass & Bioenergy* **35**, Supplement 1 (2011). Reprinted with permission. Copyright (2011) Elsevier.

Introduction

In the previous chapter the CFB gasification test rig belonging to the Energy Technology section at TU Delft was described. Also the main process parameters and feedstock characteristics were given. Although the process of steamoxygen blown gasification of biomass in a fluidized bed is not new, comprehensive experimental results in the open literature, using a circulating fluidized bed are rather scarce. In this chapter the experimental results obtained during this work are presented and discussed. The focus of the experiments was to observe the influence of the process parameters, mainly lambda, steam-to-biomass ratio, biomass fuel used, choice of the bed material and possible additives on the product gas composition, carbon conversion, cold gas efficiency and the operability of the gasifier.

4.1 Research questions addressed, the test matrix & test cases

The progress beyond the state of the art in any discipline requires answers to questions that mark that state of the art. In this work the questions to be addressed were mainly related to the influence of various parameters (λ , SB*, fuel, bed material, additive, etc.) on the process of steam-O₂ blown gasification of biomass in a Circulating Fluidized Bed gasifier. The quality of the product gas should be then assessed in terms of hydrogen yield and tar concentration, while the assessment of the stability of the gasification of fuels with high ash and alkali metal content. The criteria for the assessment and possible optimization of the process were imposed by the intended application for the product gas, namely the synthesis of liquid transportation fuels.

A test matrix was set up to indicate the necessary experiments that should give answers to questions indicated above. From the beginning a Base Case was defined being gasification of A-wood using a sand bed without any additives. The reason for defining this as a Base Case is the fact that gasification of A-wood, being an "easy" fuel in a fluidized bed reactor with "standard" bed material, should proceed reliably before any attempts are undertaken to look for improvements. Table 4.1 gives a global overview of the variations of bed material / fuel / additive combinations during different stages of the project. A mixture of steam and oxygen was used as the fluidization / oxidation medium during all the experiments reported in this paper. The gasification campaigns 2006 and 2008-1 were mostly focused on the investigations of the effects of varying process parameters like λ , SB and temperature, together with reactor operability issues. During the campaigns 2008-2, 2009-1 and 2009-2 parameters λ and SB were kept rather constant and the emphasis was put on the effects of bed materials different from

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| | | | | Gasi | fication ca | mpaign | | |
|-------------------------------|---------------------|------------|------|---------|-------------|---------|---------|--|
| Bed | Fuel | Additive | 2006 | 2008-1 | 2008-2 | 2009-1 | 2009-2 | |
| | | | Oct | Apr-May | Jul-Aug | Jan-May | Oct-Dec | |
| Sand | A-wood | I | 8 | 4 | 4 | ı | ı | |
| Sand | B-wood | ı | ı | 2 | 1 | ı | ı | |
| Sand | B-wood | kaolin | ı | 1 | | | ı | |
| Sand | miscanthus | kaolin | ı | က | 2 | ı | ı | |
| Magnesite | A-wood | ı | ı | ı | 3 | 2 | 1 | |
| Magnesite | B-wood | ı | ı | ı | | 2 | ı | |
| Magnesite | miscanthus | ı | ı | c, | | 3 | 1 | |
| Magnesite | straw | $kaolin^a$ | ı | c C | | ı | 2 | |
| Olivine (untr.) | A-wood | I | ı | ı | | 2 | ı | |
| Olivine (untr.) | B-wood | kaolin | ı | ı | | 1 | 1 | |
| Olivine (untr.) | miscanthus | kaolin | ı | ı | | ı | 1 | |
| Olivine (tr.) | B-wood | kaolin | ı | ı | · | 2 | 1 | |
| Olivine (tr.) | miscanthus | kaolin | I | I | ı | ı | 1 | |
| No. of exp ^s : | subtotal: | 54 = | 8 | 16 | 10 | 12 | ω | |
| No. of \exp^s : | 2005: | 13 | | | | | | |
| No. of exp ^s : | total: | 67 | | | | | | |
| ^a kaolin used only | during the last exp | eriment | | | | | | |

| L | able 4.2: Pro | cess param | heters and n | nain measu | rement resu | ults from eig | ht selected | experiments | OCTANN-MAG |
|---------------------------|-------------------------------|-------------|----------------|----------------|----------------|----------------|----------------------|------------------------|------------------------|
| | date: | 25-Jul-2008 | 25-Apr-2008 | 23-Jul-2008 | 26-May-2008 | 30-May-2008 | 28-Apr-2009 | 13-May-2009 | 07-Dec-2009 |
| | fuel: | A-wood | B-wood | miscanthus | miscanthus | straw | B-wood | B-wood | miscanthus |
| | bed material: additive: | sand - | sand kaolin | sand kaolin | magnesite - | magnesite - | olivine(U) kaolin | olivine(900) kaolin | olivine(900) kaolin |
| Steam | kg h−1 | 11.4 | 12.3 | 10.8 | 12.6 | 12.3 | 11.7 | 11.4 | 19.5 |
| 0_2 | $\mathrm{kg}\mathrm{h}^{-1}$ | 4.4 | 3.2 | 4.4 | 4.4 | 3.8 | 4.6 | 4.6 | 7.09 |
| Biomass | $\mathrm{kg}\mathrm{h}^{-1}$ | 13.2 | 10.3 | 15.6 | 10.5 | 10.6 | 11.1 | 11.7 | 15.6 |
| Air | $\mathrm{kg}\mathrm{h}^{-1}$ | 1.2 | 1.3 | 1.2 | 1.8 | 1.7 | 1.7 | 1.4 | 1.9 |
| N_2 | $\mathrm{kg}\mathrm{h}^{-1}$ | 2.1 | 4.3 | 2.1 | 5.1 | 3.2 | 2.0 | 2.7 | 2.9 |
| Mean riser T | ç | 835 | 821 | 831 | 836 | 831 | 827 | 830 | 837 |
| Gas inlet T | °C | 360 | 360 | 360 | 397 | 360 | 364 | 360 | 360 |
| P _{gage} CFB out | mbar | 29 | 52 | 76 | n.m. | 38 | n.m. | n.m. | n.m. |
| X | $\mathrm{kg}\mathrm{kg}^{-1}$ | 0.28 | 0.26 | 0.24 | 0.36 | 0.35 | 0.34 | 0.32 | 0.38 |
| SB^* | $\mathrm{kg}\mathrm{kg}^{-1}$ | 1.0 | 1.4 | 0.85 | 1.4 | 1.5 | 1.2 | 1.1 | 1.5 |
| $H_{2}0:0_{2}$ | $mol mol^{-1}$ | 4.6 | 6.8 | 4.4 | 5.1 | 5.7 | 4.5 | 4.4 | 5.0 |
| CO_2 , dnf | Movol | 31.0 | 30.7 | 31.7 | 42.6 | 45.3 | 35.6 | 36.0 | 35.9 |
| CO, dnf | Movol | 33.7 | 31.7 | 31.4 | 12.7 | 12.7 | 28.7 | 30.1 | 30.7 |
| H_2 , dnf | 70 vol | 21.8 | 21.9 | 22.8 | 35.9 | 32.0 | 21.2 | 19.4 | 21.5 |
| CH_4 , dnf | Movol | 8.9 | 8.6 | 9.5 | 5.5 | 5.8 | 8.0 | 8.3 | 8.5 |
| C_2H_4 , dnf | Movol | 2.8 | 3.3 | 2.6 | 1.3 | 1.4 | 3.1 | 3.7 | 2.6 |
| C_2H_2 , dnf | Movol | 0.43 | 0.50 | 0.34 | 0.055 | 0.15 | 0.48 | 0.55 | 0.40 |
| N_2 , dry | 70 vol | 13.8 | 31.5 | 12.6 | 29.8 | 28.0 | 22.0 | 18.7 | 15.8 |
| H_2O , raw | %vol | 59 | 57.1 | 56.6 | 49.0 | 58.0 | 67.1 | 53.1 | 62.8 |
| BTX, dnf | $g \mathrm{m}^{-3}$ (STP) | 38 | 33 | 42 | 6.5 | 23 | n.m. | n.m. | n.m. |
| PAH, dnf | $\mathrm{gm^{-3}}$ (STP) | 8.3 | 10.1 | 11.4 | 2.2 | 3.7 | 12.6 | 12.8 | 11.3 |
| Phenolics, dnf | $g m^{-3}$ (STP) | 2.2 | 4.4 | 4.6 | 0.40 | 1.2 | 1.9 | 1.7 | 2.0 |

sand on the gas composition and tar production.

In order to present the results of the gasification experiments in a transparent way, the results have been grouped as presented below. The letter following the Test Case identifier refers to the fuel used in that experiment: A (A-wood), B (B-wood), M (Miscanthus), S (1997 Dutch straw).

- Base Case (BC): A-wood, sand as bed material;
- Test Case 1 (SC): sand as bed material, B-wood (SC-B) and Miscanthus (SC-M) as fuel, and eventually the use of an additive to counteract agglomeration;
- Test Case 2 (MC): magnesite as bed material, with any of the four fuels considered here (MC-A, MC-B, MC-M, MC-S);
- Test Case 3 (OC): olivine as bed material with A-wood, B-wood and Miscanthus as fuel. For some experiments thermally pre-treated olivine was used. "900"indicates a batch treatment at the temperature between 900 and 1000°C for 8 hours. "1200" refers to a similar treatment, but at 1200°C. "U" indicates the use of untreated (fresh) olivine. So "OC(900)-M1" refers to the first experiment of the "Test Case 3"-series with olivine as bed material pre-treated at 900°C and Miscanthus as fuel.

4.2 Base Case and Test Cases results

4.2.1 Overview

Out of the 67 experiments mentioned in Table 4.1, 61 evaluation periods have been selected for further analysis. The criteria for the selection of those evaluation periods were:

- the operation of the gasifier should be in steady state, meaning that all mass and energy flows are constant over longer time frame (here: tens of minutes order of magnitude). Short term variations (here: tens of seconds order of magnitude) are inherent to this kind of process, and are caused, e.g., by variations in the particle size distribution of the fuel, screw feeding of the fuel, on-off control of the reactor heating system, etc. However, those short term variations do not affect the steady state as considered on long term basis;
- there should be a complete set of measurements taken during the considered steady state. The required data set consists of main gas components analysis (NDIR and (micro-)GC), tar analysis (SPA), water content of the raw gas (gravimetric or FTIR) and the process data of the gasifier (data log).

Figures 4.1–4.5 present the key process data for the evaluation periods of Base Case and the three Test Cases introduced above. Table 4.2 presents the process data and main measurement results from eight selected experiments. The complete overview of the experimental results can be found in Appendix A. All evaluation periods are in each case grouped by the kind of fuel, and sorted

by λ in ascending order. The only exception is the Test Case MC-A where, in view of nearly constant stoichiometric oxygen ratio, the sorting has been done by SB^{*}, in order to illustrate the effect of that variable on the gas composition.

4.2.2 Base Case

The Base Case as defined in this work partly represents a well-established condition in the gasification technology (fluidized bed gasification of clean wood) with the relatively novel aspect of the use of steam and oxygen as fluidization and oxidation media. Steam-oxygen gasification itself is not new, but the detailed reporting on applied process conditions and measurement results are still scarce in the open literature. The Base Case experiments can be divided in two groups: first four test are carried out at relatively constant SB* ratio, but with crushed A-wood pellets; whereas the last four tests have been carried out with "normal" pellets while applying more variation in SB*. The use of the crushed pellets was dictated by initial problems with the flow of particles through the solids outlet of the cyclone, but after a slight modification there normal pellets could be used. The results from the Base Case and Test Cases confirm that an increase in λ will lead to a decrease in the concentrations of the combustibles. Here, with "combustibles" is referred to the sum of the concentrations of H_2 , CO, CH_4 and C_2 -components; light hydrocarbons and tar are considered separately. The highest value is 73% for λ of 0.18 (BC-1). This effect is well-known and confirmed by numerous earlier publications. Noticeable is also the fluctuation of the amount of combustibles, as well as the concentration of the measured polyaromatic (PAH) and phenolic tar compounds with the variation of SB* (BC-1 to BC-4). This is according to the earlier observations that the dependence of tar concentration on steam-to-biomass ratio has a hyperbola-like shape [78]. Further increase in SB* (BC-5 till BC-8) seems to have a positive effect on tar reduction, see Table 4.3. However, this conclusion cannot be put unambiguously as there is an important difference between these two groups of experiments, namely the fuel particle size distribution. The roughly assessed Sauter diamter (d_{32}) of the crushed pellets is approximately 50% of that of the original pellets (3.5 and 6.9 mm, respectively). It can be concluded, that a decreased particle size has an adverse effect on the tar concentration in the gas. This can be supported by the theory, that the amount of tar produced during gasification strongly depends on the interaction of big, volatile aromatic structures with the char during the pyrolysis stage. (Poly)aromatic chains that are given a longer residence time inside a char particle will be cracked into smaller molecules, leading to lower tar concentrations in the product gas. This is clearly





Figure 4.1: Main gasification parameters, gas composition and tar concentration for the BC



Figure 4.2: Main gasification parameters, gas composition and tar concentration for the SC



Figure 4.3: Main gasification parameters, gas composition and tar concentration for the MC-A and MC-B



Figure 4.4: Main gasification parameters, gas composition and tar concentration for the MC-M and MC-S





Figure 4.5: Main gasification parameters, gas composition and tar concentration for the OC

observed here. Experiments BC-3 and BC-6 are carried out under very similar process conditions, but the amount of measured PAH en Phenolics is significantly lower for BC-6 (37 and 39%, respectively). On the other side smaller particle size distribution will lead to a higher burn-out rate (higher carbon conversion); this is confirmed by the mass balance of those two experiments (see Section 4.4).

The effect of $SB^* > 1$ is less pronounced than for the lower values of that variable. However, as mentioned before, due to the hyperbolic relation between tar conversion and steam-to-biomass ratio, this behavior has been expected.

Table 4.3: Average applied SB* and average measured tar concentrations for the two groups of Base Case experiments

| | Avg. BC-1 till BC-4 | Avg. BC-5 till BC-8 | Change [%] |
|-----------------------|---------------------|---------------------|------------|
| SB* | 0.92 | 1.3 | +41 |
| Meas. PAH (dnf) | 15 | 8.9 | -40 |
| Meas. Phenolics (dnf) | 3.9 | 3.5 | -9 |

4.2.3 Test case 1

Test Case 1 ("Sand case", SC) was defined to test the operation of the gasifier with basic bed material (sand), but with fuels more demanding than clean wood. Both fuels tested here, B-wood and miscanthus, have higher ash content than A-wood. In addition, miscanthus ash is rich in alkali compounds, which are known to be problematic in terms of agglomeration and defluidization phenomena. More on this topic is discussed in Section 4.3.4.

The gasification conditions applied during Test Case 1 are similar to the Base Case (BC). Also the results are comparable, although the amount of measured combustible components seems to be lower for SC-B than for the BC. This even when taking into account that the concentrations of the C_2 are not available for the measurements SC-B2, SC-B3 and SC-M2. This could be explained by the fact that the B-wood pellets were the biggest of all fuels applied, which could have led to a worse burnout characteristics. The amount of tar for both SC-B and SC-M is comparable with BC-5 till BC-8. In SC-M the first step in SB* (from 0.85 to 1.3) leads to a clear decrease in the quantity of measured tar, but the second step (to 1.6) does not cause any further reduction of the concentration of PAH or Phenolics. The concentration of the BTX is decreasing with increasing SB*.

Gasification of demolition wood (B-wood) or energy crops (miscanthus) is more beneficial from the sustainability point of view than the gasification of clean wood (A-wood). Therefore it is very promising that the results regarding the yield of combustible compounds and tar are similar to those from the Base Case. The challenges, however, are mainly posed by the ashes and their composition. The phenomena related to alkali metals will be commented upon later. In addition, demolition wood might contain amounts of trace elements (often heavy metals) that may cause unacceptable emissions. This topic falls, however, outside the scope of this research.

4.2.4 Test case 2

The main initial objective of Test Case 2 ("Magnesite Case", MC) was to test the promising properties of magnesite in terms of the resistance to agglomerate formation during the gasification of alkali-rich fuels. The test results indeed confirmed those expectations allowing the gasification of miscanthus without any additives even up to 11 hours. With sand such duration of the operation would not be possible. Next to that, an additional benefit of the application of magnesite has been observed, namely its activity as, presumably, a WGS and hydrocarbon-converting catalyst. The main evidence of the activity of the new bed material was a clearly increased H_2 :CO ratio, from below 1 during the BC and SC to over 2 for the MC.

The results of MC-A will be discussed in detail in Chapter 5. In addition tests MC-A2 till MC-A5 have been performed to investigate the influence of the SB* ratio on the product gas composition and the amount of measured tar. As can be seen in Figure 4.4 the increase in SB* does not lead to a clear change in tar concentration. The summed concentration of PAH and Phenolics equals 3.7 g m^{-3} (STP) for MC-A1 which is a reduction of about 8% compared to the average measured in MC-A2 and MC-A3. This difference falls almost within the error limits of the measurement. A measurable difference in the concentrations of PAH and Phenolics can be observed between the MC-A and MC-M cases. Table 4.4 presents the averaged results of light hydrocarbons and tar measurements carried out for the cases mentioned before. The decrease is especially pronounced for the PAH compounds, while the Phenolics fluctuate within the error margin. In addition the combination of magnesite as bed material and miscanthus as fuel led to the lowest PAH concentration (2.2 g m⁻³ (STP), dnf) measured during the 67 gasification experiments carried out at Delft University of Technology within the CHRISGAS project (see also Figure 4.6).

4.2.5 Test case 3

The results obtained from Test Case 2 were highly promising from the in-situ gas upgrading and tar reduction point of view. Nonetheless magnesite also has its drawbacks, as per the earlier mentioned low attrition resistance, and its price being higher than that of quartz sand. Although the authors are convinced that the benefits of the use of magnesite as bed material justify those drawbacks, they were also aware of the existence of other promising bed material candidates. Devi [51, 50] investigated the effect of olivine on the conversion of naphthalene in a small bench-scale reactor where gasification conditions had been simulated. One of the conclusions of that research was that a thermal pre-treatment (calcination) of the bed material causes the migration of iron molecules towards the surface of the particle. This effect could contribute to the increase of catalytic activity of olivine on tar cracking reactions and has been demonstrated in the bench-scale reactor mentioned above. The main objective of Test Case 3 ("Olivine case", OC) was to investigate the effect of fresh and pre-treated olivine on tar conversion under real gasification conditions.

4.2.5.1 Pre-treatment

The fresh olivine that was supposed to be used as bed material was pre-treated at two different temperatures: 900 and 1200°C. Also an attempt has been made to pre-treat a batch at 1000°C, but due to the limitations of the oven that was used initially, the maximum temperature reached was 980°C. That led to the division of applied olivine into three categories:

- fresh (untreated) olivine;
- olivine pre-treated at temperature between 900 and 1000 $^{\circ}\mathrm{C}$; and
- olivine pre-treated at 1200°C.

In all cases the duration of the treatment was 8 hours (hold time at setpoint) plus the time necessary to heat-up and cool-down the batch (ca. $200^{\circ}C h^{-1}$).

4.2.5.2 Results

The results presented in this work consider the experiments carried out with two different fuels, namely B-wood and miscanthus. Figure 4.5 shows the main results in terms of gasification parameters, gas composition and tar concentration. Immediately it is clear that the gas composition is similar to the Base Case and Test Case 1. This means that the kind of olivine used here (fresh or pre-treated) does not have any noticeable influence on, e.g., water-gas shift equilibrium, as was observed in Test Case 2. The measured amount of PAH and Phenolics is comparable to their amounts measured in SC-B and SC-M. During the analysis of the SPA samples collected during the 2009-2 gasification campaign the GC analysis method was changed slightly, which allowed the detection and quantification of a number of PAH heavier than pyrene. As those components were not considered in the earlier results, they have been shown separately from other PAH in Figure 4.5, in order not to bias the comparison of the measured tar data. Unfortunately, the effect of the pre-treatment of olivine

| Case | MC-A (averages) | SD | MC-M (averages) | SD | Rel. diff. [%] |
|--------------|--------------------|--------------|--------------------|-------|-------------------|
| λ | 0.35 | 0.021 | 0.33 | 0.042 | -7.1 |
| SB* | 1.15 | 0.23 | 1.26 | 0.15 | 9.7 |
| Hydrocarbons | and tar, dnf | $[g m^{-3}]$ | STP)] | | |
| Benzene | 14.4 | 0.794 | 15.1 | | 5.2 |
| MAH | 8.11 | 1.25 | 4.96 | | -39 |
| PAH | 3.54 | 0.378 | 2.57 | 0.393 | -27 |
| Phenols | 0.468 | 0.147 | 0.308 | 0.117 | -34 |
| Measured tar | 12.1 | 1.17 | 7.84 | | -35 |

Table 4.4: Differences in the concentrations of different hydrocarbons between the gasification experiments with A-wood and miscanthus

cannot be assessed unambiguously based on the obtained results. What is clear and remarkable is that the total percentage of measured combustibles increases with increasing λ (case OC-M). In the cases presented before exactly the opposite could be seen. Also the total percentage of the measured main gas components is observed to increase with the olivine pre-treatment temperature, both for OC-B as OC-M, from 96.8 to 103.3% by volume and from 94.8 to 99.6% by volume, respectively. Obviously the value exceeding 100% is a consequence of measurement inaccuracies, nonetheless the trend is clear. The increase in the the total percentage of the measured main gas components is an indication of the fact that less unknown or non-measurable species are present in the gas. Such species could be tar. However, the results of the SPA analysis do not give a clear confirmation of that hypothesis. It can be seen that the Phenolic species decrease sharply with increasing treatment temperature, however, on the other hand PAH are increasing. The sum of $C_x H_u$ hydrocarbons is rather constant; the remaining possibility is that benzene or 1-ring aromatic tar compounds are being converted at a higher rate if the bed material has been treated under the more severe conditions. Unfortunately, due to the problems with the adsorption of the light hydrocarbons in the sampling line (on the silica gel beads used as a desiccant), no reliable values for BTX have been recorded to confirm the above.

4.3 Overall comparison

4.3.1 H₂ and other combustibles

One of the main objectives of the CHRISGAS project was to investigate the possibilities for the production of clean and hydrogen-rich synthesis gas. Therefore the concentration of H₂ and other combustibles in the product gas received considerable attention during the experiments. Process parameters λ and SB^{*}, and also the choice of the bed material have an important influence on the gas composition and hydrogen yield. The following observations can be made based on the results of the experiments carried out within this work:

- the lowest hydrogen concentrations are obtained during the BC, SC and OC; all with sand or sand-like bed materials. The H_2 concentrations on dnf basis do not exceed 25% by volume;
- for the BC and OC the hydrogen concentration (initially) seems to increase slightly with increasing lambda value. This could be explained by the increased tar conversion at higher lambda, and also seems to be confirmed by the tar analysis data. However, in the BC the tests with the highest lambda value had also been performed with the highest SB*, so the effect of enhanced availability of steam should also be taken into account. From the literature it is known that the increase of SB* from ca. 0.6 to up to ca. 1.2 to 1.5 will still lead to increased conversion of tar (and therefore increased hydrogen yield), although that effect will diminish when SB* will increase further beyond these values. This has also been discussed earlier;
- in terms of the effect on hydrogen production the performance of olivine as bed material (OC) is similar to that observed in the BC. The presence of magnesite (MC) leads to a significant increase in hydrogen concentration at the expense of carbon monoxide. This was already made clear during one of the experiments in SC with A-wood where magnesite was solely used as an additive; the measured hydrogen concentration was approximately 50% higher than in the BC [145]. As stated earlier, simultaneous decrease of the CO concentration points towards the effect on homogenous water-gas shift reaction. Furthermore, the effect of magnesite is not limited to the water-gas shift reaction. Also the concentrations of methane, C_2 -compounds and tar are reduced;
- the highest hydrogen concentration is achieved in MC, during miscanthus gasification. Values close to 40% by volume were measured during five experiments. It should be mentioned that hydrogen concentrations measured during miscanthus gasification are clearly higher than the values measured during the gasification of other fuels under similar process

conditions. This could be a confirmation of the special properties of miscanthus ash, which was already suspected based on previous experience with this fuel at Delft University of Technology.

4.3.2 Light hydrocarbons and tar

The formation of tar is nearly inevitable in fluidized bed gasification, as due to moderate reactor temperature and relatively short gas residence time long hydrocarbon chains cannot be fully converted to short(er) molecules. However, different steps can be taken to reduce the amount of produced tar. The work within this project was focussed on the primary measures: the measures taken in the gasifier itself.

The effect of λ , SB^{*} and the choice of the bed material has already been globally discussed in the earlier subsections. Most of the attention has concentrated on the polyaromatic and phenolic fraction of tar, as these compounds not only cause the most problems in downstream applications, but also contain a significant fraction of the total heating value of the product gas stream. ECN [171] proposed a classification of tar which is based on the composition, detectability, water solubility and condensation behavior of the individual compounds:

- Class 1 GC undetectable tar.
- Class 2 heterocyclic compounds: tar, highly water soluble, e.g., phenol, cresols.
- Class 3 aromatic compounds: single ring, do not pose condensation and solubility problems, e.g., toluene, xylene, styrene.
- Class 4 light polyaromatic hydrocarbons: 2 and 3-ring compounds condense at relatively high concentrations at moderate temperatures, e.g., naphthalene, fluorine.
- Class 5 heavy polyaromatic hydrocarbons: 4 7 rings, condense at high temperatures at low concentrations. Examples: fluoranthene, pyrene, chrysene.

Figure 4.6 shows the overall results of tar measurement grouped and averaged per case and fuel. The only exception is the olivine case, where in this graph the grouping has been done by the applied treatment instead of fuel. The upper graph shows the sum of the concentrations of the analyzed and combustible gaseous compounds and the minimal and maximal concentrations of Class 4 and Class 5 tar (summed up) and the minimal and maximal concentrations of Class 2 tar. It was decided to sum up Class 4 and Class 5 tar for the sake of clarity of Figure 4.6. The bottom graph shows the contribution of each Class (except Class 1), to the total tar measured in each case. It has to be stressed



Figure 4.6: Overview of all Test Cases: minimum and maximum PAH and Phenolics concentrations and total measured and combustible gas fraction (top); contribution of each tar class to the total amount of tar measured, toluene and xylenes not included (bottom) here, that in the calculation of the fractions, to obtain the best comparison between cases the contribution of the BTX-compounds and the Class 5 PAH heavier than pyrene have not been taken into account. The reason for this is, that these species have not been quantified (reliably) in each of the cases presented here, and therefore would lead to biased comparisons.

Figure 4.6 (top) largely illustrates what already has been concluded in previous sections, but it gives an overall comparison of the results related to tar. In Figure 4.6 (bottom) two interesting things can be observed. First, the averaged results of MC-S show a clear shift from Class 4 to Class 2 tar. From the data presented in earlier sections it can be seen that the average SB* applied in MC-S is 1.5, while the average of other cases is 1.2. Additionally, MC-S is the only case where magnesite has been used together with kaolin. It is difficult to conclude here what was exactly the cause of that shift between Class 2 and Class 4, but these two variables could be taken into consideration. Second, a shift from Class 2 to Class 4 tar (i.e., the opposite as in MC-S) can be observed in OC, as the bed material pre-treatment temperature increases. This would imply an addition of for instance two phenol molecules with the simultaneous dehydrogenation and dehydration reactions leading to the formation of acenaphthylene. This would be confirmed by the increasing concentration of that compound, which has been actually observed here. However, the proof of such a mechanism and other detailed considerations of the fate of hydrocarbons under different process conditions require further in-depth investigations and therefore fall outside the scope of this overview paper.

4.3.3 H₂:CO ratio

The main application of the clean and hydrogen-rich syngas produced during the CHRISGAS project was intended to be the synthesis of liquid transportation fuels, like FT-diesel or DME. For these processes the molar (volumetric) ratio between H_2 and CO should be close to 2 in order to obtain proper synthesis conditions. Basing the experimental data presented in previous sections the following remarks can be made about this important ratio:

- the BC results show the H₂:CO ratio to be typically between 0.50 and 0.60 and a maximum at 0.8;
- SC shows the values of H_2 :CO ratio of the same order of magnitude as the BC. The values are generally slightly higher though (0.6–0.7). The same is valid for the OC (0.7–0.8). The tests with A-wood (SC-A) with magnesite as additive, where the ratio has increased to 1.2–1.4 depending on the amount of additive fed, are an exception. This has been presented elsewhere [145] in detail;
- MC shows obvious increase in the H₂:CO ratio. The average value is about 2.4, the minimum 1.7 and maximum 2.7; the highest values have been

measured during MC-M experiments.

According to the results described here, only the operation with magnesite as bed material (MC) yields high-quality product gas. The gas produced in other Test Cases will require more extensive upgrading especially in terms of tar removal and water-gas shift. This result is very promising for the future implementation of the process on industrial scale and also for the Värnamo plant. In the 1990s a lot of experience was obtained with the operation of the gasifier with magnesite as bed material. The extension of that experience with the results of this project could lead to the simplification of the process flow diagram and therefore to the successful demonstration of this powerful biomass-to-syngas technology on industrial scale.

Table 4.5: Overview of the tested bed material / additive / biomass combinations and the problems observed

| | Sand | Sand &kaolin | Olivine | Olivine &kaolin | Magnesite | Magnesite &kaolin |
|------------|------------|-----------------|------------|--------------------|-----------|----------------------|
| A-wood | stable | - | stable | - | stable | - |
| B-wood | S (7h) + A | stable | S (5h) + A | stable | stable | - |
| Miscanthus | A (<1.5h) | stable | - | stable | stable | - |
| Straw | - | - | - | - | A (<0.5h) | S(1.5h) + D |
| 0 1 1 1 | | | | | | |

Symbols used:

stable: no agglomeration occurred, stable operation possible during multiple hours S (7h) + A: stable operation for x hours, but agglomerates found in the bed after the experiment

A (<1.5h): agglomeration and defluidization occurred within x hours

S (1.5h) + D: stable operation of the gasifier for x hours , but problems related to the deposition of KCl from vapor phase occurred downstream the HT filter, see Figure 4.7

4.3.4 Effect of the choice of fuel and bed material combination on the operability of the gasifier

From Table 3.2 it is clear that all fuels used within this work, except A-wood, contain an increased amount of alkali elements, and especially potassium. As stated earlier, these elements will interact with silica present in the reactor (either from the bed material or the ash), and at temperatures above approximately 750°C sticky eutectics will be formed that will deposit on the bed material particles leading to agglomeration and defluidization phenomena. This process is accelerated by the presence of chlorine, as this element acts as a shuttle for alkali metals in their vaporization. Based on the composition of the fuels it was expected that A-wood would not cause any problems with fluidization,

while miscanthus and especially straw would very probably lead to agglomeration of a sand bed if no countermeasures are taken. B-wood has a composition and potential behavior in between the two cases above, but from experience it was rather expected to cause agglomeration [91, 14]. The results of the gasification tests related to ash effects are summarized in Table 4.5. As expected, only A-wood can be gasified using a sand bed without problems. B-wood and miscanthus led to agglomerate formation if no countermeasures were taken, while in view of the poor outlook no attempt was made to gasify straw using a sand bed. As explained in Section 3.3.2 magnesite had been shown to be a very effective bed material in terms of counteracting (postponing) the agglomeration. This observation has been confirmed during the experiments performed in this work, as both B-wood and miscanthus could be gasified without any additional measures. These measures involved in this case the use of an additive, to act as an alkali getter and to avoid the formation of the sticky deposits. Based on the previous experience kaolin was chosen as an additive (see Section 3.3.3). Its use gave very satisfactory results; allowing reliable operation with B-wood and miscanthus on the sand bed as well as olivine bed.

Gasification of straw proved to be challenging, even when magnesite was used as bed material. In fact, agglomerates were formed also during those tests, but most likely their origin was in the straw ash itself, i.e., the interaction between alkali and silica from the ash. Finally the decision had been taken to use kaolin also during straw gasification on magnesite bed. This seemed to solve the problem with defluidization, but unfortunately caused new problems (fouling) to the colder parts of the process located down the line. This is shown in Figure 4.7, which presents a picture of the inner part of the V-cone[®] flowmeter located downstream the process (see Figure 3.2) after short period of operation with straw. The gap between the wall and the bluff body is completely blocked by an alkali deposit. That deposit was analyzed by XRF, and the results confirmed that it consists mainly of an alkali salt, namely KCl.

4.4 Mass balance and process bench marks

In order to verify the consistency of the measurements and to gain more insight into the fate of the main elements (C, H, N, O) a material balance (mole balance) was set up for each case studied. Most of the data necessary to perform this operation came directly from the steady-state data. One crucial figure that is not listed among that data is the total flow rate of the gas leaving the gasifier. Although Figure 3.2 indicates the presence of a flow meter in the outlet line, that measurement has only been used in the first eight Base Case experiments (BC-01 till BC-08). For later experiments a different approach for calculating the total flow rate was applied in the first instance. It is based on the assumption that nitrogen fed into the reactor does not undergo any chemical reactions and thus the amount leaving the reactor should be the same as the input flow.



Figure 4.7: The space between V-cone[®] flowmeter wall and its bluff body entirely blocked by alkali deposits (white ring) consisting mainly of KCl

The amount (volume fraction) of nitrogen in the product gas is measured on dry basis as indicated in Table 3.1. Applying the law of mass conservation (no accumulation of mass takes place in the reactor) and with the assumption of nitrogen remaining inert, the molar flow of dry product gas can be estimated using the following simple equation:

$$\dot{\Phi}_{tot, dry gas} = \frac{\dot{\Phi}_{N_2, in}}{y_{N_2, dry}} [kmol \cdot h^{-1}]$$
(4.1)

The contribution of the carbon in the solids (char, ashes) to the total carbon flow is calculated from the elemental C balance – it is assumed that all the solids leaving the reactor (fly ash) consist of carbon. More detailed information about the material balance introduced above can be found in Chapter 5. There also two mass balances from two different cases (BC-16 and MC-A01) are presented in detail. For all the cases presented in earlier sections a mass balance discrepancy has been determined. This discrepancy is the result of the measurement errors or incomplete measurements and in practice can never be eliminated completely. It is defined as follows:

$$MBD_{absolute} = \dot{\Phi}_{out} - \dot{\Phi}_{in} \tag{4.2}$$

$$MBD_{relative} = \frac{\dot{\Phi}_{out} - \dot{\Phi}_{in}}{\dot{\Phi}_{in}} \cdot 100\%$$
(4.3)



Figure 4.8: Overview of all Test Cases: mass balance discrepancy, carbon conversion, cold gas efficiency and solid carbon (fly ash) flow rate

Figure 4.8 shows the average relative MBD for all discussed cases, grouped in the same way as in Figure 4.6. The error bars show the minimum and maximum relative MBD for each group. For most of the cases the discrepancy is negative, meaning that outgoing mass (or mole) flow is lower that the incoming flow. This situation is more justifiable, as even with very accurate determination of the input it is clear that not all the constituents of the product gas are quantified. This is especially true in case of gasification where the composition of the product gas is very complex including a wide range of hydrocarbons. Furthermore the method of the calculation of the total flow and the gravimetric water measurement are considered to be the primary sources of material balance discrepancies (listed in order of importance). Figure 4.8 also presents two important process benchmarks:

$$CC = \left(1 - \frac{\dot{\Phi}_{C,residue}}{\dot{\Phi}_{C,feed}}\right) \cdot 100\%$$
(4.4)

$$CGE = \frac{LHV_{gas}[MW]}{LHV_{fuel}[MW]} = \frac{\sum \dot{\Phi}_i \cdot LHV_i}{\dot{\Phi}_{fuel} \cdot LHV_{fuel}}$$
(4.5)

As already indicated before, the highest carbon conversion was achieved with milled fuel particles in the Base Case. Olivine (fresh and pre-treated) showed the relatively lowest carbon conversion, which obviously is linked with the highest (calculated) solid carbon flow rate out of the system. The initial results of the quantification of the mass of the collected filter ashes from various experiments show too high dispersion to confirm or deny this calculated result. The main fraction of the unconverted (fine) carbon particles is expected to be found downstream of the gasifier as the accumulation of carbon in the reactor is found to be negligible compared to the total carbon throughput during an average test run. The reason for the decreased carbon conversion in OC has been primarily sought in different fluidization behavior of olivine. Afterwards it had been observed that especially in OC(U) and OC(1200) the ratio between the applied fluidization velocity (u_{fl}) and the transport velocity of the particular bed material (u_{tr}) was too low (see Figure 4.8). However, this does not fully explain the reduced carbon conversion, as u_{fl} : u_{tr} applied in OC(900) is above 1 and still the carbon conversion is lower than in SC and MC. Another possible reason could be the use of B-wood as fuel (large particles, low conversion) which would be in line with the reduced carbon conversion in SC-B, or the use of an additive (in line with MC-S, but contradicting to SC-M). However, from the available data it is difficult to isolate the individual effect of those variables on carbon conversion.

4.5 Operability of the test rig – design issues

The listing of the experimental results presented in Appendix A shows that although the duration of all the experiments was limited to one working day, in most cases relatively long and stable operation was achieved. In the longest experiment performed, the steady state operation lasted even for 13 hours, which considering the size of the test rig and the amount of people involved (no operator shifts) can be considered as "long". This proves the suitability of the CFB gasifier at TU Delft for performing of the biomass gasification tests under different operating conditions.

During the experimental work several observations have been made about the effect of the design of certain parts of the gasifier on the operability and reliability of the test rig. The most were:

• diameter of the solids exit of the cyclone is critical. If a too low value is chosen it will inevitably lead to the blockage of the cyclone with unconverted fuel particles, which on its turn will lead to the loss of bed material in the reactor (see Figure 4.9). Cyclone designs are usually optimized for fine particles, and the presence of coarse particles (few orders of magnitude larger) is often not taken into account in the calculations. However, in practice it can cause a deterioration of the performance of the cyclone.

Choosing a cyclone geometry with an extra margin in the outlet diameter will still provide sufficient separation for the operation in circulating fluidized bed mode, without compromising the reliability of operation;

- the practical length-to-diameter (L/D) ratio of the horizontal part of the L-valve is much lower than the theoretical value reported by various sources. Again here, design calculations assume a certain particle size distribution of the solids, without taking into account the presence of particles that are larger by the few orders of magnitude, as can be seen in Figure 4.10. Although the initial design of the L-valve fell in the range 5 < L/D < 10 given by the relevant literature, it turned out to be quite unreliable during the operation with biomass. The relatively long horizontal arm of the L-valve led either to the stagnation of the flow or required excessive aeration to maintain continuous operation. As this was not the desired situation the design was modified to an inclined L-valve with only a short horizontal part (L/D ~ 2);
- the presence of the thermocouples in the downcomer can cause enough resistance to obstruct the flow of the solids. Initially the downcomer was equipped with 3 thermocouples (3 mm diameter) distributed along its length. In order to protect the thermocouples from abrasion and quick wear (especially noticeable in the riser), all thermocouples have been protected by an additional tube of 6 mm outside diameter. This solution worked well for the riser, but turned out to be a problem in the downcomer. The cross sectional area of the protective tubing appeared to be too large relatively to the cross section of the downcomer, and therefore could easily cause a blockage for the packed bed flow.



Figure 4.9: Top view of the cyclone: solids exit blocked with biomass particles (left); solids exit open (right)

Probably most of the above observations will be relevant only to a laboratoryscale test rigs, due to their relatively small cross-sectional dimensions compared



Figure 4.10: Removal of hot bed material from the gasifier. Note the difference between the size of the bed material and the size of unconverted char particles

to the size of the fuel particles. This also shows that the operational problems of a large-scale power plant will often be different from the problems of a smallscale or lab-scale reactor. Nonetheless, such observations should be kept in mind regardless the scale of operation to anticipate on any possible bottlenecks.

4.6 Conclusions and recommendations

The experimental research presented in the preceding sections resulted in the important further steps taken in pushing the state-of-the-art in fluidized bed gasification technology forward. The results are not only a large amount of recorded process data that will be used for the validation of mathematical models of the process. Also operational experience and novel insights have been obtained, which may result in an improved and simplified process flow diagram of a clean syngas production plant with Circulating Fluidized Bed as the first hot conversion step. The main conclusions of this work can be summarized as follows:

- the optimal bed material and fuel combination depends strongly on the application of the product gas. In particular advanced applications, like the production of platform chemicals, synthetic transportation fuels or hydrogen will benefit from the use of magnesite as bed material;
- when sand is used as bed material the use of additive to suppress the agglomeration phenomena is necessary, unless clean wood (A-wood) will be used as the fuel. When straw is being used as the fuel the use of an additive to counteract agglomeration is necessary irrespective of the bed material used. This is caused by the fact that the alkali present in the fuel ash will form low-melting eutectics with silica, that is also present in the ash. From the agglomeration point of view olivine can be designated as fractionally better than sand – this has been proven during two 13-hours test runs with that bed material and miscanthus as fuel;
- gasification of any fuel tested in this project on a sand or olivine bed will yield similar results in terms of hydrogen concentration in the gas, tar and light hydrocarbon concentration and H₂:CO ratio;
- increasing the steam-to-biomass ratio from ca. 0.7 to ca. 1.3 will contribute to tar reduction and increased H_2 yield;
- the use of magnesite either as an additive or as a bed material leads to significant increase in hydrogen concentration in the product gas. The maximum hydrogen concentration measured was close to 40% by volume during miscanthus gasification on magnesite bed. Gasification of other fuels at similar conditions gave lower H₂ concentrations, which could be an implication of special (catalytic) properties of miscanthus ash; and

• also in terms of tar reduction and the boosting of H_2 :CO ratio magnesite has shown excellent results. The sum of measured polyaromatic and phenolic compounds could be reduced below 2 g m⁻³ (STP) on raw gas basis, and the H_2 :CO ratio increased to values between 2 and 3.

According to the results of this project, only the operation with magnesite as bed material yields high-quality product gas. The gas produced in other Test Cases will require more extensive upgrading especially in terms of tar removal and water-gas shift. This result is very promising for the future implementation of the process on industrial scale. The extension of the experience from the past with the results of this project could lead to the simplification of the process flow diagram and therefore to the successful demonstration of this powerful biomass-to-syngas technology on industrial scale.
Myślisz może, że więcej coś znaczysz, bo masz rozum, dwie ręce i chęć ... So you think that you mean something, 'cause you've got a brain, two hands and some willingness

Lady Pank, Mniej niż zero, 1983



Enhanced conversion of tar and the increase of H_2 :CO ratio by the use of calcined magnesite as the bed material in a CFB

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Introduction

Previous chapter discussed the results of the gasification experiments performed in the CFB gasification test rig of the Energy Technology section at TU Delft as a contribution to the CHRISGAS project. One of the conclusions of that section was that the quartz sand, although cheap and abundant, has certain drawbacks when used as a bed material in a biomass gasifier, mainly related to its sensitivity to bed agglomeration. Basing on the pilot-scale experience of the Värnamo gasifier it was decided to test calcined magnesite as the bed material. These tests showed not only excellent agglomeration resistance when using herbaceous kinds of biomass, but also an important improvement of the product gas quality in terms of the lower tar yield and increased H_2 :CO ratio. This chapter elaborates in detail on the latter observation, basing on an experiment when a transition was made from sand to magnesite as the bed material.

5.1 Background information

During operation, the CFB internally recirculates a certain amount of inert material, also referred to as "bed material". This bed material accumulates a part of the energy released during (partial) combustion of biomass and distributes it along the reactor, ensuring nearly constant temperature throughout the bed. A variety of bulk solids can be used as bed material - quartz sand being the mostly well-known. The drawback of quartz sand, and other bed materials containing significant amount of silica, is that they are prone to agglomerate formation when herbaceous biomass with high alkali and chlorine content in the ash is being used as fuel. These agglomerates can cause a blockage inside the reactor and therefore unscheduled maintenance interruptions in the operation.

While agglomeration may lead to difficulties in process operation and unscheduled maintenance stops, the tar produced in the gasifier may affect the downstream equipment in a negative way, resulting in the need for downstream gas treatment and upgrading. Lowering the operational temperature of the reactor below the eutectic point of the lowest melting salt would solve the problems with agglomeration. However, in that case the amount of tar produced increases sharply and also the carbon conversion is significantly reduced, which makes this option not feasible for most applications. An exception to this is the Harboøre project, where the produced tar from the updraft gasifier is stored for peak load operation [158]. One method that is commonly used in practice and has gained a lot of research focus is the use of additives. Those solids, fed to the reactor simultaneously with the fuel, are expected to counteract agglomeration, reduce the amount of tar produced, or (preferably) both. Well known additives for counteracting agglomeration are, e.g., kaolin $(Al_2Si_2O_5(OH)_4)$, calcium oxide, calcium carbonate, bauxite [8], while, e.g., dolomite, limestone and char have a positive effect on the reduction of the amount of tar formed in the gasifier. Another strategy that has been investigated by researchers is the employment of different kinds of bed material. In fluidized beds used in fuel conversion applications, quartz sand is the most common bed material, due to its abundance and low price. However, it is exactly silica, the main component of quartz sand, that very easily - especially when also chlorine is present in the fuel - forms the low melting, sticky salts with alkali from herbaceous biomass mentioned before. Therefore, a reactor operated with quartz sand as bed material, without the use of an additive, will be very prone to agglomeration. Also with respect to tar formation, sand does not seem to have any activity in promoting the tar conversion, apart from thermal cracking reactions [46]. An alternative bed material that could help to overcome the problems mentioned above could be olivine [49, 51, 50]. The fraction of silica in olivine is much lower than in sand, and due to the presence of iron it has been shown to have a catalytic effect on tar cracking reactions. However, the fraction of silica, although lower than in sand, still makes olivine sensitive to agglomeration phenomena [61]. A possible alternative here could be magnesite. This mineral contains almost no silica and is abundantly available at an acceptable price: $\in 274$ per tonne net (M-85, Integra Group, Slovakia) versus \in 161 per tonne for sand (Filcom B.V., the Netherlands). Magnesite has been used on demonstration scale in the 18 MW fuel thermal power input pressurized air-blown CFB combustor/gasifier in Värnamo (Sweden) and has shown very promising results with respect to agglomeration resistance. Those results have been confirmed during smaller scale laboratory investigations [173]. Magnesite has also been used as an alternative to sand as bed material in the atmospheric 100 kW fuel thermal power input CFBG test rig in our laboratory, initially for the same reason as its application in the Värnamo plant. During the gasification experiments it was observed, that besides excellent agglomeration resistance, magnesite has a very significant influence on the composition of the product gas. Regarding the combustible gases it was seen that the concentration of hydrogen on a dry basis rose with more than 50%, while the concentrations of carbon monoxide and hydrocarbons decreased sharply as compared to gasification using sand as bed material. The results of the investigation of the observed phenomenon just introduced are presented below.

5.2 Experimental

5.2.1 Base case

Gasification experiments have been run on the test rig described in Chapter 3. The experimental results of gasification of A-quality 6 mm wood pellets (i.e., clean wood supplied by Energy Pellets Moerdijk B.V., the Netherlands, further referred to as A-wood) with a mixture of steam and oxygen as fluidization agent and quartz sand as bed material will be used as the base case in this work. The

characteristics of the quartz sand used for the base case experiments described here can be found in Table 3.3 and in Figure 3.6. Sand consists mostly of SiO_2 , with only traces of some other elements. This is immediately its Achilles' heel, due to high agglomeration potential, as explained earlier. However, its abundance, low price, availability of various particle size ranges, and excellent attrition resistance make it a very common bed material used in many (circulating) fluidized bed reactors.

Table 3.2 in Chapter 3 shows the elemental composition of A-wood. Numerous experimental results from gasification have been obtained with this fuel – see Chapter 4 and the literature, e.g., [63, 168, 147, 146]. The combination of A-wood as the fuel and sand as the bed material was used as the base case in the investigation of the (catalytic) effect of magnesite on the product gas composition.

Figure 5.1 presents the gas analysis and reactor temperature trend lines created by plotting the gas concentrations and average reactor temperature as measured during the experiment of August 19^{th} 2008 versus time. The left part of Figure 5.1 (between 10:30 and nearly 12:00) corresponds to base case operation as described in this paragraph. Average steady state values for the process variables applied and the resulting gas composition are summarized in Table 5.1. To make the comparison easier, the concentrations of combustibles and CO_2 are given on a dry, nitrogen-free (dnf) basis. The nitrogen concentration is given on a dry basis, and the moisture content is expressed on a raw gas basis. The concentrations of the combustibles can be easily recalculated from dnf to dry basis by multiplying them with a factor $(1-y_{N_2})$.





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| Table 5.1: (| |

| | | Basecase | Magnesite I1 ^a | Magnesite I2 ^a | Magnesite bed |
|---|------------------------------|----------------------|---------------------------|---------------------------|---------------|
| | date: | 19-Aug-08 | 19-Aug-08 | 19-Aug-08 | 20-Aug-08 |
| | fuel: | A-wood | A-wood | A-wood | A-wood |
| | oxidant: | Steam-O ₂ | Steam- O_2 | Steam- O_2 | Steam- O_2 |
| | duration: | 0:16 | 0:10 | 0:10 | 0:40 |
| | t start: | 10:58 | 15:25 | 16:15 | 14:00 |
| | t end: | 11:14 | 15:35 | 16:25 | 14:40 |
| Steam flow rate | ${ m kg}{ m h}^{-1}$ | 10.8 | 10.8 | 10.8 | 10.8 |
| O ₂ flow rate | ${ m kg}{ m h}^{-1}$ | 4.40 | 4.40 | 4.40 | 4.40 |
| Biomass flow rate | ${ m kg}{ m h}^{-1}$ | 10.4 | 10.4 | 10.9 | 10.4 |
| Air (L-valve) flow rate | ${ m kg}{ m h}^{-1}$ | 0.767 | 0.768 | 0.767 | 1.04 |
| N_2 (purge) flow rate | $\mathrm{kg}\mathrm{h}^{-1}$ | 1.25 | 1.26 | 1.26 | 1.25 |
| Mean riser temperature | °C | 837 | 836 | 837 | 833 |
| Gas inlet temperature | °C | 360 | 360 | 360 | 380 |
| P _{gage} at CFB outlet | mbar | 63.5 | 19.8 | 22.5 | 31.5 |
| λ (daf) ^b | ${ m kgkg^{-1}}$ | 0.35 | 0.35 | 0.33 | 0.35 |
| SB $(ar)^c$ | ${ m kgkg^{-1}}$ | 1.0 | 1.0 | 1.0 | 1.0 |
| $H_20:0_2$ | $mol mol^{-1}$ | 4.4 | 4.4 | 4.4 | 4.4 |
| CO ₂ volume fraction (dnf) | % | 33.7 | 39.3 | 39.3 | 40.8 |
| CO volume fraction (dnf) | % | 34.0 | 23.4 | 22.1 | 16.1 |
| H ₂ volume fraction (dnf) | % | 21.9 | 28.3 | 30.2 | 36.2 |
| CH ₄ volume fraction (dnf) | % | 8.23 | 7.69 | 7.41 | 6.08 |
| C ₂ H ₄ volume fraction (dnf) | % | 2.30 | 2.08 | 2.09 | 1.23 |
| C ₂ H ₂ volume fraction (dnf) | % | 0.380 | 0.320 | 0.313 | 0.0828 |
| N ₂ volume fraction (dry) | % | 12.5 | 12.2 | 11.7 | 12.1 |
| H ₂ O volume fraction (raw) | $\%^{q}$ | 62.2 | 57.9 | n.m. | 48.2 |
| ^a magnesite as additive: intermedia | te measurements | s I1 and I2 | | | |

 c steam to biomass ratio, on mass basis d average of concentrations determined by wet/dry CH_4 and C_2H_4 FTIR measurements

 $^{\boldsymbol{b}}$ ratio of actual oxygen feed rate to stoichiometric oxygen requirement based on daf fuel

5.2.2 Pure MgO and Magnesite as an additive

The use of pure MgO, the main constituent of calcined magnesite, for tar reduction was already investigated in a downstream gas cleaning unit (packed bed) [46, 45]. There calcined magnesite, being referred to as pure MgO, was expected to have some influence on tar reduction, but only at high (>800°C) temperatures. The experiment proved that indeed MgO contributed to the reduction of the amount of tar, but the effect was less than, e.g., when dolomite or calcite was applied. Furthermore, an *increase* in CH₄ concentration was observed after the sorbent bed [46]. As the calcination of MgCO₃ takes place at $300-350^{\circ}$ C, and no recarbonisation takes place at higher temperatures, no capture of CO₂ is expected. In order to test the effects mentioned above under steam-oxygen blown gasification conditions, and to verify the effect of MgO on the composition of the product gas, after approximately 1.5 hours of steady state operation under base case conditions, the feeding of pure MgO was started. However, the feeding of MgO was quite problematic, due to the cohesive nature of the material. It was difficult to establish a stable feed rate and in nearly three hours of intended MgO feed only 0.6 kg of the additive was fed, all during the first hour of feeder operation. A slight change in the gas composition can be observed between 12:00 and 13:00; this is caused, however, by the stabilizing riser temperature, which increases from 834°C to 840°C in that period of time (see Figure 5.1) and also a slightly reduced bed density at the bottom of the riser (decreased pressure drop). An increasing pressure drop of the high-temperature filter downstream, causing less nitrogen from the feeding system overpressure to enter the gasifier is responsible for yet another slight change in the gas composition (from 13:00 till 14:30), but that effect is canceled at the moment the flow is switched to the second filter with lower pressure drop. Thus none of the changes mentioned before can be attributed to the feed of magnesium oxide, but to obtain a solid proof of the (lack of the) effect of MgO on product gas composition the experiment would need to be repeated with a stable feed of a more significant amount of that additive.

Following the feed of pure MgO, magnesite was fed to the reactor as an additive. In this case within 1 minute after the initialization of the additive flow an effect started to be visible on the CO/CO_2 analyzers, without taking into account their time lag with respect to the process, which is of 10 seconds order of magnitude. After the feeding of 0.6 kg of magnesite (the same amount as the total feed of MgO), the concentration of CO had dropped from 28.1% to 21.8% by volume, while the concentration of CO_2 had risen from 30.4% to 34.1% by volume. Increasing the feed rate of magnesite led to a steeper concentration change, while stopping the magnesite feed caused the gas composition to tend towards its original value, before the start of additive feed; see Figure 5.1. More detailed values for process conditions and the gas composition are given in Table 5.1.

5.2.3 Magnesite as bed material

In the previous paragraph an observation has been described, that an increase in magnesite feed results in a significant change of product gas composition. Therefore the limits of the effect of that mineral on the gas composition could be explored by using it as the bed material instead of as an additive. Before that experiment 7 kg of magnesite were fed to the reactor and the process was initiated. However, also in this case it was necessary to feed a certain amount of magnesite continuously, at a feed rate of approximately 3 kg h^{-1} . That was necessary to compensate for the continuous carry-over of the bed material to the filter. That carry-over was caused by the fact that the magnesite available had a smaller average particle diameter than sand, and the fraction of fines was significantly higher than that of the sand. A graph presenting the cumulative particle size distribution (PSD) of both bed materials is presented in Figure 3.6. It is clear that the sand particles are restricted to the size between ca. 200 and 470 μ m, while magnesite particle sizes are spread throughout the analysis domain; the fraction of fines in magnesite is significantly larger than in sand. The fine magnesite particles have not been separated from the gas stream in the cyclone, so they were entrained with the gas stream and finally were retained in the filter. The actual carry-over rate of the bed material was also of the order of 3 kg h^{-1} on average - this value was determined by weighing the ash extracted from the filter (which now consists mainly of the bed material) and dividing it by the duration of the operation. The phenomenon of the carry-over of the bed material was also observed in the Värnamo gasifier [110], where that effect was even desirable (the formation of a coarse filter cake with significant thickness). Therefore in order to maintain the bed inventory at a constant level, a constant feed of magnesite was necessary during the operation.

An overview of the process conditions and the gas composition is given in the leftmost column of Table 5.1. Next to the gas samples and analysis, also tar samples have been taken during every setpoint. The sampling has been carried out at least in duplo, and sometimes in triplo. The analysis of the samples yielded the concentrations of 13 PAH components and 9 oxygenated components. Figure 5.2 presents an overview of the compounds contributing to over 85% by weight of the tar components that were analyzed; the values are given on measured raw gas basis. Also concentrations of benzene are presented there. Although according to the definition benzene is not a tar compound it is included in the figure, in order to separate it from the overview of the concentrations of permanent gases and light hydrocarbons (methane and C_2 -species).

5.3 Results and discussion

The following observations have been made concerning the main gas composition measured during the base case:



Figure 5.2: Comparison of the concentrations of the most significant tar compounds; base case and magnesite bed

- the volumetric H₂:CO ratio is about 0.5 to 0.7 on raw gas basis;
- the methane concentration in the product gas is significant. The production of methane is characteristic for CFB gasifiers, both atmospheric and, even stronger, pressurized, due to the fact that the gas residence time is too short to achieve overall chemical equilibrium at the typical operating temperature window (800–950°C);
- light, volatile hydrocarbons (C₂H₂, C₂H₄, C₆H₆) and tar are present in the gas, due to the same reason as methane.

The gas analysis results presented in Table 5.1 clearly indicate a change in gas composition after the introduction of magnesite. The most striking is the increase in hydrogen concentration, from 21.9% by volume, dnf, in the base case to 36.2% when magnesite is used as bed material for otherwise similar conditions. This corresponds to an increase of 14.3%-points, or to an increase of 65.5% of the base case concentration. This is a very important result, as with the increase of hydrogen concentration and the decrease of carbon monoxide

concentration a H₂:CO ratio of about 2.3 is obtained, which is one of the requirements for, e.g., Fischer-Tropsch synthesis [71]. Although the dry concentrations are very useful to get a first impression of the composition of the gas, and they are often readily available as most analyzers cannot handle moisture in the analyzed gas, to carry out some quantitative considerations it is necessary to express the gas concentrations on a raw gas basis, thus taking water into account. This is necessary, because water also takes part in many gasification reactions, and its concentration will vary, as can be seen in Table 5.2. The hydrogen concentration in the raw gas produced during gasification using a sand bed increased with nearly 130% when the reactor was operated with magnesite as bed material, which can be considered a major improvement. The change in the H₂:CO ratio is not the only difference between the base case and the operation with magnesite, either as additive or as bed material. On a "dnf" basis a clear decrease in methane and C₂-hydrocarbons is observed - especially the latter ones being of special interest, as they are thought to play a role in the tar formation pathways. However, when considered as a fraction of the raw gas mixture, the methane concentration in fact does not seem to change, while the concentrations of C_2H_4 and C_2H_2 decrease by 27% and 70%, respectively. When looking at the absolute concentration changes it can be observed that water is the most prominently consumed reactant, and the second one is carbon monoxide, but its consumption is approximately three times less than that of water. Thus although the change in the H₂:CO ratio mentioned before would suggest that it is the homogeneous water-gas shift (WGS) reaction that is affected by the presence of magnesite, the effect of the mineral is much more complicated. If it were solely the WGS reaction, then CO and H₂O should decrease in an amount equal to the production of H_2 and CO_2 . That is, however, not the case, as stated above. Also the production of CO_2 is lower than that of H_2 , which means that either CO_2 is partially consumed by an other reaction (dry reforming, Boudouard) or H₂ is also produced via another route. Next to the effect on the main gas com-

| | | Base case | Magn.bed | Abs. diff. |
|----------|---|-----------|----------|------------|
| CO_2 | % | 11.2 | 18.6 | 7.4 |
| CO | % | 11.2 | 7.3 | -3.9 |
| H_2 | % | 7.2 | 16.5 | 9.2 |
| CH_4 | % | 2.7 | 2.8 | 0.0 |
| C_2H_4 | % | 0.8 | 0.6 | -0.2 |
| C_2H_2 | % | 0.1 | 0.0 | -0.1 |
| N_2 | % | 4.7 | 6.2 | 1.5 |
| H_2O | % | 62 | 48 | -14 |
| | | | | |

Table 5.2: Volume fractions of main components expressed on raw gas basis as measured

position, the analysis of tar samples taken during the experiments also revealed a significant and interesting effect on tar concentration and composition. Table 5.3 shows a summary of the tar content in the raw product gas. In order to allow quick comparison, instead of listing all the compounds analyzed, the tar compounds have been grouped according to the classification defined by ECN [171]. Again, although not being a tar compound, benzene is listed in this table, but it does not contribute to the total tar amount. The first observation that can be made is the clear decrease in the total amount of tar, namely 21% on a mass basis. Furthermore, the new bed material has a very large influence on the fate of Class 2 and Class 5 tar - both classes are reduced by 78% and 84%, respectively (mass basis). Although some question marks could be put on the accuracy of that observation for Class 5, as it is represented only by two compounds (fluoranthene - $C_{16}H_{10}$ and pyrene, also $C_{16}H_{10}$), the decrease of the phenolic compounds is well-quantified. The only group showing an increase in the concentration is the not really problematic class 3 tar, so the monoaromatic hydrocarbons with benzene excluded.

| Tar classes (ECN) | Base case volume fr | Magn. bed action, raw | Base case concentr | Magn. bed |
|-----------------------------|------------------------|--------------------------|-----------------------|-----------|
| | l | 70] | ling in | (317)] |
| Benzene | 2.2E-01 | 1.8E-01 | 7.8E+03 | 6.4E+03 |
| Class 2: Heterocyclic comp. | 2.3E-02 | 4.8E-03 | 1.0E+03 | 2.3E+02 |
| Class 3: MAH $ex.C_6H_6$ | 7.2E-02 | 9.5E-02 | 3.1E+03 | 4.2E+03 |
| Class 4: 2-3 ring PAH | 5.2E-02 | 2.4E-02 | 3.2E+03 | 1.4E+03 |
| Class 5: 4-7 ring PAH | 1.3E-03 | 2.1E-04 | 1.2E+02 | 1.9E+01 |
| Total tar analyzed | 1.5E-01 | 1.2E-01 | 7.5E+03 | 5.9E+03 |

Table 5.3: Summary of the tar content in the raw product gas, grouped by classes as defined by ECN [171]

5.3.1 Material balance

5.3.1.1 Mole balance - calculations

Setting up a mass (or elemental mole) balance has multiple benefits:

- it allows to compare the input and output flows and thus assess the consistency of the measurement results;
- possibly it allows the calculation (estimation) of some known but not quantified process flows;

• it can help identifying the measurement errors and possible unknown process flows, e.g., leakages (Data Reconciliation).

To be able to gain more insight into the fate of the main elements (C, H, N, O) in the transition from the base case to magnesite bed, a mole balance is set up. Most of the data necessary to perform this operation can be found in Table 5.1. One crucial figure that is not listed among the data mentioned before is the total flow rate of the gas leaving the gasifier. Although Figure 3.2 indicates the presence of a flow meter in the outlet line, there are two issues related to this measurement: the measured variable is the pressure difference and the flow rate is calculated from that value, gas temperature and composition, and the geometry of the V-cone. During the experiments described in this article, there were problems with the accurate measurement of the pressure difference in the V-cone, which will greatly affect the accuracy of the measurement. The second issue is that the flow meter is located downstream the filter, while the gas composition has been measured downstream the gasifier. Due to the significant residence time in the gas ducts and the filter (ca. 10 s) the gas composition could change leading to an even greater loss of accuracy of the flow returned by the V-cone calculation. Therefore a different approach for calculating the total flow rate is applied in the first instance. It is based on the assumption that nitrogen fed into the reactor does not undergo any chemical reactions and thus its amount leaving the reactor should be the same as the input flow. As mentioned in the description of the gasifier, the nitrogen input flow is measured using mass flow controllers and consists of the nitrogen in the air used for L-valve control, nitrogen for purging of the differential pressure sensors connections and nitrogen used for creating an overpressure in the bunker system compared to the gasifier. The amount (volume fraction) of nitrogen in the product gas is measured on dry basis as indicated in Table 3.1. Applying the law of mass conservation (no accumulation of mass takes place in the reactor) and with the assumption of nitrogen remaining inert, the molar flow of dry product gas can be estimated using the following simple equation:

$$\dot{\Phi}_{tot, dry gas} = \frac{\dot{\Phi}_{N_2, in}}{y_{N_2, dry}} [kmol h^{-1}]$$
(5.1)

However, during the experiments it has been observed, that there is a leakage of nitrogen from the bunker system to the surroundings. This happens near the rotary shaft seals of the dosing feeders. Recently those leakages have been quantified by applying a flow restriction at the outlet of the main feeder (and therefore pressurizing the bunker system) and measuring the amount of the gas that still slipped through the restriction. The input flow of the gas was controlled at a constant setpoint. The difference between the input flow and the slip flow represents the leakage anywhere else in the bunker system. This leakage is directly proportional to the pressure in the bunker system. As the pressure in the bunker system is measured continuously during the experiments, the leakage can be taken into account properly when setting up the material balance. Here, the leakage flow is subtracted from the total nitrogen input flow before calcu-

lating the total molar flow of the dry gas. $\dot{\Phi}_{dry \ gas}$ represents here the molar flow of dry gas including BTX. The molar flow rate of the raw gas can be calculated dividing the dry flow rate by the factor $(1-y_{H_2O})$. Now knowing the total dry molar flow rate , the elemental mole flows can be calculated from the measured gas and tar concentrations. The gas concentrations measured on dry basis and reported in Table 5.1 have been normalized before carrying out the balance calculations. The equations used for the calculations of component and elemental molar flow rates are summarized below and the results are presented in Table 5.4 and Table 5.5 for the base case and magnesite case, respectively. The tables present only the main elements C, H, O and N. Minor elements S, Cl (from the fuel) and Ar (from air) are not included in the table due to the limited space, but are included in the calculations.

$$\dot{\Phi}_{tot, dry gas} = \frac{\left(\dot{\Phi}_{N_2, in} - \dot{\Phi}_{N_2, leakage}\right)}{y_{N_2, dry}} [kmol h^{-1}]$$
 (5.2)

$$\dot{\Phi}_i = \dot{\Phi}_{tot, dry gas} \cdot y_i [kmol h^{-1}]$$
(5.3)

where *i* stands for any of the components measured on dry basis: CO, CO₂, H₂, CH₄, C₂H₂, C₂H₄, C₆H₆, C₇H₈, C₈H₁₀, N₂, O₂.

$$\dot{\Phi}_{H_2O} = \frac{\dot{\Phi}_{tot, dry gas}}{1 - y_{H_2O}} - \dot{\Phi}_{tot, dry gas} = \frac{\dot{\Phi}_{tot, dry gas}}{\frac{1}{y_{H_2O}} - 1}$$

$$\dot{\Phi}_{tar} = \left(\sum \frac{C_{PAH, j}}{MW_j} + \sum \frac{C_{Phenolics, k}}{MW_k}\right) \cdot \dot{\Phi}_{tot, dry gas} \cdot V_{m, STP} \cdot 10^{-6}$$
(5.4)
(5.5)

C represents the measured tar concentrations in [mg m⁻³ (STP)], subdivided in PAH (index j) and Phenols (index k) compounds. Further MW_j and MW_k are the molar masses of tar compounds j and k respectively, in [kg kmol⁻¹]. The not identified tar components are assumed to have average molecular formulas of $C_{11}H_9$ and C_7H_8O for respectively PAH and Phenolic compounds. $V_{m,STP}$ represents the molar volume at standard temperature and pressure (0°C, 101325 Pa) in [m³ kmol⁻¹]. The total molar raw gas flow is calculated by summing up the dry flow, moisture flow and tar flow:

$$\dot{\Phi}_{tot, \ raw \ gas} = \dot{\Phi}_{tot, \ dry \ gas} + \dot{\Phi}_{H_2O} + \dot{\Phi}_{tar}$$
(5.6)

The elemental molar flow of element "*elem*" (being C, H, N, S and O) is obtained by multiplying the molar flow of the component "*cmp*" with the number

| | | Table | 5.4: Mole | balance | for the l | oase case | | | |
|-------------------------------|-------|----------------------|-----------------------|----------------------|------------------|----------------------|-----------------------|----------------------|-----------|
| In $[kmol h^{-1}]$ | U | $\mathrm{H}_{comb.}$ | $H_{moist.}$ | \mathbf{H}_{total} | Z | $\mathbf{O}_{comb.}$ | $\mathbf{O}_{moist.}$ | \mathbf{O}_{total} | Total in |
| Fuel (ar) | 0.406 | 0.536 | 0.095 | 0.631 | 0.002 | 0.253 | 0.047 | 0.300 | 1.339 |
| Steam | | | 1.199 | 1.199 | | | 0.599 | 0.599 | 1.798 |
| 0_2 | | | | | | 0.275 | | 0.275 | 0.275 |
| Air | 0.000 | | 0.002 | 0.002 | 0.041 | 0.011 | 0.001 | 0.012 | 0.054 |
| N_2 | | | | | 0.090 | | | | 0.090 |
| Total [kmol h ⁻¹] | 0.406 | 0.536 | 1.295 | 1.831 | 0.132 | 0.539 | 0.647 | 1.186 | 3.555 |
| Total [kg h^{-1}] | 4.876 | 0.541 | 1.305 | 1.846 | 1.843 | 8.620 | 10.358 | 18.978 | 27.56 |
| | | | | | | | | | |
| Out $[kmol h^{-1}]$ | C | $\mathrm{H}_{comb.}$ | $\mathbf{H}_{moist.}$ | \mathbf{H}_{total} | Z | $\mathbf{O}_{comb.}$ | $\mathbf{O}_{moist.}$ | \mathbf{O}_{total} | Total out |
| C_6H_6 | 0.016 | 0.016 | | 0.016 | | | | | 0.003 |
| C_7H_8 | 0.004 | 0.004 | | 0.004 | | | | | 0.001 |
| C_8H_{10} | 0.003 | 0.004 | | 0.004 | | | | | 0.000 |
| C_2H_2 | 0.003 | 0.003 | | 0.003 | | | | | 0.002 |
| $\mathrm{C_2H_4}$ | 0.019 | 0.037 | | 0.037 | | | | | 0.009 |
| CH_4 | 0.033 | 0.133 | | 0.133 | | | | | 0.033 |
| CO | 0.139 | | | | | 0.139 | | 0.139 | 0.139 |
| CO_2 | 0.136 | | | | | 0.272 | | 0.272 | 0.136 |
| H_2 | | 0.176 | | 0.176 | | | | | 0.088 |
| N_2 | | | | | 0.115 | | | | 0.057 |
| $\rm NH_3$ | | 0.000 | | 0.000 | 0.000 | | | | 0.000 |
| 0_2 | | | | | | 0.000 | | 0.000 | 0.000 |
| H_2O | | | 1.537 | 1.537 | | | 0.769 | 0.769 | 0.768 |
| Tar - PAH&Phen. | 0.009 | 0.008 | | 0.008 | | 0.000 | | 0.000 | 0.001 |
| Leakage | | | | | 0.017 | | | | |
| (Fly) ash (calc.) | 0.045 | | | | | | | | |
| Total out: | 0.406 | 0.381 | 1.537 | 1.918 | 0.132 | 0.411 | 0.769 | 1.179 | 3.635 |
| Total in: | 0.406 | 0.536 | 1.295 | 1.831 | 0.132 | 0.539 | 0.647 | 1.186 | 3.555 |
| Out - in = | 0.000 | -0.156 | 0.243 | 0.087 | 0.000 | -0.128 | 0.121 | -0.007 | 0.080 |
| Rel. diff. | 0.000 | -29.05 | 18.74 | 4.744 | 0.000 | -23.76 | 18.74 | -0.566 | 2.253 |

| $\bigcirc 4$ | Table 5.5: H _{comb} . 0.539 | Mole ba H _{moist} 0.095 1.199 | $\frac{ \text{H}_{total} }{\text{H}_{634}}$ 0.634 1.199 | the mag N 0.002 | gnesite ca O _{comb.} 0.254 | lse O _{moist.} 0.047 0.599 | $\begin{array}{c} \mathrm{O}_{total} \\ \mathrm{0.302} \\ \mathrm{0.599} \end{array}$ | Total in 1.345 1.798 |
|----------------------|--|---|---|-----------------------|---|--|---|----------------------------|
| 00 | | 0.002 | 0.002 | 0.055 0.089 | 0.275 0.015 | 990.0 | 0.016 0.016 | 0.01 |
| 08 0.539 99 0.543 | | 1.296 1.306 | 1.835 1.849 | 0.145 2.038 | 0.544 8.701 | 0.648 10.37 | $1.192 \\ 19.07$ | 3.580 27.87 |
| H H H | | $H_{moist.}$ | H_{total} | Z | $O_{comb.}$ | $O_{moist.}$ | \mathbf{O}_{total} | Total ou |
| 12 0.012 04 0.004 | | | 0.012 | | | | | 0.002 |
| 04 0.005 | | | 0.005 | | | | | 0.001 |
| 01 0.001 | | | 0.001 | | | | | 0.000 |
| 14 0.028 | | | 0.028 | | | | | 0.007 |
| 31 0.123 | | | 0.123 | | | | | 0.031 |
| 84 | | | | | 0.084 | | 0.084 | 0.084 |
| 07 | | | | | 0.413 | | 0.413 | 0.207 |
| 0.367 | | | 0.367 | | | | | 0.183 |
| | | | | 0.139 | | | | 0.069 |
| 0.000 | | | 0.000 | 0.000 | | | | 0.000 |
| | | | | | 0.000 | | 0.000 | 0.000 |
| | | 1.088 | 1.088 | | | 0.544 | 0.544 | 0.544 |
| 03 0.003 | | | 0.003 | | 0.000 | | 0.000 | 0.000 |
| 48 | | | | 0.007 | | | | |
| 08 0.544 1 | | .088 | 1.632 | 0.145 | 0.497 | 0.544 | 1.041 | 3.227 |
| 08 0.539 | | 1.296 | 1.835 | 0.145 | 0.544 | 0.648 | 1.192 | 3.580 |
| 00 0.005 | | -0.208 | -0.203 | 0.000 | -0.047 | -0.104 | -0.151 | -0.353 |
| 00 0.971 | | -16.05 | -11.05 | 0.000 | -8.557 | -16.05 | -12.63 | -9.870 |

5.3 Results and discussion

of moles of *elem* per mole *cmp*:

$$\dot{\Phi}_{elem} = n_{elem,cmp} \cdot \dot{\Phi}_{cmp} \tag{5.7}$$

The contribution of the carbon in the solids (char, ashes) to the total carbon flow is calculated from the elemental C balance. It is assumed that all the solids leaving the reactor consist of carbon - the detailed consideration of the ash and bed material balance is outside the scope of this paper.

5.3.1.2 Mole balance - results

The mole balance presented in previous subsection allows the assessment of the consistency of the measurements carried out, and it provides data for the calculation of a number of interesting benchmarks of the process. "Balance closure" is a measure that shows to which extent the law of mass conservation is fulfilled. Theoretically, in a system without mass accumulation, the sum of output flows should be equal to the sum of the input flows, giving a closure of 100%. In practice, however, due to measurement errors or incomplete measurements this can never be achieved. In this paper the preference is given to an alternative term: "material balance discrepancy" (MBD), defined as follows:

$$MBD_{absolute} = \dot{\Phi}_{out} - \dot{\Phi}_{in} \tag{5.8}$$

$$MBD_{relative} = \frac{\dot{\Phi}_{out} - \dot{\Phi}_{in}}{\dot{\Phi}_{in}} \cdot 100\%$$
(5.9)

This definition is perhaps little bit more intuitive, and represents difference between the mass output and input as percentage of the input. This value can be both positive and negative and thus gives additional information, compared to balance closure, which in fact shouldn't exceed 100%. The following conclusions can be drawn from the balances presented above:

- the relative overall mole balance discrepancy (MBD) is lower for the base case, compared to magnesite case;
- the MBD for the elements C and N are zero: this is of course correct as those elemental balances were used to calculate the solid carbon flow and total gasifier outlet flow rate, respectively;
- the calculation results suggest, that the total MBD of the magnesite case balance can be attributed to the MBD of elements H and O. This would indicate either an (increased) error in water measurement or formation of a hydroxide (OH) containing compound, that has not been measured. The last hypothesis could be supported, by the fact that the ratio of absolute MBDs of the elements H and O is close to unity, while in case of water

| | | Base case | Magnesite case |
|------------------------------------|----------------------------------|-----------|----------------|
| Carbon conversion | % | 88.9 | 88.2 |
| Cold gas efficiency | % | 72.5 | 70.4 |
| H ₂ :CO ratio | $\mathrm{mol}\mathrm{mol}^{-1}$ | 0.63 | 2.2 |
| Analyzed tar conc. (ex. C_6H_6) | $\mathrm{g}\mathrm{m}^{-3}(STP)$ | 7.4 | 5.8 |
| PAH & Phenols | $\mathrm{g}\mathrm{m}^{-3}(STP)$ | 4.3 | 1.7 |

Table 5.6: Calculated process benchmarks: carbon conversion (CC) and cold gas efficiency (CGE). Also H_2 :CO ratio and calculated raw gas tar concentrations are included

that ratio is of course 2. However, the H-balance is extremely difficult to close; obviously not all minor compounds present in the product gas have been measured. In case of very heavy tar components, even small quantities can contain amounts of H that would definitely contribute to the total content of that element in the gas in the gas. Of course heavy tar also contains large amounts of C-element, but as the total amount of carbon is nearly an order of magnitude larger than that of H-element, the error in the C-balance caused by the lack of heavy tar data will be much less pronounced than the effect on the H-balance.

To double-check the value for the water content an other, independent, measurement method should be applied. Typically gravimetric measurement is performed, eventually followed by, e.g., Karl-Fischer titration. Unfortunately, due to technical problems the gravimetric water measurement has not been performed during the experiments described here.

From the data presented in the molar balance, some important process benchmarks can be calculated. Two of them will be discussed here: carbon conversion (CC) and cold gas efficiency (CGE).

$$CC = \left(1 - \frac{\dot{\Phi}_{C,residue}}{\dot{\Phi}_{C,feed}}\right) \cdot 100\%$$
(5.10)

$$CGE = \frac{LHV_{gas}[MW]}{LHV_{fuel}[MW]} = \frac{\sum \dot{\Phi}_i \cdot LHV_i}{\dot{\Phi}_{fuel} \cdot LHV_{fuel}}$$
(5.11)

From the Table 5.6 it can be seen, that CC of the base case is marginally higher than of magnesite case. CGE efficiency is 2.1%-point higher for the base case. Carbon conversion is relatively low, but this is rather common for smaller test rigs. On contrary, the CGE efficiency is relatively high for this kind of process. Despite the slightly lower CC and CGE benchmark, the biggest advantage from magnesite case is the increased H₂:CO ratio, which is nearly directly suitable for

| | Base case [kmo | Magn. case of h^{-1}] | Rel. diff. [%] |
|--------|-------------------|--------------------------|-------------------|
| CH_4 | 0.033 | 0.031 | -6.97 |
| CO | 0.139 | 0.084 | -39.6 |
| CO_2 | 0.136 | 0.207 | 52.1 |
| H_2 | 0.088 | 0.183 | 108 |
| H_2O | 0.768 | 0.544 | -29.2 |

Table 5.7: Change in molar flow rates of the key components – comparison between the base case and the magnesite case.

Fischer-Tropsch synthesis. Also the reduction of tar and in particular the potentially problematic PAH is a great benefit of the magnesite bed over sand bed. Table 5.7 presents the change in molar flow rates of the key components of the product gas. Next to the positive effect on the WGS reaction and the reduction of tar components (see Table 5.6) also an effect on methane conversion becomes clear.

5.3.2 The influence of the presence of magnesite

The experimental results shown above form a clear evidence of the fact that the presence of magnesite has a significant effect on the composition of gas produced during the gasification of biomass in a CFB. At this stage it is very interesting to make an attempt to explain the changes that occur in the process that finally lead to the upgraded gas composition. Equations 5.12 to 5.22 present a summary of the main chemical reactions identified to occur during the process of gasification. When Table 5.7 is recalled, the shift from CO and water to H_2 and CO_2 can be clearly observed. This immediately points towards reaction 5.18 that possibly moves towards the equilibrium. However, from the stoichiometry of reaction 5.18 it is clear that the amount of moles of the species involved should change by the same quantity. That is not the case here, as the absolute decrease of CO and H₂O does not match with the increase of H₂ and CO₂. That can be partially explained, when reactions 5.19, 5.21 and acetylene wet reforming (not in the list) are taken into this consideration. The three reactions mentioned above produce a mixture of hydrogen and carbon monoxide, with as a consequence an increased hydrogen concentration and relatively low carbon monoxide concentration as compared to the hypothetical effect of merely reaction 5.18. In this approach, still, a part of the decreased water content cannot be explained - on one hand it could be caused by the reason mentioned at the beginning of this section, but also tar reforming reactions could further decrease the water content.

Decrease of CH_4 concentration is an important observation. In the literature [46] it has been observed, that the concentration of methane increased after the product gas passed over a secondary bed made up of different solids, among others magnesite (referred to as MgO). However, only a nickel steam reforming catalyst was able to reduce the volume fraction of methane below 1%, as at temperatures around 800–900°C the reaction 5.19 is rather slow when no catalyst is present.

| Partial oxidation reaction | $C(s) + \frac{1}{2}O_2 \to CO$ | $-111 MJ kmol^{-1}$ (5.12) |
|----------------------------|---|--------------------------------|
| Combustion reaction | $CO + \frac{1}{2}O_2 \to CO_2$ | $-283 MJ \ kmol^{-1}$ (5.13) |
| Combustion reaction | $H_2 + \frac{1}{2}O_2 \to H_2O$ | $-242 \ MJ \ kmol^{-1}$ (5.14) |
| Boudouard reaction | $C(s) + CO_2 \rightarrow 2CO$ | $+172 MJ kmol^{-1}$ (5.15) |
| Water-gas reaction | $C(s) + H_2O \rightarrow CO + H_2$ | $+131 MJ kmol^{-1}$ (5.16) |
| Methanation reaction | $C(s) + 2H_2 \to CH_4$ | $-75 MJ kmol^{-1}$ (5.17) |
| Water-gas shift reaction | $CO + H_2O \rightarrow CO_2 + H_2$ | $-41 MJ kmol^{-1}$ (5.18) |
| Methane wet reforming | $CH_4 + H_2O \rightarrow 3H_2 + CO$ | $+206 MJ kmol^{-1}$ (5.19) |
| Methane dry reforming | $CH_4 + CO_2 \rightarrow 2H_2 + 2CO$ | $+247 MJ kmol^{-1}$ (5.20) |
| Ethylene wet reforming | $C_2H_4 + 2H_2O \rightarrow 4H_2 + 2CO$ | $+206 MJ kmol^{-1}$ (5.21) |
| Ethylene dry reforming | $C_2H_4 + 2CO_2 \rightarrow 2H_2 + 4CO$ | $+292 MJ kmol^{-1}$ (5.22) |

5.3.3 Equilibrium calculations

In order to support the elaborations above, simple equilibrium composition calculations have been carried out using the software package FactSage, version 5.4.1. The simulation was based on the actual input data: fuel flow and composition, oxidant and fluidizing agent flows, recirculation and purge flows, pressure and temperature. As the program assumes complete carbon conver-

sion, which is not the case in the gasifier, a part of the fuel-C is subtracted from the input to mimic this condition. Typically, carbon conversion in a small-pilot scale CFB gasifier should be around 90% [167], which is also confirmed by the material balance calculations presented in previous section. Three simulations have been run, at 100%, 90%, and 77.5% carbon conversion. The second value is close to the carbon conversion obtained from the material balance, while the third value has been chosen so, that the calculated CO concentration closely matches the measured CO fraction. Table 5.8 presents the overview of the results, and the following remarks can be made:

- during the experiments with magnesite as bed material hydrogen concentration clearly shifts closer towards equilibrium, compared to the base case; so do also carbon dioxide and water;
- the increase in hydrogen concentration can be very likely attributed to the change of the reaction coordinate of WGS reaction and wet hydrocarbon reforming;
- in order to achieve the match between the measured and simulated CO concentration a very poor carbon efficiency would be required. Although the material balance calculations show higher value, it is recommended to check this figure by determining the amount and carbon content of the fly ash;
- in equilibrium conditions $C_x H_y$ are not present; they have been converted to H_2 and CO.

| | | Base case | Magn. bed | CC = 1.0 | CC = 0.90 | CC = 0.775 |
|----------|---|-----------|-----------|----------|-----------|------------|
| CO_2 | % | 12.0 | 17.6 | 17.2 | 17.3 | 17.1 |
| CO | % | 12.1 | 6.95 | 12.0 | 9.70 | 7.04 |
| H_2 | % | 7.77 | 15.7 | 26.6 | 24.0 | 20.2 |
| CH_4 | % | 2.93 | 2.63 | - | - | - |
| C_2H_4 | % | 0.818 | 0.532 | - | - | - |
| C_2H_2 | % | 0.135 | 3.58E-2 | - | - | - |
| N_2 | % | 5.07 | 5.93 | 4.81 | 4.95 | 5.15 |
| H_2O | % | 59.4 | 50.8 | 39.5 | 44.0 | 50.5 |

Table 5.8: Measured gas compositions and equilibrium compositions calculated with FactSage 5.4.1, in terms of raw gas volume fractions

The investigations towards the background of magnesite having such a positive effect on the gas composition as described above is out of the scope of this thesis, but will be carried out as a recommended future work. At this moment preliminary conclusions with that respect could be drawn based on the composition of magnesite, namely the presence of iron, and calcium. Iron is a wellknown catalyst for many chemical reactions that include hydrocarbons [51, 120, 127]. The combination of calcium and magnesium resembles dolomite, which has been proven to have an effect on the reduction of hydrocarbons present in the gasifier product gas. Of course the conditions in the gasifier are quite harsh for any type of catalyst, but the continuous feed of magnesite seems to compensate for the loss of activity.

5.4 Conclusions and outlook

In this chapter a significant effect of magnesite on the composition of the gas produced during steam/oxygen-blown gasification of biomass in a Circulating Fluidized Bed Gasifier (CFBG) has been proved experimentally. First a base case has been defined with quartz sand as bed material; A-quality wood was used as a fuel and the main operational parameters being gasification temperature, λ and steam-to-biomass ratio were set to approximately 835°C, 0.35 and 1.0 respectively. Then the two test cases were defined: addition of magnesite during base case operation, and the use of magnesite as the bed material. Already from the first test case a change in the gas composition as compared to the base case was observed in terms of increased hydrogen production and lower carbon monoxide concentrations. During the second test case a further change in the gas composition was noted. The hydrogen concentration increased by 66% on a dry, nitrogen-free basis (dnf) and by more than 100% on a raw gas basis, as compared to the base case, which corresponds to hydrogen volume fractions (dnf) of 36.2% and ca. 16%, respectively. Further effects observed were the decrease in methane and C_2 -hydrocarbons concentrations, increase in CO_2 production and a significant decrease of the water content (from ca. 60% to ca. 50% by volume, raw gas basis). Also a reduction in the total tar content has been observed, with an almost complete elimination of oxygenated hydrocarbons (Phenolics). The total concentration of PAH and Phenolics decreased to a value as low as 1.7 g m $^{-3}$ (STP) on raw gas basis.

In order to get more insight into the changes in the gas chemistry, first an elemental mole balance have been set up to verify the correctness of the measurements. Based on the differences in the concentrations of species in the base case and the second test case it could be concluded that in general the conditions in the reactor move towards the equilibrium in the presence of magnesite. The largest effect originates from the homogeneous water-gas shift reaction, as it contributes the most to the increased hydrogen production, but also the reactions involving (higher) hydrocarbons provide a significant contribution. Finally, a simple equilibrium calculation based on the actual input streams has been carried out using FactSageTMsoftware. Those results confirmed the postulate that the conditions in the reactor significantly moved towards the equilibrium, when magnesite was applied.

At this moment it is not clear yet which mechanism is responsible for that desired effect of magnesite. The presence of iron has been hypothesized as being a catalyst for the reactions that cause the gas composition change. It is recommended for the future work to closely investigate the role of magnesite, including a thorough characterization of the "fresh" and "used" material, and the modeling activities.

Czego wciąż mi brak? Co tak cenne jest? Że ta nienazwana myśl rysą jest na szkle What am I still lacking? What is so valuable? That unnamed thought is a crack in the glass Urszula, Rysa na szkle, 1999

6

Steady-state modeling of a steam-oxygen blown CFB biomass gasifier

Introduction

Experimental research described in previous chapters provided a large amount of new information about a steam-oxygen blown CFB gasification process and the most important of all is that the experiments/test runs are the only way to show that this process really works. However, running a large amount of experiments can be (very) expensive, especially if relatively large test rigs or large amounts of expensive materials (e.g., catalysts) are used. By using relatively simple mathematical models to characterize the biomass and the bed material, together with the simplified description of the fluidization process and the mass & heat transfer, a tool can be created that will provide a cheap way to deliver design parameters for a full scale reactor. The main drawback of any model is that it will always be only a simplification of the reality and it will never be smarter than the person or a group of people that implemented it.

This chapter describes the further development of an existing steady-state model capable of simulating industrial-scale Circulating Fluidized Bed coal combustors and boilers, extending it to the biomass gasification processes, also performed at small pilot scale. A global description of functionality of the model is given, the newly implemented features are presented and finally the results of a simulation are compared with the experimental data, as well as with the simulation results of another, commercial, simulation package.

6.1 Motivation to develop own CFB gasifier model

Over the years many researchers made attempts to develop a model of the fluidized bed gasification process [86, 72, 32, 69, 43, 162]; the most recent and a very comprehensive review about the modeling of biomass gasification in a fluidized bed is given by Gómez-Barea [67]. Another extensive overview is given by De Jong [41]. The researchers mentioned above either set-up a model using some kind of simulation software or developed their own code to simulate the fluidization & gasification process or one of its aspect, e.g., pyrolysis, tar conversion, reaction kinetics. De Souza-Santos developed a comprehensive simulation software able to model fixed, bubbling and circulating fluidized beds, both in combustion and in gasification mode [43]; this software is commercially available [36]. However, the use of an existing models has a number of practical limitations, the main being the lack of the access to the source code and its documentation. A model with many degrees of freedom needs also many adjustable parameters. The fit between model calculations and experimental results may, very likely, only be obtained over a very short range of values for those parameters, requiring a proper insight into the meaning of each parameter and equation in the model. Until now no model is available that is able to simulate all phenomena of interest to the researchers working on fluidized bed gasification, therefore often an adaptation to one's need may be necessary. This

is not possible without the access to the source code. Also the understanding or fixing of modeling bugs that are present even in the commercial software is impossible in that way. On the other hand setting up a new model from scratch may not be the most efficient way to proceed either. Therefore it was decided to use an *available* model code developed for a *similar process* and extend it with features necessary to simulate gasification of biomass in a CFB.

6.2 Description of the model

6.2.1 Starting point: an existing CFB combustor model

The model of a Circulating Fluidized Bed for thermal conversion of a solid organic fuel described in this work is based on the CANMET BFB combustor model developed by Preto [131]. This model was selected by the IEA-AFBC Working Group for further development to assemble their experiences with an overall model [75], for the first time documented by Van den Bleek in 1990. [165]. In 1991 the group decided to extend the BFB model with CFB features, aiming at the simulation of industrial-scale coal-fired CFB boilers. Extensive modeling and validation efforts have been made at TU Delft by Hannes [75], and the final version of the code developed by this researcher (further referred to as "the IEA model") was used as a starting point for this work.

The main features of the IEA model are:

- steady-state approach, no dynamic aspects taken into account;
- only the CFB riser and cyclone are modeled, the downcomer and loop seal are represented as recirculation mass flows and temperatures;
- 1.5-dimensional discretization: in the axial direction the riser is divided in a freely chosen number of cells (a cascade of stirred tanks), while in the radial direction a distinction is made between the core phase (in the center of the riser) and the annulus phase (region near the wall). The bubble phase, if present, is also considered as a core-annulus structure, but with a very fast mixing between these phases;
- a particle size distribution (PSD) of all the solids present in the reactor (i.e., fuel, bed material, additives) is considered, including its development caused by various physical (drying, fragmentation, attrition) and chemical (gas-solid reactions) processes;
- possible staged admission of the fluidization medium (air), and possible recirculation of the flue gas to maintain the fluidization velocity at part load;

- solid fuel treatment: drying and devolatilization times are calculated for each particle size class. The amount of the released moisture and the amount and the composition of the volatiles are calculated for each discrete cell;
- a number of homogeneous (i.e., without any catalytic effect) gas phase reaction kinetics expressions, in particular related to the oxidation of the volatiles and to the NO_x formation. Heterogeneous reactions (gas phase reactions including a catalytic intermediate step) representing the conversion of ammonia and NO_x are also included;
- heat transfer equipment to extract the sensible heat generated during the combustion process. It includes membrane walls, tube bundles in the freeboard and an external heat exchanger (ash cooler).

6.2.2 Model layout

As already mentioned in Section 6.2.1 the IEA model describes the riser of a CFB as a cascade of stirred tanks in the axial direction, while in the radial direction a distinction is made between the core and the annulus phase. Also the existence of a dense bed zone (bubble phase) is determined, and if such a region exists (which is not absolutely necessary, as in the case of turbulent fluidization) the mixing between the core and the annulus is set to a sufficiently high value, in order to preserve the core-annulus cell structure and to simplify the computational treatment of the problem.

The discretization of the reactor and the corresponding gas and solids flows are depicted in Figure 6.1. In addition, Figure 6.2 presents an overview of the external flows and also indicates the compartments related to these flows. All flows between the cells, the core and the annulus presented in Figures 6.1 and 6.2 are *scalars*, therefore their directions are defined by their definitions and no negative mass flows are possible. The mixing flows are an exception to this, as their positive direction is determined by the name of the variable, e.g., MCAX means a net mixing flow from core to annulus when the value is greater than zero, and from annulus to core otherwise. Each variable in the code that represents a flow is a three-dimensional array, e.g., for solids Mxxxx(I,K,P) where I, K and P refer to the particle size class, cell and phase, respectively. For gases Yxxxx(J,K,P) J refers to the corresponding gaseous specie, while the meaning of K and P is equal to the one introduced above.

The number of cells in the riser discretization can be chosen arbitrarily, with a maximum set to 200. As in all finite-elements calculations the cell grid should be more refined in areas where large spatial gradients are expected.

The input for the model consists of:

- the geometry of the riser and the cyclone;
- the number of cells for the discretization of the different riser compartments;
- the gas and solids feed rates;
- heat exchanging equipment (membrane walls and freeboard tubes), if present;
- solid materials properties: PSD, chemical composition (fuel), physical properties;
- pressures and (initial) temperatures;
- a number of constants and calculation options.

An example of an input file is given in Appendix B.

6.2.3 Solids balances

The solids input streams defined in the input file consist of a fuel and its composition, an additive, and the bed material. Table 6.1 presents the corresponding identifiers in the model code. The distribution of the solids among the riser cells and the determination of the internal and external solids mass flow rates is performed as one of the first calculation steps – see fourth and fifth calculation block in Figure 6.3. One of the main assumptions of the model is that the mass flows of the particles remain constant throughout the calculation, only the fraction (load) of reactive species (e.g., char) may vary. Such an approach allows the performance of the size distribution calculation *before* the mass and energy balance iteration loops, leaving only the char (carbon) balance calculation inside the iteration loop. In the previous work an initial attempt to balance the char as pure carbon with a separate size distribution caused calculation instabilities that have been solved by the approach described above [75].

As a starting point an initial population balance calculation is performed to determine a preliminary distribution for the final population calculations of the additive, bed material and ash (materials 2–4). This initial calculation is done using a single material class representing the total solid bed inventory (material 5: BED). Finally, material 1 (COAL) is not taken into account during the flow calculations and is only used to calculate the release of fuel moisture and volatile matter to the gas phase.

More detailed information about mathematical balances is given in Appendix C.



Figure 6.1: The discretization scheme used in the IEA model to describe the riser of a CFB reactor, including the corresponding gas and solids flows, and the auxiliary equipment



Figure 6.2: Main external flows and the compartments important for the calculation procedure. Stream names in capital letters are equal to these used in the program code



Figure 6.3: Global calculation sequence of the IEA model. Solid lines indicate the iteration loops before modifications, the dashed lines indicate the modified iteration loops

| Solid material | Material ID (M) | Name |
|---------------------------|-----------------|---------------------|
| Fuel | 1 | COAL |
| Additive | 2 | LIME |
| Bed material | 3 | INERT |
| Fuel ash | 4 | COKE^{a} |
| Total solid bed inventory | 5 | BED |

Table 6.1: Solid species considered by the IEA model

^{*a*} the name used in the IEA code is misleading, as in fact all variables that refer to COKE contain merely ash flow rates or holdups

6.2.4 Gas balances

In the IEA model the gas flows are treated in terms of molar flow rates. The total molar flow rate in the system is calculated before the iteration loop from the sum of all the input flows and the fuel moisture and volatile matter release. This approach does not take into account the change of molar flow rate due to non-equimolar gas-phase reactions. No back-mixing was allowed in the gas phase, see also Figure 6.1. More detailed information about mathematical balances is given in Appendix C.

6.2.5 Energy balance

The average cell temperatures are calculated using the enthalpy balance, which considers the convective gas and solids flows, heat released or consumed by the chemical reactions, and the heat transferred to the wall and the heat exchanging equipment, if present. The basis for the energy balance is the differential Fourier equation:

$$(n_g c_{p,g} + m_s c_{p,s})\frac{dT}{dt} = (u_g n_g c_{p,g} + u_s m_s c_{p,s})\frac{dT}{dz} + \dot{\Phi}_{reac} + \dot{\Phi}_{heatexch}$$
(6.1)

from which the total balance system is solved. The more detailed description and the energy balance equations are given in Appendix C.

6.2.6 Solid fuel conversion

Upon the introduction into a hot fluidized bed the solid fuel will release the moisture (drying) and the volatile matter (devolatilization / pyrolysis) leaving a solid residue consisting of fixed carbon and ash – the char. Besides carbon no other elements are assumed to be present in char; also no chemical composition of ash has been defined, and the ash is assumed to remain inert throughout

the process. As already mentioned earlier, the mass distribution and solids flows in the riser remain constant after having been calculated, while the amounts of reactive species are considered as loads of their carriers. Based on this approach the carbon content of char (further referred to as "char-C") is considered as a load of ash. The input of char-C, originating from the solid pyrolyzed fuel is therefore given by:

$$\dot{m}_{char_C,in} = \dot{m}_{ash,in} \cdot \frac{x_{fixed_C}}{x_{ash}} \quad [kg_C \ s^{-1}]$$
(6.2)

The equation above is implemented in the model code in the subroutine CHARBL as:

The amount of char-C on the ash particles for all size classes and each discrete cell is calculated from a set of linear equations

$$A \cdot \bar{x} = \bar{b} \tag{6.3}$$

where A is a matrix containing the *ash* flow rates $[kg_{ash} s^{-1}]$ between the cells, \bar{b} the vector containing the carbon input flow rates per cell $[kg_C s^{-1}]$, and \bar{x} the vector with unknown carbon load of the ash $[kg_C kg_{ash}^{-1}]$. This equation is solved using a linear equation solver routine based on the LU decomposition, yielding the values in \bar{x} . For clarification it is mentioned that the implemented solver stores the calculated unknowns in the same vector as where the right hand-side terms have been stored, i.e., B(K). This result is obtained for a single particle size class I, therefore it is stored in two char-C load arrays COKCO (I, K) (core) and COKAN (I, K) (annulus), and the calculation is repeated for all the size classes.

After the calculation of the amount and the composition of the released volatiles, and the char-C loads, the formation of the products of combustion is calculated using Arrhenius-type reaction kinetics for the homogeneous and heterogeneous gas-phase reactions. The shrinking particle model is used to describe the reactions involving char-C, as in a fluidized bed environment the ash layer is likely to detach leaving an exposed, porous, carbonaceous core available for the interaction with gaseous reactants.

6.2.7 Convergence criteria

Figure 6.3 shows that the main iterative part of the model involves a mass balance loop inside an energy balance loop. The mass balance loop involves the calculation of the char particle size distribution, the char combustion rates, and the gas species concentrations. In addition, in the energy balance loop local
temperatures are calculated via the energy balance (see Appendix C). The convergence criteria for the mass- and energy balance iterations are defined as follows:

mass balance residual =
$$\frac{r_{char,(N)} - r_{char,(N-1)}}{r_{char,(N)}}$$
(6.4)

$$energy \ balance \ residual = \frac{T(NCELLS, core)_{(N)} - T(NCELLS, core)_{(N-1)}}{T(NCELLS, core)_{(N-1)}} + \frac{T(1, core)_{(N)} - T(1, core)_{(N-1)}}{T(1, core)_{(N-1)}}$$

(6.5)

In Equation 6.4 the char reaction rate calculated in the current iteration step (N) is compared to the char reaction rate calculated in the previous step (N-1) and the relative deviation should be less than the tolerance given by the user in case of convergence. Similar consideration applies to the energy balance (Equation 6.5), only there the temperatures in the first and last riser cells are compared across the iterations.

6.2.8 New assumptions and necessary extensions of the existing model

The purpose of the IEA model was to simulate coal combustion in CFB boilers. The aim of this work, however, is to extend the existing CFB combustor model to gain the ability to simulate the gasification of biomass. This has consequences for some of the assumptions made in the IEA model, in particular for the calculation of the total gas flow, the fuel devolatilization routine and the chemical reactions part. Table 6.2 gives an overview of these assumptions made in the IEA model and their limitations for the simulation of the gasification process. The necessary extensions or alternative approach in the gasification model will be presented and discussed in Section 6.3.

6.3 Upgrading from CFB combustor to CFB gasifier model

6.3.1 Source terms for total gas flow calculation

6.3.1.1 Source terms due to non-equimolar gas-phase reactions

Considering a chemical gas-phase reaction

$$aA + bB \longrightarrow cC + dD$$
 (6.6)

Table 6.2: Assumptions made in the IEA model and their limitations for the simulation of the gasification process

| Model aspect | IEA assumption | Gasification model |
|-------------------------------------|--|---|
| Total molar gas flow calculation | Single total molar gas flow calculation <i>before</i> the iteration loop | Total molar gas flow calculation should include a source term that considers the changes due to the non-equimolar re- actions (in particular tar decomposition reactions and wet methane reforming). These changes depend on the reaction ki- netics that are calculated <i>inside</i> the itera- tion loop |
| Devolatilization of solid fuel | Volatiles composition limited to CO, NH_3 , NO, H_2 and SO_2 | Methane and higher polyaromatic hydro- carbons (tar) are important constituents of the product gas from a fluidized bed gasifier, and they originate from the pro- cess of fuel pyrolysis. Omitting them in the calculation of the pyrolysis gas composi- tion will lead to inaccurate and not realis- tic final gas composition results |
| Chemical reactions with char | Char reacts only with oxygen | Water gas reaction and (to a lesser extent) Boudouard reaction also play a role in the gasification process, contributing to car- bon conversion |
| Homogeneous gas- phase reactions | Only reactions involving the com- bustion of volatiles and the formation of NO_x implemented | Important gasification reactions missing, e.g., water-gas shift, methane reforming, tar decomposition, etc. No tar species in- cluded in the model |

if the sum of the stoichiometric coefficients a and b is equal to the sum of c and d, then the molar amount of the reaction products is equal to the amount of the reactants, and the reaction is called equimolar. According to the above, the oxidation reactions of CO and H_2 are non-equimolar as 1.5 moles of the reactants give 1 mole of the product:

$$\operatorname{CO} + 0.5\operatorname{O}_2 \longrightarrow \operatorname{CO}_2$$
 (6.7)

$$H_2 + 0.5O_2 \longrightarrow H_2O$$
 (6.8)

In relation to the calculation of the total molar gas flow the error caused by assuming the above reactions as being equimolar may be acceptable in case of a combustion process. This is due to the presence of a large amount of nitrogen that, together with the excess oxygen, contributes to roughly 80% of the volume of the flue gas. Thus the error in the total mole flow will be 33% of the total CO and H_2 fraction originating from pyrolysis stage, which would correspond to an error of approximately 6–7% in the total mole flow. This error can be subsequently compensated by the increased calculated fractions of gaseous species, which will ultimately be normalized for final representation. This is the procedure followed by the IEA model; such an approach can be justified by a simpler calculation procedure and by a reduced CPU time as less calculations are carried out inside the iteration loop.

Under gasification conditions the amount of chemical reactions involving the main species is much higher than in combustion. Most of these reactions are non-equimolar and the difference between the amount of reactants and the products can be large, as, e.g., in case of wet methane reforming reaction (Equation 5.19). The modified model contains a source term, YSRC (K) [mol s⁻¹], in which the net formation rate of gaseous species is stored for every cell. The source term is a product of the sum of stoichiometric coefficients (reactants multiplied with -1) and the reaction rate, and summed up over all implemented reactions. This source term is used in the GASFLO routine that calculates the total molar gas flow in every cell, which is indicated by the "Gas flows" calculation block in Figure 6.3.

6.3.1.2 Source terms due to gas released during reactions of solid carbon

A similar approach to the one presented in Section 6.3.1.1 can be applied to gassolid reactions involving solid carbon. From the reaction equations

$$C(s) + 0.5O_2 \longrightarrow CO$$
 (6.9)

 $C(s) + H_2O \longrightarrow CO + H_2$ (6.10)

$$C(s) + CO_2 \longrightarrow 2CO$$
 (6.11)

it is clear that reaction 6.9 has a net yield of 0.5 mol of gas per mole solid carbon, while reactions 6.10 and 6.11 have a net yield of 1 mol of gas. Hence these reactions will influence the total molar gas flow in the reactor.

The calculation of the solid carbon combustion reaction rate (RRCOMB [mol s⁻¹]) was already implemented in the IEA model, but it was not linked to the gas flow calculation. This was modified in the gasification model. First, the solid carbon reaction rates were extended with the terms considering the water-gas and Boudouard reactions (see Section 6.3.3.2). Subsequently, the source terms were added to the GASFLO routine.

6.3.1.3 Location of the call of the GASFLO routine

As mentioned in Section 6.2.8 in the IEA model the calculation of the molar gas flows was performed before the main iteration loops. However, to take into account the source terms related to the non-equimolar gas-phase reactions and the reactions involving solid carbon it was necessary to move the GASFLO routine into the mass balance iteration loop, see Figure 6.3.

6.3.2 Devolatilization / pyrolysis model

Mathematical modeling of the devolatilization / pyrolysis process is in fact a science on its own. Although both in the combustion and in the gasification processes it is just an intermediate step in the conversion of a solid fuel, the course of the devolatilization process will influence the overall process and the final gas composition, unless chemical equilibrium conditions are reached, which is not the case in a fluidized bed.

The devolatilization model proposed in the IEA model was considered to be too simple to simulate biomass gasification, as it did not involve any hydrocarbons being formed during the pyrolysis step. In his thesis Hannes [75] already indicated the existence of another, more complicated, model (coal devolatilization model by Merrick), but did not fully implement it in the code. Alternatively, other dedicated biomass pyrolysis models like, e.g., FG-DVC or FG-Biomass (Advanced Fuel Research, Inc.) could be applied [4]. This would be possible by linking the output of the external model with the Fortran code. However, as a starting point it was decided to use the modified Merrick approach, keeping the other option as a recommendation for future research.

The devolatilization model proposed by Merrick [113] is based on an empirical approach and valid for coals with volatiles content between 16 and 38% by mass. As the volatiles content is one of the main differences between coal and biomass, the original empirical relations would not be suitable for the biomass case. The global structure of the model, however, was believed to be useful, if modified with the data from biomass pyrolysis experiments.

| | | | | 5 | 2 | | | | |
|------------|-----------------|-------------------|--------|-----------------|----------------------|----------------|-------------|-----------------|---|
| | | | | | | | | | |
| U U | Η | X | N | S | 1-V | 1.31H | 0.22H | 0.32X | $\left[\begin{array}{c} 0.15X \end{array} \right]$ |
| | | | | | | | | | |
| Char | CH_4 | $\mathrm{C_2H_6}$ | CO | CO_2 | Tar | H_2 | ${ m H_2O}$ | NH_3 | $[H_2 S]$ |
| | | | | | • | | | | |
| 0 | 0.0588 | 0 | 0 | 0.9412 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0.1765 | 0 | 0.8235 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0.1111 | 0.8889 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | μ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.85 | 0.082 | 0.049 | 0.009 | 0.01 | 0 | 0 | 0 | 0 | 0 |
| 0.2727 | 0 | 0.7273 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| 0.4286 | 0 | 0.5714 | 0 | 0 | 0 | 0 | 0 | H | 0 |
| 0.8 | 0.2 | 0 | 0 | 0 | 0 | 0 | μ | 0 | 0 |
| 0.75 | 0.25 | 0 | 0 | 0 | 0 | Ч | 0 | 0 | 0 |
| $^{-}0.98$ | 0.002 | 0.002 | 0.01 | 0.006 | - | 0 | 0 | 0 | 0 |

6.12)

The core of the Merrick model is the set of linear equations

$$A\bar{x} = \bar{b} \tag{6.13}$$

The vector \bar{x} contains the (unknown) mass fractions of species considered to be formed during devolatilization. The vector \bar{b} contains the chemical analysis of the fuel on dry, ash-free basis (the first five rows) and a set of empirical relations related to the devolatilization process. Finally, the matrix A contains the elemental mass balances (the top rows) and the correlations (bottom rows). The original coal devolatilization model as proposed by Merrick is given by Equation 6.12; note that oxygen (element O) is denoted by "X" to avoid any confusion with the number zero. It can be noted that the first five rows in *m*-th column give the chemical composition of the *m*-th specie in the vector \bar{x} in terms of mass fractions of the elements C, H, O, N and S.

In order to make the model suitable to simulate the devolatilization of biomass new empirical relationships must have been determined. This was done partly based on the literature data and partly on own small-scale experiments. Devolatilization of clean wood and miscanthus have been extensively studied by De Jong [42] by means of a TG-FTIR setup under slow heating rate conditions. The researchers measured the amounts of volatile matter released, as well as the amount of char. The composition of the volatiles was also determined -17 gaseous species were measured directly, while the amount of tar was determined by difference. Although the analysis of the gaseous species is quite extensive, no hydrogen yield is reported, as this gas is not detected by the FTIR. However, it is very relevant to determine the hydrogen yield from pyrolysis, at least to check its presence in the pyrolysis products. In addition, it is desirable to confirm the calculated tar yield and, if possible, determine the composition of tar. To obtain this information, an own set of experiments has been carried out involving a Heated Grid (HG) reactor, an FTIR spectrophotometer and a micro gas chromatograph (micro-GC). The experimental setup is depicted in Figure 6.4. The full description of the approach and the results are given elsewhere [68]. The gases released during pyrolysis were forced by suction through a Solid Phase Adsorption (SPA) tube, where the condensable species (tar) were collected. Such setup allowed the measurement of the main gaseous species, including H₂, as well as of the amount and the composition of tar released; see also Table 6.3 for an overview. The number of gaseous species analyzed by FTIR was lower than in the work carried out by De Jong et al., but the main focus of own experiments was the direct measurement of hydrogen and tar.

In order to use the experimental data to develop the modified empirical relations in the Merrick model, the experimental data had to be processed to match the original set of linear equations. The development of a new extended set of linear equations and empirical relations to describe the devolatilization / pyrolysis process is outside the scope of this work. The following assumptions were made:



Figure 6.4: Heated Grid (HG) setup used for the small scale pyrolysis experiments schematic (top) and photo (bottm). Legend: 1–heated stainless steel plate, 2–Pt/Pt-Rh thermocouple, 3–optical duct for the FTIR, 4–circulation pump, 5–power connector, 6–thermocouple connector, 7–SPA sampling tube, 8–lid, 9–stainless steel extension tube, 10–micro-GC sampling line connection, 11–FTIR. Adapted from [68, 157]

| Type of analysis | Species quantified |
|-----------------------------------|--|
| Fourier Transform Infrared (FTIR) | CO_2 , CH_4 , C_2H_4 , CO , C_2H_2 COS, HCN, |
| ThermoElectron Nicolet 5700 | H_2O , NH_3 |
| 0.19 m optical length, | |
| resolution 0.125 $\rm cm^{-1}$ | |
| Varian CP4900 micro-GC | BTX (benzene, toluene, xylenes) |
| module: CP-Sil 5 CB, 4m | |
| Varian CP4900 micro-GC | N_2 , H_2 , CO, CO ₂ , CH ₄ |
| module: CP-COX, 1m | |
| Solid Phase Adsorption (SPA) | PAH, Phenolics |

Table 6.3: Analysis equipment used during the bench-scale pyrolysis experiments

- char consists of carbon only;
- the organic species quantified by De Jong [42] and by Goosens [68] but not included in the Merrick model have been grouped as "Light Organic Compounds" (LOC, C_2H_6 -equivalent), meant to substitute ethane in the devolatilization model;
- tar, according to the analysis, is assumed to consist of C, H and O only;

In addition, the atomic composition of tar $(C_x H_y O_z)$ has been determined using Least Squares method applied to an objective function consisting of elemental mass balance deviations squared:

$$F = Min \sum ((C_{biomass} - C_{measurements})^{2} + (H_{biomass} - H_{measurements})^{2} + \cdots + (O_{biomass} - O_{measurements})^{2})$$
(6.14)

This approach was necessary, as of all the analyses described above, the tar analysis contained the highest error – this is due to (still) imperfect sampling of tar in the HG. In general, the measured amount of tar was very low, with a maximum yield of 0.08% by mass of the initial biomass sample, while 20% by mass or more can be expected from the literature.

Table 6.5 presents an overview of the data that have been the basis for the modified empirical correlations. The conversion of hydrogen and oxygen contained in the fuel to respectively CH_4 and C_2H_6 -equivalent, and CO and CO_2 is reported in the last four rows of the table. The modified correlations in the Merrick model can be calculated by dividing the conversion percentage by the percentage of

| Element: | С | Н | Ν | S | 0 |
|---|-------|-------|-------|-------|-------|
| CH ₄ | 0.749 | 0.251 | 0.000 | 0.000 | 0.000 |
| C ₂ H ₆ -equivalent | 0.455 | 0.085 | 0.000 | 0.000 | 0.460 |
| CO | 0.429 | 0.000 | 0.000 | 0.000 | 0.571 |
| CO_2 | 0.273 | 0.000 | 0.000 | 0.000 | 0.727 |

Table 6.4: Elemental composition (mass fractions) of the four species considered in the empirical correlations of the Merrick's model

the mass of the element involved in the gas molecule to which the correlation will apply. These mass percentages are reported in Table 6.4; the molecular formula of C_2H_6 -equivalent has been derived from the total yields of the hydrocarbons other than tar and methane measured by de Jong et al. and during own experiments. From the data in Tables 6.5 and 6.4 new correlation constants can be calculated:

- fuel-H to CH_4 : 0.207 · H
- fuel-H to C_2H_6 -equivalent: $0.254 \cdot H$
- fuel-O to CO: 0.130 · X
- fuel-O to CO_2 : 0.068 · X

The novel aspect of quantifying the hydrogen yield during the pyrolysis experiments definitely leads to a more complete characterization of the gases released during fast pyrolysis experiments. Although the use of a micro-GC allows fast quantification of hydrogen and therefore is an improvement of the HG-FTIR setup, it has to be stated that the values for hydrogen yields from the HG experiments presented above should be considered as "initial", and the error in these values is likely relatively high. This is related to the fact that the amount of hydrogen released as H₂ is very low, and combined with the low biomass sample mass the H₂ volume fraction inside the HG is also low – approximately 100 ppmv was expected [68]. The detection limit of the CP-COX module for hydrogen depends on its configuration, and for this case has been estimated at approximately 10 ppmv. Therefore it should be possible to quantify hydrogen release by means of a micro-GC, but the repeatability of this measurement is still to be assessed. The repeatability of the CO, CO₂ and CH₄ measurements was acceptable, and also the values measured by the FTIR and the micro-GC independently were most of the time in agreement with each other, which indicates that the sampling must have been done properly. Unfortunately, the proper quantification of the tar yield was still lacking, as mentioned before. It should also be critically assessed whether the SPA method is the right way to sample Table 6.5: Mass yields of the elements C, H, N, S and O per unit mass of A-wood (daf). All values obtained from own HG experiments at the heating rate of 600 K s⁻¹, except the LOC composition (derived from [42], heating rate 1.67 K s⁻¹). The bottom rows show the newly derived correlations for the modified Merrick pyrolysis model. All numbers represent mass percentages

| Element: | С | Н | Ν | S | 0 |
|---|------|------|------|------|------|
| Char | 7.06 | 0.00 | 0.00 | 0.00 | 0.00 |
| Tar | 39.8 | 3.90 | 0.00 | 0.00 | 27.4 |
| Hydrogen | 0.00 | 0.19 | 0.00 | 0.00 | 0.00 |
| Methane | 0.88 | 0.30 | 0.00 | 0.00 | 0.00 |
| Water (pyr.) | 0.00 | 1.18 | 0.00 | 0.00 | 9.35 |
| Carbon monoxide | 2.37 | 0.00 | 0.00 | 0.00 | 3.16 |
| Carbon dioxide | 0.79 | 0.00 | 0.00 | 0.00 | 2.11 |
| Ammonia | 0.00 | 0.01 | 0.04 | 0.00 | 0.00 |
| Subtotals: | | | | | |
| Char | 7.06 | 0.00 | 0.00 | 0.00 | 0.00 |
| Tar | 39.8 | 3.90 | 0.00 | 0.00 | 27.4 |
| Gas: permanent | 4.04 | 1.66 | 0.00 | 0.00 | 14.6 |
| Gas: LOC (ethane-equivalent) | 0.66 | 0.12 | 0.00 | 0.00 | 0.66 |
| Gas: other | 0.00 | 0.01 | 0.04 | 0.00 | 0.00 |
| Total | 51.5 | 5.70 | 0.04 | 0.00 | 42.7 |
| Biomass composition (daf) | 51.4 | 5.70 | 0.22 | 0.02 | 42.7 |
| Fuel-H to CH ₄ | | 5.21 | | | |
| Fuel-H to C ₂ H ₆ | | 2.15 | | | |
| Fuel-O to CO | | | | | 7.40 |
| Fuel-O to CO ₂ | | | | | 4.94 |

tar produced during such experiments. Finally, also the quantification of char is not trivial and prone to errors: the proximate analysis of the fuel indicates approximately 13% by mass of fixed carbon present in the fuel, while the experiments yield only ca. 7%. This, however, can be (partly) explained by the fact that the analysis of the fuel is based on a low heating rate measurement, which yields more char than the high heating rate process as the heated grid.

Considering the above, the derived modified Merrick devolatilization / pyrolysis model represents a significant and necessary improvement of the IEA code to allow the simulation of biomass gasification process. With the working implementation in the Fortran code, this part can be refined further, as better experimental data become available. This is also recommended for the future research.

6.3.3 **Gasification reactions**

6.3.3.1 Homogeneous gas phase reactions

As already stated in Section 6.2.8, only oxidation reactions and a relatively detailed NO_{τ} chemistry have been taken into account in the IEA model. In order to simulate gasification processes the subroutine dealing with gas phase reactions had to be extended at least with the most important gasification reactions. Table 6.6 presents an overview, both of the reactions already implemented in the IEA model and the newly implemented gasification reactions, including their kinetic parameters.

Table 6.6: Gas phase reactions implemented in the original IEA model and the newly implemented gasification reactions

| No. | Reaction equation | Pre-exp. fac- tor (k_0) $[m^3mol^{-1}s^{-1}]$ | E _a /R ^a [K] | Lit. source |
|-------------------|--|---|---------------------------------------|---|
| IEA m | odel | | | |
| R1 | $CO + 0.5O_2 \longrightarrow CO_2$ | $1.3 \cdot 10^{8}$ | $-126 \cdot 10^3 / R$ | [82] ^b |
| R2 | $H_2 + 0.5O_2 \longrightarrow H_2O$ | $2.2 \cdot 10^{6}$ | $-109 \cdot 10^3 / R$ | [115] ^b |
| R3 | $CH_4 + 1.5O_2 \longrightarrow CO + 2H_2O$ | $1.0 \cdot 10^{9}$ | $-203 \cdot 10^3 / R$ | [174, 52] ^b |
| R4 | $C_2H_6 + 2.5O_2 \longrightarrow 2CO + 3H_2O$ | $1.0 \cdot 10^{9}$ | $-10 \cdot 10^{3}$ | |
| R5 | $\rm H_2S + 1.5O_2 \longrightarrow SO_2 + H_2O$ | $1.0 \cdot 10^{9}$ | $-24 \cdot 10^{3}$ | |
| R6 | $N_2O \longrightarrow N_2 + 0.5O_2$ | $5.2 \cdot 10^{9}$ | $-27 \cdot 10^{3}$ | |
| R7 | $NO + \frac{2}{3}NH_3 \longrightarrow \frac{5}{6}N_2 + H_2O$ | $2.45 \cdot 10^{14}$ | $-27.68 \cdot 10^{3}$ | |
| R8 | $\mathrm{NH}_3 + \frac{5}{4}\mathrm{O}_2 \longrightarrow NO + 1.5\mathrm{H}_2\mathrm{O}$ | $2.21 \cdot 10^{14}$ | $-38.16 \cdot 10^{3}$ | |
| Newly | <i>i</i> mplemented | | | |
| R9 | $CO + H_2O \longrightarrow H_2 + CO_2$ | 2.778 | $-12.56 \cdot 10^{3}$ | [85] ^c , [109] ^{b, c} |
| R10 | $C_x H_y O_z + (x + y - z) O_2 \longrightarrow x CO + \frac{y}{2} H_2 O$ | $1.58 \cdot 10^{7}$ | $-201 \cdot 10^3 / R$ | $[32]^{b,d}$ |
| R11 | $CH_4 + H_2O \longrightarrow 3H_2 + CO$ | $3.0 \cdot 10^5$ | $-125 \cdot 10^3 / R$ | [88] ^b |
| R12 | $C_x H_y O_z \longrightarrow \frac{y}{4} CH_4 + zCO + (x - z - \frac{y}{4})C(s)$ | $3.7 \cdot 10^7$ | $-145 \cdot 10^3 / R$ | [164] ^b |
| ^a exce | of the reactions no. 3, 6, 8 and 12, where $k_0 \pmod{m^{-3} s^{-1}}$ | | | |

^b values taken from [67], original source listed in the table

^c equilibrium-limited, equilibrium constant $\mathbb{K}_{WGS} = \frac{y_{H_2}y_{CO_2}}{y_{H_2O}y_{CO}} = 0.029 exp(4094T^{-1})$ ^d original reaction equation: $CH_xO_y + zO_2 \longrightarrow (\frac{x}{2} - y - 2z + 2)CO + (y + 2z - \frac{x}{2} - 1)CO_2 + \frac{x}{2}H_2O_2$ modified to avoid z being an independent variable

Reactions involving solid carbon as reactant 6.3.3.2

In the IEA model, the only reaction involving the solid carbon as a reactant was the char oxidation reaction. Using a shrinking particle model, introduced in Section 6.2.2, the carbon combustion reaction rate is calculated for each cell, yielding also the production rates of CO and CO₂, and the consumption rate of O2. However, under gasification conditions, solid carbon will also react with other gases. In this work, two additional carbon reactions have been implemented: the water-gas reaction and the Boudouard reaction, see Table 6.7. The Table 6.7: Chemical reactions involving solid carbon as reactant implemented in the original IEA model and the newly implemented gasification reactions

| No. | Reaction equation | Lit. source |
|--------|---|-------------|
| IEA r | nodel | |
| S1 | $C(s) + (1.5 - 0.5\Phi)O_2 \longrightarrow (\Phi - 1)CO + (2 - \Phi)CO_2^a$ | [75] |
| | | |
| Newl | y implemented | |
| S2 | $C(s) + CO_2 \longrightarrow 2CO$ | [164] |
| S3 | $C(s) + H_2O \longrightarrow H_2 + CO$ | [164, 135] |
| $S4^b$ | $\mathbf{C}(\mathbf{s}) + 2\bar{\mathbf{H}}_2 \longrightarrow \mathbf{C}\bar{\mathbf{H}}_4$ | |

 a Φ is the split factor between CO and CO₂ dependent on the particle size and the temperature of the surroundings. Φ =1 – only CO₂ is formed; Φ =2 – only CO is formed.

 $^{\boldsymbol{b}}$ reaction considered, but not implemented in the model

reaction mechanism of the reaction S1 will, however, significantly differ from the reactions S2 and S3. The reaction with oxygen (combustion reaction) is very fast and will therefore be diffusion-limited, meaning that the reaction takes place mainly on the surface of the particle. This is also the assumption used in the IEA code, as mentioned in Section 6.2.2. The gasification reactions, like the water-gas and the Boudouard reaction are significantly slower, and therefore they will occur also inside the particle (kinetically limited reaction). Van den Aarsen [164] performed gasification experiments in a fluidized bed, and used the data to derive an Arrhenius-type surface reaction rate for the Boudouard reaction:

$$RR = 7.2 \exp\left(-\frac{166156}{RT}\right) c_{CO_2}^{0.83} \quad \left[mol_C \ m^{-2} \ s^{-1}\right]$$
(6.15)

The reaction rate equation mentioned above has been implemented in the model. Regarding the water-gas reaction a factor 2 between the reactivity of the watergas and the Boudouard reaction was reported by Rensfelt [135, 164], therefore the reaction rate of the water-gas reaction was set to be a double of the Boudouard reaction rate. The methanation reaction (reaction S4 in Table 6.7) could also be considered for implementation. However, as the reaction rate of the methanation reaction is one order of magnitude lower than the reaction rate of the water-gas reaction, this reaction is of secondary importance in this work, and therefore not added to the gas-carbon reaction scheme.

The approach to model the carbon gasification reactions described above should be considered as a starting point. The model should be extended with a testing routine that, based on the Biot and Thiele numbers, will assess whether the chosen particle reaction model is appropriate. Based on the outcome of such a test, the necessity to implement a more complicated diffusion-based particle reaction model may emerge.

6.3.3.3 Tar decomposition reactions

In the IEA model no tar species or tar reactions have been implemented. As indicated in Section 2.2 "tar" is an umbrella term for various kinds of larger hydrocarbons produced during gasification. Therefore a choice needs to be made in which detail tar will be considered in the model. Corella [31] proposed a 6lump model (benzene, 1-ring excl. benzene, naphthalene, 2-ring excl. naphthtalene, 3-ring and larger, phenolics), with 11 rate constants, assuming 1^{st} order reactions as an alternative to the commonly used single-lump tar model with a single apparent rate constant k_{app} based on 1^{st} order reaction assumption. Obviously the 6-lump model allows a more detailed representation of the changes in tar amount and composition when proceeding from primary tar (product of the pyrolysis process) to tertiary tar (product of the tar decomposition reactions during gasification process). Nonetheless in the initial stage of the model adaptation only the tar decomposition reactions, being tar oxidation and tar cracking have been implemented. Reaction 10 in Table 6.6 is a plain homogeneous gas-phase reaction and is treated as such. More complicated is the tar cracking reaction, as it produces solid carbon (soot). Soot formation is an important phenomenon in tar cracking and therefore it must be taken into account. Soot formed during tar cracking is a very fine material, thus it is assumed that all soot falls into the smallest size category of the solids particle size distribution. A soot formation rate is defined, which is dependent on the tar decomposition rate, and it is added to the total char (carbon) input in the char balance routine.

6.3.4 Adjustments to simulate small-scale equipment

6.3.4.1 Cyclone model

A cyclone model is a part of the CFB model to simulate the gas-solid separation downstream of the riser exit. The cyclone model implemented in the IEA code is based on the Barth model [10]. Computational complications occurred after the implementation of the geometry of the TUD CFB in the input file. This was caused by the calculation of the vortex efficiency given by

$$\eta_{vortex} = \left(1 + exp\left(-\frac{d_{p,i} - d_{p,crit}}{d_{p,crit}}\right)\right)^{-1}$$
(6.16)

with

$$d_{p,crit} = \left(\frac{18\,\mu_g\,u_{rad}\,r_{in}}{u_{in}^2\,(\rho_s - \rho_g)}\right)^{0.5} \tag{6.17}$$

It is known, that small cyclones achieve higher separation efficiencies than the large units, therefore also the critical particle diameter $d_{p,crit}$ calculated for the

TUD cyclone is lower than the one calculated for a large scale unit. Consequently, the difference between the characteristic particle diameter of a size class *i* and the critical particle diameter, which is given by the numerator of the exponent in Equation 6.16 may become relatively large for small cyclones (as is the case in the TUD CFBG) compared to large cyclones (as simulated by the IEA model). After division by the denominator, which is a relatively small number, the exponent of the function may become too large, causing computational errors (overflow). This is in particular the case for large size classes, due to a relatively large numerator, as explained above. However, in an ideal case all large particles should be separated from the gas stream and the separation efficiency will decrease with the decreasing particle diameter. Therefore, to overcome computational limitations, it is assumed that the vortex efficiency is 1 for size classes 1–7, and the calculation proceeds from size class 8 onwards [141]. Nonetheless, it is recommended to refine this assumption in the future work.

6.3.4.2 Riser exit efficiency

The gas-solids separation can already be initiated upstream the cyclone, depending on the design of the riser exit. Industrial CFBs usually employ a rightangled exit, often with a flow restriction. Such design causes the separation of the largest particles from the exit gas flow, reducing the solids load on the cyclone. In the IEA model the riser exit efficiency is taken into account, but it is not calculated as a function of process parameters, only assumed being a constant value (0.3). In case of the TUD CFB, due to the smooth bend before the cyclone entrance, the riser exit efficiency very likely is close to zero. Nonetheless, the original value was kept, and no assessment was made of the sensitivity of the model to this parameter – this aspect was outside the scope of this work.

6.3.4.3 Heat losses and external heating

The IEA model considers a number of heat exchanging devices to extract the heat from the flue gas for steam generation and to control the temperature of the reactor. These are the water jacket around the riser, heat exchanger tube bundles in the lean region and an external ash cooler, all found in industrial CFB boilers. When considering a small-scale CFB gasification unit the heat management is radically different from a large-scale combustor. Firstly, most of the gasification reactions are endothermal; secondly, the heat losses of a small unit are relatively higher compared to a large unit, due to a lower volume to external area ratio. Therefore a maximal amount of heat should be kept inside the reactor, instead of extracting it with heat-exchanging devices. To balance the heat losses without the need of combusting more product gas (see Section 3.4.1) the TUD CFB test rig is equipped with external electrical heating. Such feature

is, however, not considered in the combustor model due to the reasons mentioned above. Alternatively a simple way to take the external heat supply into account was the ash cooler implemented in the IEA model, as it can be conveniently used either as a heat sink or as a heat source. This approach allowed the simulation of the gasification experiments with the focus on the gasification chemistry. However, a further consideration of various aspects of the heat management inside the gasifier is desirable and therefore recommended for future work.

6.3.4.4 Bottom bed discharge

In order to assure long-term continuous operation the bed material is continuously refreshed in the industrial fluidized bed reactors. This requires a facility to remove the bed material, usually from the dense bed zone. Small-scale lab test rigs operated on a "single day run" basis are often not equipped with such a feature, as the bed material is fed into the reactor before the experiment and usually it is removed completely at the end of a run. However, such batch operation is not implemented in the IEA model, which requires a continuous feed of the bed material which is balanced by the bottom bed discharge and the particle "loss" in the cyclone. The main difference between the batch operation and the continuous feed-discharge operation, except the long-term stability, is the energy necessary to heat up the fresh bed material. However, considering the assumptions made regarding the energy balance in the gasification model (see Section 6.3.4.3) the continuous refreshment of the bed material should not affect the results related to the gasification directly. As the discharge of the solids also includes a fraction of unconverted char, it will affect the carbon conversion predicted by the model. The consequently reduced carbon holdup in the reactor will indirectly and to some extent affect the gas composition results. For the further fine-tuning of the model it is advised to implement the possibility of simulating the batch operation mode.

6.3.4.5 Bed material feed rate

The bed material feed rate is closely related to the amount of energy added or extracted in the ash cooler. To assure stable calculations during the iteration loops a sand feed rate was determined by running the model with different values of this variable and observing the results. Finally a value of 3.00 kg h^{-1} was found to be reliable, and this value was kept constant throughout the model development described in this work. Obviously this value represents an "imaginary" sand feed rate, as in reality no sand or a least not in such an amount was fed to the TUD CFB gasifier during the experiments. As recommended in Sections 6.3.4.3 and 6.3.4.4 the implementation of the batch operation mode in the gasifier model would allow the use of the actual value for the bed material feed rate.

6.3.4.6 Size distribution of the lime feed

The use of additives, in the IEA model considered as lime only, was outside the scope of this work, which focused on the adaptation of a CFB combustion model to simulate a gasification process. Therefore for the validation of the model experiments have been chosen where no additives were fed. In agreement with the experiment a zero lime feed rate was introduced in the input file. Nonetheless it turned out to be necessary to provide a lime particle size distribution, otherwise a computational error occurred in the preliminary population calculation. Although this can be solved easily by adapting the calculation procedure not to consider lime if its feed rate is zero, an arbitrary PSD of lime was provided in the input file instead as a quick fix [141].

6.4 Simulation results

6.4.1 Base case description

The value of any mathematical model, no matter how sophisticated will be limited if it has not been validated against a real measurement. The experimental results of gasification of A-quality 6 mm wood pellets with a mixture of steam and oxygen as fluidization agent and quartz sand as the bed material will be used as the reference case for the validation of the gasifier model presented in previous sections. Table 6.8 presents an overview of the average steady state values for the process variables applied during the experiment of August 19th 2008, and the resulting gas composition measured during this experiment. The detailed description and evaluation of this experiment was given in Chapter 5. The input file for the simulation of the case described above is presented in Appendix B. The flows of the four gas input streams have been modeled as a single flow rate with an appropriate composition – at the moment of writing this variable is not a part of the input file and has to be entered directly in the code. The composition of the fuel, given in Chapter 3 has been recalculated to dry basis for C, H, O, N, S and the ash and normalized. Although the minor elements N and S were taken into account in the fuel input, their chemical reactions have not been considered in the calculation of the gas composition (by setting the preexponential factors to zero), in order to focus on the main gaseous components. In addition, the following assumptions were made:

- homogeneous gas-phase reactions: kinetic parameter taken from the literature, or kept the same as in IEA model (e.g., for reaction 4, due to the lack of better data);
- homogeneous gas-phase reactions of minor fuel constituents (N and S): disabled;

| | date: | 19-Aug-08 |
|----------------------------------|------------------------------|----------------------|
| | fuel: | A-wood |
| | oxidant: | Steam-O ₂ |
| | duration ^a : | 0:16 |
| | t start: | 10:58 |
| | t end: | 11:14 |
| Steam flow rate | $\mathrm{kg}\mathrm{h}^{-1}$ | 10.8 |
| O_2 flow rate | $kg h^{-1}$ | 4.40 |
| Biomass flow rate | $kg h^{-1}$ | 10.4 |
| Air (L-valve) flow rate | $kg h^{-1}$ | 0.767 |
| N_2 (purge) flow rate | $\mathrm{kg}\mathrm{h}^{-1}$ | 1.25 |
| Mean riser temperature | $^{\circ}\mathrm{C}$ | 837 |
| Gas inlet temperature | $^{\circ}\mathrm{C}$ | 360 |
| P_{gage} at CFB outlet | mbar | 63.5 |
| λ (daf) | $ m kgkg^{-1}$ | 0.35 |
| SB (ar) | $kg kg^{-1}$ | 1.0 |
| | | |

Table 6.8: Overview of the process conditions applied during the evaluation period of the experiment used for the validation of the newly implemented gasifier model

^{*a*} duration of the selected evaluation period

- heterogeneous gas-phase reactions (only reactions involving nitrogen were implemented in the IEA model): disabled;
- reaction C + O₂: IEA model;
- CO / CO₂ split: IEA, parameters modified according to Van den Aarsen [164];
- C + CO₂: surface kinetics approach [164];
- C + H₂O: surface kinetics approach [164, 135];
- char density: 900 kg m^{-3} , own measurements;
- sand feed rate: 3 kg h⁻¹; the model does not allow batch operation with respect to the bed material and therefore a continuous feed rate is used that is lower than the initial amount of the bed material present in the real gasifier before the experiment. This is due to the fact that part of the bed material remains in the downcomer;
- elutriation: elutriation compartment set just below the exit compartment, as expected in a circulating fluidized bed.

Other parameters, not mentioned above, have been kept "default", meaning the same as used by Hannes during the coal combustion simulations. The objective of this part of the work was to verify the performance of the new gasifier model when solely literature-derived kinetic parameters are used in the implemented gasification reactions, and subsequently tune the kinetics to achieve a match between the simulation results and the measurements.

6.4.2 Base case results

A simulation run was performed with the model code and the input file as described in the previous section. The assessment of the results was focused on the following aspects:

- Calculations prior to the energy balance iteration loop
 - the pyrolysis submodel
- Calculations inside the energy balance iteration loop
 - the number of iteration steps necessary to achieve convergence;
 - the calculated gas composition in terms of molar fractions;
 - the calculated carbon conversion;
 - the agreement between the given input and the calculated output in terms of the elemental mass balance closures.

In the following paragraphs the above-mentioned sequence is used to present the results of the modeled base case.

6.4.2.1 Base case results: the pyrolysis sub-model

The results of the pyrolysis sub-model, i.e., the composition and the amount of the volatiles released during the pyrolysis of the fuel, depend only on the fuel composition as was shown in Section 6.3.2. Table 6.9 presents the composition of the volatiles and their total molar flow rate, while Table 6.10 contains the calculated drying and devolatilization times per fuel particle size class. The most important improvement in this sub-model as compared to the IEA model is the fact, that now also methane, light volatile hydrocarbons and tar are present in the reactor after the devolatilization step. The relatively large tar yield agrees with the expectation – particles are exposed to a very high heating rate (several hundreds of Kelvin per second) which, according to the literature, will yield a higher amount of condensable gases (tar) than in case of slow heating rate (few tens of Kelvin per minute).

The largest fuel particles considered in this base case have a diameter of approximately 7 mm, i.e., 7000 μ m. As can be seen in Table 6.10 the calculated drying and devolatilization times for these fuel particles are approximately 3

| Species | Volatiles composition | Volatiles yield |
|-------------------|---------------------------------|--------------------------|
| | $\mathrm{mol}\mathrm{mol}^{-1}$ | kg kg $^{-1}$, dry fuel |
| СО | 6.61E-02 | 5.50E-02 |
| CO_2 | 2.21E-02 | 2.89E-02 |
| O_2^{a} | 4.47E-01 | 4.25E-01 |
| H_2O | 2.94E-01 | 1.57E-01 |
| N_2 | 0 | 0 |
| \overline{SO}_2 | 0 | 0 |
| NO | 0 | 0 |
| H_2 | 3.91E-02 | 2.32E-03 |
| NO_2 | 0 | 0 |
| CH_4 | 2.49E-02 | 1.18E-02 |
| C_2H_6 | 9.16E-03 | 1.44E-02 |
| NH ₃ | 5.31E-03 | 2.68E-03 |
| N_2O | 0 | 0 |
| H_2S | 2.31E-04 | 2.34E-04 |
| Tar | 9.23E-02 | 5.88E-01 |
| Volatiles | flow [kg h ⁻¹] | 8.22^{b} |

Table 6.9: The calculated composition and the molar flow rate of the volatiles in the base case

^{*a*} there is no pure oxygen present in the volatiles; the numbers represent the amount of oxygen necessary to form the volatiles

 b normalized value, in agreement with the fuel input flow and composition. Calculated value was 7.62 kg h^{-1}, giving an equal deviation in all elemental intermediate mass balances

seconds and 40–45 seconds, respectively. Although no experimental data are available for direct validation, the order of the magnitude seems to be on the high side, considering the size of the particles. A direct assessment based on a gasification experiment is difficult, as it would require instantaneous interruption of the experiment and immediate removal of the bed inventory. This is difficult to carry out due to the still high (around 800°C) temperature in the reactor. However, an observation in a bench-scale glass fluidized bed used for demonstration purposes fired with a propane-butane mixture (see Figure 6.5) revealed devolatilization times of around 10 seconds. The conditions in the glass unit are close to pyrolysis conditions as most oxygen is used for the combustion of the gas mixture.

Figure 6.6 shows the moisture and the volatile matter release rate profiles. The volatile release profile shows three maxima: near the fuel feed point (1), near the solids recirculation point (2), and at the bottom of the riser (3). Intuitively point (1) is correctly showing the highest release rate due to the local supply of

| Size class | Diameter | Drying time | Devolatilization |
|------------|----------|-------------|------------------|
| | [µm] | [s] | time [s] |
| 1 | 16000 | 7.23 | 108 |
| 2 | 13500 | 6.24 | 70.9 |
| 3 | 9500 | 3.89 | 52.8 |
| 4 | 6800 | 2.65 | 40.2 |
| 5 | 4800 | 1.76 | 30.2 |
| 6 | 3400 | 1.17 | 22.8 |
| 7 | 2400 | 0.800 | 17.3 |
| 8 | 1700 | 0.543 | 13.1 |
| 9 | 1200 | 0.375 | 9.89 |
| 10 | 855 | 0.263 | 7.54 |
| 11 | 605 | 0.180 | 5.72 |
| 12 | 428 | 0.124 | 4.34 |
| 13 | 302 | 0.0837 | 3.29 |
| 14 | 215 | 0.0545 | 2.50 |
| 15 | 152 | 0.0332 | 1.90 |
| 16 | 108 | 0.0191 | 1.44 |
| 17 | 76 | 0.0105 | 1.09 |
| 18 | 54 | 0.00543 | 0.822 |
| 19 | 38 | 0.00272 | 0.619 |
| 20 | 16 | 0.000473 | 0.307 |

Table 6.10: The calculated drying and devolatilization times for each fuel particle size class

fresh fuel. Also points (2) and (3) show significant release rates. This is caused by two phenomena: sedimentation and recirculation. Even in the fluidized bed regime where intense mixing of the bed inventory occurs, large(r) fuel particles will tend towards the bottom of the bed, due to larger gravity forces acting upon them. This will lead to a higher holdup of these particles in the bottom part of the riser, causing higher local volatile release rates. The recirculation of the solids from the downcomer amplifies that effect. However, it has to be stressed that in the current implementation of the model the residence time in the downcomer is not taken into account. Due to a still high temperature in the downcomer the devolatilization process will proceed there, leading to a lower amount of volatiles to be reintroduced with the recirculated fuel particles. Therefore the real volatile release pattern is expected to be more flattened in the bottom part of the riser.



Figure 6.5: Glass bench scale fluidized bed unit used for demonstration purposes. Here shown while operating; reddish bed zone indicates a high temperature zone, approximately 800° C

6.4.2.2 Base case results: the iteration process

For the base case simulation the tolerances for the mass- and energy balance iterations have both been set to 1E-3 (see Section 6.2.7); the maximum number of consequent mass- and energy balance iteration loops is set to 20 and 10, respectively. In the first energy balance iteration loop the mass balance criterion is not fulfilled in the maximum number of iterations, but the first energy balance calculation yields a better starting point for next iterations, finally leading to convergence in the 2^{nd} mass balance loop of the 4^{th} energy balance loop. The problems in the first mass balance iteration could be caused by the choice of initial values for the gas composition in the code – this can be fine-tuned during the further development of the code. The typical calculation times varied from 1 to a few minutes on a dual-core 1.66 GHz PC.

6.4.2.3 Base case results: the calculated gas composition and carbon conversion

The gas composition calculated during the simulation and the comparison with the experimental data is shown in Table 6.11. It is clear that the model based solely on the literature kinetics and on the values adapted from the original (coal-based) IEA model in case of gasification significantly over-predicts the carbon conversion as well as the yields of hydrogen and carbon dioxide. As also the water fraction is lower than measured, it is concluded that the water-gas shift reaction proceeds at a too high rate; the CO consumed by this reaction



Figure 6.6: The calculated release rates of moisture and volatile matter – base case. The numbers between parentheses indicate the three maxima in the volatile matter release profile

is compensated by the combustion of char. The calculated tar yield is slightly lower than the measured value.

The tuning of the model to the experimental data involved the adjustment of the kinetic parameters related to the chemical reactions implemented in the model. Obviously the target was to obtain fair agreement between the simulation and the experiment by modifying as few parameters as possible. The strategy was to match the carbon conversion efficiency as closely as possible, and to match the yields of the main product gas components (CO, H₂, CH₄, CO₂, H₂O) preferably within 10% deviation from the experimental value. The calculated amount of tar was also considered, but its exact comparison with the experiment is more difficult due to the simple definition of "tar" in the model and the measurement inaccuracies in the experiment.

The tuning of the base case simulation was performed by modifying three preexponential factors that were related to respectively char combustion, water-gas shift and wet methane reforming reactions. The original and modified parameters are shown in Table 6.12. The results obtained with the modified parameters (see Table 6.11) are closer to the experimental values, as intended, although the 10% deviation threshold was not reached. However, it can be concluded that the default pre-exponential factor for the char combustion reaction taken from the

combustion case is far too high. Nonetheless, of the three considered reactions that consume char, still the combustion reaction is the fastest one, see Figure 6.8. Also the pre-exponential factor for the wet methane reforming reaction was taken from a publication dealing with combustion [88], but its downward adjustment was not as high as in case of char combustion reaction. Finally it is clear that the water-gas shift reaction proceeds at a much lower rate than reported in the literature; this could be plausible if the data in the literature were derived from a catalytic reaction, but it is not explicitly stated [109]. This shows, however, that there is a very strong potential to improve the quality of the gas (in terms of the hydrogen yield) exiting the gasifier by using either an additive or a bed material which acts as a catalyst on the water-gas shift reaction. This has been successfully demonstrated experimentally for a certain kind of calcined magnesite, see Chapter 5, where the measured hydrogen yield was closer to the base case simulation with unmodified kinetic parameters. However, the modeling of the presence of catalytically active solid materials in the gasifier fell outside the scope of this research work.

Figure 6.7 (top) shows the core profiles of the main gaseous species considered in the modified IEA model. As expected, the oxygen is consumed in the bottom part of the reactor and it is depleted completely within two meters of the reactor length. The presence of oxygen leads to high combustion reaction rates, as shown in Figure 6.8 – at the bottom of the reactor the char combustion reaction proceeds at the highest rate, but as the oxygen concentration decreases the carbon monoxide combustion (reaction R1) gains preference, till the oxygen is fully depleted. The combustion of hydrogen occurs at a much slower rate. In the gasification zone the wet methane reforming reaction and the tar cracking reaction are dominating; the water-gas shift reaction is strongly inhibited, as already mentioned above. It is also clear, that other gas-char reactions have a very limited effect on the final gas composition, due to their slow reaction rates. It is worth noting that the local maximum in the CO profile at the bottom of the reactor was also reported by Kersten, see Figure 6.7 (bottom) [90].

Figure 6.9 presents the axial temperature profiles in the riser. The calculated profile matches well with the (interpolated) experimental data, but it has to be kept in mind, that the wall temperature and the temperature at the solids reentry point have been fixed in the input file in order to mimic the presence of the external heating elements.

6.4.2.4 Base case results: the elemental mass balance closure

To verify the correctness of the calculations performed by the model and to reveal possible errors an elemental mass balance has been prepared. The mass balance compares the flows of the elements calculated after the pyrolysis stage and the gasification stage with the elemental gas and solids input. The mass balance for the tuned base case is given in Table 6.13.





Figure 6.7: Volume fractions of the main gas components: axial profiles calculated with the modified IEA model (top); axial profiles calculated by Kersten, reproduced from [90] (bottom)



Figure 6.8: Calculated reaction rates of the prevailing chemical reactions – axial profiles



Figure 6.9: Calculated axial temperature profiles and the measured values

Table 6.11: Calculated and measured gas composition (volume fractions on wet gas basis), total product gas flow and the carbon conversion in the base case. The calculations have been performed using literature kinetics as well as modified kinetics to match the carbon conversion to the experimental value

| Species | Unit | Calculated | Calculated | Measured |
|----------------------------|-----------------------|------------|------------|------------|
| CO | 0% | 9 101 | 9 920 | 11.1 |
| CO. | 70 0% | 18 29 | 14.26 | 11.1 |
| O_2 | 70 % | 0.000 | 0.000 | 0.00 |
| H_2O | % | 43.91 | 57.17 | 62.2 |
| N_2 | % | 5.010 | 5.333 | 4.73 |
| SO_2 | ppm | 0.000 | 0.000 | n.m. |
| NŐ | ppm | 0.000 | 0.000 | n.m. |
| H_2 | % | 21.82 | 9.43 | 7.24 |
| $\bar{NO_2}$ | ppm | 0.000 | 0.000 | n.m. |
| $\overline{CH_4}$ | % | 1.539 | 3.577 | 2.72 |
| $C_2 H_6$ | ppm | 549.6 | 170.8 | 9E3 |
| NH ₃ | ppm | 1150 | 1224 | n.m. |
| N_2O | ppm | 0.000 | 0.000 | n.m. |
| H_2S | ppm | 50.08 | 53.31 | n.m. |
| Tar | ppm | 1497 | 1641 | see below |
| Sum | $\%_{vol}$ | 100.2 | 100.6 | |
| Tar | $g m^{-3}$ (STP) | 14.3 | 15.7 | 15.3^{a} |
| Gas flow | ${ m mol}{ m h}^{-1}$ | 1310 | 1225 | 1399^{b} |
| $\mathrm{C}\mathrm{C}^{c}$ | % | 98.3 | 89.0 | 89 |

 $^{\boldsymbol{a}}$ the sum of tar (measured polyaromatic and phenolic compounds) and benzene

 b calculated from the gaseous input of $\rm N_2$ and its fraction measured in the product gas, assuming that $\rm N_2$ remains inert.

^c carbon conversion efficiency

Table 6.12: Parameters used for the tuning of the base case simulation with original and new values

| Modified parameter | Original value | New value | Location |
|---------------------------------|----------------|-----------|-----------------------|
| Char combustion, k ₀ | 8.0 | 0.01 | input file |
| Water-gas shift, k_0 | 2.778 | 0.01 | main code, HOMOGR.FOR |
| CH_4 wet reforming, k_0 | 3.0E5 | 1.0E5 | main code, HOMOGR.FOR |

| Table 6.13: centage of | Elementa the input | l mass balan | ce for the t | uned base | e case. A | ll mass fl | ows given | ı in kg h | - ¹ , deviatio | ons given a | s per- |
|---------------------------|-----------------------|--------------------|-------------------|--------------------|-----------|----------------|----------------|---------------|---------------------------|------------------|---------|
| Species | Solids in dry | Fuel moist. ar | Vola fuel dry | Dev [%] vola-in | Gas in | Total in ar | Gas out wet | Filter dry | Bott.ash dry | Total out wet | Dev [%] |
| Moisture | | 0.842 | • | | | | | | | | |
| C | 4.894 | | 3.593 | 0.000 | 0.000 | 4.894^a | 4.354 | 0.1950 | 0.412 | 4.968 | 1.528 |
| Η | 0.542 | 0.094 | 0.543 | 0.005 | 1.200 | 1.836 | 1.848 | | | 1.848 | 0.626 |
| 0 | 4.061 | 0.749 | 4.061 | 0.000 | 14.18 | 18.99 | 19.03 | | | 19.03 | 0.223 |
| Z | 0.021 | | 0.021 | 0.004 | 1.841 | 1.862 | 1.862 | | | 1.862 | 0.007 |
| s | 0.002 | | 0.002 | -0.008 | 0.000 | 0.002 | 0.002 | | | 0.002 | 0.005 |
| Ash | 0.037 | | 0.037 | | | 0.037 | | 0.011 | 0.026 | 0.037 | 0.001 |
| Volatiles | 8.220 | | | | | | | | | | |
| Fixed C | 1.301 | | 1.301 | 0.000 | | | | | | | |
| Inert | 3.000 | | | | | 3.000 | | 0.000 | 3.000 | 3.000 | 0.000 |
| Lime | 0.000 | | | | | 0.000 | | | | 0.000 | |
| Total | 12.56 | 0.842 | 9.558 | | 17.22 | 30.62 | 27.09 | 0.2060 | 3.446 | 30.75 | 0.421 |
| ^a the sum of | the carbon pro | esent in the volat | tiles and the fix | ted carbon | | | | | | | |

The mass balance closure after the devolatilization step is excellent, but this is of course due to the normalization applied in the pyrolysis module. The total closure deviation of the process overall is still below 1%, except for carbon. There are a number of reasons for these deviations to occur: firstly, the use of iterative calculation routines, which inherently introduce a certain error that eventually propagates throughout the simulation. Secondly, deviations can be introduced by simplified assumptions. During their calculation the char reaction rates are related to respectively oxygen, water and carbon dioxide fractions in the *core* cells. Later in the simulation, the calculation of the yields of gaseous species that originate from char reactions is done for both core and annulus regions, using a common char reaction rate, but dedicated (i.e., core and annulus) gas fractions. This approach can introduce (small) mass balance deviations, due to the differences in gas composition between the core and the annulus regions - these are visualised in Figure 6.10 for the three gases that react with char.



Figure 6.10: Volume fractions of O_2 , H_2O and CO_2 shown as axial core and annulus profiles

6.4.3 Model sensitivity analysis

In order to test the plausibility and the robustness of the extended IEA model a simple sensitivity analysis has been performed. This included the perturbation of three process variables, namely the stoichiometric oxygen-to-fuel ratio (lambda), the PSD of the fuel, and the density of char, and the assessment of the changes in the results compared with the base case. The correct model response to the variations of lambda is one of the basic criteria for the assessment of the functionality of the model, while the PSD of the fuel and the density of char are known to cause computational problems or inaccuracies as it is very difficult to determine their actual values a priori.

Tables 6.14, 6.15 and 6.16 show the results of the sensitivity tests. Columns marked with "BC" contain the results of the base case simulation and the perturbations of the test variables are related to this case. The perturbation of lambda, both below the base case value (-19%) and above the base case value (+5%) causes no convergence problems. Also the trends of the results are in agreement with the expectations and the experimental values; with the increasing lambda

- the carbon conversion increases;
- less CO is formed, in favor of CO₂;
- the yield of hydrocarbons (methane and tar) decreases;
- the average temperature in the riser increases.

Hydrogen fraction remains fairly constant, which has also been observed during the experiments (see Chapter 4, Figure 4.1), although when considered on a dry, nitrogen-free basis the calculated hydrogen fraction shows a minimally decreasing trend with increasing lambda, while the measured trend is the opposite. The differences, however, are very small, 1% (relative) order of magnitude. In the test cases where lambda was increased by 10% and 20% with respect to the base case, the convergence criterion of the mass balance iteration was not met within the given maximum number of iteration steps (i.e., twenty). Increasing the maximum number of the iteration steps to 100 yielded the same result. The calculated char reaction rate (see Section 6.2.7) oscillates, causing the residual to remain above the threshold value. The reaction rate and the residual are shown in Figure 6.11 as a function of the mass balance iteration loop number for the base case (convergence) and for the lambda increased by 10% case (no convergence). To illustrate this further, columns 5 and 6 in Table 6.14 show the values calculated in two subsequent iteration steps – it is clear that although the values follow the correct trends for an increasing lambda, they cannot be accepted as a final result, because of their dependency of the number of the iteration steps passed. At this stage it is not clear which part of the model keeps the simulation from convergence, but it is recommended to check the calculation of the gas fractions in the annulus (subroutine FUNCV and others). Figure 6.12 shows the axial profiles of O_2 , CO_2 and H_2O calculated in the last iteration step of the non-converging simulation with a lambda 10% higher than the base case. The annulus profiles at the bottom of the reactor have a clearly rougher

| Table 6.14: Sensitivity analysis - model response to the changes in stoichiomet- |
|--|
| ric oxygen-to-fuel ratio (lambda). BC indicates base case conditions |

| Investigated parameter | | | | | | | | | |
|-------------------------------------|----------|----------|----------|--------|------------|--------|--|--|--|
| Lambda | 0.28 | 0.34 | 0.36 | 0.38 | 0.38 | 0.41 | | | |
| % change | -19 | BC | 4.8 | 9.6 | 9.6 | 19 | | | |
| Convergence | | | | | | | | | |
| No. of MB loops | 3 | 2 | 2 | 20^a | $21^{a,b}$ | 20^a | | | |
| No. of EB loops | 3 | 4 | 4 | 10^a | 10^a | 10^a | | | |
| Relative elemental r | nass bal | ance dev | viations | [%] | | | | | |
| С | 1.216 | 1.528 | 0.885 | 0.986 | -0.156 | 0.957 | | | |
| Н | 0.484 | 0.626 | 0.370 | 0.437 | -0.113 | 0.430 | | | |
| 0 | 0.174 | 0.223 | 0.145 | 0.209 | 0.027 | 0.189 | | | |
| Ν | -0.010 | 0.007 | 0.002 | -0.000 | -0.001 | 0.001 | | | |
| S | -0.012 | 0.005 | 0.000 | -0.003 | -0.003 | -0.003 | | | |
| Ash | 0.001 | 0.001 | -0.001 | -0.001 | -0.001 | -0.001 | | | |
| Carbon conversion | [%] | | | | | | | | |
| Solid-C | 84.8 | 87.4 | 88.2 | 88.9 | 89.0 | 89.8 | | | |
| Gas-C | 86.0 | 89.0 | 89.1 | 89.9 | 88.8 | 90.7 | | | |
| Product gas compos | ition an | d flow | | | | | | | |
| CO [%] | 11.5 | 9.92 | 9.28 | 8.92 | 8.34 | 7.93 | | | |
| CO ₂ [%] | 11.2 | 14.3 | 15.2 | 16.0 | 16.4 | 17.6 | | | |
| O ₂ [%] | 0 | 0 | 0 | 0 | 0 | 0 | | | |
| H ₂ O [%] | 56.4 | 57.2 | 57.5 | 57.6 | 57.9 | 58.1 | | | |
| N ₂ [%] | 7.62 | 5.33 | 4.77 | 4.19 | 4.22 | 3.04 | | | |
| H ₂ [%] | 9.34 | 9.43 | 9.44 | 9.48 | 9.28 | 9.56 | | | |
| CH ₄ [%] | 3.65 | 3.58 | 3.53 | 3.49 | 3.51 | 3.41 | | | |
| C ₂ H ₆ [ppm] | 305 | 170 | 130 | 122 | 93 | 74 | | | |
| NH ₃ [ppm] | 1209 | 1224 | 1231 | 1233 | 1243 | 1242 | | | |
| H ₂ S [ppm] | 52 | 53 | 53 | 53 | 54 | 54 | | | |
| Sum [%] | 100.5 | 100.6 | 100.3 | 100.7 | 99.63 | 100.7 | | | |
| Tar [g m $^{-3}$ (STP)] | 16.6 | 15.7 | 15.3 | 14.9 | 15.1 | 14.2 | | | |
| Gas flow [mol h^{-1}] | 1241 | 1226 | 1221 | 1214 | 1218 | 1206 | | | |
| Temperatures [°C] | | | | | | | | | |
| Avg. core T | 832 | 833 | 834 | 835 | 835 | 837 | | | |
| Avg. annulus T | 839 | 840 | 841 | 841 | 841 | 842 | | | |

^a convergence criterion not reached within maximum number of iteration loops

^b maximum number of mass balance iteration loops increased by one

| Investigated parameter | | | |
|----------------------------------|-----------|-----------|--------|
| Mean particle diameter $[\mu m]$ | 2513 | 5024 | 10046 |
| % change | -50.0 | BC | 100 |
| Convergence | | | |
| No. of MB loops | 2 | 2 | 5 |
| No. of EB loops | 4 | 4 | 5 |
| Relative elemental mass bala | nce devia | ations [% | 6] |
| С | 1.139 | 1.528 | 1.028 |
| Н | 0.481 | 0.626 | 0.249 |
| 0 | 0.189 | 0.223 | -0.008 |
| Ν | 0.001 | 0.007 | -0.020 |
| S | -0.003 | 0.005 | -0.022 |
| ash | 0.001 | 0.001 | 0.001 |
| Carbon conversion [%] | | | |
| Solid-C | 88.8 | 87.4 | 86.7 |
| Gas-C | 89.9 | 89.0 | 87.7 |
| Product gas composition and | l flow | | |
| CO [%] | 10.2 | 9.92 | 9.47 |
| CO2 [%] | 14.1 | 14.3 | 14.6 |
| O2 [%] | 0 | 0 | 0 |
| H2O [%] | 57.1 | 57.2 | 57.3 |
| N2 [%] | 5.34 | 5.33 | 5.36 |
| H2 [%] | 9.26 | 9.43 | 9.47 |
| CH4 [%] | 3.60 | 3.58 | 3.55 |
| C2H6 [ppm] | 232 | 170 | 129 |
| NH3 [ppm] | 1225 | 1224 | 1229 |
| H2S [ppm] | 53 | 53 | 53 |
| Sum [%] | 1.005 | 1.006 | 1.003 |
| Tar $[g m^{-3} (STP)]$ | 17.3 | 15.7 | 15.0 |
| Gas flow [mol h^{-1}] | 1226 | 1226 | 1223 |
| Temperatures [°C] | | | |
| Avg. core T | 832 | 833 | 834 |
| Avg. annulus T | 839 | 840 | 840 |

Table 6.15: Sensitivity analysis – model response to the changes in PSD of the fuel. BC indicates base case conditions

Table 6.16: Sensitivity analysis – model response to the changes in char density. BC indicates base case conditions

| r | | |
|----------|---|---|
| | | |
| 750 | 900 | 1050 |
| -17 | BC | 17 |
| | | |
| 2 | 2 | 20^a |
| 4 | 4 | 10^a |
| ss balan | ce devia | tions [%] |
| 0.959 | 1.528 | 0.307 |
| 0.397 | 0.626 | 0.142 |
| 0.157 | 0.223 | 0.076 |
| 0.007 | 0.007 | -0.000 |
| 0.005 | 0.005 | -0.003 |
| 0.001 | 0.001 | -0.001 |
| | | |
| 89.0 | 87.4 | 87.0 |
| 90.0 | 89.0 | 87.3 |
| on and f | low | |
| 10.4 | 9.92 | 9.23 |
| 14.1 | 14.3 | 14.7 |
| 0 | 0 | 0 |
| 56.9 | 57.2 | 57.5 |
| 5.33 | 5.33 | 5.37 |
| 9.37 | 9.43 | 9.42 |
| 3.60 | 3.58 | 3.51 |
| 198 | 170 | 113 |
| 1223 | 1224 | 1231 |
| 53 | 53 | 53 |
| 1.004 | 1.006 | 1.006 |
| 15.9 | 15.7 | 15.2 |
| 1229 | 1226 | 1218 |
| | | |
| 833 | 833 | 835 |
| 840 | 840 | 841 |
| | 750 -17 2 4 ss balan 0.959 0.397 0.157 0.007 0.005 0.001 89.0 90.0 on and f 10.4 14.1 0 56.9 5.33 9.37 3.60 198 1223 53 1.004 15.9 1229 833 840 | $\begin{array}{ccccc} 750 & 900 \\ -17 & BC \\ 2 & 2 \\ 4 & 4 \\ \begin{array}{c} \textbf{ss balance devia} \\ 0.959 & 1.528 \\ 0.397 & 0.626 \\ 0.157 & 0.223 \\ 0.007 & 0.007 \\ 0.005 & 0.005 \\ 0.001 & 0.001 \\ \end{array}$ |

^{*a*} convergence criterion not reached within maximum number of iteration loops

shape than the annulus profiles calculated for the (converging) base case simulation (see Figure 6.10). This rough shape of the axial annulus profiles has been observed in all non-converging simulations – further investigations are necessary to determine its cause.



Figure 6.11: Char reaction rate and the residual for the base case and a case with lambda 10% higher than in the base case

Contrary to the variations in lambda the two test cases involving a significant change in the particle size distribution of the fuel converged. Basically the change in PSD significantly influenced only two of the evaluated parameters, see Table 6.15. Firstly, the carbon conversion went down with increasing average fuel particle diameter, as expected. This is due to the lower reactivity of the coarse fuel particles compared to the fine fuel particles, as a relatively larger part is inaccessible for the gaseous reactants (diffusion limited reactions). Secondly, the amount of tar in the product gas went down with the increasing average fuel particle diameter. Such behavior is indeed reported by the literature, as larger fuel particles impose longer residence times of the released volatiles inside the particle, which leads to a better contact between tar and char. This is beneficial for the decomposition of tar, as biomass char is known to catalyze tar conversion reactions. However, no catalyzed char decomposition reactions are taken into account in the modified IEA model, therefore the seemingly correct effect of the fuel PSD on the amount of tar produced should be sought in the changing release rate of the volatiles, in which tar is the main fraction – larger particles



Figure 6.12: Volume fractions of O₂, H₂O and CO₂ shown as axial core and annulus profiles in a non-converging simulation ($\lambda = 1.1 \lambda_{basecase}$)



Figure 6.13: Changing axial profiles of the volatile release rates with the increasing PSD of the fuel

lead to lower release rate of the volatiles, as shown in Figure 6.13.

The char density perturbation (see Table 6.16) lead to a converging simulation for lower char density than the base case value, while the simulation with higher char density did not converge. Apart from the fluidization behavior (not evaluated here) the influence of the char density on the gas composition results is almost negligible.

6.4.4 Test cases -description and main results

In order to further test the usability of the model four well-quantified steady states were selected from the available experimental data to be compared with the simulation results. The summary of the input data is given in Table 6.17. In line with the base case simulation three wood gasification experiments have been selected. In addition one miscanthus gasification test was selected because during that experiment additional measurements of the axial gas concentration profiles in the riser have been performed, which would allow a comparison with the axial profiles calculated by the model. As no ash composition and no interaction phenomena between the ash and the bed material were taken into account by the model, in this case miscanthus was treated in the same way as wood with a slightly different ultimate analysis. Two additional assumptions were made for the miscanthus case:

- only fluidization medium composition and flow, and the biomass feed rate were changed in order to reflect the corresponding values of oxygen-to-fuel ratio, the steam-to-biomass ratio and the fluidization velocity. Other variables like particle size distribution of the fuel, the average temperature of the riser, char density, etc. were kept the same as in the base case;
- although during the experiment with miscanthus olivine was used as the bed material no changes have been made to the particle size distribution of the bed material or to the kinetic parameters of the gasification reactions. First part of this assumption is justified by the fact that the PSD of olivine is very similar to that of sand used in the base case; second part is justified by the observation that no significant tar reduction and no significant change in gas composition was achieved by using the available type of olivine (see Section 4.2.5).

The last row of Table 6.17 indicates that none of the first three wood simulations converged. Two test cases ($\lambda = 0.27$ and $\lambda = 0.37$) fall outside the range of converging simulations as tested in previous section (Table 6.14). As also indicated there, the reason for the simulations not to converge remains under investigation. Test case with $\lambda = 0.28$ did not converge as well, despite its similarity to the base case conditions except a slightly lower steam-to-biomass ratio and the a higher throughput of biomass.

| | date: fuel: oxidant: | 08-Apr-2008 A-wood Steam-O ₂ | 15-Apr-2008 A-wood Steam-O ₂ | 25-Jul-2008 A-wood Steam-O ₂ | 15-Apr-2008 A-wood Steam-O ₂ | 02-Dec-2009 Miscanthus Steam-O ₂ |
|-------------------------|----------------------------|---|---|---|---|---|
| Steam flow rate | kgh^{-1} | 12.9 | 12.6 | 11.4 | 12.6 | 12.3 |
| O_2 flow rate | $kg h^{-1}$ | 4.60 | 3.20 | 4.40 | 3.20 | 5.00 |
| Biomass flow rate | $kg h^{-1}$ | 10.2 | 10.3 | 13.2 | 10.3 | 13.5 |
| Air (L-valve) flow rate | $kg h^{-1}$ | 1.30 | 1.30 | 1.22 | 1.30 | 1.48 |
| N_2 (purge) flow rate | kgh^{-1} | 4.87 | 4.58 | 2.12 | 1.58^{a} | 2.72 |
| Mean riser temperature | °C | 837 | 826 | 837 | 838 | 852 |
| λ (daf) | $kg kg^{-1}$ | 0.37 | 0.27 | 0.28 | 0.27 | 0.32 |
| SB w/w (ar) | $kg kg^{-1}$ | 1.3 | 1.2 | 0.9 | 1.2 | 0.8 |
| Convergence | | no | no | no | no | yes |

Table 6.17: Overview of process conditions of the simulated test cases taken from the steady-state experimental data

^a nitrogen input flow reduced with 3 kg h⁻¹ to test its influence on the simulation convergence

A comparison between the calculated and measured gas composition at the exit of the gasifier for the miscanthus test case is given in Table 6.18. The results of the model are in a very good agreement with the experiment, with CO, H_2O and H_2 each showing a relative deviation below 5%. Unfortunately during the evaluated steady state of this experiment no tar measurement has been done. However, as indicated earlier a gas composition measurement has been performed at three different positions along the riser. Figure 6.14 shows the calculated profiles and the discrete measurements. As no measurements of the water vapor fraction were performed, the gas fractions in the figure are given on dry and nitrogen-free basis (except N_2 , which is given on dry basis). The following remarks can be made regarding the presented data:

- oxygen and methane show a close match between the measurement and the calculations;
- carbon dioxide matches closely at three points, but the deviation is high near a maximum predicted by the model (shortly above the fuel feed point);
- the measured hydrogen profile is rather flat, while the calculated one is monotonically increasing. Nonetheless the final fractions are in good agreement;
- the measured carbon monoxide profile indicates a maximum just above the fuel feed point, while the calculated trend shows a much lower maximum near the recirculation point. The differences between the simulation and the measurement are high, up to 200% (relative). Only the last point (riser exit) is acceptable;
- for nitrogen the difference between the simulation and the measurement is the largest. This is, however, caused by the simplification in the model
that all the nitrogen is injected with the fluidization medium at the bottom of the riser, while in reality nitrogen is added at several points along the riser as purge flows of the pressure sensors and the bunker system, and as the L-valve aeration. For this reason the measured N_2 fraction is low at the bottom of the reactor and increases towards the top as nitrogen flows enter the reactor. On the other hand the simulation predicts a high initial fraction which decreases along the axial coordinate as the amount of moles of gaseous species increases due to the decomposition of large(r) molecules.

The considerations presented above are very important for the validation of the model, as the capability of calculating the axial profiles is one of the main benefits of this model. In this way different reactor modifications could be modeled to check their effect on the product gas composition, mainly regarding the amount of tar and the yield of combustible non-condensable gases.

| Species | Unit | Simulation | Experiment |
|--------------------------|---|------------|--------------|
| СО | % | 9.82 | 9.66 |
| CO_2 | % | 13.6 | 12.2 |
| O_2 | % | 0. | 0. |
| H_2O | % | 54.8 | 57.4 |
| N_2 | % | 9.24 | 7.07 |
| H_2 | % | 7.69 | 7.60 |
| CH_4 | % | 4.08 | 3.20 |
| Sum | % | 100.5 | 98.1 |
| Tar | $\mathrm{g}\mathrm{m}^{-3}(\mathrm{STP})$ | 26.1 | n.m. |
| Gas flow | ${ m mol}{ m h}^{-1}$ | 1484. | 1949^{a} . |
| $\mathrm{C}\mathrm{C}^b$ | % | 86.3 | 72. |

Table 6.18: Calculated and measured gas composition (volume fractions on wet gas basis), total product gas flow and the carbon conversion in the miscanthus test case

 a calculated from the gaseous input of $\rm N_2$ and its fraction measured in the product gas, assuming that $\rm N_2$ remains inert.

^b carbon conversion efficiency

6.4.5 Comparison with commercial modeling software (CSFMB [®] / CeSFaMBTM)

From the previous paragraphs of this chapter it is clear that comparing to the original IEA model intended for the simulation of coal combustion in Circulating Fluidized Beds, the extended model is capable of simulating the gasification



Figure 6.14: Calculated and measured axial gas composition profiles for the miscanthus test case. Gas composition given in terms of dry, N_2 -free gas, except for nitrogen which is given on dry basis

of biomass. However, it is also clear that although major steps in the model development have been achieved by implementing the alternative pyrolysis module and extending the reactions scheme with gasification reactions, this model still has to be considered as "work in progress". In order to better assess the intermediate results of the work done sofar it is helpful to compare the results of own work to available alternatives. In this case a short comparison will be made between the results of the base case simulation described earlier and the same case simulated by the commercially available simulation software CSFMB®, recently renamed by the developer to CeSFaMBTM. The acronym CSFMB stands for "Comprehensive Simulator of Fluidized and Moving Beds"; the work has been initiated and is under continuous development by the University of Campinas in Brazil [43]. It is a steady-state model that considers three hydrodynamic phases: bubble, emulsion and freeboard. It is outside the scope of this work to give a thorough description of the CSFMB model – extensive documentation is available [44]. At the Energy Technology Section at TU Delft attempts have been made to use this software to simulate both large-scale gasification pilot plants and small-scale laboratory equipment. Some results of the small-scale modeling activities are presented below.

To compare the simulation results of the extended IEA model and CSFMB,

the gasifier geometry and the experimental data from the base case experiment (see Section 6.4.1) have been used as the input for CSFMB. The same approach has been chosen as in case of the extended IEA model: first perform simulations with default model parameters and then perform modification of the kinetic parameters to tune the simulation. The results presented in Table 6.19 indicate

Table 6.19: CSFMB simulation results using default and modified kinetic parameters. Results from the extended IEA model and experimental results included for comparison. Gas composition given in molar fractions

| Variable | Unit | CSFMB | CSFMB | Ext. IEA | Ext. IEA | Experiment |
|----------|---------------------|---------|----------|-----------------------|-----------------------|------------|
| | | default | modified | litbased ^a | modified ^a | |
| СО | % | 7.15 | 10.9 | 9.10 | 9.92 | 11.1 |
| CO_2 | % | 17.0 | 12.2 | 18.3 | 14.3 | 11.2 |
| O_2 | % | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| H_2O | % | 57.8 | 62.8 | 43.9 | 57.2 | 62.2 |
| N_2 | % | 4.98 | 5.00 | 5.01 | 5.33 | 4.73 |
| H_2 | % | 12.9 | 6.81 | 21.8 | 9.43 | 7.24 |
| CH_4 | % | 0.138 | 1.78 | 1.54 | 3.58 | 2.72 |
| Tar | % | 0.00 | 0.399 | 0.148 | 0.164 | 0.15 |
| Tar | ${ m g}{ m m}^{-3}$ | 0.00 | 22.8 | 14.3 | 15.7 | 15.3 |
| | (STP) | | | | | |
| CC | % | 73.4 | 81.0 | 98.3 | 89.0 | 88.9 |

^a see Section 6.4.2.3 and Table 6.11

that the CSFMB simulation with default kinetic parameters leads to similar directions in the deviations of CO, CO_2 , H_2 and CH_4 fractions. Surprising is the total absence of tar in the default simulation. CSFMB has a more complex model for the fate of gaseous hydrocarbons, as next to the lumped tar specie, methane and light volatiles consisting of C_2H_4 , C_2H_6 , C_3H_6 and C_3H_8 , also benzene is included in the scheme. Contrary to the modified IEA model with literaturederived reaction kinetics, CSFMB calculates a carbon conversion that is lower than the experimental one.

To obtain a better match between the simulation and the experiment, the preexponential factors of seven gaseous chemical reactions have been modified. This included a strong reduction of the rates of the water-gas shift, tar decomposition and the oxidation of light hydrocarbons reactions. The pre-exponential factor of the tar hydro-cracking reaction was increased to yield more methane. The modified kinetics lead to a good agreement between the experiment and the simulation for the main gaseous components, but also to a high over-prediction of the tar yield. The calculated carbon conversion remains below the



Figure 6.15: Volume gas fractions of the main gas components – axial profiles calculated with CSFMB[®]

experimental value.

For comparison with the modified IEA model also the axial gas composition profiles calculated with CSFMB[®] were examined, see Figure 6.15. Comparing these profiles with the ones in Figure 6.7 higher gradients for oxygen decay and CO₂ formation can be noticed. The fractions of CO and H₂ have local maxima at the height of approximately 0.5 m above the distributor, and in general the curves are less smooth in this zone than the ones calculated with the modified IEA model. This behavior can be attributed to the fact that CSFMB[®] explicitly considers the presence of a dense bed zone, which according to the simulation has a dynamic depth of 0.491 m. The modified IEA model did not predict the presence of a typical dense bed zone (i.e., bubble-emulsion phase), which considering the fact that the test rig was operated rather in a turbulent or even fast fluidization regime (see Section 2.3.1) is a plausible result. Therefore the gas fraction profiles are smoother as there is no real dense bed to freeboard transition. Above the 1 m level the CSFMB® and modified IEA profiles are similar, except for hydrogen fraction: in the CSFMB® simulation it is tending towards a maximum, while it is monotonically increasing in the modified IEA model results.

The strong points of the CSFMB software are the ability to simulate few different types of reactors, an extensive input file that allows the taking into account various features of the reactor (water cooling, external heating, detail of the gas distribution plate, etc.) and the technical support available to the user. On the other hand, although the simulation results of the base case were generated successfully it was observed that also this model, despite being a commercial product, has a number of shortcomings. The main issue was the sensitivity to certain input variables, e.g., the PSD and the heating value of the fuel, the density of the bed material and the initial guesses for the maximum and the minimum values for fixed carbon conversion. In case of the particle size distribution and the heating value even very small differences in the input allowed or prohibited the simulation from convergence. In reality such differences obviously would not lead to the (de)stabilization of the functioning of the equipment. The simulations including the presence of a catalytically active ash or solid are possible, but they require a direct input of additional kinetic parameters.

6.5 Conclusions and recommendations for future modeling work

An existing mathematical model of the process of the combustion of coal in a Circulating Fluidized Bed reactor has been upgraded to simulate also the biomass gasification process. The main objective of this modeling effort has been achieved: the model is now able to simulate a gasification process in a Circulating Fluidized Bed, taking into account the hydrodynamics of the reactor, the pyrolysis of the biomass fuel, the kinetics of gasification reactions including tar conversion and the char reactions. The use of the reaction kinetics has an important advantage over equilibrium models that employ additional (empirical) subroutines to "correct" the gas composition, as it allows easier extension of the model with new reaction schemes based on the kinetic data determined experimentally.

The developed model is already able to simulate laboratory gasification equipment and predict the response of the gasifier to the perturbations of process parameters within a limited range. It has the potential to be used as a design aid for new gasification plants based on the fluidized bed technology and to help in the assessment of an intended change in the operational parameters of the existing gasifiers. Compared to the commercially available CSFMB [®] / CeSFaMB TM package the flexibility of the input and the amount of the simulation options is still limited, but having the access to the source code the model can be extended depending on the needs and interests of the research group. This also allows easier tracing and solving of bugs and modeling errors.

Basing on the experience from this work the following recommendations can be given for future activities on the improvement of the presented model (in order of importance):

- check the hydrodynamics part, especially the equations for the core, annulus and mixing flows, and the formation of the bubble phase. The latter can be validated with the available pressure drop data from the gasifier test rig. It is suspected that the instabilities in the hydrodynamics part (flows possibly becoming very small) cause convergence problems in the mass balance iteration loop;
- investigate the reason for the lack of convergence in the simulations with certain lambda and char density values;
- check the cause for the need to normalize the volatiles flow rate in the pyrolysis subroutine;
- check the validity of the char surface reaction model (Thiele modulus, Biot number);
- include a (simple) model of the downcomer in order to take into account the particle residence time in that part of the reactor;
- rework the heat transfer modules, to gain the possibility to simulate a certain amount of heating power;
- determine the kinetic parameters for the water-gas shift reaction in the presence of different kinds of bed material. For instance, no literature data is present on the kinetics of WGS on magnesite. Such study could be performed in a bench-scale fixed bed reactor where conversions of a mixture of CO and steam are measured at various temperatures;
- add the possibility to simulate batch operation;
- perform the calculations of the solids distribution and flows in every iteration loop (to take into account the soot generated by tar decomposition);
- refine the assumption of all the soot going to the smallest particle size class;
- refine or improve the pyrolysis / devolatilization subroutine either by performing more small scale measurements with the heated grid setup to increase the accuracy of the calculated parameters in the Merrick matrix, or by coupling the modified IEA model with external pyrolysis models (e.g., FG-Biomass);
- check the cyclone submodule regarding the calculation of the separation efficiency calculation. Also the development of an indicator of the chocking of the solids exit at certain solids fluxes and particle size distributions would be of great value for the equipment designers.

Heal the world, make it a better place, for you and for me and the entire human race

Michael Jackson, Heal the World, 1992

Overall conclusions, recommendations and outlook

7.1 Conclusions

In the previous chapters of this book the results of the research on the steamoxygen blown gasification of woody and herbaceous biomass in a Circulating Fluidized Bed gasifier were described. The research was focused on the study of the gas quality optimization in terms of syngas components and the reduction of the tar content in the raw product gas. After undergoing the cleaning and upgrading steps this gas should be ready for use in the synthetic biomassbased transportation fuels production process. In addition, the operability of the test rig with ash-rich herbaceous fuels was investigated, as well as the aspects related to the availability of biomass and the optimal plant size. Finally, a mathematical model of the gasifier was developed based on an existing combustor model.

The following conclusions can be drawn from this research:

Literature review part

- approximately 50–55% of world's current primary energy demand could be covered by biomass that is available on a sustainable basis and competitive prices;
- the size of the biomass conversion plant, irrespective of the employed technology, should match the local supply of biomass in order to avoid long-distance shipping. Only then one can speak about truly sustainable and renewable energy management;
- the gasification process proves to be a very suitable choice for the conversion of solid biomass, when compared to combustion and pyrolysis, mainly when the production of advanced secondary energy carriers is intended, but also when a CHP application is planned;
- if the gasification process is to be carried out at large industrial scale the fluidized bed technology shows the best balance between the advantages and the disadvantages;
- gas produced in the fluidized bed gasification process is not yet of the syngas quality. The design of the gas cleaning and upgrading system will depend on the process that will use the gas and can be very demanding both in terms of the removal efficiency of the impurities as in terms of the gas temperature matching between the gas cleaning and the next downstream steps;
- although nowadays a few (C)FB biomass gasifiers are being operated at industrial scale using woody (thus "easy") fuels, the production of advanced secondary fuels has not left the demo-scale yet.

Experimental part

- steam-oxygen blown circulating fluidized bed biomass gasification is a powerful fuel conversion technology able to produce hydrogen-rich *product gas* from solid biomass;
- the optimal bed material and fuel combination depends strongly on the application of the product gas. For a co-combustion application and clean, woody biomass fuels sand as bed material may suffice;
- if production of secondary energy carriers, and in particular synthetic fuels, from biomass is intended, then a significant improvement of gas quality in terms of reduced tar content and increased H₂:CO ratio can be achieved by using calcined magnesite as bed material;
- as pure magnesium oxide had no influence on the gas composition, and the influence of calcined magnesite was major, the activity of calcined magnesite should be sought in the presence of iron and / or calcium elements in the mineral;
- the origin of the bed material will strongly influence its catalytic activity. The olivine used in this research had no significant influence on tar conversion inside the gasifier, while the olivine used by other researchers showed very promising results in that respect;
- the average measured tar concentrations (in terms of PAH and Phenolic compounds on raw gas basis) and H_2 :CO ratio with sand as bed material and clean wood pellets as fuel was 3.7 g m⁻³ (STP) and 0.68 respectively. The minimum tar concentration and the maximum H_2 :CO ratio were achieved with magnesite as bed material and miscanthus as fuel the sum of measured polyaromatic and phenolic compounds in the raw gas was reduced below 2 g m⁻³ (STP), while the H_2 :CO ratio increased to over 2.5;
- the agglomeration and defluidization phenomena can be successfully suppressed by either using an additive to the sand or olivine bed (both bed materials rich in silica) or by using magnesite as bed material without additive (very low amount of silica in the bed material). This strategy worked well for B-wood and for miscanthus;
- with straw, containing a very high amount of ash and a very high fraction of alkali metals therein (2% of K by weight, as received), it was necessary to use an additive, but rather due to ash-ash interaction rather than to bed material-ash interaction. In addition, evaporation of KCl and the use of a filter operated practically at process temperature caused severe deposition problems on the cooler process parts downstream the gas cleaning unit;

- increasing steam-to-biomass ratio from ca. 0.7 to ca. 1.3 will contribute to tar reduction and an increased H₂ yield;
- the benefit of using magnesite instead of sand as the bed material is threefold: a significantly improved H_2 :CO ratio, a reduced amount of tar in the product gas, and a stable operation with more difficult (herbaceous) fuels.

Modeling part

- the developed model of a CFB biomass gasifier, which is an extension of an existing model of a large-scale CFB coal combustor is capable of simulating the operation of a small-scale laboratory biomass gasification test rig;
- the developed model needs further improvement, in particular regarding the stability of the calculations, further refinement of the pyrolysis & reaction kinetics model and the validation of the hydrodynamics calculations;
- despite a much more extensive user interface, a large number of simulation options, and an already long development process, also CSFMB [®] / CeSFaMB TMsuffers from the sensitivity to certain process variables – this leads to instable solutions of the calculations (no convergence). However, the lack of access to the source code makes the investigation of such problems very complicated if not impossible.

7.2 Recommendations

The following recommendations for future research can be given based on the results and the experience gained from this work:

- the integration of water-gas shift catalysis in the gasifier by using magnesite as the bed material and the integration of the reforming step in the high-temperature filter by using catalytic filter candles would significantly simplify the flow sheet of the biomass gasification and gas cleaning facility, also reducing the investment costs (2 units of operation less to construct);
- in this research only one kind of calcined magnesite was tested. However, it is likely that as in the case of olivine the origin of the mineral may play an important role regarding its catalytic activity in the gasifier. This is thought to be related especially to the content of iron and calcium in the mineral. Therefore it is recommended to compare the activity of magnesite from different sources by performing appropriate gasification tests;

- in the literature no data on the catalytic activity of magnesite on the watergas shift reaction could be found. Therefore bench-scale experiments targeted at the determination of the kinetic parameters of the water-gas shift reaction over magnesite should be performed. Similar consideration applies to the tar conversion reactions;
- due to the low attrition resistance of magnesite a considerable amount of this material is elutriated from the gasifier causing an increase of the dust load in the gas. Therefore the influence of the presence of fine magnesite particles on the high-temperature filter behavior should be investigated;
- pressurized gasification with magnesite as bed material should be investigated in a modeling study, as initial equilibrium calculations showed a potential CO₂ capture effect by the recarbonization of CaO present in magnesite at reactor pressures above 20 bar;
- the cyclone calculations found in the literature are focused on the cyclone separation efficiency for a single type of solid. For a circulating fluidized bed biomass gasifier, where the cyclone needs to handle a mixture of bed material (small particles, high density) and char (large particles, low density) these calculations are insufficient, as the determined cyclone geometry will be based on a compromise between the separation efficiency and pressure drop. However, the design of the solids outlet is of key importance, as a too small cross-section will lead to the blockage by the char particles and the loss of bed material via the gas outlet. Some calculations or rules-of-thumb should be developed as a guideline for such cyclone applications;
- the design of the loop seal in the small pilot unit should be also investigated: the L-valve is a simple solution but it requires excessive aeration if a large amount of char particles is present or when alkali-rich fuels are used (with additive). A more efficient and reliable loop seal type should be tested, for example a "seal pot";
- the mathematical model of the gasifier should be developed further. The attention should primarily focus on the general stability of the model, also for the process conditions that are more remote from the ones tested in this work, and the development of the feedback routines indicating the possible reasons for the lack of convergence. Furthermore the hydrodynamics part should be checked and validated (e.g., with pressure drop data from the gasifier), and the pyrolysis module should be extended further (e.g., by performing own fundamental devolatilization / pyrolysis experiments or by coupling the model with existing pyrolysis models like FG-Biomass). In addition, reaction kinetics scheme could be extended also with the heterogeneous reactions involving the presence of catalytic bed materials.

7.3 Outlook

The introduction of the production of advanced fuels from biomass to the community is very close. What is needed are the initiatives to build and commission the full demonstration plants that should soon become fully commercially operational. Now the governments and private companies are, in general, still hesitating. This is due to the fact that some aspects of the process are still not well-developed or not reliable enough. Here the academia and the R&D companies come into the picture – they should provide the necessary final technology push. The integrated gasification-filtration-upgrading test rigs as the unit in the Process & Energy laboratory at TU Delft provide excellent facilities to develop and test various aspects of the biomass conversion process under realistic process conditions but still on an easily manageable scale. Now being a part of the European FP7 "BRISK" infrastructures consortium, the experimental work supported my mathematical modeling and fundamental research will continue, giving the possibility to carry out the recommendations given here and in other scientific publications from our group. Hopefully these "little steps for men" will lead to a "large step for mankind"!



| General information | BC-01 | BC-02 | BC-03 | BC-04 | BC-05 | BC-06 | BC-07 | BC-08 | BC-09 | BC-10 | BC-11 | BC-12 | BC-13 | BC-14 | BC-15 | BC-16 |
|--------------------------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|--------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| bate [dd-mm-yyyy]: | 10-17- 2006 | 10-18- 2006 | 10-19- 2006 | 10-19- 2006 | 10-20- 2006 | 10-20- 2006 | 10-23- 2006 | 10-23- 2006 | 8-4- 2008 | 10-4- 2008 | 10-4- 2008 | 15-4- 2008 | 15-7- 2008 | 17-7- 2008 | 25-7- 2008 | 19-8- 2008 |
| iuel: | A-wood milled | A-wood | A-wood | A-wood | A-wood | A-wood | A-wood | A-wood | A-wood |
| 3ed material: | sand | sand | sand | sand | sand | sand | sand | sand | sand |
| Additive: | 1 | | | | | | | | | | | | | | | |
| Total duration of the run: | 7:00 | 2:49 | 8:00 | 8:00 | 7:53 | 7:53 | 9:32 | 9:32 | 5:24 | 7:08 | 7:08 | 4:59 | 5:40 | 4:19 | 4:17 | 7:48 |
| Duration of the evaluation period: | 0:30 | 0:35 | 0:28 | 0:30 | 1:10 | 0:35 | 0:30 | 0:30 | 0:54 | 3:04 | 1:25 | 2:57 | 0:13 | 0:31 | 0:17 | 0:16 |
| Start time of the evaluation period: | 17:49 | 11:50 | 12:00 | 17:00 | 15:40 | 20:00 | 13:00 | 18:00 | 11:38 | 11:50 | 15:53 | 10:57 | 13:10 | 11:02 | 10:36 | 10:58 |
| End time of the evaluation period: | 18:19 | 12:25 | 12:28 | 17:30 | 16:50 | 20:35 | 13:30 | 18:30 | 12:32 | 14:54 | 17:19 | 13:54 | 13:23 | 11:33 | 10:53 | 11:14 |
| Input flows [kg h ⁻¹] | | | | | | | | | | | | | | | | |
| Steam (primary) | 9.5 | 8.7 | 8.1 | 11.9 | 9.5 | 9.7 | 10.1 | 10.1 | 12.9 | 12.6 | 13.2 | 12.6 | 10.8 | 10.8 | 11.4 | 10.8 |
| Oxygen (primary) | 4.16 | 3.88 | 3.89 | 3.58 | 3.09 | 3.23 | 3.40 | 3.42 | 4.58 | 4.60 | 4.00 | 3.20 | 4.40 | 4.40 | 4.40 | 4.40 |
| Air (L-valve recirculation) | nitrogen | 1.32 | 0.88 | 1.25 | 1.31 | 1.22 | 0.80 | 1.22 | 0.77 |
| Nitrogen (purge flows) | 4.41 | 4.74 | 4.46 | 5.87 | 5.12 | 5.04 | 3.48 | 5.00 | 4.87 | 4.73 | 4.70 | 4.58 | 2.30 | 2.24 | 2.12 | 1.74 |
| Biomass | 15.6 | 10.8 | 11.2 | 15.6 | 10.8 | 11.2 | 11.3 | 11.0 | 10.2 | 10.4 | 10.4 | 10.3 | 10.3 | 10.6 | 13.2 | 10.4 |
| Bed material | 1 | i. | | | | | | | | 1 | | | | | | |
| Additive | | | , | | , | | , | , | | , | , | | | | | , |
| Temperatures [°C] | | | | | | | | | | | | | | | | |
| Riser (average of 7 TCs) | 845 | 851 | 850 | 837 | 846 | 846 | 847 | 847 | 824 | 805 | 798 | 813 | 841 | 841 | 835 | 832 |
| Riser el. heating (average) | 850 | 850 | 850 | 848 | 850 | 850 | 850 | 850 | 830 | 810 | 807 | 826 | 842 | 842 | 839 | 825 |
| Gas inlet | 360 | 360 | 360 | 360 | 360 | 360 | 360 | 360 | 366 | 364 | 363 | 360 | 360 | 360 | 360 | 360 |
| Pressures [mbar] | | | | | | | | | | | | | | | | |
| Gage pressure at CFB outlet | n.m. | 47.3 | 48.2 | 55.9 | 50.1 | 39.8 | 52.8 | 78.9 | 63.5 |

| Process parameters | | | | | | | | | | | | | | | | |
|---|------|------|------|------|------|------|------|------|------|------|------|-------|-------|------|------|------|
| Fluidization velocity (u _{fl}) [m s ⁻¹] | 3.8 | 3.6 | 3.4 | 4.5 | 3.7 | 3.8 | 3.7 | 3.9 | 3.9 | 3.8 | 3.8 | 3.6 | 3.3 | 3.2 | 3.3 | 3.2 |
| Stoich. oxygen ratio (λ) | 0.21 | 0.28 | 0.27 | 0.18 | 0.22 | 0.23 | 0.24 | 0.24 | 0.37 | 0.36 | 0.32 | 0.27 | 0.35 | 0.34 | 0.28 | 0.35 |
| Steam-to-biomass ratio (SB) | 0.61 | 0.80 | 0.72 | 0.76 | 0.88 | 0.87 | 0.89 | 0.92 | 1.3 | 1.2 | 1.3 | 1.2 | 1.0 | 1.0 | 0.0 | 1.0 |
| H2O:O2 ratio [mol mol ⁻¹] | 4.0 | 4.0 | 3.7 | 5.9 | 5.5 | 5.3 | 5.3 | 5.2 | 5.0 | 4.9 | 5.9 | 7.0 | 4.4 | 4.4 | 4.6 | 4.4 |
| Main gas components [%vol] | | | | | | | | | | | | | | | | |
| H ₂ dnf | 18.7 | 17.5 | 18.8 | 19.1 | 19.7 | 19.8 | 18.2 | 18.0 | 25.4 | 19.1 | 20.1 | 20.8 | 28.5 | 23.1 | 21.8 | 21.9 |
| CO dnf | 36.5 | 38.8 | 38.9 | 40.7 | 40.4 | 39.4 | 42.2 | 42.4 | 23.8 | 32.7 | 32.2 | 35.0 | 28.9 | 30.7 | 33.7 | 34.0 |
| CH4 dnf | 10.4 | 9.4 | 9.4 | 10.6 | 10.1 | 10.1 | 10.0 | 9.8 | 7.4 | 8.0 | 8.3 | 8.9 | 7.5 | 8.2 | 8.9 | 8.2 |
| CO ₂ dnf | 23.3 | 26.7 | 26.0 | 21.2 | 24.3 | 24.5 | 24.1 | 23.9 | 37.7 | 33.9 | 33.3 | 28.4 | 31.4 | 34.1 | 31.0 | 33.7 |
| $N_2 dry$ | 18.4 | 26.7 | 24.7 | 28.7 | 29.2 | 26.9 | 20.8 | 27.3 | 30.4 | 30.8 | 32.3 | 31.6 | 10.9 | 15.9 | 13.8 | 12.5 |
| H ₂ O wet | 40.0 | 52.0 | 52.0 | 57.0 | 50.0 | 46.0 | 45.0 | 42.0 | 57.2 | 59.9 | 45.5 | 59.1 | 53.8 | 48.9 | 59.0 | 62.2 |
| Minor components [%wal] | | | | | | | | | | | | | | | | |
| C ₂ H ₄ dnf | 2.4 | 2.1 | 2.1 | 2.3 | 2.1 | 2.1 | 2.3 | 2.1 | 0.86 | 0.68 | 0.66 | 3.0 | 2.0 | 2.5 | 2.8 | 2.3 |
| C ₂ H ₂ dnf | 0.48 | 0.47 | 0.45 | 0.47 | 0.45 | 0.45 | 0.47 | 0.46 | 0.32 | 0.39 | 0.38 | 0.44 | 0.33 | 0.42 | 0.43 | 0.38 |
| NH3 wet | n.m. | 0.010 | 0.021 | n.m. | 0.15 | n.m. |
| Measured tar [g m ³ (STP)] | | | | | | | | | | | | | | | | |
| BTX dnf | n.m. | 9.4 | 12 | 13 | 14 | 11 |
| PAH raw | 8.2 | 5.5 | 5.6 | 4.1 | 4.4 | 5.5 | 5.6 | 5.6 | 1.7 | 2.1 | 2.7 | 2.9 | n.m. | n.m. | 2.9 | 3.3 |
| Phenolics raw | 2.1 | 1.0 | 1.4 | 1.3 | 1.4 | 1.5 | 1.3 | 1.5 | 0.8 | 1.2 | 1.7 | 1.4 | n.m. | n.m. | 0.76 | 1.0 |
| Process benchmarks | | | | | | | | | | | | | | | | |
| Carbon conversion [%] | 96 | 96 | 96 | 73 | 92 | 96 | 95 | 98 | 85 | 83 | 79 | 90 | 143 | 85 | 83 | 68 |
| Cold gas efficiency [%] | 67 | 55 | 57 | 60 | 56 | 58 | 63 | 57 | 61 | 59 | 58 | 62 | 123 | 70 | 72 | 72 |
| H ₂ : CO ratio [-] | 0.51 | 0.45 | 0.48 | 0.47 | 0.49 | 0.50 | 0.43 | 0.43 | 1.1 | 9.0 | 9.0 | 0.6 | 1.0 | 0.8 | 9.0 | 0.6 |

| Country in the second s | CC D01 | CU DUU | oud Up | CC DU | | | CO MINT | | | CU MID | CC A11 | CU 410 | CU 412 |
|--|-----------|-----------|-----------|-----------|------------|------------|------------|------------|------------|------------|-----------|-----------|-----------|
| General muonnanon | | 20-202 | ong-ne | 3C-D0# | CUIVI-DC | SC-IVIDO | CUIVI-DC | OUIVI-DC | SUIVI-JS | | | 20-217 | CIN-DC |
| Date [dd-mm-yyyy]: | 17-4-2008 | 22-4-2008 | 22-7-2008 | 25-4-2008 | 7-5-2008 | 7-5-2008 | 13-5-2008 | 15-5-2008 | 23-7-2008 | 23-7-2008 | 19-8-2008 | 19-8-2008 | 19-8-2008 |
| Fuel: | B-wood | B-wood | B-wood | B-wood | miscanthus | miscanthus | miscanthus | miscanthus | miscanthus | miscanthus | A-wood | A-wood | A-wood |
| Bed material: | sand | sand | sand | sand | sand | sand | sand | sand | gung | sand | pues | sand | pues |
| Additive: | 1 | | | kaolin | kaolin | kaolin | kaolin | kaolin | kaolin | kaolin | MgO | magnesite | magnesite |
| Total duration of the run: | 6:55 | 2:12 | 4:25 | 6:24 | 4:13 | 4:13 | 6:30 | 6:35 | 5:17 | 5:17 | 7:45 | 7:45 | 7:45 |
| Duration of the evaluation period: | 0:51 | 0:36 | 0:19 | 0:20 | 0:33 | 0:21 | 0:33 | 1:19 | 0:24 | 0:24 | 0:10 | 0:10 | 0:10 |
| Start time of the evaluation period: | 12:48 | 14:28 | 10:10 | 11:37 | 14:47 | 12:36 | 12:20 | 12:44 | 13:06 | 15:36 | 12:45 | 15:25 | 16:15 |
| End time of the evaluation period: | 13:40 | 15:05 | 10:30 | 11:57 | 15:20 | 12:58 | 12:53 | 14:04 | 13:30 | 16:00 | 12:55 | 15:35 | 16:25 |
| Input flows [kg h ⁻¹] | | | | | | | | | | | | | |
| Steam (primary) | 13.2 | 13.5 | 10.8 | 12.3 | 13.8 | 13.2 | 13.2 | 11.7 | 10.8 | 10.8 | 10.8 | 10.8 | 10.8 |
| Oxygen (primary) | 4.20 | 3.80 | 4.40 | 3.20 | 4.80 | 4.80 | 4.00 | 3.20 | 4.40 | 4.40 | 4.40 | 4.40 | 4.40 |
| Air (L-valve recirculation) | 1.29 | 1.48 | 0.68 | 1.29 | 0.47 | 0.47 | 0.86 | 1.85 | 1.12 | 1.22 | 0.77 | 0.77 | 0.77 |
| Nitrogen (purge flows) | 2.10 | 5.11 | 2.05 | 4.31 | 2.24 | 2.30 | 4.58 | 4.16 | 2.12 | 2.11 | 1.77 | 1.79 | 1.76 |
| Biomass | 6.6 | 10.0 | 12.7 | 10.3 | 10.3 | 11.1 | 6.7 | 10.4 | 14.0 | 15.6 | 10.3 | 10.4 | 10.9 |
| Bed material | | | 0.3 | 0.7 | 0.5 | 0.6 | 0.6 | 0.5 | | 0.4 | | 0.1 | , |
| Additive | 1 | 0.1 | | , | | , | 0.01 | 0.02 | 0.2 | | low | 1.7 | 1.6 |
| Temperatures [°C] | | | | | | | | | | | | | |
| Riser (average of 7 TCs) | 838 | 826 | 835 | 821 | 844 | 840 | 833 | 826 | 837 | 831 | 835 | 833 | 833 |
| Riser el. heating (average) | 838 | 825 | 847 | 832 | 840 | 836 | 834 | 834 | 840 | 839 | 828 | 828 | 829 |
| Gas inlet | 358 | 360 | 360 | 360 | 360 | 360 | 360 | 360 | 360 | 360 | 360 | 360 | 360 |
| Pressures [mbar] | | | | | | | | | | | | | |
| Gage pressure at CFB outlet | 50.9 | 61.8 | 63.4 | 52.2 | 56.3 | 52.3 | 61.1 | 55.6 | 60.2 | 76.4 | 75.8 | 19.8 | 22.5 |

| Process parameters | | | | | | | | | | | | | |
|---|------|------|------|------|-------|-------|------|------|------|------|------|------|------|
| Fluidization velocity (un) [m s ⁻¹] | 3.8 | 3.7 | 3.2 | 3.4 | 4.0 | 3.9 | 3.7 | 3.2 | 3.2 | 3.1 | 3.2 | 3.3 | 3.3 |
| Stoich. oxygen ratio (\lambda) | 0.34 | 0.31 | 0.27 | 0.26 | 0.38 | 0.35 | 0.35 | 0.28 | 0.26 | 0.24 | 0.35 | 0.35 | 0.33 |
| Steam-to-biomass ratio (SB) | 1.3 | 1.3 | 0.9 | 1.2 | 1.3 | 1.2 | 1.4 | 1.1 | 0.8 | 0.7 | 1.0 | 1.0 | 1.0 |
| H2O:O2 ratio [mol mol-1] | 5.6 | 6.3 | 4.4 | 6.8 | 5.1 | 4.9 | 5.9 | 6.5 | 4.4 | 4.4 | 4.4 | 4.4 | 4.4 |
| Main gas components [%vol] | | | | | | | | | | | | | |
| H2 dnf | 20.0 | 20.8 | 19.1 | 21.9 | 15.8 | 17.9 | 18.8 | 22.2 | 23.2 | 22.8 | 22.3 | 28.3 | 30.2 |
| CO dnf | 31.1 | 30.4 | 34.2 | 31.7 | 32.3 | 34.0 | 30.7 | 32.2 | 31.3 | 31.4 | 32.0 | 23.4 | 22.1 |
| CH4 dnf | 8.1 | 8.1 | 9.4 | 8.6 | 7.2 | 8.1 | 7.7 | 8.4 | 9.1 | 9.5 | 8.4 | 7.7 | 7.4 |
| CO ₂ dnf | 34.8 | 34.4 | 30.3 | 30.7 | 33.4 | 33.3 | 31.3 | 31.2 | 32.7 | 31.7 | 35.3 | 39.3 | 39.3 |
| N2 dry | 19.4 | 36.3 | 12.3 | 31.5 | 14.2 | 15.3 | 28.1 | 32.0 | 13.3 | 12.6 | 12.0 | 12.2 | 11.7 |
| H ₂ O wet | 65.7 | 62.0 | 24.3 | 57.1 | 60.3 | 61.3 | 56.9 | 54.4 | 56.9 | 56.6 | 62.6 | 57.9 | n.m. |
| Minor components [%vol] | | | | | | | | | | | | | |
| C ₂ H ₄ dnf | n.m. | n.m. | 2.6 | 3.3 | n.m. | n.m. | 2.0 | n.m. | 2.4 | 2.6 | 2.3 | 2.1 | 2.1 |
| C ₂ H ₂ dnf | n.m. | n.m. | 0.43 | 0.50 | n.m. | n.m. | 0.42 | n.m. | 0.34 | 0.34 | 0.39 | 0.32 | 0.31 |
| NH3 wet | n.m. | 0.18 | n.m. | 0.18 | 0.071 | 0.071 | n.m. | n.m. | 0.13 | n.m. | n.m. | n.m. | n.m. |
| Measured tar [g m ⁻³ (STP)] | | | | | | | | | | | | | |
| BTX dnf | 9.4 | 7.3 | 29 | 9.7 | 10 | 11 | 8.5 | 12 | 14 | 16 | 11 | 10 | n.m. |
| PAH raw | 2.5 | 1.8 | n.m. | 3.0 | n.m. | n.m. | 2.2 | 2.2 | n.m. | 4.3 | n.m. | 2.5 | n.m. |
| Phenolics raw | 0.89 | 0.86 | n.m. | 1.3 | n.m. | n.m. | 1.1 | 1.2 | n.m. | 1.8 | n.m. | 0.83 | n.m. |
| Process benchmarks | | | | | | | | | | | | | |
| Carbon conversion [%] | 76 | 26 | 88 | 83 | 76 | 73 | 104 | 84 | 83 | 82 | 88 | 96 | n.m. |
| Cold gas efficiency [%] | 54 | 54 | 72 | 70 | 51 | 51 | 81 | 65 | 68 | 70 | 70 | 76 | n.m. |
| H ₂ : CO ratio [-] | 9.0 | 0.7 | 0.6 | 0.7 | 0.5 | 0.5 | 0.6 | 0.7 | 0.7 | 0.7 | 0.7 | 1.2 | 1.4 |

| General information | MC-M01 | MC-M02 | MC-M03 | MC-M04 | MC-M05 | MC-M06 | MC-M07 | MC-M08 | MC-S09 | MC-S10 | MC-S11 | MC-S12 | MC-S13 | MC-S14 |
|--------------------------------------|------------|------------|------------|------------|------------|------------|------------|------------|-----------|-----------|-----------|-----------|------------|------------|
| Date [dd-mm-yyyy]: | 22-5-2008 | 20-5-2008 | 26-5-2008 | 26-5-2008 | 3-2-2009 | 5-2-2009 | 9-2-2009 | 2-11-2009 | 29-5-2008 | 30-5-2008 | 30-5-2008 | 30-5-2008 | 19-11-2009 | 27-11-2009 |
| Fuel: | miscanthus | straw'97 | straw'97 | straw'97 | straw'97 | straw'97 | straw'97 |
| Bed material: | magnesite | magnesite | magnesite | magnesite | magnesite | magnesite | magnesite |
| Additive: | , | ı | , | , | , | , | , | , | 1 | , | , | | , | kaolin |
| Total duration of the run: | 4:30 | 5:50 | 4:54 | 4:54 | 8:28 | 7:31 | 7:21 | 10:21 | 3:05 | 3:10 | 3:10 | 3:10 | 5:01 | 2:53 |
| Duration of the evaluation period: | 0:48 | 0:50 | 1:22 | 0:54 | 0:40 | 2:20 | 0:53 | 2:42 | 2:12 | 0:29 | 0:23 | 0:12 | 60:0 | 0:18 |
| Start time of the evaluation period: | 14:02 | 14:27 | 12:43 | 15:24 | 10:40 | 12:50 | 11:02 | 14:38 | 10:30 | 9:10 | 11:12 | 13:33 | 12:12 | 19:09 |
| End time of the evaluation period: | 14:51 | 15:18 | 14:06 | 16:18 | 11:20 | 15:10 | 11:55 | 17:20 | 12:42 | 9:39 | 11:35 | 13:45 | 12:21 | 19:27 |
| Input flows [kg h ⁻¹] | | | | | | | | | | | | | | |
| Steam (primary) | 11.4 | 13.8 | 12.6 | 12.6 | 11.7 | 12.2 | 11.1 | 11.1 | 11.1 | 12.0 | 12.3 | 12.9 | 14.1 | 15.4 |
| Oxygen (primary) | 3.80 | 3.20 | 4.40 | 4.40 | 4.00 | 4.00 | 4.00 | 4.40 | 4.40 | 3.80 | 3.80 | 3.20 | 5.00 | 6.00 |
| Air (L-valve recirculation) | 0.56 | 0.49 | 1.77 | 1.77 | 1.18 | 1.42 | 1.41 | 1.67 | 1.15 | 1.70 | 1.71 | 1.71 | 1.85 | 129 |
| Nitrogen (purge flows) | 2.76 | 2.69 | 5.12 | 5.12 | 237 | 2.39 | 2.33 | 2.87 | 5.23 | 4.82 | 3.21 | 4.45 | 3.79 | 2.97 |
| Biomass | 11.1 | 9.0 | 10.5 | 10.1 | 11.0 | 11.2 | 12.4 | 10.7 | 10.3 | 26 | 10.6 | 10.4 | 20.2 | 12.2 |
| Bedmaterial | 5.5 | 1 | 8.3 | 0.4 | 2.8 | 2.6 | 20 | | 8.4 | 8.5 | 8.5 | 8.5 | 42 | 4.3 |
| Additive | , | 7.4 | 1.9 | 6.5 | | , | | 2.8 | 5.4 | 32 | 3.6 | 7.3 | , | 0.8 |
| Temperatures [°C] | | | | | | | | | | | | | | |
| Riser (average of 7 TCs) | 837 | 827 | 836 | 840 | 856 | 824 | 821 | 829 | 834 | 830 | 831 | 806 | 817 | 841 |
| Riser el. heating (average) | 838 | 830 | 835 | 837 | 835 | 833 | 832 | 844 | 834 | 831 | 832 | 813 | 831 | 844 |
| Gas inlet | 360 | 360 | 397 | 383 | 368 | 360 | 360 | 360 | 360 | 360 | 360 | 360 | 360 | 360 |
| Pressures [mbar] | | | | | | | | | | | | | | |
| Gage pressure at CFB outlet | 76.4 | 55.0 | 80.0 | 31.9 | 75.3 | 71.3 | 24.8 | 80.0 | 31.0 | 32.5 | 38.1 | 47.2 | 80.0 | 80.0 |

| Process parameters | | | | | | | | | | | | | | |
|--|-------|------|-------|------|-------|-------|-------|------|------|------|------|------|------|------|
| Fluidization velocity (u _f) [m s ⁻¹] | 3.2 | 3.7 | 3.8 | 3.8 | 3.1 | 3.2 | 3.2 | 3.1 | 3.4 | 3.3 | 3.3 | 3.3 | 3.3 | 3.4 |
| Stoich. oxygen ratio (λ) | 0.28 | 0.29 | 0.36 | 0.38 | 0.32 | 0.31 | 0.28 | 0.36 | 0.40 | 0.39 | 0.35 | 0.31 | 0.24 | 0.46 |
| Steam-to-biomass ratio (SB) | 1.0 | 1.5 | 1.2 | 1.2 | 1.1 | 1.1 | 0.0 | 1.0 | 1.1 | 1.2 | 1.2 | 1.2 | 0.7 | 1.3 |
| H2O:O2 ratio [mol mol ⁻¹] | 5.3 | 7.7 | 5.1 | 5.1 | 5.2 | 5.4 | 4.9 | 4.5 | 4.5 | 5.6 | 5.7 | 7.2 | 5.0 | 4.5 |
| Main gas components [%wol] | | | | | | | | | | | | | | |
| H ₂ dnf | 39.1 | 39.7 | 35.9 | 33.9 | 38.9 | 39.3 | 39.1 | 33.3 | 29.5 | 29.9 | 32.0 | 32.2 | 30.3 | 27.2 |
| CO dnf | 15.6 | 12.0 | 12.7 | 13.5 | 14.6 | 14.4 | 15.6 | 14.6 | 12.2 | 13.1 | 12.7 | 12.6 | 13.9 | 15.5 |
| CH4 dnf | 5.7 | 5.2 | 5.5 | 5.8 | 5.9 | 5.9 | 5.9 | 5.2 | 5.4 | 5.7 | 5.8 | 5.9 | 9.5 | 9.9 |
| CO ₂ dnf | 37.6 | 41.5 | 42.6 | 42.2 | 38.9 | 38.9 | 37.6 | 41.5 | 46.4 | 45.4 | 45.3 | 44.3 | 36.2 | 42.7 |
| N2 dry | 14.7 | 16.1 | 29.8 | 30.0 | 12.8 | 12.0 | 14.3 | 19.8 | 33.5 | 35.4 | 28.0 | 34.3 | 14.2 | 12.9 |
| H ₂ O wet | 53.3 | 63.2 | 49.0 | 51.8 | 52.8 | 50.4 | 54.2 | 55.9 | 30.5 | 59.3 | 58.0 | 61.5 | 62.2 | n.m. |
| Minor components [%00] | | | | | | | | | | | | | | |
| C ₂ H ₄ dnf | 1.1 | n.m. | 1.3 | n.m. | 1.5 | 1.4 | 1.5 | 1.7 | 1.2 | 1.4 | 1.4 | 1.5 | n.m. | 1.4 |
| C ₂ H ₂ dnf | 0.043 | n.m. | 0.055 | n.m. | 0.071 | 0.087 | 0.092 | 0.10 | 0.13 | 0.15 | 0.15 | 0.15 | n.m. | 0.15 |
| NH3 wet | 0.11 | n.m. | 0.11 | n.m. | 0.18 | 0.18 | 0.18 | 0.16 | 0.13 | n.m. | 0.12 | n.m. | n.m. | n.m. |
| Measured tar [g m ³ (STP)] | | | | | | | | | | | | | | |
| BTX dnf | 7.1 | 5.2 | 6.5 | 7.1 | 2.8 | 0.6 | 6.0 | n.m. | 9.3 | 5.8 | 6.8 | 6.2 | n.m. | n.m. |
| PAH raw | n.m. | n.m. | 0.79 | 0.74 | 1.0 | 1.3 | 1.1 | n.m. | 1.5 | 0.71 | 1.1 | 0.79 | n.m. | n.m. |
| Phenolics raw | n.m. | n.m. | 0.14 | 0.16 | 0.072 | 0.16 | 0.12 | n.m. | 0.34 | 0.24 | 0.37 | 0.40 | n.m. | n.m. |
| Process benchmarks | | | | | | | | | | | | | | |
| Carbon conversion [%] | 20 | 75 | 84 | 91 | 92 | 101 | 88 | 81 | 87 | 87 | 72 | 78 | 53 | 167 |
| Cold gas efficiency [%] | 57 | 55 | 62 | 63 | 26 | 80 | 72 | 57 | 56 | 59 | 50 | 56 | 41 | 119 |
| H ₂ : CO ratio [-] | 2.5 | 3.3 | 2.8 | 2.5 | 2.7 | 2.7 | 2.5 | 2.3 | 2.4 | 2.3 | 2.5 | 2.6 | 2.2 | 1.8 |

| General information | MC-A01 | MC-A02 | MC-A03 | MC-A04 | MC-A05 | MC-A06 | MC-A07 | MC-A08 | MC-B09 | MC-B10 |
|--------------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|------------|------------|-----------|------------|
| Date [dd-mm-yyyy]: | 20-8-2008 | 22-8-2008 | 22-8-2008 | 22-8-2008 | 22-8-2008 | 28-1-2009 | 30-01-2009 | 17-11-2009 | 18-2-2009 | 19-02-2009 |
| Fuel: | A-wood | A-wood | B-wood | B-wood |
| Bed material: | magnesite | magnesite | magnesite | magnesite |
| Additive: | | | | | | | | | | |
| Total duration of the run: | 2:54 | 5:36 | 5:36 | 5:36 | 5:36 | 4:26 | 2:09 | 10:55 | 3:49 | 4:49 |
| Duration of the evaluation period: | 0:40 | 0:33 | 0:15 | 0:11 | 0:14 | 0:48 | 1:00 | 3:30 | 0:53 | 0:00 |
| Start time of the evaluation period: | 14:00 | 11:05 | 12:40 | 14:05 | 15:20 | 12:25 | 10:25 | 10:50 | 12:10 | 0:00 |
| End time of the evaluation period: | 14:40 | 11:39 | 12:56 | 14:16 | 15:35 | 13:13 | 11:25 | 14:20 | 13:03 | 0:00 |
| Input flows [kg h ^{.1}] | | | | | | | | | | |
| Steam (primary) | 10.8 | 6.6 | 9.3 | 11.4 | 11.4 | 10.8 | 11.5 | 12.2 | 11.1 | 11.1 |
| Oxygen (primary) | 4.40 | 5.20 | 5.80 | 3.80 | 3.80 | 4.80 | 4.80 | 5.00 | 4.00 | 4.00 |
| Air (L-valve recirculation) | 1.04 | 1.03 | 1.03 | 1.03 | 1.03 | 1.03 | 1.08 | 1.66 | 1.23 | 1.22 |
| Nitrogen (purge flows) | 1.80 | 1.76 | 1.79 | 1.82 | 1.82 | 1.89 | 2.23 | 2.92 | 2.12 | 222 |
| Biomass | 10.4 | 12.6 | 13.0 | 9.4 | 9.3 | 9.6 | 10.4 | 12.0 | 10.0 | 9.5 |
| Bed material | | | | 3.5 | 3.7 | 3.1 | 1.7 | 4.5 | 2.9 | 4.2 |
| Additive | 3.6 | 4.7 | 3.5 | 0.02 | 1.0 | | 0.1 | | | 0.1 |
| Temperatures [°C] | | | | | | | | | | |
| Riser (average of 7 TCs) | 830 | 834 | 843 | 828 | 825 | 844 | 845 | 833 | 828 | 828 |
| Riser el. heating (average) | 828 | 829 | 833 | 827 | 823 | 844 | 843 | 841 | 836 | 835 |
| Gas inlet | 380 | 360 | 360 | 360 | 360 | 360 | 360 | 360 | 360 | 364 |
| Pressures [mbar] | | | | | | | | | | |
| Gage pressure at CFB outlet | 31.5 | 40.7 | 45.9 | 42.6 | 45.4 | 75.5 | 49.5 | 80.0 | 69.2 | 69.2 |

| Process parameters | | | | | | | | | | |
|---|-------|-------|-------|-------|------|-------|-------|-------|-------|------|
| Fluidization velocity (u _{ii}) [m s ⁻¹] | 3.3 | 3.2 | 3.1 | 3.3 | 3.3 | 3.1 | 3.3 | 3.2 | 3.0 | 3.0 |
| Stoich. oxygen ratio (A) | 0.35 | 0.34 | 0.36 | 0.34 | 0.34 | 0.40 | 0.38 | 0.35 | 0.33 | 0.34 |
| Steam-to-biomass ratio (SB) | 1.0 | 0.8 | 0.7 | 1.2 | 1.2 | 1.1 | 1.1 | 1.0 | 1.1 | 1.2 |
| H2O:O2 ratio [mol mol ⁻¹] | 4.4 | 3.4 | 2.8 | 5.3 | 5.3 | 4.0 | 4.3 | 4.3 | 4.9 | 4.9 |
| Main gas components [‰wi] | | | | | | | | | | |
| H ₂ dnf | 36.2 | 35.0 | 33.4 | 36.2 | 34.9 | 35.5 | 34.2 | 32.3 | 31.0 | 33.1 |
| CO dnf | 16.1 | 18.0 | 19.1 | 15.4 | 16.4 | 14.7 | 15.1 | 14.2 | 13.8 | 13.0 |
| CH4 dnf | 6.1 | 6.3 | 6.6 | 6.4 | 6.4 | 6.4 | 6.5 | 9.5 | 5.6 | 5.9 |
| CO ₂ dnf | 40.8 | 40.0 | 40.7 | 42.2 | 42.2 | 42.0 | 41.4 | 40.5 | 36.9 | 43.1 |
| N2 dry | 12.0 | 10.7 | 10.3 | 13.3 | 13.5 | 12.4 | 13.5 | 17.0 | 23.0 | 17.1 |
| H ₂ O wet | 48.2 | 41.9 | 41.4 | 55.9 | 55.7 | 52.0 | 54.1 | 58.0 | 65.0 | 60.1 |
| Minor components [%vol] | | | | | | | | | | |
| C2H4 dnf | 1.2 | 1.4 | n.m. | n.m. | n.m. | 1.9 | 1.7 | 1.6 | 2.1 | 1.9 |
| C ₂ H ₂ dnf | 0.083 | 0.064 | 0.083 | 0.091 | 0.14 | 0.087 | 0.087 | 0.095 | 0.18 | 0.15 |
| NH3 wet | n.m. | n.m. | n.m. | n.m. | n.m. | 0.018 | 0.019 | 0.019 | n.m. | 0.25 |
| Measured tar [g m ⁻³ (STP)] | | | | | | | | | | |
| BTX dnf | 11 | 11 | 12 | 8.4 | 8.6 | 1.5 | 3.8 | n.m. | 0.4 | 16 |
| PAH raw | 1.5 | 1.7 | 1.9 | 1.3 | 1.4 | 1.7 | 1.7 | n.m. | 0.71 | 1.3 |
| Phenolics raw | 0.23 | 0.27 | 0.30 | 0.14 | 0.27 | 0.075 | 0.095 | n.m. | 0.075 | 0.10 |
| Process benchmarks | | | | | | | | | | |
| Carbon conversion [%] | 88 | 82 | 84 | 85 | 85 | 88 | 83 | 75 | 44 | 84 |
| Cold gas efficiency [%] | 20 | 65 | 65 | 66 | 65 | 67 | 64 | 60 | 33 | 64 |
| H ₂ : CO ratio [-] | 2.3 | 1.9 | 1.7 | 2.4 | 2.1 | 2.4 | 2.3 | 2.3 | 2.2 | 2.6 |

| General information | OC(U)-A01 | OC(U)-A02 | OC(U)-B03 | OC(U)-B04 | OC(U)-M05 | OC(900)-B01 | OC(900)-B02 | OC(1200)-B05 | OC(900)-M06 |
|--------------------------------------|------------|------------|------------|------------|------------|--------------|--------------|---------------|--------------|
| Date [dd-mm-yyyy]: | 21-04-2009 | 24-04-2009 | 28-04-2009 | 23-10-2009 | 2-12-2009 | 13-05-2009 | 18-05-2009 | 21-10-2009 | 7-12-2009 |
| Fuel: | A-wood | A-wood | B-wood | B-wood | miscanthus | B-wood | B-wood | B-wood | miscanthus |
| Bed material: | olivine-U | olivine-U | olivine-U | olivine-U | olivine-U | olivine-T900 | olivine-T980 | olivine-T1200 | olivine-T900 |
| Additive: | | | kaolin | kaolin | kaolin | kaolin | kaolin | kaolin | kaolin |
| Total duration of the run: | 4:30 | 71:7 | 5:35 | 6:35 | 13:33 | 5:01 | 7:56 | 10:14 | 7:38 |
| Duration of the evaluation period: | 0:30 | 0:23 | 1:00 | 1:06 | 5:30 | 1:15 | 0:45 | 1:15 | 0:35 |
| Start time of the evaluation period: | 14:25 | 13:50 | 14:20 | 12:34 | 15:50 | 14:45 | 12:30 | 12:45 | 15:56 |
| End time of the evaluation period: | 14:55 | 14:13 | 15:20 | 13:40 | 21:20 | 16:00 | 13:15 | 14:00 | 16:31 |
| Input flows [kg h ⁻¹] | | | | | | | | | |
| Steam (primary) | 13.2 | 12.0 | 11.7 | 10.6 | 12.3 | 11.4 | 10.4 | 10.7 | 19.5 |
| Oxygen (primary) | 5.00 | 5.00 | 4.59 | 5.00 | 5.00 | 4.60 | 4.60 | 5.00 | 7.00 |
| Air (L-valve recirculation) | 1.47 | 1.25 | 1.72 | 0.70 | 1.48 | 1.40 | 0.54 | 0.70 | 1.85 |
| Nitrogen (purge flows) | 2.29 | 2.28 | 2.02 | 3.06 | 2.72 | 2.65 | 2.78 | 3.04 | 2.88 |
| Biomass | 12.0 | 11.5 | 11.1 | 11.6 | 13.5 | 11.7 | 11.8 | 11.4 | 15.6 |
| Bedmaterial | | | | | 1.3 | | 0.0 | 0.1 | |
| Additive | | | | 0.5 | 0.4 | | 0.4 | 9.0 | |
| Temperatures [°C] | | | | | | | | | |
| Riser (average of 7 TCs) | 837 | 841 | 827 | 834 | 811 | 830 | 833 | 839 | 837 |
| Riser el. heating (average) | 838 | 838 | 832 | 846 | 833 | 830 | 835 | 847 | 843 |
| Gas inlet | 360 | 348 | 364 | 360 | 360 | 360 | 360 | 360 | 360 |
| Pressures [mbar] | | | | | | | | | |
| Gage pressure at CFB outlet | 80.0 | 80.0 | 80.0 | 80.0 | 80.0 | 80.0 | 80.0 | 80.0 | 80.0 |

| Appendix A. Experimental data | |
|-------------------------------|--|
|-------------------------------|--|

| Process parameters | | | | | | | | | |
|--|-------|-------|------|------|------|------|------|------|-------|
| Fluidization velocity (u _{fl}) [m s ¹] | 3.6 | 3.4 | 3.3 | 2.9 | 3.2 | 3.2 | 3.0 | 3.0 | 4.5 |
| Stoich. oxygen ratio () | 0.35 | 0.36 | 0.34 | 0.34 | 0.32 | 0.32 | 0.30 | 0.33 | 0.38 |
| Steam-to-biomass ratio (SB) | 1.1 | 1.0 | 1.1 | 6.0 | 6.0 | 1.0 | 6.0 | 6.0 | 1.3 |
| H2O:O2 ratio [mol mol ¹] | 4.7 | 4.3 | 4.5 | 3.8 | 4.4 | 4.4 | 4.0 | 3.9 | 5.0 |
| Main gas components [%vol] | | | | | | | | | |
| H ₂ dnf | 27.2 | 24.0 | 212 | 18.1 | 21.4 | 19.4 | 20.6 | 21.4 | 21.5 |
| CO dhf | 23.7 | 26.7 | 28.7 | 32.1 | 27.2 | 30.1 | 29.9 | 30.0 | 30.7 |
| CH4 dhf | 7.7 | 7.9 | 8.0 | 7.8 | 9.0 | 8.3 | 8.6 | 8.5 | 8.5 |
| CO ₂ dhf | 37.4 | 37.2 | 35.6 | 34.8 | 34.4 | 36.0 | 35.0 | 39.8 | 35.9 |
| N ₂ dry | 14.4 | 15.3 | 22.0 | 18.3 | 16.6 | 18.7 | 17.2 | 21.4 | 15.8 |
| H2O wet | 62.6 | 55.2 | 67.1 | 63.4 | 57.4 | 53.1 | 52.8 | 63.6 | 62.8 |
| Minor components [%vol] | | | | | | | | | |
| C2H4 dhf | 2.5 | 2.6 | 3.1 | 3.2 | 2.5 | 3.7 | 3.3 | 32 | 2.6 |
| C2H2 dnf | 0.31 | 0.32 | 0.48 | 0.49 | 0.28 | 0.55 | 0.53 | 0.51 | 0.40 |
| NH ₅ wet | 0.019 | 0.016 | 0.21 | 0.21 | 0.14 | 0.24 | 0:30 | 0.20 | 0.094 |
| Measured tar [g m ⁻³ (STP)] | | | | | | | | | |
| BTX dhf | 2.4 | 3.6 | 1.7 | um | n.m. | 0.31 | 0.12 | um | um |
| PAH raw | 2.5 | 3.5 | 3.2 | 'nm | uu | 4.9 | 5.0 | um | 'nm |
| Phenolics raw | 0.20 | 0.25 | 0.48 | nm. | uu | 9970 | 0.72 | um | nm |
| Process benchmarks | | | | | | | | | |
| Carbon conversion [%] | 87 | 85 | 65 | 55 | 72 | 82 | 75 | 64 | 67 |
| Cold gas efficiency [%] | 69 | 99 | 49 | 40 | 55 | 62 | 57 | 45 | 50 |
| H ₂ : CO ratio [-] | 1.1 | 0.9 | 0.7 | 0.6 | 0.8 | 9.0 | 0.7 | 0.7 | 0.7 |

CFB Fortran model: base case input file

1 RRBASE RRBASE Input for the CFBC 1.0 Code File name: woodA_53.INP Riser geometry and state changes according to bed height # Level Width Length Add. Flue Tapered Wall Tubes Cells air gas 1=y,0=n ratio A/V
 interm
 interm< [m] [m2/m3] [-] 0.00 1 1.00 0.00 4 2 0.00 1.00 0.00 1.00 0.00 15 0.00 4 5.29 0.074 0.074 0.0000 0.00 1.00 0.00 0.074 0.074 0.0000 0.00 1.00 0.00 5.30 5.40 0.074 0.074 0.0000 0.00 0.00 0.00 0 0.00 0.00 0.00 0.00 0.0000 0.00 0.00 0.00 0 0.00 0.0000 8 0.00 0.00 0.00 0.00 0.00 0 0.00 0.00 0.00 0.0000 0.00 0.00 0.00 0 0 0.00 10 0.00 0.00 0.00 0.0000 0.00 0.00 0.00 0 0.00 0.00 0.0000 0.00 0.00 0.00 0.00 0 0.00 0.00 0.00 0.0000 0.00 0.00 0.00 0
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 13 0.00 0.00 0.00 0.00 0 0.00 0.00 0.00 14 0.00 0 15 0.00 0.00 0.00 0.00 0 16 0.00 0.00 0.00 0.00 0
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 17 0.00 0.00 0.00 0.00 0 0.00 0.00 0.00 0.00 0.00 0.00 18 0.00 0.00 0 0.00 0.00 19 0 20 0 Compartment according to: Elutriation CoalFeed Limefeed Recycle External Exit 4 3 3 2 2 Cyclone geometry: Number of cyclones
 1
 Total:
 Height
 Diameter
 Tube length
 Tube Diameter

 0.375
 0.102
 0.069
 0.054

 Inlet:
 Distance
 Height
 Width
 Acceleration coefficient

 0.035
 0.050
 0.020
 0.800
 Proportionality constant for eddy carrying capacity 0.010 Feed mass flows [units via Option 5] Coal Lime Inert(sand) 10.4 0.0000 3.0 External heat exchanger split ratio l=all;0=no temperature of reentered particles 1.0000 825.0000
 eve classes

 Sieve [m]
 Coal [%] Lime [%]
 Inert [%]

 2
 5600.0
 15.304
 0.0
 0.0

 2
 5600.0
 15.304
 0.0
 0.0

 3
 4000.0
 13.791
 0.0
 0.0

 4
 200.0
 2.595
 10.0
 0.0

 5
 1000.0
 3.510
 10.0
 0.0

 6
 600.0
 0.0
 20.0
 1.0

 8
 425.0
 0.0
 0.0
 57.8

 1
 200.0
 0.0
 0.0
 1.7

 2
 150.0
 1.508
 0.0
 0.3

 4
 0.0
 0.0
 0.3
 3
 90.0
 0.0
 0.3

 5
 150.0
 1.508
 0.0
 0.3
 3
 90.0
 0.0
 0.0
 0.0

 5
 0.0
 0.0
 0.0
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 5
 0.0
 0.0
 0.0
 0.0
 0.0
 0.0</ Sieve classes No 1 3 4 5 6 8 9 10 11 12 13 14 15 16 17 18 19 20
 Temperatures [C]
 Bed
 Air in
 Ambient
 Flue reci
 Wall

 830.0
 332.0
 20.0
 750.0
 848
 848.0 Absolute Drop in riser Drop in cyclone 101300.0 1957.0 740.0 Pressures [Pa] Walls Walls 0.0 Heat transfer coeff. Tubes Coal Lime Bed Char Density [kg/m3]

```
550.0 2600.0 2600.0
                                                    900.0
Sphericity [-]
                       0.710 0.710 0.710
                                                   0.710
Heat cap. [J/kg*K]
                       1260.0 840.0
                                           840.0
                                                     715.0
Attr. const.
                    0.0000000 0.0000000 0.0000000 0.0001000
Fragmentation
                        2.00 1.00
                                           1.00
                                                    1.00
Exp.Fact a*u.
                        6.00
                               6.00
                                           6.00
                                                     6.00
                    H [%dry] O [%dry] N [%dry] S [%dry]
2 5.676 42.491 0.221 0.022
Fuel:
         C [%dry]
              51.202
         Mois [%ar] Ash[%dry]
                                 Volat[%dry] Fixed C [%dry]
               8.1
                       0.388
                                  86.00
                                               13.612
Ratio: NO/(NO+N2O)
               0.60
                                 E0/RG (K) D (m/s)
Combustion
              k0 (kg/m2skPa) E0/RG (K)
0.01000 -10825.0 0.0000200
        BET surface (m2/g) Max conversion (-) ks (m/s) XCaCO3 (-)
2.0000 0.5000 0.1500 0.9000
S02
OPTIONS:
1.) elutriation model 0= Wirth, 1= Yang
2.) devolatilization model: 0: IEA 2: Merrick
3.) bottom ash treatment, 0= none, 1= segregation, 2= wind sifter, 3=both
4.) heat transfer model 0= Wirth, 1= Matmann
5.) flow rate units: 0 = nm3/s, kg/s; 1 = all kg/h
6.) free
7.) free
8.) free
9.) free
10.) free
Write state of operation to screen?
 1
Write out submodel results: 1 = yes, 0 = no
END
```



A summary of the general assumptions related to model balances:

- all reactions are assumed to take place in the riser;
- for the use of the matrix solvers it is convenient to continue the annular phase into the dense bed, if the existence of this phase is predicted. By doing so the bed and freeboard can be solved together, simultaneously. In such a case the lateral mixing between the core and the annulus should be high enough to equalize both phases to a common dense bed;
- all balances are independent of time, steady-state conditions are assumed.

C.1 Gas balances

A summary of the assumptions related to the gas balances. The new aspects of the model, as compared to the original IEA model [75], are indicated in boldface:

- the gas flows are split using the values from the pre-calculations of the bubble holdup and the annulus width;
- the gas flows are balanced as molar flow rates;
- **new:** changes caused by the reactions that are not equimolar are taken into account by introducing a source term that contains the net total molar gas formation rate in each cell, YSRC (K) [mol s^{-1}];
- the flows to be balanced are:
 - the convective flows in each phase: core, annulus (abbrev. annu) and bubble (abbrev. bubb). The values of these flows can only be equal to or greater than zero;
 - the cross flows from core to annulus (core-annu), core to bubble (corebubb), and vice-versa. Also the values of these variables can only be equal to or greater than zero. For example, if there is a flow from annulus to the core, the annu-core flow value in a cell in that region YANCO(K) will be positive, while the core-annu flow YCOAN(K) will be zero;
 - the mixing flows between the phases (coreannux and corebubbx). These variables can become positive, negative or zero.
- no gas back-mixing is allowed in the gas phase. Gas flows either in the upward direction or in the lateral direction (cross and mixing flows between the phases);
- **new:** the molar gas flows in all cells are calculated within the mass balance iteration loop (subroutine GASFLO);

• the species concentrations XGAS (J) are calculated depending on the source terms caused by the gas release, gas phase and gas-solids reactions.

The gas flows in each of the three phases are balanced based on the differential equation:

$$\frac{dn_g}{dt} = u_g \frac{\delta n_g}{\delta z} + \dot{\Phi}_{g,source} + \dot{\Phi}_{g,exchange}$$
(C.1)

which leads to the gas balance equations for each of the three phases:

$$0 \equiv \frac{dn_{g,core}(k)}{dt} = \dot{n}_{g,core} (k-1) - \dot{n}_{g,core} (k)$$

$$+ \dot{n}_{g,annu-core} (k) - \dot{n}_{g,core-annu} (k)$$

$$+ \dot{n}_{g,bubb-core} (k) - \dot{n}_{g,core-bubb} (k)$$

$$+ \dot{n}_{g,feedgas} (k) + \dot{n}_{g,feedflue} (k) + \dot{n}_{g,H_2O} (k) + \dot{n}_{g,vola} (k)$$

$$+ \dot{n}_{g,src} (k) - \dot{n}_{g,out} (k)$$
(C.2)

$$0 \equiv \frac{dn_{g,annu}(k)}{dt} = \dot{n}_{g,annu} (k-1) - \dot{n}_{g,annu} (k) + \dot{n}_{g,core-annu} (k) - \dot{n}_{g,annu-core} (k)$$
(C.3)

$$0 \equiv \frac{dn_{g,bubb}(k)}{dt} = \dot{n}_{g,bubb} (k-1) - \dot{n}_{g,bubb} (k) + \dot{n}_{g,core-bubb} (k) - \dot{n}_{g,bubb-core} (k)$$
(C.4)

For an individual gaseous component *j* Equation C.1 can be written as:

$$\frac{d(n \cdot X_j)}{dt} = u_g \frac{\delta(n \cdot X_j)}{\delta z} + \dot{\Phi}_{source,j} + \dot{\Phi}_{exchange,j}$$
(C.5)

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The combination of the above equations and assumptions for the three individual phases yields:

$$0 \equiv n_{g,core} \frac{dX_{core}}{dt} = \dot{n}_{g,core} (k-1) \cdot X_{core}(j,k-1) - \dot{n}_{g,core} (k) \cdot X_{core}(j,k)$$

$$+ \dot{n}_{g,annu-core} (k) \cdot X_{annu}(j,k) - \dot{n}_{g,core-annu} (k) \cdot X_{core}(j,k)$$

$$+ \dot{n}_{g,coreannux} (k) \cdot X_{annu}(j,k) - \dot{n}_{g,coreannux} (k) \cdot X_{core}(j,k)$$

$$+ \dot{n}_{g,bubb-core} (k) \cdot X_{bubb}(j,k) - \dot{n}_{g,core-bubb} (k) \cdot X_{core}(j,k)$$

$$+ \dot{n}_{g,feedgas} (k) \cdot X_{feedgas}(j) - \dot{n}_{g,feedflue} (k) \cdot X_{feedflue}(j)$$

$$+ \dot{n}_{g,H_2O} (k) \cdot X_{H_2O}(j) + \dot{n}_{g,vola} (k) \cdot X_{vola}(j)$$

$$- \dot{n}_{g,out} (k) \cdot X_{core}(j,k)$$

$$\pm \dot{n}_{g,reac} (j,k)$$
(C.6)

$$0 \equiv n_{g,annu} \frac{dX_{annu}}{dt} = \dot{n}_{g,annu} (k-1) \cdot X_{annu}(j,k-1) - \dot{n}_{g,annu} (k) \cdot X_{annu}(j,k)$$
$$- \dot{n}_{g,annu-core} (k) \cdot X_{annu}(j,k) + \dot{n}_{g,core-annu} (k) \cdot X_{core}(j,k)$$
$$- \dot{n}_{g,coreannux} (k) \cdot X_{annu}(j,k) + \dot{n}_{g,coreannux} (k) \cdot X_{core}(j,k)$$
$$+ \dot{n}_{g,H_2O} (k) \cdot X_{H_2O}(j) - \dot{n}_{g,vola} (k) \cdot X_{vola}(j)$$
$$\pm \dot{n}_{g,reac} (j,k)$$
(C.7)

$$0 \equiv n_{g,bubb} \frac{dX_{bubb}}{dt} = \dot{n}_{g,bubb} (k-1) \cdot X_{bubb}(j,k-1) - \dot{n}_{g,bubb} (k) \cdot X_{bubb}(j,k)$$

$$+ \dot{n}_{g,bubb-core} (k) \cdot X_{bubb}(j,k) - \dot{n}_{g,core-bubb} (k) \cdot X_{core}(j,k)$$

$$+ \dot{n}_{g,corebubbx} (k) \cdot X_{bubb}(j,k) - \dot{n}_{g,corebubbx} (k) \cdot X_{core}(j,k)$$

$$\pm \dot{n}_{g,reac} (j,k)$$
(C.8)

C.2 Solids balances

A summary of the assumptions related to the solids balances:
- first an initial, overall, population balance is solved, which yields the size distribution of the general bed inventory (material no. 5, BED);
- based on the initial population balance the size classes *i* of different solid materials *m* are balanced separately for each cell *k*;
- in the freeboard solids can flow only from core to annulus;
- in the lowest cell (*k* = 1) all material from the annulus is added to the core inventory to conserve the mass balance;
- reactive species in the solids, like carbon in the fuel char, are modeled as solid fractions. The mass flow of the particles is kept constant, only the species fractions may vary. This is done for better numerical system solubility;
- only the ash fraction of the fuel is used in the population balance calculations. The fixed carbon is treated as a load of the ash – the solid carbon balance is solved separately;
- **new:** a soot formation rate term (CPRRTC(K) and CPRRTA(K) [mol s⁻¹] for the core and the annulus, respectively) is introduced to pass the information about the amount of solid carbon formed during the tar decomposition reaction to the solid carbon balance;
- the mass of the raw fuel fed to the system is treated as a virtual fraction it is only used to calculate the source terms for evaporated fuel moisture and volatile release.

The general differential equation

$$\frac{dm_s}{dt} = u_s \frac{\delta m_s}{\delta z} + \dot{\Phi}_{s,source} \tag{C.9}$$

can be written for each phase as a function of the size class, the material and the location (cell):

$$0 \equiv \frac{dm_{s,core}(k)}{dt} = \dot{m}_{s,up} (i, k - 1, m) - \dot{m}_{s,up} (i, k, m) + \dot{m}_{s,annu-core} (i, k, m) - \dot{m}_{s,core-annu} (i, k, m) + \dot{m}_{s,feed} (i, k, m) + \dot{m}_{s,recy} (i, k, m) + \dot{m}_{s,ehe} (i, k, m) - \dot{m}_{s,out} (i, k, m)$$
(C.10)

$$0 \equiv \frac{dm_{s,annu}(k)}{dt} = \dot{m}_{s,dwn} (i, k+1, m) - \dot{m}_{s,dwn} (i, k, m) + \dot{m}_{s,core-annu} (i, k, m) - \dot{m}_{s,annu-core} (i, k, m)$$
(C.11)

The fractional balances are based on:

$$\frac{d(m_s \cdot x)}{dt} = u_s \frac{\delta(m_s \cdot x)}{\delta z} + \dot{\Phi}_{s,source} + k_r \cdot \dot{m}_s \cdot x \tag{C.12}$$

where the last term represents the influence of a chemical reaction, and k_r is a release or reaction constant that depends on the local gaseous reactants concentrations and on the local temperatures.

The discrete species balances for the core and the annulus phase can be written as:

$$\begin{split} 0 &\equiv m_{s,core} \frac{dx_{core}}{dt} = \dot{m}_{s,up} \left(i, k - 1, m \right) \cdot x_{core}(i, k - 1) \\ &\quad - \dot{m}_{s,up} \left(i, k, m \right) \cdot x_{core}(i, k) \\ &\quad + \dot{m}_{s,annu-core} \left(i, k, m \right) \cdot x_{annu}(i, k) \\ &\quad - \dot{m}_{s,core-annu} \left(i, k, m \right) \cdot x_{core}(i, k) \\ &\quad - \dot{m}_{s,coreannux} \left(k \right) \cdot x_{core}(i, k) \\ &\quad + \dot{m}_{s,coreannux} \left(k \right) \cdot x_{annu}(i, k) \\ &\quad + \dot{m}_{s,x} \left(i, k - 1, m \right) \cdot x_{core}(i, k - 1) \\ &\quad - \dot{m}_{s,x} \left(i, k - 1, m \right) \cdot x_{core}(i, k) \\ &\quad - \dot{m}_{s,x} \left(i, k, m \right) \cdot x_{core}(i, k) \\ &\quad + \dot{m}_{s,recy} \left(i, k, m \right) \cdot x_{core}(i, k + 1) \\ &\quad + \dot{m}_{s,feed} \left(i, k, m \right) \cdot x_{recy}(i) \\ &\quad + \dot{m}_{s,recy} \left(i, k, m \right) \cdot x_{core}(i) \\ &\quad - \dot{m}_{s,out} \left(i, k, m \right) \cdot x_{core}(i) \\ &\quad - \dot{m}_{s,out} \left(i, k, m \right) \cdot x_{core}(i, k) \end{split}$$

$$0 \equiv m_{s,annu} \frac{dx_{annu}}{dt} = \dot{m}_{s,dwn} (i, k+1, m) \cdot x_{annu} (i, k+1)$$

$$- \dot{m}_{s,dwn} (i, k, m) \cdot x_{annu} (i, k)$$

$$+ \dot{m}_{s,core-annu} (i, k, m) \cdot x_{core} (i, k)$$

$$- \dot{m}_{s,annu-core} (i, k, m) \cdot x_{annu} (i, k)$$

$$+ \dot{m}_{s,coreannux} (k) \cdot x_{core} (i, k)$$

$$- \dot{m}_{s,coreannux} (k) \cdot x_{annu} (i, k)$$

$$- k_r (i, k, T) \cdot m_{s,annu} \cdot x_{annu} (i, k)$$
(C.14)

C.3 Energy balance

The enthalpy balance, delivering the average cell temperatures, considers the convective flows of gas and solids, changes in formation enthalpies due to reactions and the heat transfer to the walls and, if present, the tube banks. From the differential Fourier equation:

$$(n_g c_{p,g} + m_s c_{p,s})\frac{dT}{dt} = (u_g n_g c_{p,g} + u_s m_s c_{p,s})\frac{dT}{dz} + \dot{\Phi}_{reac} + \dot{\Phi}_{heatexch}$$
(C.15)

the total balance system to be solved is the following:

$$\begin{split} 0 &= (n_{g}c_{p,g} + m_{s}c_{p,s}) \frac{dT_{core}(k)}{dt} = \\ &\sum_{j=1}^{nj} [[n_{g,core}(k-1) \cdot X_{core}(j,k-1) - n_{g,core}(k) \cdot X_{core}(j,k) \\ &+ (n_{g,annu-core}(k) + n_{g,annucorex}(k)) \cdot X_{annu}(j,k) \\ &- (n_{g,core-annu}(k) + n_{g,annucorex}(k)) \cdot X_{core}(j,k) \\ &+ n_{g,feedgas}(k) \cdot X_{feedgas}(j) + n_{g,feedflue}(k) \cdot X_{core}(j,n_k) \\ &+ n_{g,fuc}(k) \cdot X_{hgo}(j) + n_{g,vola}(k) \cdot X_{vola}(j) \\ &- n_{g,out}(k) \cdot X_{core}(j,k) + n_{from}(j)] \\ &+ \sum_{j=1}^{nj} [n_{g,core}(k-1) \cdot c_{p,g,core}(j,k-1) \cdot X_{core}(j,k-1) \cdot T_{core}(k-1) \\ &- n_{g,core}(k) \cdot c_{p,g,core}(j,k-1) \cdot X_{core}(j,k-1) \cdot T_{core}(k-1) \\ &+ (n_{g,annu-core}(k) + n_{g,annucorex}(k)) \cdot c_{p,g,annu}(j,k) \cdot X_{annu}(j,k) \cdot T_{annu}(k) \\ &- (n_{g,core-annu}(k) + n_{g,annucorex}(k)) \cdot c_{p,g,ore}(j,k) \cdot X_{core}(j,k) \cdot T_{core}(k) \\ &+ n_{g,feedflue}(k) \cdot c_{p,g,feed}(j) \cdot X_{feedgas}(j) \cdot T_{in} \\ &+ n_{g,feedflue}(k) \cdot c_{p,g,feed}(j) \cdot X_{foedgas}(j) \cdot T_{in} \\ &+ n_{g,goat}(k) \cdot c_{p,g,feed}(j) \cdot X_{core}(j,k) \cdot T_{core}(k)] \\ &+ \sum_{m=2}^{m} \sum_{i=1}^{ni} [m_{up}(i,k-1,m) \cdot c_{p,s}(m) \cdot T_{core}(k-1) \\ &- n_{up}(i,k,m) \cdot c_{p,s}(m) \cdot T_{core}(k) \\ &+ (m_{annu-core}(i,k,m) + m_{annucorex}(i,k,m)) \cdot c_{p,s}(m) \cdot T_{annu}(k) \\ &- (n_{core-annu}(i,k,m) + m_{coreannux}(i,k,m)) \cdot c_{p,s}(m) \cdot T_{annu}(k) \\ &- (n_{core-annu}(i,k,m) + m_{coreannux}(i,k,m)) \cdot c_{p,s}(m) \cdot T_{annu}(k) \\ &- (n_{eore}(j,k) - T_{oore}(j,k) \cdot T_{core}(k-1) \\ &+ n_{w}(i,k-1,m) \cdot c_{p,s}(m) \cdot T_{core}(k-1) \\ &+ m_{w}(i,k-1,m) \cdot c_{p,s}(m) \cdot T_{core}(k-1) \\ &+ m_{w}(i,k-1,m) \cdot c_{p,s}(m) \cdot T_{core}(k-1) \\ &+ m_{w}(i,k-1,m) \cdot c_{p,s}(m) \cdot T_{core}(k) \\ &+ m_{feed}(i,k-1,m) \cdot c_{p,s}(m) \cdot T_{core}(k) \\ &+ m_{ehe}(i,k-1,m) \cdot c_{p,s}(m) \cdot T_{core}(k) \\ &+ m_{out}(i,k,m) \cdot c_{p,s}(m) \cdot T_{core}(k) \\ &+ m_{out}(i,k,m) \cdot c_{p,s}(m) \cdot T_{core}(k) \\ &+ m_{ehe}(i,k-1,m) \cdot c_{p,s}(m) \cdot T_{core}(k) \\ &+ m_{out}(i,k,m) \cdot c_{p,s}(m) \cdot T_{core$$

$$\begin{aligned} 0 &= \frac{1}{2} (n_g c_{p,g} + m_s c_{p,s}) \frac{dT_{annu}(k)}{dt} = \\ &\sum_{j=1}^{n_j} [[\dot{n}_{g,annu} \ (k-1) \cdot X_{annu}(j,k-1) - \dot{n}_{g,annu} \ (k) \cdot X_{annu}(j,k) \\ &+ (\dot{n}_{g,core-annu} \ (k) + \dot{n}_{g,coreannux} \ (k)) \cdot X_{core}(j,k) \\ &- (\dot{n}_{g,annu-core} \ (k) + \dot{n}_{g,annucorex} \ (k)) \cdot X_{annu}(j,k)] \cdot h_{form}(j)] \\ &+ \sum_{j=1}^{n_j} [\dot{n}_{g,annu} \ (k-1) \cdot c_{p,g,annu}(j,k-1) \cdot X_{annu}(j,k-1) \cdot T_{annu}(k-1) \\ &- \dot{n}_{g,annu} \ (k) \cdot c_{p,g,annu}(j,k-1) \cdot X_{annu}(j,k-1) \cdot T_{annu}(k-1) \\ &+ (\dot{n}_{g,core-annu} \ (k) + \dot{n}_{g,coreannux} \ (k)) \cdot c_{p,g,core}(j,k) \cdot X_{core}(j,k) \cdot T_{core}(k) \\ &- (\dot{n}_{annu-core} \ (k) + \dot{n}_{annucorex} \ (k)) \cdot c_{p,g,annu}(j,k) \cdot X_{annu}(j,k) \cdot T_{annu}(k)] \\ &+ \sum_{m=2}^{n_m} \sum_{i=1}^{n_i} [\dot{m}_{dwn} \ (i,k+1,m) \cdot c_{p,s}(m) \cdot T_{annu}(k+1) \\ &- \dot{m}_{dwn} \ (i,k,m) \cdot c_{p,s}(m) \cdot T_{annu}(k) \\ &+ (\dot{m}_{core-annu} \ (i,k,m) + \dot{m}_{coreannux} \ (i,k,m)) \cdot c_{p,s}(m) \cdot T_{annu}(k) \\ &- (\dot{m}_{annu-core} \ (i,k,m) + \dot{m}_{annucorex} \ (i,k,m)) \cdot c_{p,s}(m) \cdot T_{annu}(k) \\ &- (\dot{m}_{annu-core} \ (i,k,m) + \dot{m}_{annucorex} \ (i,k,m)) \cdot c_{p,s}(m) \cdot T_{core}(k)] \\ &- \alpha_{uube} \cdot A_{tube} \cdot (T_{annu}(k) - T_{uubl}) \end{aligned}$$

All equations are of first order. If they contain 4^{th} order radiative parts, these are linearized, to solve the system as a set of linear equations by LU-decomposition, taken from [130]. Core and annular cells were assembled in sequence arrays: $T(k) = T_{core}(k)$ $T(k+n_k) = T_{annu}(k)$

and the set of equations can be written as follows:

$$A(2n_k, 2n_k) \cdot T(2n_k) = b(2n_k)$$
(C.18)

The considered values are indicated as crosses in the matrix:

Bibliography

- ABANADES, J. C., ANTHONY, E. J., WANG, J., AND OAKEY, J. E. Fluidized bed combustion systems integrating CO₂ capture with CaO. *Environ. Sci. Technol.* 39, 8 (2005), 2861–2866.
- [2] ABU EL-RUB, Z., BRAMER, E., AND BREM, G. Experimental comparison of biomass chars with other catalysts for tar reduction. *Fuel* 87, 10–11 (2008), 2243–2252.
- [3] ABU EL-RUB, Z., BRAMER, E. A., AND BREM, G. Review of catalysts for tar elimination in biomass gasification processes. *Ind. Eng. Chem. Res.* 43, 22 (2004), 6911–6919.
- [4] Advanced Fuel Research, Inc. Functional-Group, Depolymerization, Vaporization, Cross-linking Model. http://www.afrinc.com/products/fgdvc/default.htm.
- [5] ANTAL JR, M. J., ALLEN, S. G., SCHULMAN, D., XU, X., AND DIVILIO, R. J. Biomass gasification in supercritical water. *Ind. Eng. Chem. Res.* 39, 11 (2000), 4040–4053.
- [6] ANTTIKOSKI, T. Circulating fluidized bed gasifier offers possibility for biomass and waste utilization and for substitution of natural gas by syngas from coal gasification. In *IChemI Conference "Gasification: the clean choice for carbon management"* (Noordwijk, the Netherlands, 2002).
- [7] BAIN, R. An overview of biomass gasification. In *AIChE Spring National Meeting, Conference Proceedings* (2004), pp. 375–381.
- [8] BARTELS, M. Agglomeration in fluidized beds: detection and counteraction. PhD thesis, Delft University of Technology, Delft, the Netherlands, 2008.
- [9] BARTELS, M., LIN, W., NIJENHUIS, J., KAPTEIJN, F., AND VAN OMMEN, J. R. Agglomeration in fluidized beds at high temperatures: Mechanisms, detection and prevention. *Prog Energ Combust* 34, 5 (2008), 633–666.
- [10] BARTH, W. Berechnungen und auslegung von zyklonabscheidern aufgrund neuerer untersuchungen. *Brennstoff, Waerme, Kraft 8*, 1 (1956), 1–9.

- [11] BASU, P. Combustion and Gasification in Fluidized Beds. CRC Press, 2006.
- [12] BEENACKERS, A. A. C. M., AND VAN SWAAIJ, W. P. M. Gasification of biomass, a state of the art review (keynote paper). In *Thermochemical Processing of Biomass* (1984), A. V. Bridgwater, Ed., Butterworths, pp. 91– 136.
- BERGMAN, P. C., VAN PAASEN, S. V., AND BOERRIGTER, H. The novel "OLGA" technology for complete tar removal from biomass producer gas. In *Pyrolysis and Gasification of Biomass and Waste, Expert Meeting* (Strasbourg, France, 30 September – 1 October 2002).
- [14] BIZON, K., DE JONG, W., SIEDLECKI, M., AND CHIRONE, R. Investigation of agglomeration phenomena during fluidized bed combustion of biomass in a 1 MW_{th} shallow bed boiler. In 32nd Meeting of the Italian Section of The Combustion Institute - Combustion Colloquia (Napoli, Italy, April 26–28, 2009), R. Ragucci, Ed., University of Naples Federico II, The Italian Section of The Combustion Institute, pp. V–8.
- [15] BLAMEY, J., ANTHONY, E., WANG, J., AND FENNELL, P. The calcium looping cycle for large-scale CO₂ capture. *Prog Energ Combust* 36, 2 (2010), 260–279.
- [16] BOERRIGTER, H., DEN UIL, H., AND CALIS, H.-P. Green diesel from biomass via Fischer-Tropsch synthesis: New insights in gas cleaning and process design. In *Pyrolysis and gasification of biomass and waste* (2003), A. Bridgwater, Ed., CPL Press, pp. 385–394.
- [17] BOERRIGTER, H., VAN PAASEN, S., AND BERGMAN, P. Status update of OLGA technology development. Tech. Rep. ECN-RX-03-063, ECN, November 2003.
- [18] BP. BP statistical review of world energy. Tech. rep., June 2011. http://www.bp.com/statisticalreview.
- [19] BRAGE, C., YU, Q., CHEN, G., AND SJÖSTRÖM, K. Use of amino phase adsorbent for biomass tar sampling and separation. *Fuel 76* (1997), 137– 142.
- [20] BRAGE, C., YU, Q., CHEN, G., AND SJÖSTRÖM, K. Tar evolution profiles obtained from gasification of biomass and coal. *Biomass Bioenerg* 18, 1 (2000), 87–91.
- [21] BRIDGWATER, A. V. The technical and economic feasibility of biomass gasification for power generation. *Fuel* 74, 5 (1995), 631–653.
- [22] BRIDGWATER, A. V. Renewable fuels and chemicals by thermal processing of biomass. *Chem. Eng. J.* 91, 2–3 (2003), 87–102.

- [23] Encyclopædia Britannica. http://www.britannica.com.
- [24] CAMPOY, M., GÓMEZ-BAREA, A., VIDAL, F. B., AND OLLERO, P. Air-steam gasification of biomass in a fluidised bed: Process optimisation by enriched air. *Fuel Process. Technol.* 90, 5 (2009), 677–685.
- [25] CARPENTIERI, M., CORTI, A., AND LOMBARDI, L. Life cycle assessment (LCA) of an integrated biomass gasification combined cycle (IBGCC) with CO₂ removal. *Energy Conversion and Management* 46, 11-12 (2005), 1790– 1808.
- [26] CIEMAT. BIORAISE Geographic Information System (GIS) tool for biomass resources assessment in Southern Europe. http://bioraise.ciemat.es/bioraise/intro.aspx.
- [27] CIFERNO, J., AND MARANO, J. Benchmarking biomass gasification technologies for fuels, chemicals and hydrogen production. Tech. rep., DOE NETL, 2002.
- [28] CLEETON, J., BOHN, C., MLLER, C., DENNIS, J., AND SCOTT, S. Clean hydrogen production and electricity from coal via chemical looping: Identifying a suitable operating regime. *Int. J. Hydrogen Energ* 34, 1 (2009), 1–12.
- [29] CONSTANTINOU, D. A., FIERRO, J. L. G., AND EFSTATHIOU, A. M. The phenol steam reforming reaction toward H₂ production on natural calcite. *Appl. Catal.*, *B* (2009).
- [30] CONSTANTINOU, D. A., FIERRO, J. L. G., AND EFSTATHIOU, A. M. A comparative study of the steam reforming of phenol towards H₂ production over natural calcite, dolomite and olivine materials. *Appl. Catal.*, B 95, 3–4 (2010), 255–269.
- [31] CORELLA, J., CABALLERO, M. A., AZNAR, M.-P., AND BRAGE, C. Two advanced models for the kinetics of the variation of the tar composition in its catalytic elimination in biomass gasification. *Ind. Eng. Chem. Res.* 42, 13 (2003), 3001–3011.
- [32] CORELLA, J., AND SANZ, A. Modeling circulating fluidized bed biomass gasifiers. a pseudo-rigorous model for stationary state. *Fuel Process. Technol. 86*, 9 (2005), 1021–1053.
- [33] CORELLA, J., TOLEDO, J., AND MOLINA, G. Biomass gasification with pure steam in fluidised bed: 12 variables that affect the effectiveness of the biomass gasifier. *Int. J. Oil, Gas and Coal Technology 1*, 1–2 (2008), 194– 207.

- [34] CORELLA, J., TOLEDO, J. M., AND MOLINA, G. Calculation of the conditions to get less than 2 g tar/ m_n^3 in a fluidized bed biomass gasifier. *Fuel Process. Technol.* 87 (2006), 841–846.
- [35] CRAIG, K., AND MANN, M. Cost and performance analysis of biomassbased integrated gasification combined-cycle (BIGCC) power systems. Tech. rep., NREL, 1996.
- [36] CSFMB [®] / CeSFaMB TM. Comprehensive Simulator of Fluidized and Moving Beds. http://www.csfmb.com.
- [37] CUI, H., TURN, S. Q., KEFFER, V., EVANS, D., TRAN, T., AND FOLEY, M. Contaminant estimates and removal in product gas from biomass steam gasification. *Energ Fuel 24*, 2 (2010), 1222–1233.
- [38] CURRAN, G. P., FINK, C. E., AND GORIN, E. CO₂ Acceptor Gasification Process. 1967, ch. 10, pp. 141–165.
- [39] CZERNIK, S., AND BRIDGWATER, A. V. Overview of applications of biomass fast pyrolysis oil. *Energ Fuel 18*, 2 (2004), 590–598.
- [40] DAYTON, D. Review of the literature on catalytic biomass tar destruction. Tech. Rep. TP-510-32815, NREL, 2002.
- [41] DE JONG, W. *Nitrogen compounds in pressurised fluidised bed gasification of biomass and fossil fuels.* PhD thesis, Delft University of Technology, Delft, the Netherlands, 2005.
- [42] DE JONG, W., PIRONE, A., AND WÓJTOWICZ, M. Pyrolysis of miscanthus giganteus and wood pellets: TG-FTIR analysis and reaction kinetics. *Fuel 82*, 9 (2003), 1139–1147.
- [43] DE SOUZA-SANTOS, M. Comprehensive simulator (CSFMB) applied to circulating fluidized bed boilers and gasifiers. *Open Chem. Eng. J. 2* (2008), 106–118.
- [44] DE SOUZA-SANTOS, M. Solid Fuels Combustion and Gasification: Modeling, Simulation, and Equipment Operations, 2nd ed. CRC, March 2010.
- [45] DELGADO, J., AND AZNAR, M. Biomass gasification with steam in fluidized bed: Effectiveness of CaO, MgO, and CaO-MgO for hot raw gas cleaning. *Ind. Eng. Chem. Res.* 36 (1997), 1535–1543.
- [46] DELGADO, J., AZNAR, M., AND CORELLA, J. Calcined dolomite, magnesite, and calcite for cleaning hot gas from a fluidized bed biomass gasifier with steam: Life and usefulness. *Ind. Eng. Chem. Res.* 35 (1996), 3637–3643.
- [47] DEMIRBAS, A., Ed. *Biofuels: Securing the Planet's Future Energy Needs.* Springer London, 2009.

- [48] DENNIS, J. S., AND SCOTT, S. A. In situ gasification of a lignite coal and CO₂ separation using chemical looping with a Cu-based oxygen carrier. *Fuel* 89, 7 (2010), 1623–1640.
- [49] DEVI, L., PTASINSKI, K. J., AND JANSSEN, F. J. A review of the primary measures for tar elimination in biomass gasification processes. *Biomass Bioenerg* 24 (2003), 125–140.
- [50] DEVI, L., PTASINSKI, K. J., AND JANSSEN, F. J. Pretreated olivine as tar removal catalyst for biomass gasifiers: investigation using naphthalene as model biomass tar. *Fuel Process. Technol. 86* (2005), 707–730.
- [51] DEVI, L., PTASINSKI, K. J., JANSSEN, F. J., VAN PAASEN, S. V., BERGMAN, P. C., AND KIEL, J. H. Catalytic decomposition of biomass tars: use of dolomite and untreated olivine. *Renew Energ* 30 (2005), 565–57.
- [52] DRYER, F., AND GLASSMAN, I. High-temperature oxidation of CO and CH₄. 14th Symposium (International) on Combustion, 1 (1973), 987–1003. Pittsburgh, PA, USA.
- [53] DUFOUR, A., CELZARD, A., FIERRO, V., MARTIN, E., BROUST, F., AND ZOULALIAN, A. Catalytic decomposition of methane over a wood char concurrently activated by a pyrolysis gas. *Appl. Catal., A 346*, 1-2 (2008), 164–173.
- [54] ECN. BIODAT Biomass Database. http://www.biodat.eu.
- [55] ECN. Phyllis, database for biomass and waste. http://www.ecn.nl/phyllis.
- [56] ERGUDENLER, A., AND GHALY, A. Agglomeration of silica sand in a fluidized bed gasifier operating on wheat straw. *Biomass Bioenerg 4*, 2 (1993), 135–147.
- [57] Eurostat. Country profiles. http://epp.eurostat.ec.europa.eu/portal/page/portal/eurostat/home/.
- [58] EUROPEAN COMMISSION. Directive 2001/77/EC of the European Parliament and of the Council, September 2001. The directive of 27 September 2001 on the promotion of electricity produced from renewable energy sources in the internal electricity market, http://eurlex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32001L0077:EN:NOT.
- [59] Fischer-Tropsch Archive. http://www.fischer-tropsch.org.
- [60] FRANCO, C., PINTO, F., GULYURTLU, I., AND CABRITA, I. The study of reactions influencing the biomass steam gasification process. *Fuel 82* (2003), 835–842.

- [61] FRYDA, L., PANOPOULOS, K., AND KAKARAS, E. Agglomeration in fluidised bed gasification of biomass. *Powder Technol. 181* (2008), 307–320.
- [62] GADHE, J. B., AND GUPTA, R. B. Hydrogen production by methanol reforming in supercritical water: Catalysis by in-situ-generated copper nanoparticles. *Int. J. Hydrogen Energ 32*, 13 (2007), 2374–2381.
- [63] GIL, J., AZNAR, M. P., CABALLERO, M. A., FRANCES, E., AND CORELLA, J. Biomass gasification in fluidized bed at pilot scale with steam-oxygen mixtures. product distribution for very different operating conditions. *Energ Fuel 11* (1997), 1109–1118.
- [64] GLAZER, M. P., KHAN, N. A., DE JONG, W., SPLIETHOFF, H., SCHURMANN, H., AND MONKHOUSE, P. Alkali metals in circulating fluidized bed combustion of biomass and coal: Measurements and chemical equilibrium analysis. *Energ Fuel 19*, 5 (Sept. 2005), 1889–1897.
- [65] GLUCKMAN, M., YERUSHALMI, J., AND SQUIRES, A. Defluidization characteristics of sticky materials on agglomerating bed. In *Fluidization technology, vol. 2* (1976), D. Keairns, Ed., vol. 2, Hemisphere Pub. Corp., pp. 395– 422.
- [66] GOLDEMBERG, J., Ed. World Energy Assessment: Energy and the Challenge of Sustainability. UNDP, 2000.
- [67] GÓMEZ-BAREA, A., AND LECKNER, B. Modeling of biomass gasification in fluidized bed. *Prog Energ Combust* 36, 4 (2010), 444–509.
- [68] GOOSENS, F. Investigation of the fate of tars and non-condensable gaseous compounds by means of biomass pyrolysis experiments in a heated grid reactor BSc thesis report Delft University of Technology, Delft, the Netherlands, 2009.
- [69] GRÄBNER, M., OGRISECK, S., AND MEYER, B. Numerical simulation of coal gasification at circulating fluidised bed conditions. *Fuel Process. Technol. 88*, 10 (2007), 948–958.
- [70] GUPTA, H., IYER, M., SAKADJIAN, B., AND FAN, L.-S. Enhanced hydrogen production integrated with CO₂ separation in a single-stage reactor. Tech. rep., Ohio State University, Columbus, OH, USA, March 2005.
- [71] GUPTA, R., Ed. *Hydrogen fuel Production, Transport and Storage.* CRC Press, Boca Raton, FL, USA, 2009.
- [72] HAMEL, S., AND KRUMM, W. Mathematical modelling and simulation of bubbling fluidised bed gasifiers. *Powder Technol. 120*, 1-2 (2001), 105–112.

- [73] HAMELINCK, C. N., FAAIJ, A. P., DEN UIL, H., AND BOERRIGTER, H. Production of FT transportation fuels from biomass; technical options, process analysis and optimisation, and development potential. *Energy* 29, 11 (2004), 1743–1771.
- [74] HAMELINCK, C. N., VAN HOOIJDONK, G., AND FAAIJ, A. P. Ethanol from lignocellulosic biomass: techno-economic performance in short-, middle- and long-term. *Biomass Bioenerg 28*, 4 (2005), 384–410.
- [75] HANNES, J. Mathematical Modelling of Circulating Fluidized Bed Combustion. PhD thesis, Delft University of Technology, Delft, The Netherlands, 1996.
- [76] HANPING, C., BIN, L., HAIPING, Y., GUOLAI, Y., AND SHIHONG, Z. Experimental investigation of biomass gasification in a fluidized bed reactor. *Energ Fuel 22* (2008), 3493–3498.
- [77] HEIN, D., AND KARL, J. Conversion of biomass to heat and electricity, vol. 3: Energy Technologies; subvolume C of Landolt-Börnstein numerical data and functional relationships in science and technology. New series, group 8: Advanced Materials and Technologies. Springer-Verlag, 2006, ch. 5.2, pp. 374–413.
- [78] HERGUIDO, J., CORELLA, J., AND GONZALEZ-SAIZ, J. Steam gasification of lignocellulosic residues in a fluidized bed at a small pilot scale. effect of the type of feedstock. *Ind. Eng. Chem. Res.* 31 (1992), 1274–1282.
- [79] HIGMAN, C., AND VAN DER BURGT, M. *Gasification*, 2nd ed. Gulf Professional Publishing, 2008.
- [80] HOFBAUER, H., RAUCH, R., BOSCH, K., KOCH, R., AND AICHERNIG, C. Biomass CHP plant Gussing – a success story. In *Pyrolysis and Gasification* of Biomass and Waste, Expert Meeting (Strasbourg, France, 30 September – 1 October 2002).
- [81] Holzvergaser. http://www.holzvergaser.org.
- [82] HOWARD, J., WILLIAMS, G., AND FINE, D. Kinetics of carbon monoxide oxidation in postflame gases. 14th Symposium (International) on Combustion, 1 (1973), 975–986. Pittsburgh, PA, USA.
- [83] HUBBERT, M. K. Energy from fossil fuels. Science 109, 2823 (1949), 103– 109.
- [84] IEA. Bioenergy Task 32. http://www.ieabcc.nl.
- [85] JENNEN, T. Mathematische Modellierung der Vergasung von Biomasse in dem System Zirkulierender Wirbelschichtvergaser / Gasmotor. PhD thesis, Dortmund University, Dortmund, Germany, 2000.

- [86] JENNEN, T., HILLER, R., KNEKE, D., AND WEINSPACH, P.-M. Modeling of gasification of wood in a circulating fluidized bed. *Chem. Eng. Technol.* 22, 10 (1999), 822–826.
- [87] JOHANSSON, E. Swedish tests of otto and diesel engines operated on producer gas. Tech. rep., National Machinery Testing Institute, Uppsala, Sweden, 1980.
- [88] JONES, W., AND LINDSTEDT, R. Global reaction schemes for hydrocarbon combustion. *Combust. Flame* 73, 3 (1988), 233–249.
- [89] KARELLAS, S., KARL, J., AND KAKARAS, E. An innovative biomass gasification process and its coupling with microturbine and fuel cell systems. *Energy 33*, 2 (2008), 284–291. 19th International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impactof Energy Systems – ECOS 2006.
- [90] KERSTEN, S. R. *Biomass gasification in circulating fluidized beds.* PhD thesis, Universiteit Twente, Enschede, the Netherlands, 2002.
- [91] KHAN, A. *Combustion and co-combustion of biomass in a bubbling fluidized bed boiler*. PhD thesis, Delft University of Technology, Delft, the Netherlands, 2007.
- [92] KHAN, A., DE JONG, W., JANSENS, P., AND SPLIETHOFF, H. Biomass combustion in fluidized bed boilers: Potential problems and remedies. *Fuel Process. Technol. 90*, 1 (2009), 21–50.
- [93] KHAN, A. A., AHO, M., DE JONG, W., VAINIKKA, P., JANSENS, P. J., AND SPLIETHOFF, H. Scale-up study on combustibility and emission formation with two biomass fuels (B quality wood and pepper plant residue) under BFB conditions. *Biomass Bioenerg* 32, 12 (2008), 1311–1321.
- [94] KIEL, J. Biomass co-firing in high percentages: opportunities in conventional and advanced coalfired plants, November 2008.
- [95] KINOSHITA, C. M., WANG, Y., AND ZHOU, J. Tar formation under different biomass gasification conditions. *J. Anal. Appl. Pyrolysis* 29, 2 (1994), 169– 181.
- [96] KNOEF, H., Ed. Handbook Biomass Gasification. BTG, 2005.
- [97] KNOEF, H. BTG biomass gasification, April 2008. http://www.btgworld.com/index.php?id=20&rid=8&r=rd.
- [98] KOLBITSCH, P., PRÖLL, T., BOLHAR-NORDENKAMPF, J., AND HOFBAUER, H. Operating experience with chemical looping combustion in a 120 kW dual circulating fluidized bed (DCFB) unit. *Energy Procedia* 1, 1 (2009),

1465–1472. Greenhouse Gas Control Technologies 9, Proceedings of the 9th International Conference on Greenhouse Gas Control Technologies (GHGT-9), 16–20 November 2008, Washington DC, USA.

- [99] KOLJONEN, J., KURKELA, E., AND WILEN, C. Peat-based HTW-plant at Oulu. *Bioresour. Technol.* 46, 1-2 (1993), 95–101.
- [100] KOPPATZ, S., PFEIFER, C., RAUCH, R., HOFBAUER, H., MARQUARD-MOELLENSTEDT, T., AND SPECHT, M. H₂ rich product gas by steam gasification of biomass with in situ CO₂ absorption in a dual fluidized bed system of 8 MW fuel input. *Fuel Process. Technol.* 90, 7–8 (2009), 914–921.
- [101] KUHN, J. N., ZHAO, Z., FELIX, L. G., SLIMANE, R. B., CHOI, C. W., AND OZKAN, U. S. Olivine catalysts for methane- and tar-steam reforming. *Appl. Catal.*, B 81, 1-2 (2008), 14–26.
- [102] KUNII, D., AND LEVENSPIEL, O. *Fluidization Engineering*. Butterworth-Heinemann, 1991.
- [103] KURKELA, E. Fluidized bed gasification of biomass for syngas BTL in forest industry. In *Proceedings of Bioenergy NoE Final seminar* (Brussels, Belguim, 2–3 November 2009).
- [104] LAMBERTZ, J., BRÜNGEL, N., RUDDECK, W., AND SCHRADER, R. Recent operational results of high-temperature Winkler and hydrogasification process. In Proceedings of the EPRI Conference on Coal Gasification Systems and Synthetic Fuels for Power Generation (1985), vol. 1.
- [105] LECKEL, D. Diesel production from Fischer-Tropsch: The past, the present, and new concepts. *Energ Fuel 23*, 5 (2009), 2342–2358.
- [106] LI, X. T., GRACE, J. R., LIM, C. J., WATKINSON, A. P., CHEN, H. P., AND KIM, J. R. Biomass gasification in a circulating fluidized bed. *Biomass Bioenerg* 26, 2 (2004), 171–193.
- [107] LIN, S.-Y., SUZUKI, Y., HATANO, H., AND HARADA, M. Developing an innovative method, HyPr-RING, to produce hydrogen from hydrocarbons. *Energy Convers. Manage.* 43, 9–12 (2002), 1283–1290.
- [108] LIN, W., DAM-JOHANSEN, K., AND FRANDSEN, F. Agglomeration in biofuel fired fluidized bed combustors. *Chem. Eng. J.* 96, 1–3 (2003), 171–185.
- [109] MACAK, J., AND MALECHA, J. Mathematical model for the gasification of coal under pressure. *Ind Eng Chem Process Des Dev* 17, 1 (1978), 92–98.
- [110] MÅNSON, H. VVBGC, personal communication, 2008.

- [111] MATSUMURA, Y., AND MINOWA, T. Fundamental design of a continuous biomass gasification process using a supercritical water fluidized bed. *Int. J. Hydrogen Energ* 29, 7 (2004), 701–707.
- [112] Merriam-Webster. Online Dictionary. http://www.merriamwebster.com/dictionary/.
- [113] MERRICK, D. Mathematical models of the thermal decomposition of coal: 1. the evolution of volatile matter. *Fuel 62*, 5 (1983), 534–539.
- [114] MILNE, T., EVANS, R., AND ABATZOGLOU, N. Biomass gasifier "tars": Their nature, formation, and conversion. Tech. Rep. NREL/TP-570-25357, NREL, Golden, CO, USA, November 1998.
- [115] MITANI, T., AND WILLIAMS, F. Studies of cellular flames in hydrogen oxygen—nitrogen mixtures. *Combust. Flame* 39, 2 (1980), 169–190.
- [116] NARVAEZ, I., ORIO, A., AZNAR, M., AND CORELLA, J. Biomass gasification with air in an atmospheric bubbling fluidized bed. effect of six operational variables on the quality of the produced raw gas. *Ind. Eng. Chem. Res.* 35, 7 (1996), 2110–2120.
- [117] NEEFT, J., KNOEF, H., AND ONAJI, P. Behaviour of tar in biomass gasification systems. tar related problems and their solutions. Tech. Rep. EWAB9919, Utrecht, the Netherlands, 1999.
- [118] NEEFT, J., KNOEF, H., ZIELKE, U., SJÖSTRÖM, K., HASLER, P., SIMELL, P., DORRINGTON, M., THOMAS, L., ABATZOGLOU, L., DEUTCH, S., GREIL, C., BUFFINGA, G., BRAGE, C., AND SUOMALAINEN, M. Guideline for sampling and analysis of tar and particles in biomass producer gases, version 3.3. Tech. rep., 2001.
- [119] NIEMINEN, M. Gasification of biomass and waste derived fuels for industrial applications. International Seminar on Gasification, Malmö - VTT presentation, October 2008.
- [120] NORDGREEN, T., LILIEDAHL, T., AND SJÖSTRÖM, K. Elemental iron as a tar breakdown catalyst in conjunction with atmospheric fluidized bed gasification of biomass: A thermodynamic study. *Energ Fuel 20* (2006), 890– 895.
- [121] OLOFSSON, I., NORDIN, A., AND SODERLIND, U. Initial review and evaluation of process technologies and systems suitable for cost-efficient medium-scale gasification for biomass to liquid fuels. Tech. Rep. ISSN 1653-0551 ETPC Report 05-02, University of Umea, Umeå, Sweden, 2005.
- [122] PADBAN, N. Air gasification of biomass. Investigation of product formation and problematic issues related to ammonia, tar and alkali. PhD thesis, Lund University, Lund, Sweden, 2000.

- [123] PATEL, J. Biomass gasification gas engine demonstration project. Smallwood: Creating Solutions for Using Small Trees, Sacramento, CA, USA – Carbona Corporation presentation, May 2004.
- [124] PFEIFER, C., PUCHNER, B., AND HOFBAUER, H. In-situ CO₂-absorption in a dual fluidized bed biomass steam gasifier to produce a hydrogen rich syngas. *Int J Chem React Eng* 5 (2007).
- [125] PFEIFER, C., PUCHNER, B., AND HOFBAUER, H. Comparison of dual fluidized bed steam gasification of biomass with and without selective transport of CO₂. *Chem. Eng. Sci.* 64, 23 (2009), 5073–5083.
- [126] PLASS, L., BEISSWENGER, H., LIENHARD, H., AND BIERBACH, H. Combustion / gasification in the Lurgi circulating fluid bed. In Proceedings of the EPRI Conference on Coal Gasification Systems and Synthetic Fuels for Power Generation (1985), vol. 1.
- [127] PLIETKER, B. Iron catalysis in organic chemistry: reactions and applications. Wiley-VCH, 2008.
- [128] POPULATION REFERENCE BUREAU. 2010 World population data sheet. Tech. rep., Washington DC, USA, 2010. http://www.prb.org/Publications/Datasheets/2010/2010wpds.aspx.
- [129] POWERCLEAN R, D&D THEMATIC NETWORK. Fossil fuel power generation state-of-the-art. Tech. rep., PowerClean, 2004.
- [130] PRESS, W., VETTERLING, W., TEUKOLSKY, S., AND FLANNERY, B. *Numerical Recipies in Fortran*, 2nd editon ed. Cambridge University Press, 1986.
- [131] PRETO, F. *Studies and Modelling of Athmospheric Fluidized Bed Combustion of Coal.* PhD thesis, Queen's University, Kingston, Canada, 1986.
- [132] PRINS, M. J., PTASINSKI, K. J., AND JANSSEN, F. J. More efficient biomass gasification via torrefaction. *Energy 31*, 15 (2006), 3458–3470.
- [133] RAPAGNÀ, S., GALLUCCI, K., MARCELLO, M. D., MATT, M., NACKEN, M., HEIDENREICH, S., AND FOSCOLO, P. U. Gas cleaning, gas conditioning and tar abatement by means of a catalytic filter candle in a biomass fluidizedbed gasifier. *Bioresour. Technol. 101*, 18 (2010), 7123–7130.
- [134] RAUCH, R., BOSCH, K., HOFBAUER, H., SWIERCZYNSKI, D., COURSON, C., AND KIENNEMANN, A. Comparison of different olivines for biomass steam gasification. In *Proceedings of the International Conference Science in Thermal and Chemical Biomass Conversion* (2006), A. Bridgwater and D. Boocock, Eds., vol. 1, CPL Press, pp. 799–809.

- [135] RENSFELT, E. Energy from biomass and wastes. In *Proceedings of I.G.T. conference* (Washington, DC, USA, August 1978).
- [136] RENSFELT, E. Other biomass gasification activities. ÅF BioRefinery Conference, Stockholm, Sweden – presentation, 16 November 2006.
- [137] ROLLINS, M., REARDON, L., NICHOLS, D., LEE, P., MOORE, M., CRIM, M., LUTTRELL, R., AND HUGHES, E. Economic evaluation of CO₂ sequestration technologies. Task 4, biomass gasification-based processing. Tech. Rep. DE-FC26-00NT40937, Tennessee Valley Authority, Chattanooga, TN, USA, 2002.
- [138] Roper, L.D. Future world energy. http://www.roperld.com/science/energy.htm.
- [139] ROSILLO-CALLE, F. Biomass energy an overview, vol. 3: Energy Technologies; subvolume C of Landolt-Börnstein numerical data and functional relationships in science and technology. New series, group 8: Advanced Materials and Technologies. Springer-Verlag, 2006, ch. 5.1, pp. 334–373.
- [140] SCHMIDT, J. H. Life cycle assessment of rapeseed oil and palm oil. Part 3: Life cycle inventory of rapeseed oil and palm oil. PhD thesis, Aalborg University, Aalborg, Denmark, 2007.
- [141] SEGATORI, L. Mathematical modelling of biomass gasification in a CFB reactor. Master's thesis, Delft University of Technology, Delft, the Netherlands, 2007.
- [142] SIEDLECKI, M. Own energy consumption data collection of a large detached house in Warsaw, Poland, 2011.
- [143] SIEDLECKI, M. Own energy consumption data collection of a small appartment in Amstelveen, the Netherlands, 2011.
- [144] SIEDLECKI, M., AND DE JONG, W. Biomass gasification as the first hot step in clean syngas production process gas quality optimization and primary tar reduction measures in a 100 kW thermal input steameoxygen blown CFB gasifier. *Biomass Bioenerg* 35 (2011), S40–62.
- [145] SIEDLECKI, M., NIEUWSTRATEN, R., SIMEONE, E., DE JONG, W., AND VERKOOIJEN, A. H. M. Effect of magnesite as bed material in a 100 kW_{th} steam-oxygen blown circulating fluidized-bed biomass gasifier on gas composition and tar formation. *Energ Fuel 23 (11)* (2009), 5643–5654.
- [146] SIEDLECKI, M., SIMEONE, E., DE JONG, W., AND VERKOOIJEN, A. Characterization of gaseous and condensable components in the product gas obtained during steam-oxygen gasification of biomass in a 100kW_{th} CFB gasifier. In *Proceedings of the* 15^{th} *European Biomass Conference & Exhibition* (Berlin, Germany, 2007).

- [147] SIEDLECKI, M., VAN DER NAT, K., SIMEONE, E., AND DE JONG, W. The first results of gas and solids characterization obtained during steam-oxygen gasification of biomass in a 100kW_{th} CFB gasifier. In World Renewable Energy Congress IX Book of Abstracts (Florence, Italy, 2006).
- [148] SILK, M., ACKIEWICZ, M., J., A., AND OGUNSOLA, O. Overview of Fundamentals of Synthetic Ultraclean Transportation Fuel Production. Oxford University Press, 2007, ch. 2, pp. 3–17.
- [149] SIMEONE, E., HÖLSKEN, E., NACKEN, M., HEIDENREICH, S., AND DE JONG, W. Study of the behaviour of a catalytic ceramic candle filter in a lab-scale unit at high temperatures. *Int J Chem React Eng 8*, A11 (2010).
- [150] SIMEONE, E., NACKEN, M., HAAG, W., HEIDENREICH, S., AND DE JONG, W. Filtration performance at high temperatures and analysis of ceramic filter elements during biomass gasification. *Biomass Bioenerg* 35 (2010), S87–104.
- [151] SIMEONE, E., SIEDLECKI, M., NACKEN, M., HEIDENREICH, S., AND DE JONG, W. High temperature gas filtration with ceramic candles and ashes characterisation during steam-oxygen blown gasification of biomass. *Fuel in press* (2011).
- [152] SIMS, R., SCHOCK, R., ADEGBULULGBE, A., J. FENHANN, I. K., MOOMAW, W., NIMIR, H., SCHLAMADINGER, B., TORRES-MARTÍNEZ, J., TURNER, C., UCHIYAMA, Y., VUORI, S., WAMUKONYA, N., AND ZHANG, X. 2007: Energy supply. In Climate Change 2007: Mitigation. Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA., 2007.
- [153] SIMS, R., TAYLOR, M., SADDLER, J., AND MABEE, W. From 1st to 2nd generation biofuel technologies. an overview of current industry and RD&D activities. Tech. rep., IEA Bioenergy, 2008.
- [154] SIQUEIRA, P. F., KARP, S. G., CARVALHO, J. C., STURM, W., RODRGUEZ-LEN, J. A., THOLOZAN, J.-L., SINGHANIA, R. R., PANDEY, A., AND SOC-COL, C. R. Production of bio-ethanol from soybean molasses by saccharomyces cerevisiae at laboratory, pilot and industrial scales. *Bioresour. Technol.* 99, 17 (2008), 8156–8163.
- [155] SPLIETHOFF, H. *Power generation from solid fuels*. Springer Berlin / Heidelberg, 2010.
- [156] STÅHL, K., AND NEERGAARD, M. IGCC power plant for biomass utilization, Värnamo, sweden. *Biomass Bioenerg* 15 (1998), 205–211.

- [157] TAMBOER, R. Fast pyrolysis of biomass in a heated wire mesh & FTIR laboratory setup. Master's thesis, Delft University of Technology, Delft, the Netherlands, 2007.
- [158] TEISLEV, B. Harboøre woodchips updraft gasifier and 1500 kW gas-engines operating at 32% power efficiency in CHP configuration. http://media.godashboard.com/gti/IEA/BWVgasifiersDOC.pdf.
- [159] TIJMENSEN, M. J. The production of Fischer Tropsch liquids and power through biomass gasification. Master's thesis, Utrecht University, Utrecht, the Netherlands, November 2000.
- [160] TIJMENSEN, M. J. A., FAAIJ, A. P. C., HAMELINCK, C. N., AND VAN HARDE-VELD, M. R. M. Exploration of the possibilities for production of Fischer Tropsch liquids and power via biomass gasification. *Biomass Bioenerg 23*, 2 (2002), 129–152.
- [161] TK Energi AS. http://www.tke.dk.
- [162] TOONSSEN, R., WOUDSTRA, N., AND VERKOOIJEN, A. H. Exergy analysis of hydrogen production plants based on biomass gasification. *Int. J. Hydrogen Energ* 33, 15 (2008), 4074–4082.
- [163] TURN, S., KINOSHITA, C., ZHANG, Z., ISHIMURA, D., AND ZHOU, J. An experimental investigation of hydrogen production from biomass gasification. *Int. J. Hydrogen Energ* 23, 8 (1998), 641–648.
- [164] VAN DEN AARSEN, F. G. *Fluidised Bed Wood Gasifier Performance and Modeling*. PhD thesis, Technische Hogeschool Twente, Enschede, the Netherlands, 1985.
- [165] VAN DEN BLEEK, C., BREM, G., GRUBOR, B., JOHNSSON, J., JONES, R., LANGER, V., AND VERWEYEN, N. Documentation of the IEA-AFBC model, version 1.1. Tech. rep., TNO, Apeldoorn, The Netherlands, 1990.
- [166] VAN DER DRIFT, A. Biomass gasification for second generation biofuels, August 2010. ECN-L–10-076.
- [167] VAN DER DRIFT, A., AND VAN DER MEIJDEN, C. Ways to increase the carbon conversion of a CFB gasifier. In *Proceedings of the 12th European Conference and Technology Exhibition on biomass for energy, industry and climate protection* (Amsterdam, the Netherlands, 2002).
- [168] VAN DER DRIFT, A., VAN DOORN, J., AND VERMEULEN, J. Ten residual biomass fuels for circulating fuidized-bed gasification. *Biomass Bioenerg* 20 (2001), 45–56.

- [169] VAN DER MEIJDEN, C., VAN DER DRIFT, A., AND VREUGDENHIL, B. Experimental results from the allothermal biomass gasifier "Milena". In *Proceedings of 15th European Biomass Conference & Exhibition* (Berlin, Germany, 2007).
- [170] VAN KREVELEN, D. *Coal: typology, chemistry, physics, constitution*, 3rd ed. Elsevier, 1993.
- [171] VAN PAASEN, S. Tar formation in a fluidised-bed gasifier. Tech. Rep. ECN-C–04-013, ECN, Petten, the Netherlands, March 2004.
- [172] VISSER, H. The influence of fuel composition on agglomeration behaviour in fluidised-bed combustion. Tech. Rep. ECN-C-04-054, ECN, Petten, the Netherlands, September 2004.
- [173] VUTHALURU, H., AND ZHANG, D. Remediation of ash problems in fluidised-bed combustors. *Fuel 80* (2001), 583–598.
- [174] WESTBROOK, C. K., AND DRYER, F. L. Chemical kinetic modeling of hydrocarbon combustion. *Prog Energ Combust 10*, 1 (1984), 1–57.
- [175] ZEVENHOVEN-ONDERWATER, M., BACKMAN, R., SKRIFVARS, B.-J., AND HUPA, M. The ash chemistry in fluidised bed gasification of biomass fuels. Part I: predicting the chemistry of melting ashes and ash-bed material interaction. *Fuel 80*, 10 (2001), 1489–1502.
- [176] ZUBERBÜHLER, U., SPECHT, M., AND BANDI, A. Gasification of biomass an overview on available technologies. In 1st European Summer School on Renewable Motor Fuels (August 2005).

Epilogue

Personal reflections and remarks

In the year 2002, while doing my so-called "First Assignment" (under the supervision of prof. dr. ir. A.H.M. Verkooijen by the way), I was convinced that I will never do a Ph.D. Finding an exciting assignment for the Master's thesis, graduating and going to work in a company – that was the idea at that time. At the end of the year 2003, in the final phase of my M.Sc thesis work I started to inquire if within the ET section there would be a possibility to become a *toegevoegde onderzoeker* ("added researcher"). In the year 2004, as of January 1st I started to fulfill a four-year contract as a Ph.D. candidate.

Nearly eight years later I can say that I do not regret any single day from this period. It absolutely does not mean that each day was a day of glory and victory, but often one learns the most from the defeats. As a matter of fact, I consider the time of the move of ET laboratory from the main 3mE building to the API (now P&E) building as an excellent training in the organizational and human-to-human interaction skills, although it caused the most delay in the experiments, and consequently in the finalization of the thesis. It is something you do not learn during any course, but managers, please, don't use this as an argument to force a laboratory to move!

After having browsed through this book you have probably found some more or less useful information, depending on your interests. There are some background information, some experimental data, some modeling studies. However, despite their usefulness for the people interested in this topic, occasionally I was wondering "what is the benefit of doing all this?", in a broader sense than simply obtaining an another degree. Luckily, I can conclude that this research can potentially be very useful, but it requires more than experiments and modeling. What do I exactly mean? Well, I'm quite convinced that if people in general will not change their consumptive habits, all the research done to push renewable energy forward will turn out to be useless. Therefore it is absolutely necessary to reduce the consumption of energy and other natural resources in the developed countries and show to the developing countries how to avoid making the same mistakes. Also the term "developed country" should receive a new meaning, indicating not a country where people can afford to buy things they will throw away the next day, and where traffic jams dominate the city life, but rather a country that can satisfy its daily needs without being dependent on oligopolized trade, thus matching the local demand to local supply. These are just few examples of some very complicated changes and challenges, and I would not believe that they are feasible if I would not come across people with a similar way of thinking. The time will tell how much we will be able to achieve – in joint efforts and individually.

Acknowledgements

During the work on the research presented in this thesis my path crossed with the paths of quite a number of wonderful people. From a simple "hi" in the corridor, through a short chat, through their contribution to this work either by doing work in the lab, in the workshop or behind the computer, or by giving guidance and critical but constructive feedback, to the ultimate case of giving the friendship – this really gave me wings and power to proceed! A few exceptions caused drag and irritation, but as an exception confirms the rule, thank you for this confirmation as well!

The completion of this work would not be possible without the excellent guidance by my promotors. Ad, thank you for asking difficult questions and giving critical remarks – starting from the experiments, through modeling, all the way even to the propositions – they were essential to maintain the positive gradient of the learning curve. I also appreciate our pleasant cooperation: the discussions may have been tough, but we always finished the meetings with a joke or a smile. Ad, heel hartelijk dank! Your official retirement ceremony in the Aula was a very special moment for me. Wiebren, "daily supervision" can be implemented in many different ways - the one you applied worked perfectly for me! I was very happy to be given the opportunity to continue the work on the CFB after graduating as an engineer in the first place, but the best of all was the fact that from the very beginning of the Chrisgas project you gave me a significant portion of responsibility and freedom to act in order to fulfill both the targets of the project and to fill the pages of this thesis. Your feedback on my work, and especially the modeling part, was invaluable. I also admired how you managed to keep your patience and constructive thinking in the situations where I would already had lost my temper ten times – this was a very good lesson, too! Wiebren, dank voor alles, diep uit het hart.

As a brain is nothing without a pair of hands, I really appreciate the help of the colleagues from the workshop, first ET, later P&E and DEMO, who worked on the gasification test rig. It is nor an easy nor a clean job, especially when dealing with the insulation material, or when removing the ashes from the filter, while the temperature on the top floor exceeds 35° C! Here a special "thank you" goes to Daniël van Baarle for his enthusiasm, flexibility and patience. You showed me that welding can be a real art – *Daan, bedankt!* Aad Vincenten, you somehow sensed my interest in the measurement, system and control issues, and gave

me a short but intensive course on PLC and SCADA programming. Thanks to this I was able to maintain and expand the instrumentation of the CFBG, but also assist other colleagues in these matters, which was a great thing to do. *Aad, bedankt*! A lot of practical skills, especially in the field of gas analysis, I learned from Duco Bosma. Our "off the record" conversations were often a great relief for the mind. *Duco, bedankt*!

I would also like to cordially acknowledge all other colleagues from ET, IRS, PE, ETh, FM and other departments at the TU, as well as my dear office mates from room 142: thank you for listening to my complains and for sharing the moments of joy and frustration. To all our project partners from the Chrisgas project, and especially these from Växjö, KTH, Bologna and Jülich: from my point of view we had a really nice cooperation, it was a great pleasure for me to work with you.

Of course I will not forget the "gasification team". Eleonora, I think we spent more time together breathing ashes, tar and insulation fibres than breathing the office air – *grazie*, *E*! Xiangmei, Martina, Malte – thanks for your cooperation, too. And to my students Raquel, Luca, Rob, Fabienne, Marcel, Kassa, Yaìr and Alex – your work is now a part of this book, thanks!

Ladies and gentlemen, this session is closed. It is time to move on now; let's see what the future will bring us.

Marcin

List of publications

Journal papers

M. Siedlecki, R. Nieuwstraten, E. Simeone, W. de Jong, and A. H. M. Verkooijen, "Effect of Magnesite as Bed Material in a 100 kW_{th} Steam-Oxygen Blown Circulating Fluidized-Bed Biomass Gasifier on Gas Composition and Tar Formation", *Energy & Fuels* **2009**, 23, 5643–5654

Ph. Hofmann, K.D. Panopoulos, P.V. Aravind, M. Siedlecki, A. Schweiger, J. Karl, J.P. Ouweltjes, E. Kakaras, "Operation of Solid Oxide Fuel Cell on Biomass Product Gas with Tar Levels >10 g Nm⁻³", *International Journal of Hydrogen Energy* **2009**, 34, 9203-9212

Malte Bartels, John Nijenhuis, Jasper Lensselink, Marcin Siedlecki, Wiebren de Jong, Freek Kapteijn, and J. Ruud van Ommen, "Detecting and Counteracting Agglomeration in Fluidized Bed Biomass Combustion", *Energy & Fuels* **2009**, 23, 157–169

Marcin Siedlecki, Wiebren de Jong and Adrian H.M. Verkooijen, "Fluidized Bed Gasification as a Mature and Reliable Technology for the Production of Bio-Syngas and Applied in the Production of Liquid Transportation Fuels–a Review", *Energies* **2011**, 4, 389–434

M. Siedlecki, W. de Jong, "Biomass Gasification as the First Hot Step in Clean Syngas Production Process – Gas Quality Optimization and Primary Tar Reduction Measures in a 100 kW Thermal Input Steam-Oxygen Blown CFB Gasifier", *Biomass and Bioenergy* **2011**, 35, S40–S62

E. Simeone, M. Siedlecki, M. Nacken, S. Heidenreich, W. de Jong, "High Temperature Gas Filtration with Ceramic Candles and Ashes Characterisation during Steam-Oxygen Blown Gasification of Biomass", *Fuel*, in press

Conference papers

K.V. van der Nat, M. Siedlecki, W. de Jong, N. Woudstra and A.H.M. Verkooijen, "Particle Size Characterization of Particles Present in the Producer Gas of a Steam and Oxygen Blown Biomass Circulating Fluidized Bed Gasifier", 14th European Biomass Conference Biomass for Energy, Industry and Climate Protection, 2005, Paris, France

M. Siedlecki, K. van der Nat, E. Simeone, W. de Jong, "The First Results of Gas and Solids Characterization Obtained During Steam-Oxygen Gasification of Biomass in a 100 kW_{th} CFB Gasifier", World Renewable Energy Congress IX, 2006, Florence, Italy

W. de Jong, K.V. van der Nat, E. Simeone und M. Siedlecki, "Charakterisierung von Produktgas Aus Einem 100 kW_{th} Biomassen Gefeuerten Dampf/Sauerstoff Zirkulierenden Wirbelschichtvergaser", DGMK-Fachbereichstagung Energetische Nutzung von Biomasse, 2006, Velen, Germany

M. Siedlecki, E. Simeone, W. de Jong, A.H.M. Verkooijen, "Characterization of Gaseous and Condensable Components in the Product Gas Obtained During Steam-Oxygen Gasification of Biomass in a 100 kW_{th} CFB Gasifier", 15th European Biomass Conference and Exhibition from Research to Market Deployment, 2007, Berlin, Germany

K.D. Bizon, W. de Jong, M. Siedlecki, R. Chirone, "Investigation of Agglomeration Phenomena During Fluidized Bed Combustion of Biomass in a 1 MW_{th} Shallow Bed Boiler", 32^{nd} Meeting of the Italian Section of The Combustion Institute - Combustion Colloquia, 2009, Napoli, Italy

E. Simeone, M. Siedecki, M. Nacken, S. Heidenreich, W. de Jong, "High Temperature Gas Filtration and Particle Characterisation During Steam-Oxygen Blown Gasification of Biomass", 8th International Symposium on Gas Cleaning at High Temperatures, 2010, Taiyuan, China

Marcin Siedlecki, Alexandros Litinas, Wiebren de Jong, "Biomass Gasification For Syngas Generation in a 100 kW_{th} Steam-Oxygen Blown CFB Gasifier – Gas Quality Optimization and Tar Reduction", 18^{th} European Biomass Conference and Exhibition from Research to Industry and Markets, 2010, Lyon, France

Curriculum Vitae

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