THE CHEMISTRY AND TECHNOLOGY OF FURFURAL PRODUCTION IN MODERN LIGNOCELLULOSE-FEEDSTOCK BIOREFINERIES

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Furfural, the sleeping beauty

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The Chemistry and Technology of Furfural Production in Modern Lignocellulose-Feedstock Biorefineries

Proefschrift

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- Noodles, what have you been doing all these years?

- Been going to bed early...

Sergio Leone, Once upon a time in America

to my dear

family

friends

Laura

in the order they prefer

Getting to the end of this 4+ years experience gives conflicting feelings, and this little piece of work is not the only thing I am left with after leaving Delft. I'll take with me a trunk full of people, places, and feelings I will never forget.

The people I shared this time with made it special, and for this reason I would like to thank them all.

Special thanks to Wiebren, who allowed all this to happen in the first place. Wiebren, I will always be immensely grateful to you for this great opportunity, for the fair mix of independence and responsibility you gave me, for encouraging me to a more critical scientific attitude, and for trusting my work. Thank you to my promotor, Ad Verkooijen, a real Prof.. Thank you Henk, a cheerful man and a special colleague who introduced me to the fascinating world of furfural; who left us unexpectedly for a sudden and unfortunate chance.

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Grazie infine alla mia famiglia, ai parenti, agli amici, e a tutte le persone che ho lasciato in Italia nell'unico posto che possa chiamare casa.

Gianluca

SUMMARY

This dissertation deals with biorefinery technology development, *i.e.* with the development of sustainable industrial methods aimed at the production of chemicals, fuels, heat and power from lignocellulosic biomass. This work is particularly focused on the production of furfural from hemicellulose-derived pentoses.

The possibility of producing materials, chemicals, and fuels from biomass has a long history. Unfortunately fossil resources, in particular oil, have dominated last century both in the chemical and energy sectors due to their enormous availability at relatively low cost. Nowadays, bio-based chemicals and fuels are gaining a much more favorable competitive position, not only by virtue of high oil prices and the forecasts on their future availability, but also because of the increasing public environmental awareness.

Although the use of biomass for energy, and in particular for biofuels production, has been greatly challenged recently in terms of real benefits to the environment, the technological advances in the biorefinery field offer many reasons to believe that, in the near future, biomass could be definitely the sustainable alternative to fossil resources in the chemical and also fuels industries. By a careful review of the scientific literature, and observing the recent research trends, it is noticeable that a relatively short list of high-potential biomass-derived building blocks has the potential for replacing or substituting fossil resources in nearly every industrial field.

The broad family of furan compounds represents certainly an intriguing selection of biomass derivatives for many industrial applications. Furfural is nowadays the only starting material for the production of nearly all the furan compounds. Furfural industry exists since almost a century, but it is nowadays facing a major renovation challenge in order to meet the global trend toward bio-based products, and the consequent increased demand for furfural and its derivatives.

The majority of current furfural production is still based on more or less modified versions of the original Quaker Oats process (1921). For reasons that can be related to their limited technological evolution, the production processes in use today generally suffer from low yields (around 50%), besides significant economical and environmental concerns. All these reasons hindered the expansion and modernization of the furfural industry below its actual potential. A profound technological development is a priority in order to upgrade furfural to a large-volume bio-based commodity. The integrated production of furfural within modern biorefineries is a big opportunity, and it will most probably represent the next cornerstone in the development of furfural industry.

In Chapter 1 the opportunities offered by the modern biorefinery in the broader context, and the importance of furan compounds are highlighted. In this context the enormous potential of furfural and its derivatives, both in the chemical and energy sector, is discussed. Recent advances in furfural technology are summarized, both regarding furfural synthesis and applications, eventually stating the motivation behind this dissertation, and the main achievements herein contained.

In Chapter 2 the experimental methods used in this work are carefully described. A new lab-scale titanium reactor was built in order to investigate several aspects related to the furfural formation and related reactions, and to enable liquid phase reactions under a relatively broad range of pressure, temperature and pH conditions. This test rig has allowed most of the experimental work behind this dissertation, and thus it is thoroughly described in this chapter in all the relevant aspects typical of chemical reactor engineering. The analytical and experimental methods employed in the several experimental campaigns described in this dissertation are also extensively described.

Chapter 3 concerns the reaction kinetics of furfural formation. Even considering the number of relevant works on the topic of furfural formation in acidic media, a general expression for the reaction kinetics, its dependence on the acid nature and concentration, and the potential effect of other species present in solution, is yet to be defined. Results of reaction kinetics studies related to furfural formation from xylose, xylose side reactions, and furfural destruction in acidic aqueous media are thus studied and reported.

In Chapter 4 some particular aspects of the chemistry of xylose reaction into furfural are addressed with the aim to clarify the reaction mechanism and to define new green catalytic pathways for its production. Specifically the reduction of mineral acids utilization is addressed by the introduction of alternative catalysts. In this sense the effect of chloride salts in dilute acidic solutions at temperatures between 170 and 200 °C is described. Results indicate the Cl^- ions to promote the formation of the 1,2-enediol from the acyclic form of xylose, and thus the subsequent acid catalyzed dehydration to furfural. For this reason the presence of Cl^- ions led to significant improvements with respect to the H2SO4 base case. The addition of NaCl to a 50mM HCl aqueous solution (0.18 wt%) allows to attain 90% selectivity to furfural. Among the salts tested FeCl3 shows very interesting preliminary results, producing exceptionally high xylose reaction rates.

Starting from the results discussed in chapter 4 on the effects of Cl^- ions on furfural formation in aqueous acid solution, the general effect of different halides is addressed in Chapter 5. Experimental results show the halides to influence at least two distinct steps in the reaction leading from xylose to furfural under acidic conditions, via different mechanisms. The nucleophilicity of the halides appears to be critical for the dehydration, but not for the initial enolization reaction. By combining different halides synergic effects become evident resulting in very high selectivities and furfural yields.

In Chapter 6 the combined production of hemicellulose-derived carbohydrates and an upgraded solid residue from wheat straw using a dilute-acid pretreatment at mild temperature is described. Dilute aqueous HCl solutions were studied at temperatures of 100 and 120 °C, and they were compared to dilute FeCl3 under the same conditions. Comparable yields of soluble sugars and acetic acid were obtained, affording an almost complete removal of pentoses when using 200mM aqueous solutions at 120 °C. The solid residues of pretreatment were characterized showing a preserved crystallinity of the cellulose, and a almost complete removal of ash forming matter other than Si. Results showed upgraded characteristic of the residues for thermal conversion applications compared to the untreated wheat straw.

Chapter 7 deals with the industrial processes for the production of furfural, describing in particular an innovative process patented by Delft University of Technology and based on the results contained in this dissertation. As already mentioned, the integrated production of furfural within modern biorefineries will most probably represent the next cornerstone in the development of furfural industry. The innovative process concept described in this chapter is aimed at an economically viable and environmentally sound furfural production, with reduced energy and chemicals consumption. The evaluation of process economics shows encouraging results compared to existing processes, making this concept economically attractive.

Finally, in Chapter 8 main concluding remarks are provided, as well as recommendations for future research.

Gianluca Marcotullio

SAMENVATTING

Dit proefschrift behandelt de ontwikkeling van bioraffinage technologieën, te weten de ontwikkeling van duurzame industriële methodes gericht op de productie van chemicaliën, brandstoffen, warmte en elektriciteit op basis van lignocellulose biomassa. Dit onderzoekswerk is in het bijzonder gericht op de productie van furfural uit pentose suikers, afkomstig van het hemi-cellulose deel van biomassa.

De mogelijkheid om materialen, chemicaliën en brandstoffen te produceren uit biomassa heeft al een lange geschiedenis. Helaas hebben fossiele bronnen, met name olie, de afgelopen eeuw gedomineerd in zowel de chemische als de energie sector door hun enorme beschikbaarheid tegen relatief lage kosten. Tegenwoordig verkrijgen biomassa gebaseerde chemicaliën en brandstoffen een gunstiger competitieve positie, niet alleen door de hoge olieprijzen en de voorspellingen voor wat betreft hun beschikbaarheid in de toekomst, maar ook door het toenemende milieubewustzijn van de maatschappij.

Hoewel het gebruik van biomassa voor energievoorziening, en in het bijzonder voor bio-brandstof productie, recentelijk behoorlijk is uitgedaagd in termen van werkelijke voordelen voor het milieu, bieden de technologische vorderingen op het gebied van bioraffinage veel aanleiding om te geloven dat in de nabije toekomst biomassa zeker een duurzaam alternatief kan bieden voor fossiele bronnen in de chemische en brandstofproducerende industrie. Door een zorgvuldige overzichtsstudie van de wetenschappelijke literatuur en observatie van de recente onderzoekstrends wordt duidelijk dat een relatief korte lijst van biomassa afgeleide bouwstenen met een hoog potentieel in potentie zou kunnen zorgen voor de vervanging of gedeeltelijke substitutie van fossiele bronnen in bijna elke industriële sector.

De grote familie van furaanverbindingen vertegenwoordigt zeker een interessante selectie van biomassa afgeleide componenten voor veel industriële toepassingen. Furfural is tegenwoordig het enige uitgangsmateriaal voor de productie van bijna alle furaan-verbindingen. De furfural producerende industrie bestaat al sinds bijna een eeuw, maar staat vandaag de dag voor de uitdaging om grotendeels te vernieuwen om tegemoet te kunnen komen aan de globale trend in de richting van biomassa gebaseerde producten en de bijbehorende toegenomen vraag naar furfural en haar afgeleide producten.

Het grootste deel van de huidige furfural productie is nog steeds gebaseerd op min of meer gemodificeerde versies van het originele Quaker Oats proces (1921). Vanwege hun beperkte technologische ontwikkeling worden de productieprocessen van vandaag gelimiteerd door lage opbrengsten (rond 50%) en is er zorg wat betreft zowel economische en ecologische aspecten. Al deze punten hebben de expansie en modernisering van de furfural industrie zodanig gehinderd dat zij haar actuele potentieel niet haalt. Een forse technologische ontwikkeling is nodig als prioriteit om furfural een stap verder te brengen als grootschalige biomassa gebaseerde sleutelcomponent. De geïntegreerde productie van furfural in moderne bioraffinaderijen is een veelbelovende mogelijkheid en zal zeer waarschijnlijk de volgende hoeksteen vormen in de verdere uitbouw van de furfural producerende industrie.

In hoofdstuk 1 worden de mogelijkheden geboden door de moderne bioraffinaderij in een bredere context geplaatst en wordt het belang van furaanverbindingen toegelicht. In dit verband wordt het enorme potentieel voor zowel de chemische als de energie sector van furfural en haar afgeleide componenten bediscussieerd. Recente ontwikkelingen in de furfural technologie worden samengevat, zowel met betrekking tot synthese als toepassingen, waarbij tenslotte de motivatie voor dit proefschrift wordt gegeven met het oog op de beoogde resultaten.

In hoofdstuk 2 worden de experimentele methodes die zijn toegepast in dit werk uitgebreid beschreven. Een nieuwe titanium reactor is gebouwd op labschaal om verschillende aspecten van furfural vorming en gerelateerde reacties te bestuderen en om vloeistoffase reacties mogelijk te maken in een relatief brede range van druk, temperatuur en pH-waarden. Deze testopstelling heeft het mogelijk gemaakt om het grootste deel van de experimenten in het kader van dit proefschrift uit te voeren, en dus wordt zij grondig beschreven in dit hoofdstuk gerelateerd aan alle relevante aspecten van de chemische reactor technologie. De analytische en experimentele methodes die zijn toegepast in de verschillende experimentele campagnes die in dit proefschrift zijn weergegeven staan ook uitgebreid in dit hoofdstuk beschreven.

Hoofdstuk 3 behandelt de reactiekinetiek van furfural vorming. Zelfs als wordt gekeken naar het aantal relevante studies naar furfural vorming in zure media, is het nog steeds nodig een algemene uitdrukking te definiëren voor de reactiekinetiek, waarbij de afhankelijkheid van de aard en concentratie van het zuur, alsmede het potentiële effect van andere componenten in de oplossing wordt meegenomen. Daarom worden de resultaten van de reactiekinetiek studies gerelateerd aan furfural vorming uit xylose, xylose nevenreacties en furfural afbraak in waterige, zure media bestudeerd en gerapporteerd.

In hoofdstuk 4 wordt een aantal bijzondere aspecten van de chemie van de reactie van xylose naar furfural behandeld met als doel om het reactiemechanisme op te helderen en om nieuwe groene, katalytische productieroutes te ontsluiten. In het bijzonder wordt aandacht besteed aan de reductie van mineraal zuur gebruik door de introductie van alternatieve katalysatoren. In dit kader wordt het effect van chloride zouten in verdunde zure oplossingen beschreven bij temperaturen tussen 170 en 200 °C. De resultaten wijzen op een promotie van de vorming van het “1,2-enediol” uit de acyclische vorm van xylose en de opvolgende zuur gekatalyseerde dehydratatie tot furfural. Vanwege dit effect leidde de aanwezigheid van Cl^- ionen tot significante verbeteringen in vergelijking met de H_2SO_4 basis case. De toevoeging van NaCl aan een 50 mM HCl waterige oplossing (0.18 massa%) leidt tot de realisatie van 90% selectiviteit naar furfural. Van de toegevoegde zouten vertoont $FeCl_3$ zeer interessante initiële resultaten, waarbij uitzonderlijk hoge xylose reactiesnelheden zijn behaald.

Met de besproken resultaten uit hoofdstuk 4 betreffende de effecten van Cl^- ionen op de vorming van furfural in zure, waterige oplossingen als uitgangspunt, wordt in hoofdstuk 5 het algemene effect van verschillende halides bestudeerd in hoofdstuk 5. De experimentele resultaten tonen aan dat de halides minstens twee afzonderlijke stappen in het reactieproces van xylose naar furfural beïnvloeden middels verschillende mechanismen. De mate van nucleofiel gedrag van de halides blijkt kritisch te zijn voor de dehydratatie, maar niet voor de initiële enol-vormingsreactie. Door verschillende halides te combineren komen synergie effecten aan het licht, die resulteren in zeer hoge selectiviteiten en furfural opbrengsten.

In hoofdstuk 6 wordt de gecombineerde productie van hemicellulose afgeleide suikers en een verbeterd vast residu op basis van tarwestro beschreven, gebruikmakend van een verdund zure voorbehandeling bij milde temperaturen. Verdunde, waterige HCl oplossingen zijn bestudeerd bij temperaturen van 100 en 120 °C en deze zijn vergeleken met verdunde $FeCl_3$ oplossingen onder dezelfde reactieomstandigheden. Vergelijkbare opbrengsten van oplosbare suikers en azijnzuur zijn verkregen, waarbij een bijna complete verwijdering van pentose suikers is gerealiseerd bij toepassing van 200 mM waterige oplossingen bij 120 °C. De vaste residuen van de voorbehandeling zijn hierop gekarakteriseerd, waarbij is aangetoond dat de kristalliniteit van cellulose wordt behouden en dat asvormende elementen met uitzondering van Si praktisch compleet worden verwijderd. De resultaten tonen verbeterde karakteristieken van de residuen met betrekking tot thermische conversie toepassingen in vergelijking met onbehandeld tarwestro.

Hoofdstuk 7 behandelt de industriële processen voor de productie van furfural, waarbij in het bijzonder wordt stilgestaan bij een innovatief proces dat is gepatenteerd door de Technische Universiteit Delft en dat is gebaseerd op de resultaten die staan beschreven in dit proefschrift. Zoals reeds is genoemd, zal de geïntegreerde productie van furfural in moderne bioraffinaderijen zeer waarschijnlijk de volgende hoeksteen vormen in de verdere ontwikkeling van de furfural industrie. Het innovatieve procesconcept dat is beschreven in dit hoofdstuk is gericht op een economisch haalbare en voor het milieu acceptabele furfural productie met gereduceerde energie en toegevoerde chemicaliën consumptie. De evaluatie van de proceseconomie toont veelbelovende resultaten in vergelijking met de bestaande processen, hetgeen dit concept economisch aantrekkelijk maakt.

Tenslotte worden in hoofdstuk 8 de conclusies gegeven, alsmede aanbevelingen voor toekomstig verder onderzoek.

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NOMENCLATURE

Abbreviations

a.r.	As received
AOAC	Association of Official Agricultural Chemists
CrI	Crystallinity Index
CS	Carbon steel
d.b.	Dry basis
DTG	Differential Thermogravimetric Plot
eNRTL	electrolyte Non-Random Two-Liquids
FCI	Fixed Capital Investment
FEMA	Flavor and Extract Manufacturers Association
HPLC	High Performance Liquid Chromatography
LCF	Lignocellulose-feedstock
mM	millimolar
M	molar
[X]	molar concentration of X
RON	Research Octane Number
RTD	Residence Time Distribution
SS	Stainless Steel
TGA	Thermo-Gravimetric Analysis
XRD	X-ray diffraction
XRF	X-ray fluorescence
wt	Weight

Chemicals

DMSO	Dimethylsulfoxide
FA	Furfuryl alcohol
FDCA	2,5-Furandicarboxylic acid
HMFA	5-Hydroxymethyl furoic acid
HMF	5-Hydroxymethyl furfural
MF	2-Methyl furan
MTHF	2-Methyl tetrahydrofuran
THF	Tetrahydrofuran
THFA	Tetrahydrofurfuryl alcohol

Symbols

t	Time [min]
a	Ion activity in aqueous solution [mol l^{-1}]
A	Debye-Hückel costant [$l^{0.5}$ $mol^{-0.5}$]
C	Concentration [mol l^{-1}]
E_a	Activation Energy [kJ mol^{-1}]
$\Delta H^{\ddagger}$	Enthalpy of activation [kJ mol^{-1}]
I	Ionic strength [mol l^{-1}]
k	Reaction rate constant [s^{-1}]
$\dot{m}$	Mass flow-rate [g min^{-1}]
MO_1	First momentum of the distribution curve $E(t)$ [min]
Pe	Péclet number [-]
pK_a	Sulphuric acid second dissociation constant [-]
R	Universal gas constant [kJ mol^{-1} K^{-1}]
$\Delta S^{\ddagger}$	Entropy of activation [J mol^{-1} K^{-1}]
t	Time [min]
T	Temperature [K]
V	Volume [l]
z_i	Ion charge

Greek Symbols

γ	Ion activity coefficient [-]
ϑ	Normalized residence time [-]
ρ	Density [g l^{-1}]
σ_{ϑ}	Variance of the distribution curve $E(\vartheta)$ [-]
τ	Average residence time [min]

1

INTRODUCTION

In this chapter the opportunities offered by modern biorefinery in the broader context are introduced, and the importance of furanic compounds within the biorefinery is pointed out. In this context the enormous potential of furfural and its derivatives, both in the chemical and energy sector, is discussed. Recent advances in furfural technology are summarized, both regarding furfural synthesis and applications, eventually stating the motivation behind this dissertation, and the main achievements therein contained.

To what extent is agriculture likely in the future to supply the raw materials for industry in addition to food and textiles, her main customers today? The question arose in a lecture given by Sir Harold Hartley to the Textile Institute in June 1937, later published on Nature *[14]*. It is remarkable to find such a present-day question in an almost 80 year-old lecture. In that same lecture the competition between biomass derived and fossil resources was also very current: *Of greater significance from the point of view of displacement of plant products, is the use of cracked oil gas and natural gas in the United States as starting-points for the manufacture of organic chemicals [. . .]. Here there is a direct competition with the products of the fermentation industry and wood distillation. [. . .] On the other hand, the more detailed knowledge of plant products has led to great developments in their extraction and utilization, for example, the process of fat-hardening, the conversion of molasses into alcohol, glycerin, acetone and other solvents, and the production of furfural from cereals wastes for use as solvent or as a constituents of plastics.*

The terms of the discussion around bio-fuels, in particular on ethanol high cost of production compared to gasoline, were also very clear back then: *[bioethanol] use today as motor fuel is justifiable on strategic grounds, but when petroleum supplies begin to contract, alcohol will be in a better competitive position.*

On the perspectives of bio-based material as substitutes for oil derivatives and metals: *The extent to which agricultural materials may replace minerals and metals will depend on physical properties and cost. Some plastics are suitable for replacing metals; the use of synthetic resins as adhesives, and the improvements in the manufacture of laminated wood already make it a successful rival to metal in many fields, [. . .].* In conclusion: *Such a development of the use of agricultural products would be most fortunate in view of the gradual exhaustion of our capital assets, coal and oil.*

It is clear that the possibility of producing materials, chemicals, and fuels from biomass had been envisioned already long ago. Unfortunately fossil resources, in particular oil, have dominated last century both in the chemical and energy sectors due to their enormous availability at relatively low cost. Hence only limited and specific bio-based sectors could survive.

In nowadays scenario bio-based chemicals and fuels are gaining a much more favorable competitive position, not only by virtue of high oil prices and the forecasts on its future availability, as predicted by Sir Harold Hartley, but also because of the increasing environmental awareness and the demand for of a secure, possibly domestic, energy supply.

1.1 BIOREFINERY SYSTEMS

The use of biomass for energy applications has been greatly promoted in the recent years in many countries. As far as the biomass transformations to fuels and chemicals is concerned, the production of bioethanol in particular has shown a very sharp increase [1], especially in the USA, next to Brazil which has

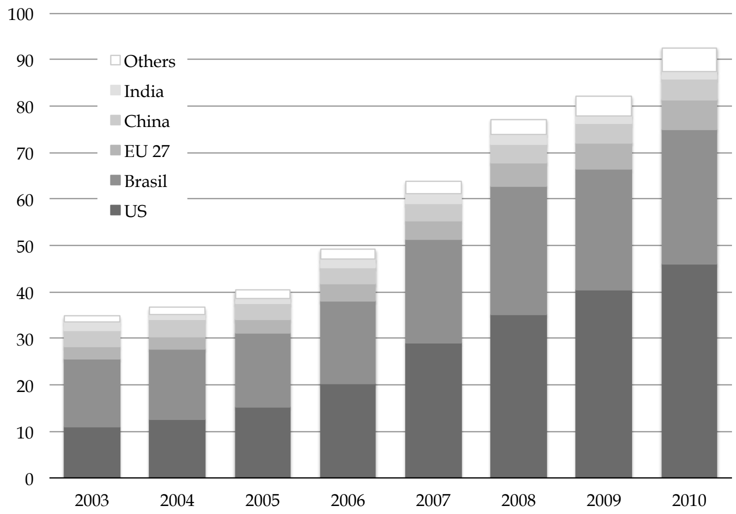


Figure 1.1: Bioethanol production in Mm^3. Raw data from [1].

a longer history of ethanol production from sugarcane molasses, see Figure 1.1. Such massive production of the so called first generation biofuels contributed also to inflame the debate on the competition between food and fuel, and more in general on the sustainability of biomass use for energy applications, which peaked together with food prices between 2007 and 2008. Important organizations such as the World Bank argued that the increase in internationally traded food prices was caused by a confluence of factors, but the most important was the large increase in biofuels production from grains and oilseeds in the US and EU [15].

Furthermore, first generation bioethanol has been seriously challenged in terms of actual CO2 emission reductions. An article appeared on Science in 2006 showed that, in some particular cases where coal was employed to power the processes for corn-based ethanol production and purification, the associated well-to-wheels CO2 emissions resulted even higher than regular gasoline [16]. If, on the one hand, the use of a domestic carbon-intensive energy resources, such as US coal, for the production of ethanol could be justified on the strategic grounds of the reduction of the dependence on imported oil, it turned out to be in clear contradiction with the environmental basis behind biofuels.

Apart from the particularly fortunate Brazilian case, it has been often recognized that first generation biofuels, besides raising concerns on the competition with food, may bring very limited environmental benefits [2, 16–18]. The proven limited reduction of greenhouse gases emissions, next to the predicted increasing pressure on food prices, water resources, biodiversity, forests and vulnerable

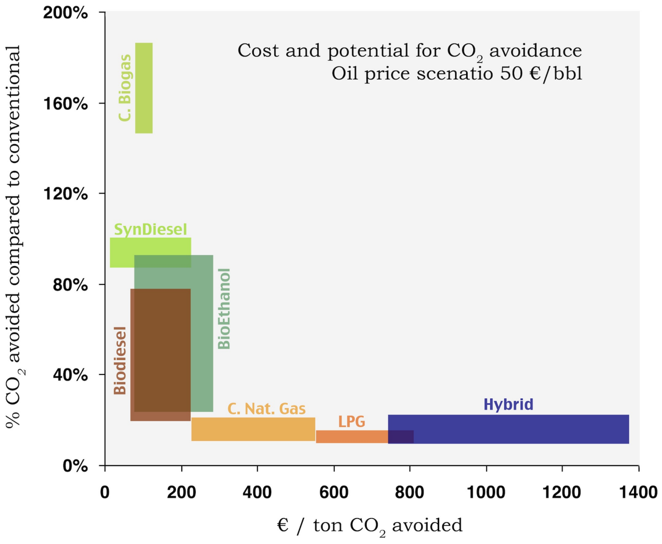


Figure 1.2: CO2 emission reduction potential and related cost. Adapted from [2]

lands, brought up the question whether, in some cases, biofuels, and in particular first generation bioethanol, could become a *cure worse than the disease* [19].

Concerning the EU context, the European Commission Joint Research Centre studied the CO2 reduction potential for a variety of alternative solutions in the transportation sector, showing that the impact on CO2 emissions and the associated costs spanned over a wide range [2], as shown in Figure 1.2.

In order to address all these issues, and drive the market towards the best practices available, it became important to introduce *sustainability criteria* associated to the biomass use in transportation. The European Commission recently approved the directive 2009/28/EC, which prescribes a minimum target of 35% CO2 emissions reduction for biofuels and bioliquids put on the market, which is set to increase to 50% in 2017 and 60% in 2018. In view of these very clear sustainability targets the development of future biofuels productions shall probably shift towards new generation and more sustainable solutions, like cellulosic ethanol, syn-diesel, furanic fuels, besides hydrogen and electricity.

Besides biofuels, also bio-based chemicals in the recent years gained a better competitive position against oil derivatives. The spectrum of possible biomass transformations routes into chemicals is very wide [4]. If on the one hand it is mostly accepted that a selection of primary biomass-derived building blocks and secondary intermediates could either replace or substitute oil derivatives in most of existing industrial applications, on the other hand it is also commonly agreed

Table 1.1: Chemical composition (on dry basis) of common lignocellulose feedstock. Source [5].

LCF	Cellulose (%)	Hemicellulose (%)		Lignin (%)
		Hexoses	Pentoses	
Softwood	40-48	12-15	7-10	26-31
Hardwood	30-43	2-5	17-25	20-25
Cereal straw	38-40	2-5	17-21	6-21
Maize straw	35-41	2	15-28	10-17
Rape straw	38-41	-	17-22	19-22
Recovered paper	50-70	-	6-15	15-25

that conversion and separation technologies are mostly lagging far behind the established oil-based refining industry [4, 10, 11, 20–22].

In view of all this, the attention is focused nowadays on the emerging field of BIOREFINERY systems, aimed at an economically and environmentally sound use of the biomass feedstock for the production of a whole range of products: form high-volume commodities, such as fuels, to high added value specialty chemicals [21].

1.1.1 *The lignocellulose-feedstock Biorefinery*

The term Biorefinery in general represents a complex system able to process different biomass feedstocks, via different technologies, in order to produce a multiplicity of products [23]. Among the potential large-scale industrial biorefineries, the so-called lignocellulose-feedstock (LCF) biorefinery holds many characteristics for future success. Lignocellulosic raw material, i.e. straw, reed, grass, wood, paper-waste, etc., is nearly ubiquitous, and normally available at relatively low cost. Carbohydrates, namely cellulose and hemicellulose, make up for about 70% of the dry weight of lignocellulosic biomass, see Table 1.1, and represent the feedstock for nearly all of the most promising bio-based building blocks and chemical intermediates, both deriving from biological and thermo-chemical conversion routes [4, 10, 11, 21]. Lignin, another important constituent of lignocellulosic biomass making up for about 25% of its weight, is by far the most important natural resource of aromatics, beside a good solid biofuel.

Global photosynthetic production of biomass is enormous, in the order of 1.7-2.0×10^{11} tons per year [24]. Needless to say, only a small fraction of it is nowadays harvested and used for food, feed and industrial applications. According to the United Nations Food and Agriculture Organization statistic data, the world production of cereals in 2008 accounted for 2.5×10^{9} tons, sugarcane production reached 1.7×10^{9} tons, whereas the forestry-derived products, such as various kind of industrial wood and wood fuel, accounted for 3.4×10^{9} m^{3}. Noteworthy,

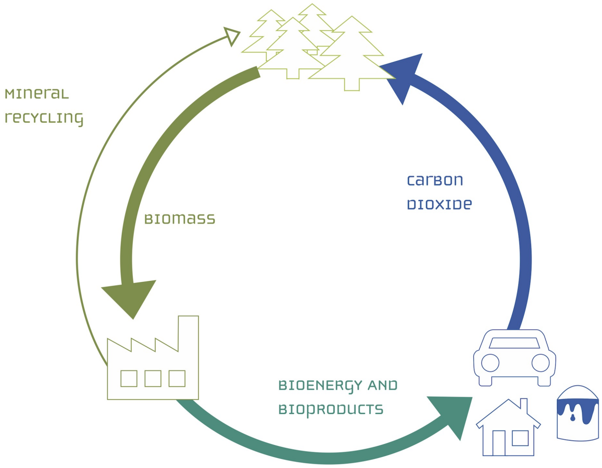


Figure 1.3: The sustainable biorefinery concept, adapted from [3]

such figures are comparable to the annual production of oil on weight basis, 3.9×10^9 tons (163 EJ) in 2008.

From the purely energetic point of view, Kim and Dale [25] estimated that about 1.5×10^9 tons (25.5 EJ) of lignocellulosic residues associated to the main agricultural crops (which are nowadays only partly used and mostly left behind during harvesting) are globally available for the production of bio-based fuels and chemicals, corresponding to a potential bioethanol production of 0.4×10^9 tons (10.7 EJ), in addition to substantial amounts of electricity and steam.

Next to agricultural residues, there is still a huge growth potential for particularly promising crops like sugarcane. The Brazilian Sugarcane Industry Association (UNICA) claims that only 10% of the suitable land for sugarcane is presently used, the remaining being mainly pastures, primarily located in South American regions not constituting a potential threat to the Amazons, and sub-Saharan Arica.

Although sugarcane holds an enormous potential as future energy crop, this is limited to specific regions of the world with appropriate climate conditions. In temperate regions like Europe, North America and the Mediterranean area, selected perennial rhizomatous grasses hold the highest potential as energy crops, namely miscanthus (*Miscanthus*), reed canarygrass (*Phalaris arundinacea*), giant reed (*Arundo donax*) and switchgrass (*Panicum virgatum*) [26]. These crops present very high yields per hectare, up to 40 ton/ha annum of dry matter, and, unlike annual crops, their need for soil tillage is limited to the year in which the crops are established. Due to the fast growth and reduced tilling, and also because of a significant below ground carbon sequestration, they present significant beneficial aspects firstly in terms of CO2 balance, but also on preventing soil erosion and degradation. Furthermore, due to the recycling of nutrients by their rhizome systems, perennial grasses have low demand for nutrient inputs, and little or no pesticide use [26, 27], besides being able of growing on a wide range of soils, including marginal or set-aside lands normally not suitable for agriculture.

Global biomass supply potential has been carefully estimated in the framework on the Netherlands Research Program on Scientific Assessment and Policy Analysis for Climate Change [28]. By taking into account the complex relationships between food, energy, and water demand, beside land uses, biodiversity, conversion processes, and many others, it was shown that biomass could contribute up to 510 EJ/y to the global primary energy demand in 2050 (estimated between 600 and 1040 EJ/y), considering:

- Agricultural and forestry residues (100 EJ/y).
- Forestry surplus (80 EJ/y).
- Energy crops production on good quality surplus agricultural and pasture lands (120 EJ/y).
- Energy crops production on water scarce, marginal and degraded lands (70 EJ/y).
- Learning in agricultural technology (140 EJ/y).

The selection of feedstock for currently developing LCF biorefineries projects reflects the geographic location, with corn stover being a preferred choice in the US, bagasse in the regions where sugarcane is already well established like Brazil, and mostly cereal straw in EU. First movers are already looking at energy crops, and at the beginning of 2011 the northern-Italy based company M&G started building a cellulosic ethanol pilot plant based of the conversion of locally grown Arundo Donax. They claim a productivity of about 11 m^3 of ethanol per ha-annum, which is about double the present productivity of Brazilian sugarcane-based ethanol [29, 30].

In view of what mentioned above, the availability of lignocellulosic feedstock does not represent the bottle-neck for the medium-term development of biorefineries. The development effort is currently focused rather on suitable conversion technologies, starting from the pre-treatment of raw biomass for its fractionation into its main constituents: cellulose, hemicellulose and lignin.

1.1.2 *Aspects of biorefinery integration*

If on the one hand LCF biorefineries at this stage are focusing on the bulk production of cellulosic ethanol as main output and source of revenues, on the other

Table 1.2: Top chemical opportunities from integrated biorefinery systems, source [10, 11].

Alcohols	Ethanol	Besides the large-scale use as biofuel, ethanol is gaining interest as chemical platform, in particular as precursor of ethylene.
Furans	Furfural	The potential of furfural as platform chemical will be discussed more extensively in this chapter.
	HMF	HMF is an appealing starting material for various chemical transformations.
	2,5-FDCA	2,5-furandicarboxylic acid has been suggested as a potential substitute for terephthalic acid in the production of polyesters. It is preferably produced by HMF oxidation.
Glycerol and derivatives		Readily available from the biodiesel industry, glycerol offers many conversion opportunities to interesting products via reduction, dehydration and fermentation.
Hydrocarbons	Isoprene	Isoprene is a high value hydrocarbon with a significant market. There are biochemical routes being developed and brought to market for producing (bio)isoprene.
	Biohydrocarbons	Production of long chain hydrocarbons from microalgae is being explored, next to biological synthesis using appropriate bacteria. Hydrocarbons in general will be of high importance for the development of the biorefinery, providing a direct drop-in interface with the petrochemical industry.
Organic acids	Lactic acid	Lactic acid is a well-recognized commercial bio-chemical produced by glucose fermentation. Its primary use is the production of polylactic acid.
	Succinic acid	Succinic acid production via biochemical transformation of sugars has been widely studied, and is close to commercial scale. Succinic acid is a high potential platform chemical for the production of C_4 intermediates.
	Hydroxypropanoic acid / aldehyde	3-Hydroxypropanoic acid and 3-hydroxypropionaldehyde (HPA) may be produced from glycerol via biological routes and offer several conversion opportunities to valuable products, such as 1,3-propanediol and acrylic acid.
	Levulinic acid	Of interest as derived with relatively high yields from C_6 sugars (via HMF). Transformation of levulinic acids into substituted pyrrolidones; lactones; levulinate esters; diphenolic acid; and ketals is being studied.
Sugar alcohols	Sorbitol	Chemical reduction of glucose is well-established, although the biochemical route is investigated. Of interest for the production of drop-in hydrocarbons via aqueous phase reforming, but also for the production of isosorbide.
	Xylitol	Preferably prepared by catalytic hydrogenation of xylose, although biochemical reduction is being investigated. It is of interest the aqueous phase reforming to hydrocarbons and the transformations to polyols.

hand their integration with value-added chemicals production does not present yet a winning set of technologies, and operators are mostly screening for the most promising options.

Bio-based chemical production is challenged by an overabundance of possible products. Integrated biorefinery development has yet to identify a core group of primary chemicals and secondary intermediates analogous to those used by the petrochemical industry. A valuable effort was done in this direction by the US Department of Energy, which produced a systematic study aimed at selecting the most promising building blocks based on the following criteria [10]:

1. **The compound or technology has received significant attention in the literature.** A high level of reported research identifies both broad technology areas and structures of importance to the biorefinery.
2. **The compound illustrates a broad technology applicable to multiple products.** As in the petrochemical industry, the most valuable technologies are those that can be adapted to the production of several different structures.
3. **The technology provides direct substitutes for existing petrochemicals.** Products recognized by the chemical industry provide a valuable interface with existing infrastructure and utility.
4. **The technology is applicable to high volume products.** Conversion processes leading to high volume functional equivalents or utility within key industrial segments will have particular impact.
5. **A compound exhibits strong potential as a platform.** Compounds that serve as starting materials for the production of derivatives offer important flexibility and breadth to the biorefinery.
6. **Scale-up of the product or a technology to pilot, demo, or full scale is underway.** The impact of a biobased product and the technology for its production is greatly enhanced upon scaleup.
7. **The biobased compound is an existing commercial product, prepared at intermediate or commodity levels.** Research leading to production improvements or new uses for existing biobased chemicals improves their utility.
8. **The compound may serve as a primary building block of the biorefinery.** The petrochemical refinery is built on a small number of initial building blocks: olefins, BTX, methane, CO. Those compounds that are able to serve an analogous role in the biorefinery will be of high importance.

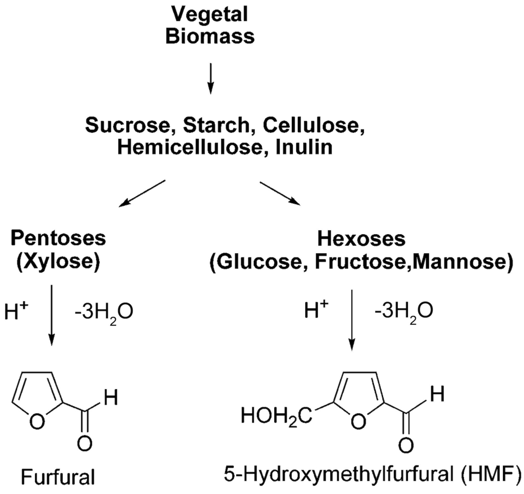


Figure 1.4: Simplified reaction pathway from biomass to furans, adapted from [4].

9. **Commercial production of the compound from renewable carbon is well established.** The potential utility of a given compound is improved if its manufacturing process is already recognized within the industry.

The screening resulted in a first selection of 15 candidates in 2004, starting from a longer list of 30 [11]. In 2010 the list was revised with the elimination of some products which turned out to be of limited interest during these years, and the introduction of others, resulting in a new list of 13 compounds based on more updated developments [10]. The 2010 list is depicted in Table 1.2.

1.1.3 *The Furans*

As shown in Table 1.2, the family of furans is of high importance for the integrated biorefinery. The dehydration of 5- and 6-carbon sugars to give furfural and (HMF) is a well-known transformation since 1832 (although the first observations may be dated back in 1821) when Dobereiner first reported the isolation of a few drops of yellow oil from the distillate obtained during the preparation of formic acid from sugar by the action of MnO2 and H2SO4. Later such "oil" was assigned the correct formula C5H4O2, but only in 1845 it was named Furfurol by the English chemist G. Fownes (Furfur-bran; oleum-oil), then changed to Furfur-al in recognition of its aldehydic nature [8].

The chemistry of the broader family of furan compounds is even older than furfural, as furoic acid was first obtained in 1780 by dry distillation of galactaric acid [8]. Already in 1953 an encyclopedic survey on the chemistry of the furans was written by Dunlop and Peters who had been involved in the field for many years within The Quaker Oats Company, first industrial producer of furfural [8].

Although many compounds of the furan series have been encountered in connection to studies of natural resources, such as furfural, HMF, furan, 5-methyl furfural, furoic acid, 5-methyl furan and others, only furfural, along with its main by-product 5-methyl furfural, is currently commercially produced from biomass. For this reason furfural represents nowadays the starting material in the manufacture of most of the furan compounds [31].

5-HYDROXYMETHYL FURFURAL (HMF) HMF is the furfural 6-carbon equivalent. The presence of two functional groups, combined with the furan ring, makes HMF an appealing starting material for various chemical transformations. Although the chemistry behind HMF formation is comparable to furfural, and hexoses are even more abundant and easily available than pentoses, contrary to furfural HMF has never been produced at industrial scale.

Interestingly, since the earliest observations, furfural could be easily recovered in a steam distillate and thus purified by virtue of its limited solubility in water. It is a matter of fact that the peculiar thermodynamics of the furfural-water system made it possible to discover furfural in the first place - from a *milky distillate* -, and to produce it at industrial scale by *rapidly distilling the aldehyde from the reaction chamber during the period of its formation* [8]. Unlike furfural, HMF is hydrophilic and only slightly volatile in aqueous solutions, therefore its recovery via steam distillation is practically impossible, and also liquid-liquid extraction results unfavorable. This fundamental difference, and the fact that HMF, like furfural, undergoes further reactions under the conditions necessary for its formation, makes any attempt of producing and purifying HMF from raw biomass inherently challenging [32].

During the last years an enormous research effort has been devoted to the synthesis and isolation of HMF, which may be grouped by catalysis type: metal catalysis and acid catalysis, the latter including homogeneous liquid, heterogeneous liquid–liquid, solid-liquid and gas-liquid. Such effort resulted in considerable improvements for the conversion of fructose to HMF, whereas the transformation of glucose, sucrose and cellulose remains challenging. For an extensive coverage of the topic of HMF synthesis and applications the reader might refer to the comprehensive reviews recently published [32, 33].

Among the vast work on HMF synthesis and isolation, remarkable results have been achieved by following alternative approaches, i.e. obtaining selected furan derivatives presenting good chemical stability and favorable purification options. Mascal and co-workers obtained the substitute furan 5-(chloromethyl)furfural with relatively high yields directly from cellulosic material, and from this intermediate could then isolate HMF and other furan derivatives [34, 35]. Following a similar strategy, the Dutch company Avantium has developed a very promising process aimed at forming a stable HMF ether derivative, namely 5-(alkoxymethyl)furfural, reacting hexoses in presence of an alcohol and an acid catalyst [36, 37]. They firstly highlighted the remarkable properties of such ethers as liquid fuels or fuel additives for transportation and aviation, although interesting options also exist for bio-based polymers applications [38]. Avantium is presently building a pilot plant in the Netherlands for demonstrating their technology [39].

1.2 FURFURAL

As already mentioned, furfural is the only compound of the furan series being directly obtained from biomass at industrial scale. Furfural production is generally carried out by hydrolysis of hemicellulose-derived pentosans into monomeric pentoses, and their subsequent acid-catalyzed dehydration into furfural. An extensive discussion on the mechanistic aspects of furfural formation from pentoses is presented in chapters 4 and 5.

The first time furfural was produced in relatively large amounts was at the beginning of 1922 in the USA by The Quaker Oats Company, and the consequent development of the furfural industry achieved a relative maturity already before the first half of the century [40–50]. With a global production of about 300 kton/y furfural is still currently the sole precursor of furyl, furfuryl, furoyl, or furfurylidene compounds in the chemical industry [31], and actually one of the most important biomass derived chemicals.

1.2.1 *Sources and production*

Furfural can be obtained by every pentosan-containing material, i.e. by cellulosic material of all kind. Curiously, being formed on heating carbohydrates, furfural, together with HMF and other furans, may be easily found in cooked, roasted or baked goods, resulting in an appreciable daily human intake. The highest concentrations of natural occurring furfural are found in cocoa and coffee (55-255 ppm), alcoholic beverages (1-33 ppm), and in wholegrain bread (26 ppm). The total potential furfural daily intake from food has been estimated in the order of 0.3 mg/kg/day [51]. Being used as flavor ingredient, furfural underwent a FEMA assessment in 1997, and it was determined to be generally recognized as safe (GRAS) [51].

Even though pentosans, namely xylans and arabinans, are present in virtually all plant materials as constituents of hemicellulose, their concentration varies depending upon the hemicellulose typology, covering a relatively wide range, see also Table 1.1.

Arabinoxylans Typical of annuals and grasses, contain a predominant xylan sugar residue in the backbone, with minor amounts of arabinofuranoside and ester-linked acetyl group substituents [52].

Glucoronoxylans Mostly found in hardwoods, have also a predominant presence of xylans, together with significant concentrations of glucuronic acids and acetyl substituents, with a molar ratio of about 10:1:7 [52].

Galactoglucomannans In contrast to hardwoods and herbaceous, softwood hemicellulose is dominated by hexosans rather than pentosans, with galactoglucomannans representing roughly 15–20% of the biomass dry weight, and xylans comprising only 7–10% [52, 53].

Therefore, arabinoxylans containing materials, such as annuals and grasses, are more suitable for furfural production, see Table 1.3. Today, like in 1922, the large availability, low cost and relatively high pentosan content of agricultural residues made them the feedstock of choice in the furfural industry. Currently corncobs and sugarcane bagasse are the dominating feedstock, the former mainly used in China and Thailand, whereas the latter is used in Dominican Republic and South Africa [31, 54].

The majority of current production is still based on more or less modified versions of the original Quaker Oats process. They mostly consist of suitable digesters loaded with acid-impregnated biomass, where steam is injected through the biomass bed at an appropriate pressure and temperature, while a furfural enriched vapor stream is constantly withdrawn. The furfural-containing stream is subsequently concentrated via azeotropic distillation and rectified via vacuum distillation, whereas the solid biomass residues are normally incinerated or disposed of. Most of the processes are run in batch mode. A more extensive discussion on furfural production process is presented in Chapter 7.

Currently the largest plant for the production of furfural (35 kton/y) is located in Dominican Republic, contiguous to a sugar mill owned by The Central Romana Corporation, a big sugar producer; whereas most of the world production capacity is located China, mainly consisting of a large number of producers with a capacity in the order of only few kilotons per year.

Many new concepts for the production of furfural have been developed and described in literature [7, 55], demonstrating a substantial research effort, although only limited progresses may be recorded on the ground of operating industrial plants.

For reasons that can be related to their limited technological evolution, the production processes in use today generally suffer from low yields (around 50%), besides significant economical and environmental concerns. All these reasons certainly contributed to the shrinking of furfural production capacity in EU and USA down to an only residual presence, and hindered the expansion and modernization of the furfural industry below its actual potential. A profound techno-

Table 1.3: Furfural production potential as estimated from the A.O.A.C. method [8, 12].

Raw material	Furfural % wt dry basis
Agricultural residues and herbaceous	
Corncobs	23.4
Oat hulls	22.3
Bagasse	17.4
Olive press cake	16.6
Straw	16.0
Beet pulp	17.0
Arundo Donax	17.9
Hardwoods	
Birch (paper)	13.2
Maple (red)	10.1
Beech (American)	11.5
Softwoods	
Spruce (white)	7.0
Pine (jack)	7.4
Fir (balsam)	6.3

logical development is a priority in order to upgrade furfural to a large-volume bio-based commodity.

1.2.2 *Advances in the synthesis of furfural from pentoses*

The innovation effort in the field of furfural production covers few main aspects, with reaction catalysis certainly being the most active area, especially focused on the use of solid acids, but also non-aqueous reaction media are being tested, besides innovative options for furfural separation.

Many researchers consider the use of homogeneous catalysts, such as aqueous sulfuric or hydrochloric acid, to be the main disadvantage in furfural production. In particular, many environmental and economic concerns are associated to the use of large amounts of strong mineral acids, along with neutralizing agents and the consequent spent wastes [38, 54]. In this view several attempts have been made towards the introduction of heterogeneous catalysis in furfural production, with the particularly active contribution of the group of prof. Valente and co-workers at University of Aveiro. A variety of solid acid catalysts, namely

Table 1.4: Comparison of heterogeneous catalysts used in the dehydration of xylose to furfural.

Catalyst	**Solvent**	**Temp.**	**Res. time**	**S /%**	**Y /%**	**Ref.**
MCM-41-SO3Hc	W-T	140°C	24 h	83	76	[60]
eHTiNbO5-MgO	W-T	160°C	4 h	60	55	[61]
PSAZ-MCM-41	W-T	160°C	4 h	49	39	[64]
ZSM-5	W	200°C	0.3 h	n.a.	46	[57]
Nafion-117	DMSO	150°C	2 h	66	60	[66]
Dealumin. HNu-6(2)	W-T	150°C	4 h	53	48	[62]
H-mordenite 13	W-T	260°C	0.05 h	98	98	[58]
H-mordenite 11	W-T	170°C	0.5 h	96	26	[56]
$SO4^{2-}$*/12%ZrO2-Al2O3/SBA-15*	W-T	160°C	4 h	53	53	[65]
Amberlyst-15 / Hydrotalcite	N,N-DMF	100°C	1 h	51	37	[67]

Furfural selectivity (S) and yield (Y) are highlighted. Water-Toluene (W-T), Water (W), Dimethylsulfoxide (DMSO), and N,N-dimethylformamide (N,N-DMF) are used as solvent systems.

zeolites [56–58]; microporous and mesoporous niobium silicalites [59]; micro-mesoporous sulfonic acids [60]; layered titanates, niobates and titanoniobates [61]; delaminated aluminosilicates [62]; cesium salts of 12-tungstophosphoric acid and mesoporous silica-supported 12-tungstophosphoric acid [63], bulk and mesostructurated sulfated zirconia [64, 65], nafion 117 [66] and a combination of different acid and basic solid catalyst [67], have been tested for the dehydration of xylose to furfural. In general, the results achieved so far in the area of solid catalysis in furfural production are quite promising as shown in Table 1.4, especially in view of the future improvements expected by fine-tuning of the catalysts properties and reaction conditions [38]. In particular, outstanding results have been reported when using zeolites at relatively high temperatures (Table 1.4, entries 4,7 and 8), both in terms of furfural selectivity, yield, and short residence time. Nevertheless research in this field is developing quickly, and, although strong indications already exist, it is too early to select the best solid catalyst. Moreover, in view of the industrial implementation of solid catalysts, many aspects are still to be carefully evaluated, such as: catalysts deactivation and regeneration; water compatibility; leaching and poisoning; and economic viability. For a more extensive discussion on this topic the reader might refer to the published reviews [38, 68].

When solid acids are employed the reaction is usually carried out using an aqueous–organic biphasic solvent system. In the aqueous phase the reaction of sugars takes place, whereas the organic phase is used, as alternative to the traditional steam distillation, to readily extract the furfural formed so to avoid its uncontrolled decomposition. Toluene is normally a preferred choice as organic extracting agent due to its high affinity with furfural, although methylisobutylketone (MIBK), isobutyl acetate, ethyl acetate, THF and a series of C_5 alcohols have been tested for this purpose [69–72]. Supercritical CO2 has also been tested for furfural extraction with interesting results [73–76], whereas organic [77, 78], polar aprotic solvents [79], and ionic liquids [80] have been studied in replacement of the aqueous phase. Furfural formation in uncatalyzed liquid hot water [81, 82], and with the application of microwave has also been recently reported [83, 84].

1.3 APPLICATIONS OF FURFURAL AND ITS DERIVATIVES

The combination of the furan ring and the aldehyde function, make furfural a very versatile chemical with peculiar solvent, resin precursor and biological properties. In all these applications furfural may be used as such or, more often, in the form of its derivatives of hydrogenation, mainly furfuryl alcohol (FA). The number of potential uses of furfural, as reported in literature, is gigantic [5, 7, 8, 31, 85], see Figure 1.5. The reason why current uses of furfural are limited to few main applications is the combined result of several factors, certainly including the enormous expansion of the petrochemical industry during last century, but also the limited evolution of the furfural industry.

The furan chemistry lived its golden age during the first half of the 20^{th} century, and an unmatched review book published in the monographic series of the American Chemical Society in 1953, entitled The Furans [8], testifies to the surprising activity in this field. Such volume, regrettably not printed anymore, contained thousands of references to scientific publications, and a vast collection of patents covering the field of furans, which in 1953 had already reached the number of 3500. Despite the enormous effort resulting in a more than 800 pages, the authors, by their own admission, could not achieve a full coverage on all the aspects regarding the furans. Yet they achieved an impressive collection of synthesis methods and properties regarding furfural; furan and homologous; halogen and nitro derivatives; furanols and furylamines; furan metallic compounds; furan alcohols, acids, aldehydes and ketones; and an enormous number of derivatives of hydrogenation. Moreover they reported many fields of application where furans showed interesting results: as chemical intermediates; pharmaceuticals; fungicides and preservatives; insecticides; herbicides; selective solvents; and resins and polymers precursors. Although out-of-date, every researcher involved with furans today should look through this very intriguing book, at least to avoid the very likely and frustrating chance of repeating something already done before 1953.

A clear sign of decline of the furan chemistry came in 1961, when Du Pont abandoned its furfural-based process for the production of nylon, preferring the more economical petroleum derivatives.

Interest around furans slowly picked up during the last couple of decades, and it is now increasing due to the high oil prices, the environmental drive, and the widely proven versatility of this series of chemical compounds. A very interesting and updated book on furfural and its derivatives [7], and a huge number of recent scientific contributions testify to the renewed interest.

In the following paragraphs an attempt is made to summarize the more important current uses of furfural and derivatives, and the upcoming fields of application.

1.3.1 *Furfural as solvent*

Furfural has excellent solvent characteristics due to some very important aspects descending from its chemical structure:

- The aromatic character of the furan ring and its polarity gives furfural good solvent selectivity toward aromatics, and in general unsaturated compounds.
- Furfural has an intermediate polarity, and for this reason it is only partially soluble both in highly polar substances like water, and in highly apolar substances like saturated hydrocarbons. Furfural presents a miscibility gap with many C_6 or higher paraffins and olefins [8]. Because of this peculiar property furfural is a versatile extracting agent easy to recover by steam distillation.
- Despite the misleading darkening of furfural at room conditions (which is due to the formation of very minor amounts of coloring compounds), furfural exhibits very good thermal stability at most operating temperature levels [7, 8].

Because of its properties, furfural has been used as selective solvent in many applications [7, 31, 47, 85, 86]. The knowledge on the processes involving furfural or furan compounds as solvents in industry is vast, and reviewing it goes far beyond the scopes of this thesis. Nevertheless a short collection of the most common applications may be exposed here.

FURFURAL IN THE REFINING INDUSTRY The extraction of aromatic components by using selective solvents is currently one of the basic operations in the process of obtaining lubricating oils, and furfural is the solvent most commonly used [87]. Such practice was started in 1933 by a subsidiary of The Texas Company [8], and it is aimed at achieving a low viscosity index, i.e. low viscosity variations of the oil with temperature, by reducing its aromatic content via furfural extraction. The content of sulfur compound was also reduced.

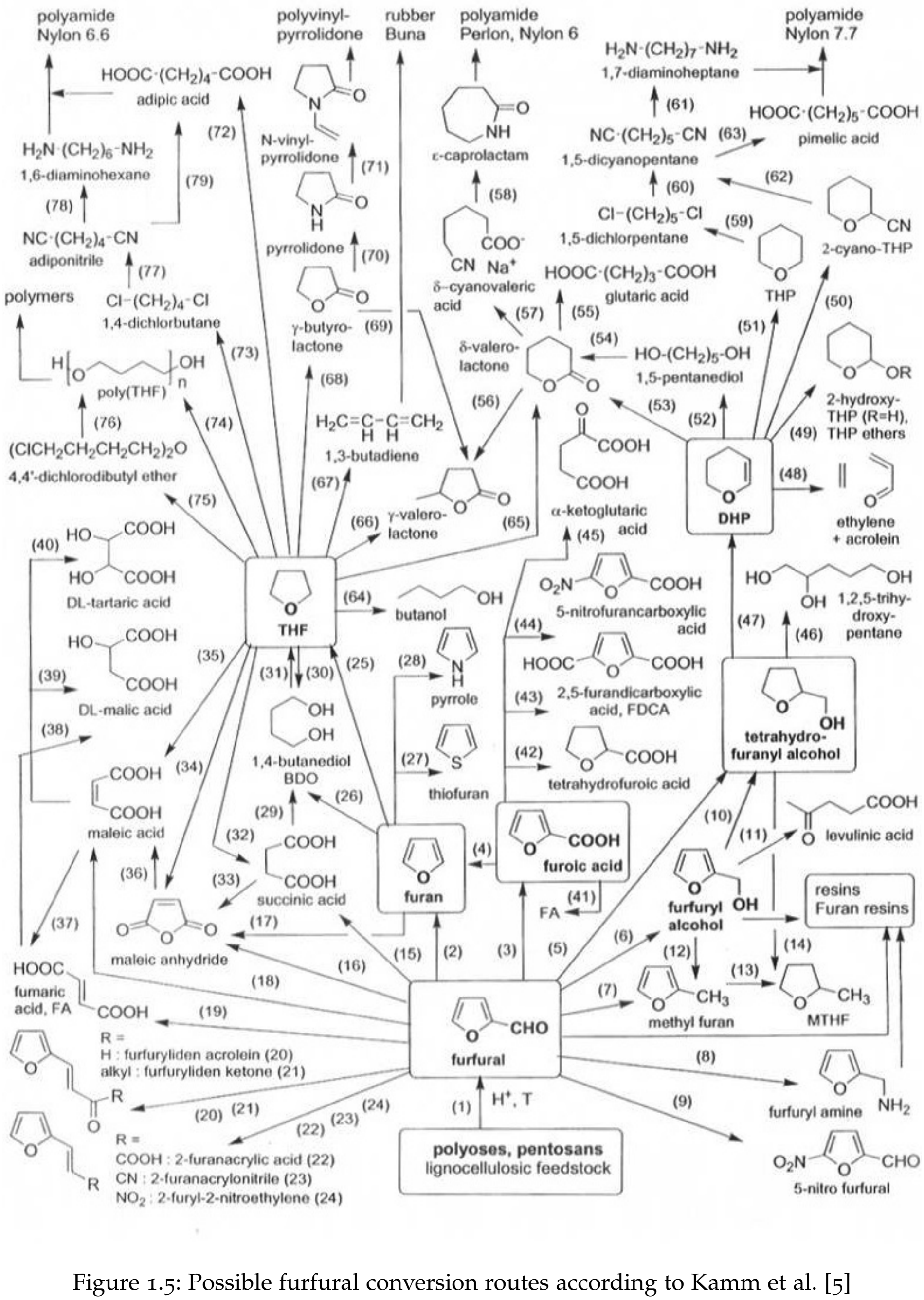


Figure 1.5: Possible furfural conversion routes according to Kamm et al. [5]

Based on the same principle, solvent extraction of aromatics and sulfur compounds may be applied for diesel fuel upgrading. It has been reported that furfural extraction reduced extensively virgin gas-oils sulfur content and improved its burning characteristics such as the cetane number [8].

The selective action of furfural towards unsaturated hydrocarbons is exploited also in the refining of lighter hydrocarbons. Namely, in the purification of 1,3-butadiene from a complex mixture of C_4 hydrocarbons, where simple distillation would not be practical due to the very similar boiling points of mixture components. The addition of a selective solvent, such as furfural, acts changing the relative volatility of the different compounds in the mixture, enabling their separation by extractive distillation [7, 8, 31].

Due to its solvent characteristics, furfural may also be used in vegetable oil refining, carboxylic acids extraction from aqueous solutions, and also as reactive solvent and wetting agent in the manufacture of phenolic resins, abrasive wheels, brake linings and refractory products [31].

Some furfural derivatives of hydrogenation are also important industrial solvents. In particular tetrahydrofurfurul alcohol (THFA) is used as water-miscible, high-boiling, biodegradable solvent for dyes, printing inks, pesticides and herbicides [31]. Another interesting product of furfural hydrogenation is methyltetrahydrofuran (MTHF), which is gaining interest as solvent in organometallic reactions where a strong Lewis base such as tetrahydrofuran (THF) is required. Due to the partial mutual solubility and the low boiling azeotrope of MTHF/water mixtures, MTHF can be used to conveniently recover and dry the products of reaction, and be easily recycled [88].

1.3.2 *Tetrahydrofuran synthesis*

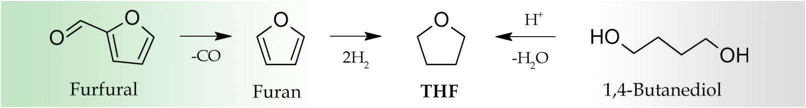


Figure 1.6: Competing furfural and petroleum-based routes to THF

Among all the compounds of the furan series, tetrahydrofuran (THF) deserves a particular mention, as, contrary to what could be expected, it is not derived from furfural or any other furan intermediate.

With an annual production in the order of one Mton, THF largely exceeds furfural production, and it is mainly used as precursor of polytetrahydrofuran (PTHF), important in the production of thermoplastic polyurethanes, elastic fibers e.g. Spandex or Lycra, molded elastomers, and copolyesters or copolyamides.

A smaller proportion finds use as a solvent, as an extracting agent, and as the preferred medium for organometallic syntheses [7, 89].

Preferential industrial processes for obtaining THF involve the catalytic dehydration and cyclization of 1,4-butanediol to THF, see Figure 1.6. The key intermediate 1,4-butanediol may be obtained via different processes, all involving fossil resources [89].

The more logical, bio-based, process involving the decarbonylation of furfural to furan and its subsequent hydrogenation to THF, is very well-known as it was employed between 1949 and 1961 by Du Pont in the manufacture of nylon [8]. The Du Pont process involved four steps with furan, THF, and 1,4-dichlorobutane as intermediates to adiponitrile, but was abandoned in 1961 because tetrahydrofuran could be made more economically from petrochemicals [31].

Interestingly in the last years, due to high oil prices and the local availability of raw material, the furfural-based process for making THF is being reintroduced in China with an initial capacity of 35 kton/y and substantial expansion perspectives [90].

1.3.3 *Furfural as precursor for resins and polymers*

Polymerization of furfural is a well-known reaction, but it has no industrial importance [31]. On the other hand, furfural copolymers with phenol, phenol-formaldehyde resins or ketones have drawn significant interest [7, 91]. In particular, when furfural is used in substitution of formaldehyde in phenol-formaldehyde formulations, the ensuing resins exhibit interesting properties such as improved flow/cure characteristic, solvent tolerance and reduced brittleness, although the polymerization reaction, especially when acid-catalyzed, is more difficult to control [7, 8].

FURFURYL ALCOHOL RESINS When considering the current production of resins from furan compounds, FA is by far the dominating precursor used for numerous industrial applications. The mechanism of FA acid-catalyzed polymerization has been studied extensively for decades, and the complex structure of poly-FA has been elucidated by Gandini and co-workers [92]. The peculiar characteristic of FA-derived resins is a highly cross-linked structure giving them good mechanical and thermal properties, alongside an outstanding chemical resistance. Such resins are used in a variety of applications including sand cores and molds for metal casting; corrosion-resistant fiberglass-reinforced plastics; low flammability and low smoke generating composites and foams; carbonaceous products; corrosion-resistant polymer concretes and impregnating agents for wood modification [91]. Although the patent literature covering the subject of FA- and furfural-based resin formulations for different uses is vast, the use of

FA resins in the worldwide foundry industry remains by far the leading application. The production of FA-based resins for use as binders to produce sand cores and molds for metal castings is currently responsible for the majority of furfural consumption [31].

WOOD MODIFICATION Next to the traditional use in the foundry industry, another application for FA resins is recently gaining commercial interest, i.e. its use as impregnating agent for the production of modified wood. Research concerning modification of wood with FA, sometimes referred to as "furfurylation", was initiated by Dr. Alfred Stamm in the early 1950's, but only recently such technique was brought to commercial scale thanks to the pioneer work of few companies, such as the Norwegian Kebony ASA [93, 94].

Furfurylation, originally developed to substitute the toxic - in some countries now banned - CCA (Copper Chromium Arsenic) treatments, gives to wood an improved dimensional stability, hardness, moisture barrier and resistance to microbial and insect decay, by direct grafting of the FA polymer onto the wood cell walls [95, 96]. The result is a durable, non-toxic, heavy metals-free, directly disposable wood with a very good environmental profile. European or North American wood species treated in this way could be conveniently employed in substitution of tropical teak. The commercial development of furfurylated wood is at its infancy, with an annual production in the order of few thousand tons, but the potential growth is enormous as industrial wood consumption is in the order of 0.9×10^9 m^3 [97].

FURAN-BASED POLYMERS Besides resins, furans are increasingly seen as building blocks for the production of copolymers, polyesters and Diels-Alder systems from renewable resources, capable of replacing fossil-based conventional and high-tech materials. The possibilities of furan chemistry are vast, and the exploitation of furan derivatives for the synthesis of macromolecular materials can be planned strategically in a fashion that resembles closely the approach adopted in the petrochemical industry. A whole original area of polymer science can be built starting from the first-generation furan building blocks, i.e. furfural and HMF. For an overview of the most recent advances in furan polymers the reader may refer to the work of Gandini and co-workers [92, 96, 98, 99].

1.3.4 *Furfural as agricultural nematocide*

It is known from literature that furfural may control plant-parasitic nematodes without adversely affecting crop growth and yield [100]. Very interestingly, it has been shown that furfural do not kill nematodes directly, but act stimulating the development of antagonistic bacteria, thus controlling nematodes in a biological fashion [7]. In view of the phasing out of methyl bromide, and considering that furfural has low acute and ecological toxicity, is non-systemic (not taken up by plants) and safely applicable to soils via water solutions, it is likely to gain a very interesting position as biomass-derived active ingredient in nematocide formulations for agriculture.

Based on these results, the South African sugar and furfural producer Illovo Sugar Ltd. introduced a furfural-based agricultural nematocide with the trade name of Crop Guard^{TM}, which is already registered at the South African Department of Agriculture for different crops. Data have also been submitted to the US Environmental Protection Agency for the same formulation under the name of Multiguard Protect^{TM} by Agriguard Company LLC, USA.

1.4 FUTURE PERSPECTIVES OF FURFURAL AS LIQUID FUELS PRECURSOR

The focus on biofuels for transportation covers a much wider spectrum than ethanol and common biodiesel, incorporating virtually the whole range of biomass transformation technologies [101]. Furfural and furans are no exception, and they have been often addressed as interesting sugar-derived intermediates for the synthesis of biofuels or fuel additives.

In a purely chemical view, biomass derived sugars are highly oxygenated molecules, and need necessarily to be dehydrated, condensed to larger molecules and thus hydrogenated to higher hydrocarbons similar to the constituents of gasoline, diesel and jet fuel. In this perspective, it is noteworthy that both pentoses and hexoses lose three water molecules upon reaction to furfurals, at the same time totally preserving their carbon content (opposite to ethanol), and heating value. The resulting unsaturated, lower oxygen content (furan) molecules, although not indicated for direct use as transportation fuels, are very interesting starting materials for intriguing synthetic pathways to compounds with superior fuel characteristics [102–104].

FURFURAL DERIVATIVES OF HYDROGENATION A straightforward method for upgrading furfurals to suitable liquid fuels is by direct hydrogenation/hydrogenolysis. In this way molecules with higher chemical stability may be attained, presenting also higher heating values due to the hydrogen uptake and eventual oxygen elimination.

The technical knowledge on catalytic hydrogenation of furfural is well established, and by a careful selection of the catalysts and operating conditions quantitative yields of selected molecules may often be approached [7, 8, 31, 45, 58]. Thanks to such selectivity, a whole set of ensuing molecules may be obtained, with a variety of key properties such as octane number, energy density, volatility, polarity, viscosity, water solubility and oxygen content, that might be rationally exploited when formulating novel and optimized fuel blends.

Apart from the odd use of FA as main component of the rocket propellant called "furaline" [7, 8], the first reported tests on furan derivatives as regular gasoline additives may be dated back to 1941, when furfural and few selected derivatives of hydrogenation, namely FA, 2-methylfuran (MF), THFA and MTHF were tested in blends with gasoline [105]. MTHF resulted the only derivative presenting a proper chemical stability and an octane number comparable to - 1940's - gasoline, thus eligible to be used as liquid fuel. Nevertheless, the MTHF unsaturated homologue MF exhibited higher octane number and no appreciable gums formation up to about 20 vol% mixture with gasoline, whereas FA, despite an octane rating comparable to MF, presented an objectionable (but predictable) tendency to polymerization. THFA showed an octane number comparable to MTHF, but, unexpectedly, a higher polymerization tendency was reported, probably due to its lower volatility rather than its reactivity.

Furans use in liquid fuel blends remained apparently dormant until recently, when MTHF was picked up as one of the main components of the so-called P-series alternative fuels [106–109]. Despite its relatively low RON (86), MTHF has been found to favor a better blending of ethanol with C_5 hydrocarbon mixtures, resulting in an alternative fuel formulation with optimized properties that could be directly used in flexi-fuel vehicles [110, 111]. MF has also been reconsidered as bio-based octane enhancer due to its remarkable RON (131), low water solubility and good energy density [58, 104], whereas THFA has been used in low concentrations as anti-icing agent in jet fuels in Russia, due to its melting point below -80°C [112, 113].

SYNTHETIC FUELS DERIVED FROM FURANS Besides direct hydrogenation, furfurals well-known reactivity offers more options to obtain synthetic liquid fuels. By controlled reactions involving furfurals, such as aldol condensation, alkylation and etherification, larger molecules may be obtained, that can undergo subsequent hydrogenation/hydrogenolysis to higher alkanes. Due to the variety of possible synthetic pathways, a whole range of ensuing molecules may be obtained for direct replacement of gasoline, diesel and also jet-type fuels.

Prof. Dumesic and co-workers at University of Wisconsin have done extensive work in this sense, testing numerous controlled condensation reactions of furfurals with acetone, or their self-condensation after ring hydrogenation [104, 114–118]. The resulting higher-carbon content molecules underwent a subsequent hydrogenation/hydrogenolysis step to yield higher alkanes with interesting overall yields.

A similar approach has been recently used by prof. Corma and co-workers [119], who exploited the reactivity of the furan ring at the 5^{th} position for the hydroxyalkylation/alkylation of MF with butanal or other aldehydes. The resulting molecules underwent subsequent hydrogenation/hydrodeoxygenation steps to obtain branched alkanes with comparatively high yields. The organic fraction obtained after such multi-step process presented an excellent pour point (-90°C) and cetane number (70.9), thus excellent diesel-range characteristics.

Similarly, the Amsterdam based company Avantium developed an interesting approach to furanic biofuels, in particular focusing on several 2- or 2,5-ring-hydrogenated furan ethers. The compounds selected present very interesting properties in terms of solubility with regular diesel, cetane number, heating values and good results on engine tests. Due to their properties they also represent an option as bio-based jet fuels [36, 37, 39]. Of particular interest is the furfural and ethanol derivative ethyltetrahydrofurfuryl-ether, presenting superior cetane number, high heating value and good results on engine tests in terms of exhaust emissions [39].

1.5 ECONOMICAL ASPECTS OF FURFURAL INDUSTRY

FURFURAL SUPPLY AND DEMAND In the last decades, the global furfural production capacity has been shrinking or stagnating in most of the countries, with the only exception of China, which currently holds the leadership in furfural and furfuryl alcohol production. As already mentioned, furfural current production generally suffers from low yields, and significant economical and environmental concerns mainly due to its limited technological evolution, furthermore it is characterized by a high number of relatively small producers. As a result, current furfural supply is unstable and volatile, with exchange prices topping 2500 $/ton in the last years mainly because of supply shortages [90]. Yet, investing in new furfural capacity using current technologies is considered a risky enterprise by most operators.

The demand for furfural comes from established businesses, and more recently from few emerging applications such as wood modification, and THF synthesis in China. As mentioned above, there is a multitude of potential downstream applications, but the expansion of furfural demand has to face a stagnating supply. In a scenario of increasing furfural availability experts envision a substantial growth of furfural demand up to 1 Mton/y by 2020, only considering the expansion of traditional businesses [90]. In addition, the global trend toward bio-based products, and rising cost of oil derivatives, is stimulating the demand for furfural for new applications. As shown in Figure 1.7, the cost of production of the main oil derivatives in the last years has been in the range of 1 k$/ton, making furfural an appealing candidate as platform chemical when available at lower and stable prices. The challenge is now in the hands of innovative furfural producers willing to implement novel and disruptive technologies.

Concerning the potential of furfural derivatives as transportation fuels, the competition with oil derivatives is more severe considering the lower energy density of furfural. When comparing the production cost of current fuels on $/GJ basis, as shown in Figure 1.8, furfural would be a competitive alternative in a cost

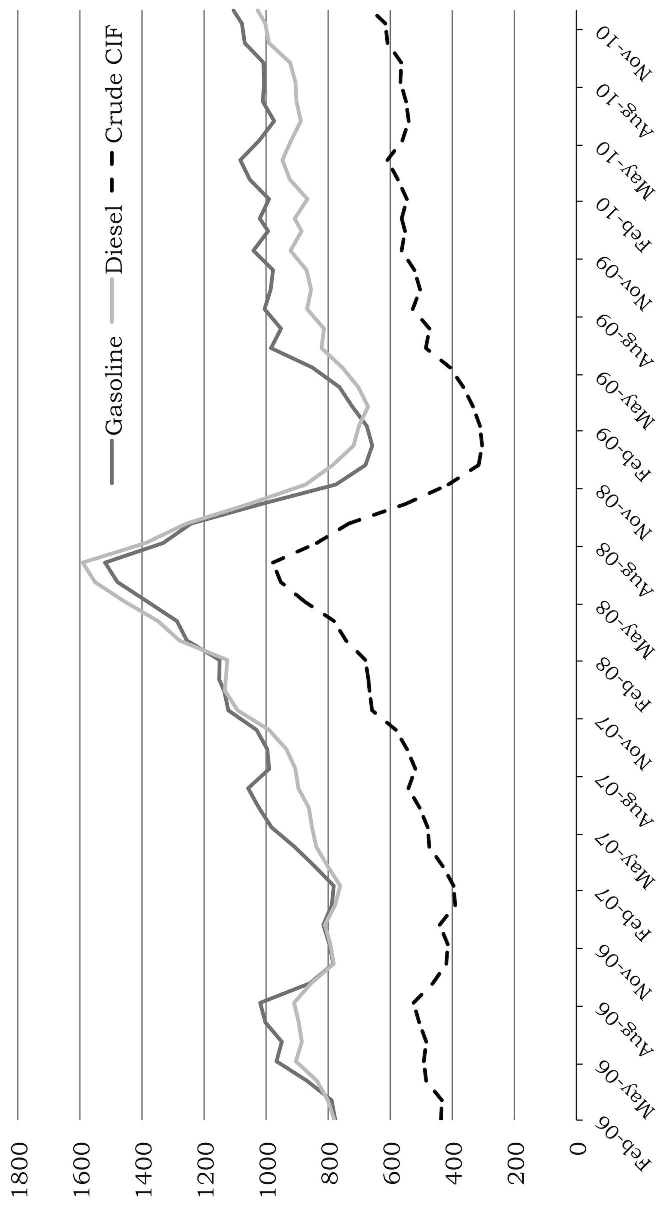


Figure 1.7: Oil exchange price (CIF WTI), and production cost of gasoline and diesel expressed in US$/ton, source [6].

range of 500 $/ton, whereas its fully hydrogenated derivative THFA around 600 $/ton. Current market prices for furfural and derivatives are significantly higher, although they could reach those cost levels when produced in a considerably larger scale, and adopting innovative technologies, as discussed in Chapter 7.

1.6 MOTIVATION AND SCOPE

Despite the relative simplicity of current production processes, there are still some questions that must be addressed concerning the chemistry of C_5 sugars which might lead to significant improvements in furfural production. Although it is well known that C_5 sugars like xylose can be converted quantitatively into furfural under acidic conditions [7, 120–122], there are many aspects which deserve further investigation, especially concerning the reaction mechanisms and kinetics of both furfural formation and destruction under the same conditions of pH and temperature.

The objective of this research is to address some unsolved issues regarding the chemistry and technology of furfural, which may be summarized as follows:

1. Better understanding of the chemistry of furfural formation, in particular addressing the contradicting theories reported by different authors in the scientific literature on the mechanistic aspects of xylose dehydration.
2. To seek in the chemistry of furfural formation the answer to the so-called "paradox of furfural yields" pointed out by Zeitsch [7], concerning the discrepancy in the furfual yields from pentoses obtained in industrial processes (50-60%), in laboratory tests (70%), and in the analytical chemistry (close to 100%).
3. The development of optimal xylose production conditions from raw biomass in view of the development an integrated biorefinery based on furfural production.
4. Finally, developing an innovative furfural production process in order to fit the economical and environmental requirements of the modern biorefinery industry.

1.7 OUTLINE

This dissertation is divided in 8 chapters and is organized in the following way:

In Chapter 2 the experimental methods used in this work are carefully described. A new dedicated test rig is described in all the relevant aspects typical of chemical reactor engineering, and the analytical and experimental methods employed in the several experimental campaigns are also extensively described. Chapter 3 concerns the reaction kinetics of furfural formation. The dependence

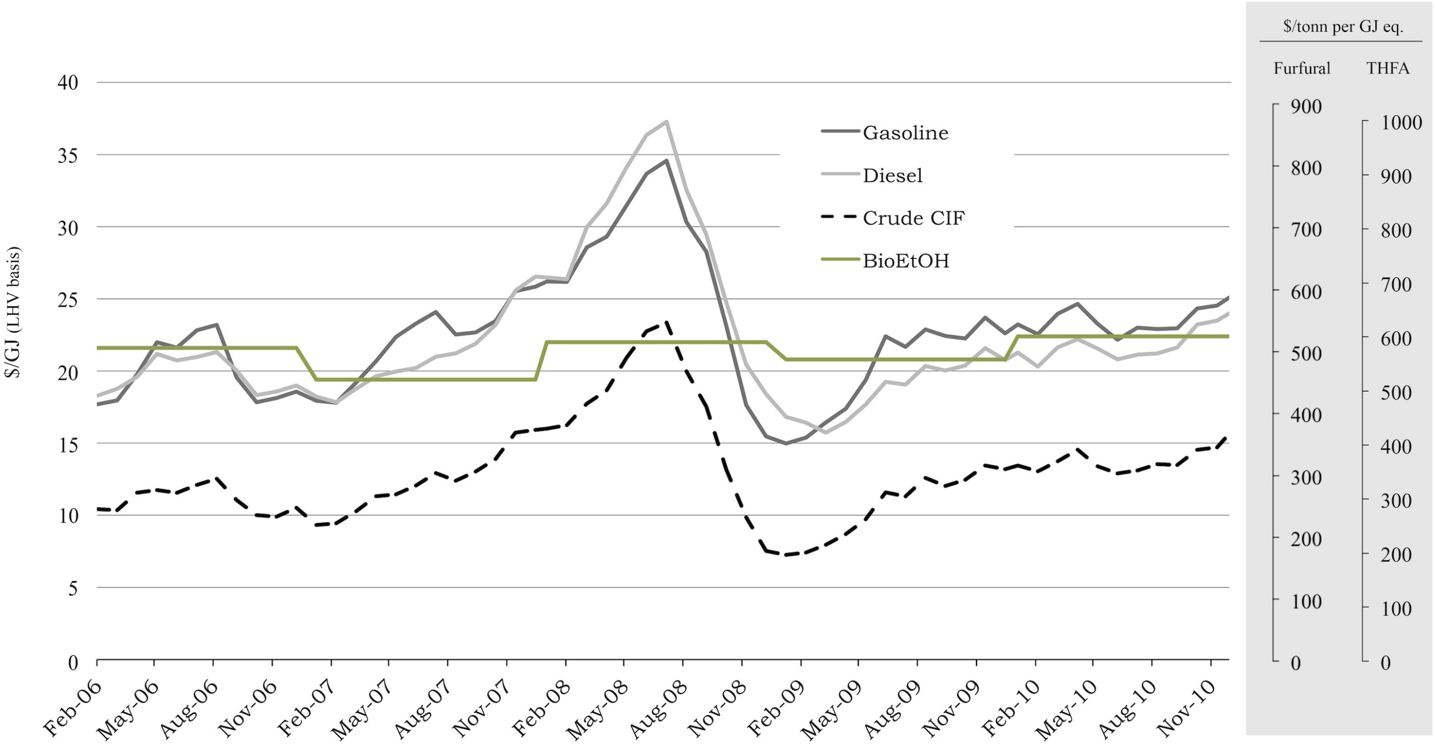


Figure 1.8: Oil exchange price (CIF WTI), and production cost of gasoline, diesel and bioethanol in US$/GJ (LHV basis), source [1, 6].

of furfural formation reactions on the acid nature and concentration is discussed, and a suitable reaction kinetic model is introduced and described.

In Chapter 4 some particular aspects of the chemistry of xylose reaction into furfural are addressed with the aim to clarify the reaction mechanism and to define new green catalytic pathways for its production. In particular the effect of chloride salts in dilute acidic solutions at temperatures between 170 and 200 °C is described, obtaining a better understanding of furfural formation mechanism. Starting from the results discussed in chapter 4, the general effect of different halides is addressed in Chapter 5, showing interesting synergistic effects, and revealing more about the furfural mechanism of formation.

In Chapter 6 the combined production of hemicellulose-derived carbohydrates and an upgraded solid residue from wheat straw using a dilute-acid pretreatment at mild temperature is described. The solid residues of pretreatment are also characterized showing a preserved crystallinity of the cellulose, and upgraded characteristics for thermal conversion applications.

Chapter 7 deals with the industrial processes for the production of furfural, describing in particular an innovative process patented by Delft University of Technology based on the results contained in this dissertation. The innovative process concept described in this chapter is aimed at an economically viable and environmentally sound furfural production from biomass hydrolisates, with reduced energy and chemicals consumption.

Finally in Chapter 8 an overview of the main conclusions is presented, and some recommendation are provided for future research.

2

EXPERIMENTAL METHODS

In order to investigate several aspects related to the furfural formation and related reactions, a new lab-scale titanium reactor has been designed and built in order to enable liquid phase reactions under a relatively broad range of pressure, temperature and pH conditions. Such test rig has allowed most of the experimental work behind this dissertation, and it is thoroughly described in this chapter in all the relevant aspects typical of chemical reactor engineering. The analytical and experimental methods employed in the several experimental campaigns described in this dissertation are also extensively described in this chapter.

The contents of this chapter have been adapted from:

Marcotullio, G.; Cardoso, M. A. T.; De Jong, W. and Verkooijen, Ad H.M. (2009) Bioenergy II: Furfural Destruction Kinetics during Sulphuric Acid-Catalyzed Production from Biomass, *International Journal of Chemical Reactor Engineering*: Vol. 7: A67

2.1 MATERIALS

Xylose reagent grade (Sigma-Aldrich, $\geq$99%) and Furfural reagent grade (Sigma-Aldrich, 99%) were used as model compounds in the experiments, and for HPLC calibration. Furfural was further purified via vacuum distillation. Concentrated HCl (36.5 – 38%wt), H_2SO_4 (95-98%wt), and acetic acid (99-100%wt) were purchased from J.T.Baker. Pure $FeCl_3$ hexahydrate, NaCl, $CaCl_2$ dihydrate, KCl, KBr, KI, $KHSO_4$ and $CaCO_3$ were purchased from Merck.

For the experiments discussed in chapters 3, 4 and 5, acidic aqueous solutions of xylose (or furfural) were prepared with demi-water, then added with known amounts of inorganic salts, and fed to the tube reactor after stirring to ensure a complete dissolution of the solids.

2.1.1 *Analysis of the reaction products*

Analysis of the reaction products was carried out by means of an HPLC apparatus equipped with a Resex ROA-Organic acid column, 8% cross linked H^+, 300×7.80 mm, or alternatively with a Resex RHM-Monosaccharide column, 8% cross linked H^+, 300×7.80 mm (Phenomenex Inc., Torrance, CA, USA). A Marathon XT auto-sampler (Separations, Ambacht, NL) was used to enhance reproducibility. Quantification of the components was carried out by means of both Refractive Index detector (Varian Model 350) and UV detector (Varian Model 310 Pro Star) in series.

The mobile phase consisted of a 0.005 N H_2SO_4 solution in demineralized water. The HPLC was operated at a flow rate of 0.6 ml/min, at a column temperature of 80 °C.

2.2 EXPERIMENTAL SETUP

The experimental setup consists of a coiled tube reactor immersed in a thermostatic oil bath. The reactor is made of titanium grade 2 (Merinox, Alblasserdam, NL) to ensure high resistance to corrosion and minimal catalytic effects. The tube reactor has an external diameter of 3.2 mm, internal diameter of 1.7 mm, and a length of 4.40 m. The reactants are fed to the reactor by a Waters HPLC pump, while the reaction temperature is precisely controlled and kept constant by the oil bath. The reaction solution is rapidly heated up to the set temperature by an electrical heater consisting of an insulated aluminum block which encloses the tube reactor for a length of approximately 15 cm. Downstream the reactor the solution is cooled down by means of a double pipe heat exchanger fed with tap water, see figure 2.1.

In the range of process conditions considered, the flow in the tube reactor is within the laminar region as the maximum Reynolds number achieved in this

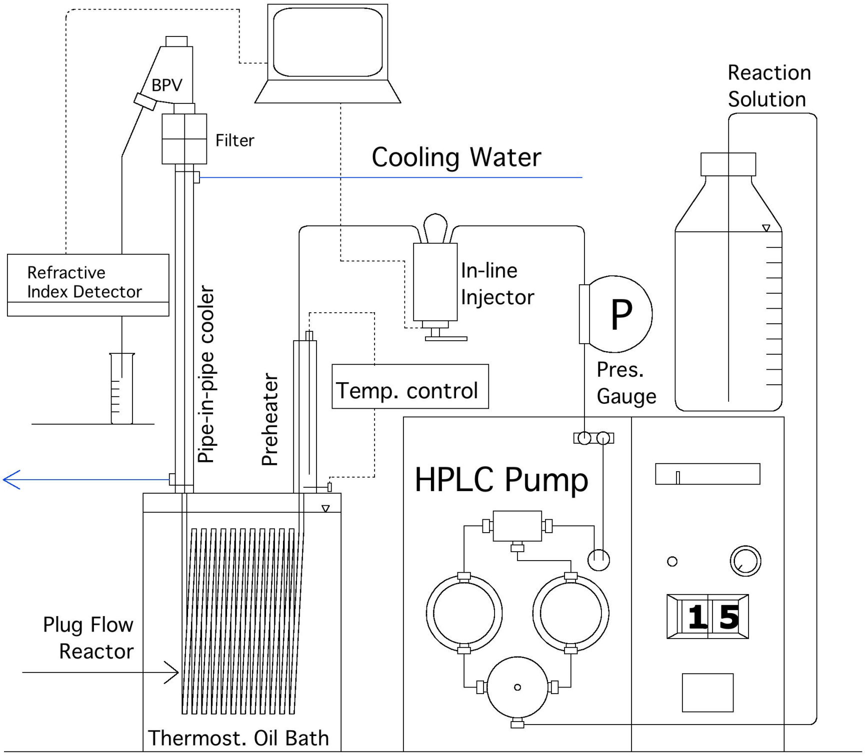


Figure 2.1: Representation of the experimental setup. The refractive index detector, injector and the computer were only used for the testing purposes described in this chapter, but not during the experimental campaigns.

work is around 320. This implies the need of a careful evaluation of the residence time distribution (RTD) along the reactor. To accurately determine the RTD, tests were carried out injecting a small volume of a tracer solution (50%vol formic acid in water) in the proximity of the reactor inlet through an in-line injector, see figure 2.1, and detecting its concentration distribution in time at the reactor outlet by means of a refractive index detector. This procedure was repeated for various conditions of flow rate and temperature and the detector and the injector were connected to a terminal for data collection and processing.

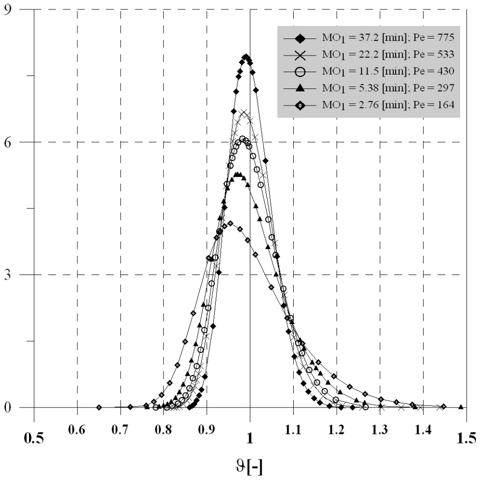


Figure 2.2: Dimensionless $E(\vartheta)$ for different flow-rates, at $T = 180^{o}C$

In figure 2.2 some experimental RTD curves $E(\vartheta)$ are depicted. All the curves are normalized, ϑ being a dimensionless time scale:

$$\vartheta = \frac{t}{MO_1} \quad where \quad MO_1 = \int_0^{\infty} tE(t)dt \quad and \quad \int_0^{\infty} E(t)dt = 1$$

The quantity MO_1 is the first momentum of the normalized RTD curve $E(t)$, which represents the average residence time of a molecule in the reactor. Normalized variance σ_ϑ can be easily calculated by integration of the RTD curves. It is relevant to estimate Péclet (Pe) number for all curves using equation (2.1):

$$\sigma_\vartheta^2 = \frac{2Pe - 2 + 2e^{-Pe}}{Pe^2} \quad \Rightarrow \quad Pe \simeq \frac{2}{\sigma_\vartheta^2}\, for\, Pe > 100 \tag{2.1}$$

as the Pe number gives an indication of how axial dispersion counteracts the spreading effect due to the laminar velocity profile. In the cases investigated Pe varies from 164 to 775, while MO_1 varies from 2.76 to 37.21 min. A higher Pe number means a behavior closer to an ideal plug-flow reactor, as shown in figure 2.2 where RTD curves present an asymmetrical shape which approaches a sharper Gaussian distribution when the residence time becomes longer and Pe higher, [123].

Considering a first order reaction, and knowing $E(t)$, real conversion rates can be calculated by applying equation (2.2):

$$\frac{C}{C_0} = \int_0^{\infty} e^{-kt} E(t)dt \tag{2.2}$$

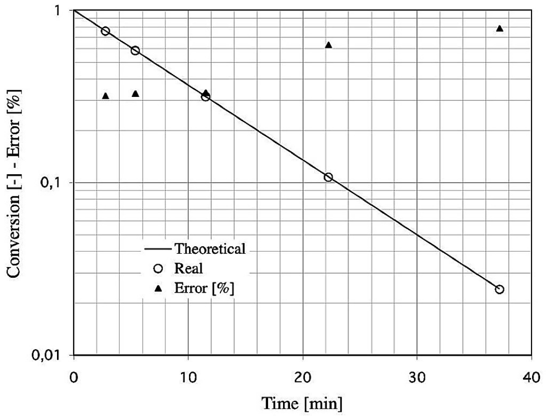


Figure 2.3: Theoretical and real conversion rates when $k = 0.1[min^{-1}]$

These values are shown to very closely approach the theoretical conversion rates calculated as $(C/C_0) = e^{-kt^*}$ when $t^* = MO_1$ as shown in figure 2.3 for a hypothetical case. Thus, when MO_1 is taken into account as the average residence time in the reactor, uncertainties due to the laminar flow spreading effect can be neglected even at higher flow-rates and shorter residence times. In this case the reactor can be considered as an ideal plug-flow reactor.

2.2.0.1 *Main reactor characteristics validation*

Since the entire length of the tube is not at reaction temperature and in order to precisely assess the average time of the reactant under actual reaction conditions, the length of the tube at those conditions needed to be estimated. This was done by residence time measurements as described below.

The tube reactor was considered to be the sum of a two portions of tube in series at different temperatures, being the volume V_H at reaction temperature and V_R at room temperature. Temperature transitories were neglected and instantaneous temperature increments were assumed to occur within the length of the two heat exchangers. For simplicity V_H and V_R are assumed to be constant for all conditions of temperature and flow rates. Thus the total volume between the injector and the detector is $V_{tot} = V_H + V_R$; in the same way the average residence time in the reactor can be considered to be the sum of the average residence time in the high temperature portion of the reactor, which is the one of interest for the reaction, and the average residence time in the rest of the volume, being then $\tau_{tot} = \tau_H + \tau_R$. Considering $\dot{m}$ to be the mass flow rate and ρ the density of the solution, by the mass conservation one derives:

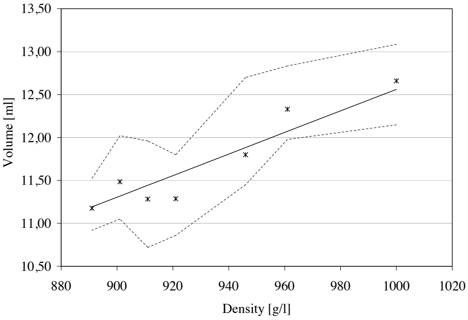


Figure 2.4: Apparent reactor volume V^* against solution density ρ_H. (*) Averaged measured values at constant T; $(\cdots)$ measurement dispersion; (-) model used in this work

$$\tau_R = \frac{\rho_R V_R}{\dot{m}}; \qquad \tau_H = \frac{\rho_H V_H}{\dot{m}} \tag{2.3}$$

which results in:

$$\tau_{tot}\dot{m} = V_{tot}\rho_R + V_H\left(\rho_H - \rho_R\right) \tag{2.4}$$

When the reactor is at room temperature, for every $\dot{m}$:

$$\dot{m} = \frac{V_{tot}}{\tau^0_{tot}}\rho_R \tag{2.5}$$

where τ^0_{tot} is the average residence time in the reactor when the reaction temperature equals the room temperature. τ^0_{tot} can be measured directly by detecting the tracer solution at the outlet of the reactor. Combining equations (2.4) and (2.5) results in the following equation:

$$V^* = \frac{\tau_{tot}}{\tau^0_{tot}}V_{tot} = V_R + V_H\frac{\rho_H}{\rho_R} \tag{2.6}$$

The volume V^* in equation (2.6) represents the total apparent volume of the reactor which decreases as the solution density ρ_H decreases with increasing reaction temperature. Experimental assessment of V^* variation with ρ_H allows the estimation of V_H and V_R. In this way the average residence time τ_H can be calculated by equation (2.3) for every $\dot{m}$ and temperature. Operating with very diluted solutions, density ρ_H was assumed to closely approach that of water and it was computed, given pressure and temperature, using the highly accurate thermodynamic model for water included in the RefProp package by NIST, [124], where the FluidProp package was used as interface, [125]. Experimental results are shown in figure 2.4 where V^* is plotted against ρ_H. The solid line in the figure 2.4 was drawn given V_H, which was derived by estimating the temperature profile along the tube, and deriving V_R by least square fitting. As shown in figure 2.4 the average error introduced by using the calculated reaction residence time is always less than 3%, and can be mostly regarded as the result of the pump flow rate variation.

2.2.0.2 *Operations*

After achieving the desired temperature in the oil bath and pre-heater, the flowrate $\dot{m}$ was set in order to get the desired τ_H. The operating pressure was kept always around 60 bar by means of a back-pressure regulator, which is higher than the saturated pressure of water in the temperature range considered to ensure entirely liquid phase operation in the reactor. For each set of temperature and flow rate $\dot{m}$ conditions the system was run for a time longer than the corresponding $\vartheta = 1$ (see figure 2.2) to ensure that steady state was achieved and then a sample was recovered in a vial at the reactor outlet and analyzed. The operation was carried out for every desired τ_H, and every set of temperature and initial pH.

2.3 METHODS USED FOR WHEAT STRAW PRETREATMENT

2.3.1 *Materials*

The wheat straw used in this work came form Spain, and it was made available within the FP6 European project Biosynergy. The straw was ground, passed through a 1.4 mm sieve and stored in a Polyethylene container at room temperature. Pure monomeric sugars (99%), D-xylose, L(+)arabinose, and D(+)glucose used as reference materials were purchased from Sigma-Aldrich. Concentrated HCl (36.5 – 38%wt), H_2SO_4 (95-98%wt), and acetic acid (99-100%wt) were purchased from J.T.Baker. Pure $FeCl_3$ hexahydrate, NaCl, $CaCl_2$ dihydrate, and $CaCO_3$ were purchased from Merck.

2.3.2 *Wheat straw pretreatment procedures*

Borosilicate glass bottles of 50 ml internal volume with membrane screw cap (Duran) were used in this work to carry out the reactions. Wheat straw samples of 2g (a.r.) were mixed with 10ml of solution directly inside the glass reactor. The solutions employed in this work were pure water and dilute solutions of HCl or $FeCl_3$ (100-200 mM in pure water). After the preparation of the sample the bottle was sealed and placed in a ventilated oven, which was then set to the desired temperature (100 - 120°C). For all the pretreatments the reaction time was 120 min, and it was counted starting when the oven reached the aimed temperature. The actual temperature inside the glass bottles could not be measured.

The reactions were carried out in static conditions as no stirring was employed. After the desired residence time, the reaction was ended by quenching the bottle in a water bath at room temperature. The contents of the bottle were thus collected using a spatula into a vacuum filtering device. The bottle was repeatedly cleaned from the remaining traces of solids using ultra-pure water, which was thus poured onto the filter cake in order to ensure a better washing of the solids. The liquid filtrate was collected and made up to 50 ml with ultra-pure water using an appropriate volumetric flask and, after pH measurement, it was stored in a refrigerator for further analysis. The solid residue was dried at room temperature and weighed after 24 hours.

All pretreatments were performed in duplicates and averaged data are presented. Raw measurement data such as carbohydrates concentration in the filtrates, filtrates pH and sample weight loss showed limited deviations between duplicates, the average deviation being in the range of ±8%.

2.3.3 *Analytical methods*

2.3.3.1 *Liquid filtrates analysis*

Monomeric sugars (MS) and acetic acid concentrations in the filtrates were measured by means of an HPLC apparatus equipped with a Resex RHM - Monosaccharide column, 8% cross linked H^+, 300×7.80 mm, (Phenomenex Inc., Torrance, CA, USA). A Marathon XT auto-sampler (Separations, Ambacht, NL) was used to enhance reproducibility. All components were quantified by means of a Refractive Index detector (Varian Model 350). A 0.005 N H_2SO_4 solution was used as the eluent at a flow rate of 0.6 ml/min with a column temperature of 80°C and a run time of 25 min. No appreciable amounts of furfurals were found in the filtrates.

In order to quantify the soluble sugars in oligomeric form (OS), 10 ml of liquid filtrate was added with 0.4g HCl solution (36.5 – 38wt%) and underwent a second hydrolysis step at 120 °C for one hour. Sugar standard samples of known concentration were also subjected to the same treatment at the same conditions to quantify the sugar loss (SL) during such step (always in the order of few percent). The hydrolysate was added with $CaCO_3$ until neutral pH and then analyzed. The total pentoses content measured after the second hydrolysis step was corrected for the sugar loss considered as the fraction of sugars disappeared after the second hydrolysis step on the initial. For this correction a conservative hypothesis was taken considering only the monomeric fraction MS to be subjected to loss reactions. The OS were thus calculated as the measured sugars in the hydrolysate minus MS*(1-SL), whereas the total sugars were MS+OS. Such method employed for the quantification of soluble oligomeric sugars did not give any information on their degree of polymerization.

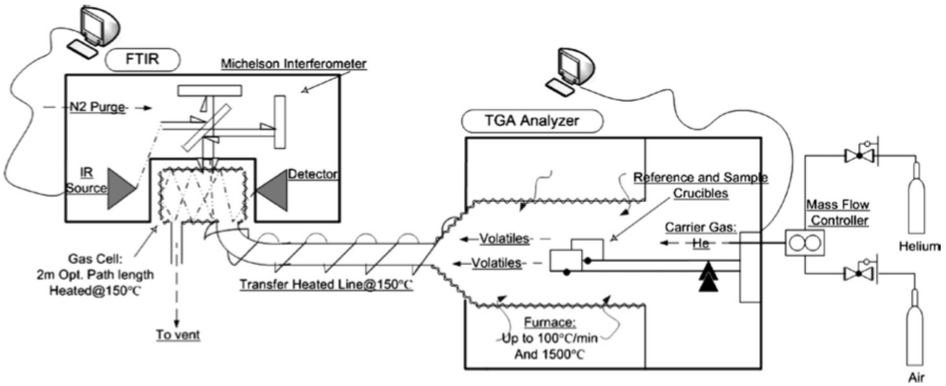


Figure 2.5: TG-FTIR set-up at TU Delft Process and Energy Laboratory

The yield of total sugars was calculated on the basis of the untreated wheat straw composition. The composition analysis of the wheat straw used in this work was made available within the framework of the European FP6 research project Biosynergy and fully presented by Huijgen et al. [13]. The reported content of the main polysaccharides is: xylan 21.5, arabinan 2.1, glucan 34.6 wt% d.b.. No biochemical composition analysis of the untreated wheat straw, nor of the residues of pretreatments, was directly carried out in this work.

2.3.3.2 *Thermo-gravimetric analysis of the solid residues*

The untreated wheat straw and the solid residues of the pretreatments were analyzed using a Thermo-Gravimetric setup SDT Q600 produced by TA Instruments, USA, used in a configuration similar to what was reported in previous works from our group [126], and shown in Figure 2.5 in its complete configuration including online FTIR detector (not used in this work). The residues were manually ground and placed in an alumina cup in amounts varying from 4 to 6 mg. The samples were kept at 50 °C for 45 min under a flow of 100 ml/min of nitrogen. The temperature was then ramped up at a rate of 10 °C/min to 120 °C and kept constant for 15 min in order to thoroughly dry the sample. Moisture was quantified as the weight loss at the end of this period. The temperature was then increased again at 10 °C/min to 550 °C where the sample was kept isothermal for 20 min, and it was finally combusted in air (100 ml/min) at this temperature for 20 min. The residue after the isothermal period at 550 °C is regarded as char, the residue after combustion is regarded as "ash" whereas the fixed carbon is quantified as the difference between the char and the ash.

2.3.3.3 *X-ray analysis of the solid residues*

X-ray diffraction (XRD) and X-ray fluorescence (XRF) were used to examine the physical characteristic of untreated wheat straw, as well as pretreated samples. X-ray diffraction analysis of untreated and pretreated solid samples can give information regarding the crystallinity index of the cellulose in the wheat straw samples, whereas XRF was used for elemental analysis of the solid residues.

XRD analysis was carried out using a Bruker D5005 diffractometer equipped with Huber incident-beam monochromator and Braun PSD detector. The X-ray powder diffraction patterns were recorded in a Bragg-Brentano geometry. The samples of untreated wheat straw and the pretreated solid residues were scanned from 2θ=5° to 60° with a step size of 0.038°. All samples were measured under identical conditions. Cu Kα radiation source (α = 0.154056 nm) was used and around 20 mg of sample was deposited on a Si<510> wafer and was rotated during measurement. Data evaluation was done with the Bruker program EVA.

The crystallinity index (CrI) was defined as follows:

$$CrI = \frac{I_{002} - I_{am}}{I_{002}} 100$$

where I_{002} and I_{am} are the intensity of diffraction at 2θ=22.6° (crystalline region) and at 2θ=16,2° (amorphous region) respectively, as already described in literature [127].

Semi-quantitative multi-element analysis of all inorganics (C, H, O, and N are not measured) was carried out using a Philips PW2400 X-ray wavelength dispersive Fluorescence Spectrometer. Data evaluation was done with Uniquant (5.0) software. Samples of wheat straw solid residues of pretreatment, of about 1 gram each, were pressed into pellets of 27mm diameter and analyzed.

All the X-ray analysis were carried out at the Department of Materials Science and Engineering of the Delft University of Technology.

3

REACTION KINETICS IN FURFURAL PRODUCTION

Even considering the number of relevant works on the topic of furfural formation in acidic media, a general expression for the reaction kinetics, its dependence on the acid nature and concentration, and the potential effect of other species present in solution, is yet to be established. Results of reaction kinetics studies related to furfural formation from xylose, xylose side reactions, and furfural destruction in acidic aqueous media are reported in this chapter.

The contents of this chapter have been adapted from:

Marcotullio, G.; Cardoso, M. A. T.; De Jong, W. and Verkooijen, Ad H.M. (2009) Bioenergy II: Furfural Destruction Kinetics during Sulphuric Acid-Catalyzed Production from Biomass, *International Journal of Chemical Reactor Engineering*: Vol. 7: A67

Marcotullio G., Heidweiller H., de Jong W., Reaction kinetics assessment for selective production of furfural from C_5 sugars contained in biomass, *in proceedings of 16th European Biomass Conference and Exhibition* - From Research to Market, pp. 1-6, ETA, June 2008, Valencia - Spain.

3.1 FURFURAL FORMATION AND DESTRUCTION IN ACIDIC CONDITIONS

Many relevant studies on the chemistry of furfural, its mechanism and kinetics of formation and destruction in aqueous acidic solution, have been published from the 1940s up to now [7, 50, 120–122, 128–137]. By reviewing the literature available on this topic, a limited agreement emerges between different studies, which are often carried out under different temperature conditions, using different catalysts in a wide concentration range, or using different raw materials at different initial concentrations. In this dissertation it will be shown that the chemistry of furfural formation has a complex dependence on catalyst type, and secondary reactions may become relevant when increasing the initial concentrations of reactants.

In this chapter experimental results are presented concerning furfural formation in aqueous acidic solutions from pure D-xylose, and furfural destruction under similar conditions. A relatively narrow range of conditions is investigated, which is considered relevant both from the analytical point of view, and for industrial application. In particular, reaction temperature is varied between 150 and 200 °C, and a dilute-acid media is employed in order to resemble industrial operations. Sulfuric acid is chosen as model catalyst, at concentrations between 145.5 and 36.4 mM (pH between 0.81 and 1.36 at 298 K). Furthermore initial reactants concentration is kept in the dilute range - the initial concentration of furfural varied between 60 and 72 mM, and that of D-xylose varied between 7 and 133 mM - in order to limit second order reactions.

Different reaction kinetic mechanisms leading from xylose to furfural have been proposed in literature, from more simple ones to more complicated [7, 8, 120–122, 133], but almost all of them can be expressed in a simplified way as depicted in Figure 3.1. Even if simple such a scheme of reaction enables to accurately fit the experimental results under the conditions of interest for this work, thus it is chosen for describing the reaction. As the initial sugar concentration is kept in the dilute range, second order reactions between furfural and intermediates can be ruled out; the effect of increasing initial sugar concentration is presently being studied and it will be discussed elsewhere. Such approximation allows for describing the reaction rates by a relatively simple analytical expression:

$$\begin{cases} r_{D-Xylose} = \frac{dC_X}{dt} = -(k_1 + k_2)C_X \\ r_{Intermediate} = \frac{dC_i}{dt} = k_1 C_X - k_{1b} C_i \\ r_{Furfural} = \frac{dC_F}{dt} = k_{1b} C_i - k_3 C_F \end{cases} \tag{3.1}$$

Reaction intermediate(s) have never been clearly identified in literature, nevertheless, judging from experimental results, their concentration can be assumed to be low and not varying significantly with time. Hence steady-state approximation can be introduced for the intermediate resulting in $dC_i/dt = k_1 C_X - k_{1b} C_i \cong 0$

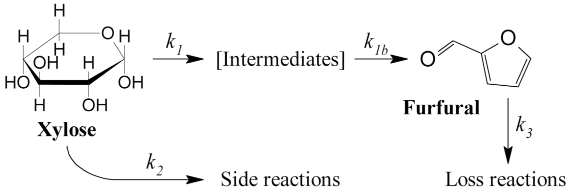


Figure 3.1: Simplified scheme for furfural formation from D-xylose

and then ${}^{dC_F}/_{dt} \cong k_1 C_X - k_3 C_F$. Introducing this assumption makes the integration easier and the concentration of xylose and furfural can be written as:

$$\begin{cases} C_X(t) = C_{X_0} e^{-(k_1+k_2)t} \\ C_F(t) = C_{X_0} \left(\frac{k_1}{k_3-k_1-k_2}\right) \left(e^{-(k_1+k_2)t} - e^{-k_3 t}\right) \end{cases} \tag{3.2}$$

where the initial furfural concentration $C_{F_0} = 0$ and C_{X_0} is the initial xylose concentration. The maximum molar yield of furfural can also be analytically derived as a function of the three main kinetic parameters as:

$$\frac{C_{Fmax}}{C_{X_0}} = \frac{k_1}{k_1+k_2} \left[\left(\frac{k_1+k_2}{k_3} \right)^{\frac{k_3}{k_3-k_1-k_2}} \right] \tag{3.3}$$

3.2 KINETICS OF FURFURAL DESTRUCTION

Furfural is a very reactive compound and is known to easily polymerize in both acid and basic environment following various routes. Moreover, in aqueous acidic media, the furan heterocycle is reported to undergo ring opening resulting in aliphatic open-chain products [98]. For these reasons, under the same conditions of temperature and acidity employed for its production, furfural degrades at an appreciable rate, posing a major issue when designing industrial production processes.

In order to better quantify the furfural rate of destruction under specific conditions, specific experimental studies have been performed using pure furfural as model compound in acidic aqueous solutions. Under the conditions considered in this work the reaction rate of furfural destruction presents a first order behavior with respect to furfural concentration, hence furfural-furfural polymerization reactions leading to resins seem unlikely to take place, in agreement with earlier observations [50, 120].

The model proposed here postulates the protonation of the furfural molecule and its subsequent reaction, resulting in the following simple first order rate equation:

$$\frac{dC_F}{dt} = -k_3 C_F \tag{3.4}$$

The kinetic parameter k_3 may be easily derived by least square fitting starting from experimental measurements. As expected, the k_3 show a clear dependence on temperature as well as on H_2SO_4 initial concentration. Nevertheless, a simple correlation with initial $H_3O^+_{aq}$ concentration resulted inadequate to predict the measured results.

Thermodynamics of electrolytes in liquid hot water need to be considered in the first place. It is known from literature that the second dissociation constant of sulphuric acid varies significantly with temperature and with the ionic strength of the solution [138–140], and neglecting such effects might lead to significant uncertainties, as observed by some authors [7, 133]. In particular, within the range of conditions of interest for this work, the bisulfate ion becomes a very weak acid ($pKa_2 \simeq 4$) [138], thus aqueous sulphuric acid can be considered with good approximation monoprotic and only dissociated into H_3O^+ and HSO_4^-. For this reason the H_3O^+ concentration at reaction conditions may be assumed to equal the initial acid concentration, see Table 3.1. Nevertheless, when considering the formulation $k_3 = k_3^*[H_3O^+]$, and an Arrhenius temperature correlation for k_3^*, the model results inadequate when compared to experimental results. In particular, at constant temperature, the reaction rate presents a less than linear dependence on $[H_3O^+]$ (H_3O^+ molar concentration), thus the correlation between k_3 and acid concentration has an higher complexity.

When studying acid catalyzed reactions of organic compounds, a common approach is to make use of the acidity function $H_\circ$ proposed by Hammett in 1934 [141], which takes into account a complex correlations derived from the equilibrium between a weak base and its protonated form in an acidic solutions. On the other hand, the complicated Hammett acidity function for low acid concentration approaches the $pH = -Log(a_{H_3O^+})$ [142]. Considering the range of conditions employed in this work in terms of temperature, pressure and ionic strength, the general formulation for dilute solutions may be considered acceptable. Based on these considerations, the ion activity $a_{H_3O^+}$ was used in the kinetic formulation instead of the simple $[H_3O^+]$, which possibly accounts for the lower "availability" of the ions with increasing ionic strength as well as for the changing dielectric characteristics of the solvent induced by temperature [142, 143]. When using the formulation $k_3 = k_3^*\, a_{H_3O^+}$, the resulting rate constant k_3^* shows a clear Arrhenius dependence on temperature in the range of conditions considered, as depicted in Figure 3.2. Thus $a_{H_3O^+}$ may be considered an adequate measure of the acid catalytic activity on furfural destruction. Deviation of two measurements at lower temperature can be explained by the amplification of

Table 3.1: H_3O^+ molar concentration $[H_3O^+]$ and relative activity coefficient $\gamma_{H_3O^+}$ at various temperature and initial acid concentration as estimated by the eNRTL model

	Initial H_2SO_4 molar concentration			
	0.145 M	0.109 M	0.073 M	0.036 M
T /°C	$[H_3O^+]$ ($\gamma_{H_3O^+}$)	$[H_3O^+]$ ($\gamma_{H_3O^+}$)	$[H_3O^+]$ ($\gamma_{H_3O^+}$)	$[H_3O^+]$ ($\gamma_{H_3O^+}$)
190	0.146 (0.566)	0.109 (0.607)	0.073 (0.660)	0.036 (0.739)
180	0.146 (0.573)	0.110 (0.614)	0.073 (0.667)	0.036 (0.744)
170	0.146 (0.578)	0.110 (0.620)	0.073 (0.673)	0.036 (0.750)
160	0.147 (0.583)	0.110 (0.625)	0.073 (0.678)	0.036 (0.754)

measurement errors in a range of conditions where furfural concentration decay is more difficult to quantify. In this temperature range the reaction is very slow and thus k_3 values rather small ($\sim 10^{-5}\, s^{-1}$).

Individual ion activity for the ionic species i may be defined as: $a_i = \gamma_i [C_i]$, where γ_i represents the individual activity coefficient and $[C_i]$ the molar concentration. In general, from the Debye-Hückel theory, the ions activity coefficient can be related to the ionic strength I in dilute solutions according to the equation:

$$\log_{10} \gamma_i = -A z_i^2 I^{1/2}$$

where z is the ion charge and A is a constant dependent on temperature, density and dielectric constant of the solvent. Although simple, such correlation might be inadequate in a wider range of conditions, and especially at ionic strength higher than about 0.1 M. For this reason, some authors have made use of either the Pitzer model [138, 144], or the electrolytes NRTL (eNRTL) model [145]. In this work the latter model was chosen, where the commercial software Aspen Plus^{TM} was used for its implementation. Individual ion activity coefficients under actual reaction conditions could thus be estimated, see Table 3.1.

The solid line in figure 3.2, was drawn by least square fitting of the experimental measurements and it refers to the Arrhenius formulation $k_3^* = Aexp(-\frac{E_a}{RT})$ where ln(A)=26.64 [s^{-1}] and the activation energy E_a=125.1 [kJ/mol]. From these kinetic parameters enthalpy and entropy of activation could easily be derived, resulting in $\Delta H^\ddagger$=E_a-RT=121.1 [kJ/mol] and $\Delta S^\ddagger = R\left(\ln k_3^* - \ln T - 23.76 + \frac{\Delta H^\ddagger}{RT}\right)$ = -35.7 [J/molK] at 473K. The negative value for the activation entropy shows a decrease in entropy across the transition state, which in this case could mean the association of the furfural molecule with the proton forming a more ordered intermediate [143].

As far as the activation energy is concerned, these results are in disagreement with earlier studies, which reported much lower values for this reaction, namely

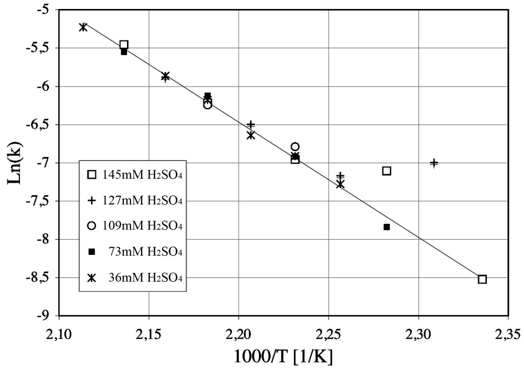


Figure 3.2: k_3^* $[s^{-1}]$ Arrhenius plot in the temperature range 150-200 °C

20 kcal/mol (83.7 kJ/mol) [50]. Rather than to differences in reaction rate measurements, such disagreement might be explain due to the different modeling done by the authors. In particular, major discordances are generated when considering the non-ideality of the acid solution, i.e. ions activity, as well as the sulphuric acid second dissociation constant variation with temperature. Nevertheless, despite the different modeling, good agreement is observed when comparing the experimental measurement reported in the same work [50] with those predicted by using the model proposed here under the same conditions (0.1 N H_2SO_4 at 160 °C for 180 min). In this case the deviation in terms of predicted and measured furfural concentration in time is always lower than 7%.

With respect to the furfural destruction reaction products, in the same work [50] it was claimed that formic acid had been identified, which was suggested to result from the hydrolytic fission of the furfural aldehyde group. In this work formic acid could not be clearly identified and quantified, and by a qualitative analysis of the HPLC-UV chromatograms, its presence, if cannot be excluded, can be regarded as marginal under the tested conditions. Formic acid detected during furfural production from pentosans might rather be considered as the result of parallel sugar reactions [133], whereas a stronger evidence of rehydration of the furfural molecule to components like reductic acid has been reported [130].

Preliminary subsequent studies using HCl as acid catalyst instead of H_2SO_4, have shown some inconsistencies namely in the rate of furfural destruction, which appears to be faster than what could be expected by using the reaction kinetics proposed in this work. Nevertheless a similar dependence on temperature was evidenced. Such results suggest a more complex mechanism involving not only the H_3O^+ ion but also the anions HSO_4^- and Cl^-, which might play a role in the catalysis of the reaction.

3.3 KINETICS OF FURFURAL FORMATION FROM XYLOSE

Similarly to furfural, D-xylose reaction rate presents a first order reaction rate with respect to its initial concentration under the conditions considered. Hence the expected second order loss reactions, such as condensation reactions involving xylose, furfural and the intermediates of reaction, may be neglected in the range of dilution considered in this work, and this is in agreement with earlier observations [50, 121].

In order to derive the raw values of the main kinetic parameters k_1, k_2, k_3 in equations (3.2), a least-square minimization fitting to experimental results was performed. The model showed very good agreement with the experimental measurements in the whole range of conditions considered.

Remarkably, the three kinetic parameters showed a similar dependence on acid concentration, thus, as evident from eq. 3.3, no significant improvements in terms of maximum furfural yield may be achieved increasing acid concentration within the range of interest for this work. This is an important observation when considering the acid use in furfural production, evidencing that, in the dilute range, acid concentration has a direct influence only on xylose rate of reaction, but not on selectivity toward furfural. Different catalysts influence on furfural selectivity will be discussed more in details in the following chapters.

Similarly to what shown in the previous section for furfural reaction, when describing the acid influence on xylose reaction rate H_3O^+ activity $a_{H_3O^+}$ is preferably considered, resulting in the formulation:

$$k_X = k_1 + k_2 = k_X^* \, a_{H_3O^+}$$

Using such formulation for k_X^* , similarly to k_3^* , shows a clear Arrhenius dependence on temperature in the range of conditions considered.

$$\ln(k_X^*) = 31.86 - \frac{133.3 \, [kJ/mol]}{RT} \, [s^{-1}]$$

$$\ln(k_3^*) = 26.64 - \frac{125.1 \, [kJ/mol]}{RT} \, [s^{-1}]$$

The activation energy of both reactions is of similar magnitude, thus no significant furfural yield increase may be achieved by varying the reaction temperature in the range considered. When considering the transition state model for k_X^*, the calculated values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are respectively 129.4 [kJ/mol] and 7.8 [J/molK] at 473K. Remarkably, the positive value of $\Delta S^\ddagger$ indicates the increased degrees of freedom of the activated state, which is a strong indication of xylose ring opening being involved in the transition state. Hence protonation, ring opening and subsequent dehydration are seemingly the key steps in the reaction of xylose to furfural. More indications in this sense will be provided in chapter 4.

If defining a reliable formulation for xylose and furfural reaction rates (k^*_X and k^*_3) is of major interest for reactor engineering purposes in the furfural industry, the analysis of k_1 and k_2 is important for the optimization of furfural selectivity and yield. In particular, experimental results showed that xylose side-reactions rate (k_2) and xylose-to-furfural reaction rate (k_1) are related to acidity and temperature in a very similar manner. Consequently, the resulting selectivity toward furfural, expressed as k_1/k_2, remains relatively unchanged across the whole range of conditions considered - around 77% -, displaying an objectionable limit to furfural yield from xylose. Similar results were reported earlier [122]. Such "selectivity limit" is in apparent disagreement with the commonly reported quantitative furfural yields from pentoses when performing the classic standard method for biomass pentosans-content estimation [7, 8, 12]. Such disagreement suggests that different reaction mechanisms might take place under different conditions, indicating that xylose dehydration to furfural goes beyond the commonly accepted specific-acid catalysis. This observation stimulated further experimental work, which led to original results regarding furfural formation mechanism from xylose, selectivity and overall yield, that will be exhaustively discussed in the following chapters.

Regarding the influence of initial xylose concentration, it is important to remind that higher sugar concentrations may lead to a significant decrease in overall furfural yield due to the occurrence of second order loss reactions. Such effect is known from past studies, but, although some reaction mechanisms have been proposed [7, 31], the products of such reactions have never been isolated. The influence of second order reactions have been quantified only in terms of furfural yield losses compared to the dilute conditions. In this study some tests have been performed in this sense, confirming earlier observations [122]. In particular it was shown that an increase in initial xylose concentration from 0.1 to 1.5 wt% led to a maximum furfural yield drop from about 70% to 58%. Furthermore, analyzing the experimental results it emerged that the lower furfural yield was the result of an increased apparent furfural destruction rate, i.e. an increased apparent k_3 compared to the actual parameter estimated by using furfural as model compound in the absence of other species (sugars or derivatives). Such deviation appeared only when increasing initial xylose concentration. Considering also that xylose reaction rate remained virtually unchanged during those tests, and that under similar conditions furfural showed a first order reaction rate, the increased furfural rate of disappearance might be explained by its reaction with other compounds than xylose or furfural itself, possibly involving intermediates of reaction or side products.

3.4 CONCLUSIONS

The results reported in this chapter regard xylose reaction and furfural destruction reaction kinetics in the temperature range 150 – 200 °C and H_2SO_4 concentration between 36 and 145 mM. Initial reactants concentration was kept in a relatively narrow range of dilution in order to observe the rate of furfural and xylose reaction in dilute acid solutions in the absence of second order reactions effects, mostly occurring at higher reactants concentrations.

The kinetic models proposed, although simple, present a good agreement with the measured reaction rates. The kinetic constants are related to the acid concentration via the ion activity $a_{H_3O^+}$ to better account for the thermodynamics of the electrolytes in solution, which may be accurately estimated by means of the eNRTL model. Moreover, no significant formation of formic acid from furfural from furfural decay was observed, contrary to earlier studies.

The influence of temperature on the rate constants k_X^* and k_3^* showed a clear agreement with the Arrhenius law, the activation energies being respectively 133.3 and 125.1 kJ/mol and the pre-exponential factors $68.65 \cdot 10^{12}$ and $3.71 \cdot 10^{11}$ s^{-1}. From the transition state theory a strong indication emerges of ring opening being involved in the activated state of xylose reaction to furfural.

4

CHLORIDE IONS ENHANCE FURFURAL FORMATION FROM XYLOSE IN DILUTE AQUEOUS ACIDIC SOLUTIONS

In this chapter some particular aspects of the chemistry of D*-xylose reaction into furfural are addressed with the aim to clarify the reaction mechanism and to define new green catalytic pathways for its production. Specifically the reduction of mineral acids utilization is addressed by the introduction of alternative catalysts. In this sense chloride salts were tested in dilute acidic solutions at temperatures between 170 and 200 °C. Results indicate the* Cl^- *ions to promote the formation of the 1,2-enediol from the acyclic form of xylose, and thus the subsequent acid catalyzed dehydration to furfural. For this reason the presence of* Cl^- *ions led to significant improvements with respect to the* H_2SO_4 *base case. The addition of NaCl to a 50mM HCl aqueous solution (0.18 wt%) allows to attain 90% selectivity to furfural. Among the salts tested* $FeCl_3$ *shows very interesting preliminary results, producing exceptionally high xylose reaction rates.*

The contents of this chapter have been adapted from:

Marcotullio, G. and de Jong, W. Chloride ions enhance furfural formation from D-xylose in dilute aqueous acidic solutions, *Green Chem.*, 2010, 12, 1739-1746

4.1 INTRODUCTION

Novel and green concepts for furfural production are required in order to minimize the carbon footprint and waste streams related to furfural industry. To this aim a deeper comprehension of the chemistry of pentoses is required in the first place, as well as the establishment of new catalytic pathways for their conversion into furfural.

In view of the understanding of the mechanisms behind the quantitative conversion of pentoses into furfural, it is interesting to recall the old standard methods for the estimation of pentosans content of plant material [7, 8, 12], where nearly 100% of the initial pentosans can be recovered as furfural by distilling atmospherically the raw material in a 12 wt% HCl solution saturated with NaCl. Evidently such reaction conditions are just prohibitive for any industrial scale application due to the high chemicals utilization. Nevertheless a deeper understanding of the reaction mechanism taking place under those conditions is necessary in order to approach the same yields under significantly milder conditions. The acid choice was not a case, since it is known from literature that different acids catalyze differently the dehydration of pentoses into furfural [8], and among strong acids HCl is reported to be the preferable choice [7, 8]. Such observation suggests that the mechanism of furfural formation might go beyond specific acid catalysis, i.e. involving ionic species other than H_3O^+. Also very important is the role played by NaCl which, besides the salting-out effect enhancing the separation of furfural during distillation, was reported to increase sugars reaction rate. Such effect was thought to be the combined result of the higher boiling temperature and of the increased activity coefficient of the acid [8, 146].

More recently it was shown that the addition of KCl, NaCl, $CaCl_2$, $MgCl_2$ or $FeCl_3$ to pure water increased the reaction rate of both xylose and xylotriose at 180°C. This effect was more pronounced for xylotriose than for xylose [136]. Similar results were reported in recent works when treating corn stover with diluted inorganic salts [147, 148]. A peculiar catalytic effect of $FeCl_3$ on hemicellulose hydrolysis was also evidenced in these works, and $FeCl_3$ in water was shown to be significantly more effective than a strong acid solution of the same pH. In particular it was shown that Fe^{3+} and Cl^- ions are both responsible for this effect [148]. Gravitis et al. [149] reported the metal cations to catalyze the reaction of biomass derived carbohydrates to furfural proportionally to their ionization potential, mentioning an increasing effectiveness for K^+, Na^+, Ca^{2+}, Mg^{2+}, Fe^{3+}.

Furthermore metal salts, and especially metal chlorides, have been shown to have significant effects in microwave aided hydrolysis of chitosan [150], the hydrolysis of ethers and amines in near and supercritical water [151], but also on hemicellulose and cellulose hydrolysis both in solid state [152, 153], and in dilute aqueous solution [136, 147, 148]. Some metal chlorides have also been shown to affect the dehydration of glucose and fructose to HMF in ionic liquids [154].

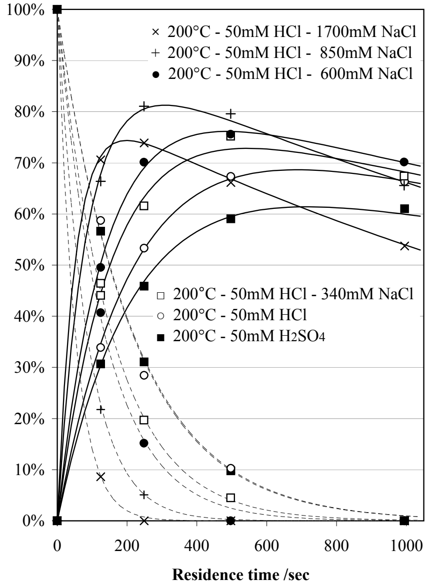


Figure 4.1: Effect of NaCl addition on xylose reaction rate and furfural yield. Xylose (dotted line) and furfural dimensionless concentration (solid line) as from equation (3.2) after fitting to the experimental results.

In view of what mentioned above, in this work the use of different chloride salts for furfural production is addressed, evaluating the role of the different electrolytes in solution in terms of xylose rate of reaction and furfural selectivity and yield, with the aim of exploring new catalytic pathways leading to high furfural yields with a reduced mineral acid usage.

4.2 EXPERIMENTAL RESULTS AND DISCUSSION

Figure (4.1) shows the results of xylose dehydration in dilute aqueous acid solutions with the addition of different amounts of NaCl. Initial xylose concentration is constant for all the experiments in this work, and equal to C_{X_0}= 33.3 mM. The reaction rate of xylose in two equimolar solutions of HCl and H_2SO_4 at 200 °C does not show a significant deviation, nevertheless furfural yield is significantly higher in the former case with respect to the latter. The second dissociation constant of H_2SO_4 is known to decrease markedly with temperature [138, 139], to such an extent that H_2SO_4 can be considered with very good approximation to be monoprotic at 200 °C ($pKa_2 \simeq 4$), and consequently the H^+ concentration of two equimolar solutions of HCl and H_2SO_4 can be assumed to be equal at those conditions. The different results in terms of furfural yield can thus be ascribed

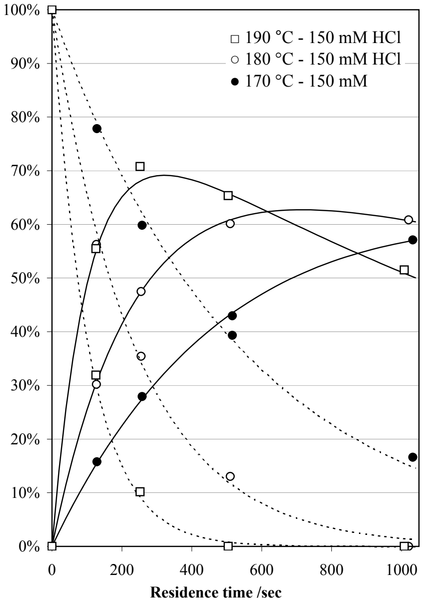


Figure 4.2: Effect of temperature on xylose reaction rate and furfural yield in 150mM HCl. Xylose (dotted line) and furfural dimensionless concentration (solid line) as from equation (3.2) after fitting to the experimental results.

to the presence of different anions in solution, in particular Cl^- having a more beneficial effect than HSO_4^-.

In the presence of increasing amounts of NaCl in dilute aqueous HCl a clear increase in xylose reaction rate is immediately evident and surprisingly higher furfural yields are achieved, see Figure (4.1). Thus NaCl is confirmed [146] to affect xylose reaction rate already at relatively low concentrations in acidic solutions, although, contrary to what was believed before [8, 146], this effect can neither be ascribed to the increased activity of the acid, nor to the increased boiling temperature or the salting-out effect. From the Debye-Hückel theory the ions activity coefficient γ can be related to the ionic strength I in dilute solutions according to the equation $log_{10}\gamma_i = -A\, z_i^2\, I^{1/2}$, in which the expression z is the ion charge and A a constant dependent on temperature, density and dielectric constant of the solvent [143].

Thus, under these conditions of dilution, increasing the salt concentration leads to a decrease of the ions activities, and consequently to a decreased acid activity. Furthermore the reaction is carried out at constant and controlled temperature in liquid solution without any separation by steam stripping, thus boiling point raise or salting-out effect do not play any role in this case.

In the previous chapter, where the action of H_2SO_4 catalyst was studied in the same range of conditions used in this work, increasing the temperature led to negligible variations in terms of furfural selectivity and yield. Contrary to this result, in Figure (4.2) it is shown how a significant increase of furfural yield can be obtained raising the temperature from 170 to 190 °C when dilute HCl is used instead of H_2SO_4.

Considering these results, it can be postulated that the ionic species in solution other than H^+ induce a change in the reaction mechanism, and Cl^- ions seem to be the main responsible for this effect.

Different salts, namely KCl, NaCl, $CaCl_2$ and $FeCl_3$, were also tested in 50 mM aqueous HCl, keeping a constant Cl^- molarity in every solution. Results showed very similar reaction behavior for the three salts KCl, NaCl and $CaCl_2$, both in terms of xylose reaction rate and furfural yield. For these three salts the concentration of Cl^- in solution seems to be the main feature for the kinetics of xylose reaction, the different cations seemingly playing only a minor role, Figure (4.3).

A significantly different behavior was observed when adding $FeCl_3$, where the xylose reacted so fast that no sugar could be detected already after a residence time of 124 seconds, thus, even if the exact value could not be derived, the reaction rate appeared to be more than 10 times larger than in the other cases. Hence the Fe^{3+} ion itself can be considered to have a relevant catalytic effect on the reaction of xylose. On the other hand, furfural maximum yield was lower when adding $FeCl_3$ compared to the other cases, which accounted for 62% of the initial xylose, in agreement with what was shown earlier when treating corn stover under very similar conditions [148].

The addition of electrolytes to the water can generally induce significant changes by attracting or orienting its molecules, or change its ordered short range structure and in general its interaction with the solute. Similar effects are responsible for the vapor pressure increase of aqueous electrolytes solutions, for salting-out or salting-in effects [155], or colloids precipitation as first studied by Franz Hofmeister more than a hundred years ago [156]. In the same way these effects could be regarded as responsible for the reported results in terms of xylose reaction rates and furfural yield. Nevertheless, especially when considering dilute solutions, Hofmeister effects are normally not so dependent on the nature of the electrolytes but rather on the total ion concentration, whereas, by carefully considering the results shown in Figures (4.1), (4.2) and (4.3), it becomes evident the the nature of the ions is very important even in very dilute solutions. Furthermore when comparing the results for $CaCl_2$ with those for KCl and NaCl we can notice that, even if the total ions concentration in solution is 25% lower in the first case if compared to the other two, the results are very similar to each other. Thus a direct contribution of the ions to the chemistry of the reaction, rather than a change of the solvent-reactant interactions, can be considered to play the major role.

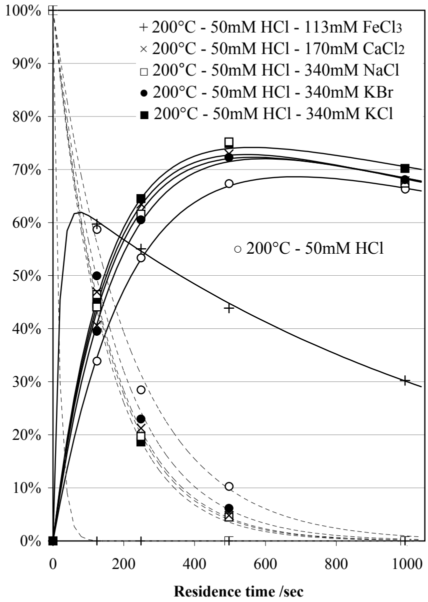


Figure 4.3: Effect of different chloride salts on xylose reaction rate and furfural yield. Xylose (dotted line) and furfural dimensionless concentration (solid line) as from equation (3.2) after fitting to the experimental results.

Xylose reaction in two equimolar solutions of KCl and KBr was also studied at the same conditions of temperature and acidity, Figure (4.3). The reaction resulted to be about 15% slower in KBr with respect to KCl, even though faster than in the absence of any added salt, while the furfural maximum yield was comparable in both cases, see also Table (4.1). This last result denotes the addition of metal halides in general to aqueous acidic solutions to potentially have surprisingly beneficial effect in terms of xylose conversion into furfural, and further results in this sense will be exposed in the next chapter where where the effect of different ions of the series I, Br and Cl will be thoroughly discussed.

4.2.1 *Mechanism of furfural formation from pentoses*

Contradictory theories exist in literature concerning the mechanism of furfural formation from pentoses. On the one hand many authors considered the reaction to proceed via the acyclic form of the pentoses, through a first 1,2-enediol formation and subsequent three dehydration steps yielding furfural [131, 135]. On the other hand, other authors believed the reaction to take place starting from the pyranose form of the pentoses [121], which recently was postulated to take place by the action of H^+ on a specific position of the pyranose ring, leading

Table 4.1: Condensed results from kinetic experiments.

Entry	Acid	Acid / mM	Salt	Salt wt%	Total Cl^- / mM	Temp. / ºC	$k_X/10^{-4}$ [s^{-1}]	$k_1/10^{-4}$ [s^{-1}]	$k_2/10^{-4}$ [s^{-1}]	$k_3/10^{-4}$ [s^{-1}]	Selectivity$^{\pm}$ [%]	Max. Yield* [%]
1	HCl	150	-	-	150	170	18.5	13.68	4.83	1.5	73.9	59.2
2	HCl	150	-	-	150	180	42.0	31.5	10.5	2.5	75.0	62.7
3	HCl	150	-	-	150	190	95.0	77.9	17.1	5.3	82.0	69.1
4	H_2SO_4	50	-	-	-	200	46.2	32.6	13.6	2.0	70.6	61.4
5	HCl	50	-	-	50	200	46.7	37.3	9.4	2.2	79.9	68.7
6	HCl	50	KCl	2.5	390	200	67.3	54.9	12.4	1.7	81.6	74.1
7	HCl	50	NaCl	2.0	390	200	64.5	52.84	11.7	2.2	81.9	72.8
8	HCl	50	KBr	4.1	390$^{\bullet}$	200	57.0	46.7	10.3	2.2	82.0	72.0
9	HCl	50	$CaCl_2$	2.5$^{\diamond}$	390	200	63.0	51.0	12.0	2.0	81.0	72.3
10	HCl	50	$FeCl_3$	3.1$^{\mp}$	390	200	> 600	> 400	> 200	8.0	65.7	62.0
11	HCl	50	NaCl	3.5	650	200	74.4	63.1	11.3	2.2	84.8	76.1
12	H_2SO_4	50	NaCl	3.5	600	200	78.7	65.1	13.6	2.0	82.7	75.3
13	HCl	50	NaCl	3.5	390	210	175.0	144.4	30.6	4.0	82.5	75.5
14	HCl	50	NaCl	5.0	906	200	119.1	107.4	11.6	3.4	90.2	81.3
15	HCl	50	NaCl	10.0	1762	200	196.8	159.4	37.4	4.3	81.0	74.4
16	Formic acid	220	NaCl	10.0	1712	200	66.5	42.2	24.3	0.2	63.5	62.1
17	HCl	50	NaCl	5.0	906	170	11.7	9.1	2.6	0.6	77.7	65.7
18	HCl	50	NaCl	5.0	906	185	39.5	32.4	7.0	1.1	82.2	74.3
19	HCl	50	-	-	50	170	9.6	7.1	2.4	0.4	74.5	65.6
20	HCl	50	-	-	50	185	29.5	21.0	8.5	0.9	71.2	63.7
21	HCl	100	NaCl	5.0	956	200	184.1	161.4	22.7	5.1	87.7	79.2

$^{\pm}$ Calculated as k_1/k_X.* Maximum furfural yield calculated from (3.3). $^{\bullet}$ Considered as $[Cl^-] + [Br^-]$. $^{\diamond}$ $CaCl_2$ dihydrate. $^{\mp}$ $FeCl_3$ hexahydrate.

to a first dehydration and structure rearrangement yielding the furanose ring and subsequent dehydration to furfural [133, 137]. It has been demonstrated that after reacting xylose-1-^{14}C in 12% aqueous HCl the "aldehydic" carbon of the pentose at C-1 position was found nearly completely at the aldehyde group of the final product, 2-furaldehyde-α-^{14}C [129]. Such result is perfectly aligned with the former theory, whereas it cannot be explained according to the mechanism proposed in the latter. Furthermore, in analogy to the reaction of xylose to furfural, an isomerization reaction of glucose to fructose has been shown to take place in acidic conditions at high temperature, proving this to be the first step in the reaction leading from glucose to HMF [132]. Besides, ketopentoses, which present a significantly higher proportion of acyclic form in water solution if compared to aldopentoses [157, 158], react much faster in water yielding furfural proportionally to the acidity of the solution [135]. From all these evidences provided by different authors throughout the years, the former theory appears to be strongly supported, whereas the latter fails to comply with some of the earlier works. For these reasons, in this work, the first theory is considered for the interpretation of the results.

A strong indication was also provided of the 1,2-enediol intermediate to be irreversibly formed from the aldopentoses in acidic conditions, showing on the other hand a partial equilibration with the keto form [135]. Such indication is in agreement with the general aldoses reluctance to isomerization in acidic conditions [132], and thus, since enolization reactions are normally reversible, the 1,2-enediol formation from xylose in acidic conditions can be considered to be the rate limiting step in the formation of furfural. In analogy with this, HMF is known to be formed much faster from fructose than from glucose in acidic conditions, and fructose has often been measured in the reaction from glucose to HMF, indicating aldose isomerization to take place as intermediate step [132, 159].

4.3 EFFECT OF THE CL$^-$ ION ON FURFURAL KINETICS OF FORMATION

Based on the results obtained in this work, it seems reasonable to postulate that one particular step among the multi-step reaction from xylose to furfural to be catalyzed by both H$^+$ and Cl$^-$, this particular step being the formation of the 1,2-enediol intermediate. Thus the mechanism depicted in Figure (4.4) can be drawn, which appears in agreement with the results obtained in this work and with what was observed in previous works. In such mechanism the presence of Cl$^-$ favors the formation of the 1,2-enediol **2**, which can equilibrate with both the aldo **1** and keto **3** form of the sugar, and reacts to furfural **4** in presence of an acid.

Accordingly, it is evident from the experimental results that, with increasing chloride salts concentration, xylose reacts significantly faster to furfural, while no significant effect is observed on the side reactions, resulting in a remarkable

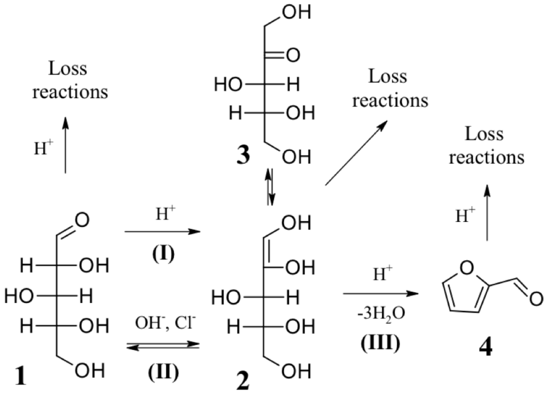


Figure 4.4: Simplified reaction scheme involving chlorides

selectivity improvement. When the salt concentration becomes higher than a certain threshold with respect to [H$^+$], the increasing selectivity trend to furfural is inverted and a small drop is observed, Figure (4.1). This can be due to the larger concentration of the intermediate(s) which are prone to undergo loss reactions, including possible condensation reactions with furfural. In the simplified kinetic model proposed here this effect results in an increase of k_2, as it is observed for 10 wt% NaCl , see Table (4.1); entry 15. As mentioned before, **2** and **3** are more reactive than **1**, also in absence of acids [135, 159], yielding furfural proportionally to the acidity. Accordingly, the faster xylose reaction and the poor furfural yields obtained using a weak acid in presence of 10 wt% NaCl (Table (4.1); entry 16) can be explained due to the relatively high pH in presence of a relatively large concentration of chloride salts. In addition, comparing the results when using different strong acids like HCl and H_2SO_4 led to different results as discussed before, Figure (4.1), whereas in the same conditions, when a larger concentration of chloride salt is also present, results are very similar (Table (4.1); entries 11-12), meaning the H$^+$ source does not significantly influence the reaction when a larger concentration of Cl$^-$ is also present.

Hence, even if the reaction of xylose can be catalyzed by chloride salts by favoring the 1,2-enediol formation, the presence of a strong acid is necessary in order to favor the selectivity toward furfural. This conclusion is in agreement with what was previously shown for ketopentoses, where higher acidity influenced the selectivity to furfural not influencing so much the sugars rate of reaction [135].

The mechanism in Figure (4.4) helps also explaining the Arrhenius plot depicted in Figure (4.5). In this plot the natural logarithm of the total xylose reaction rate kinetic parameter $k_X = k_1 + k_2$ divided by [H$^+$] is plotted against

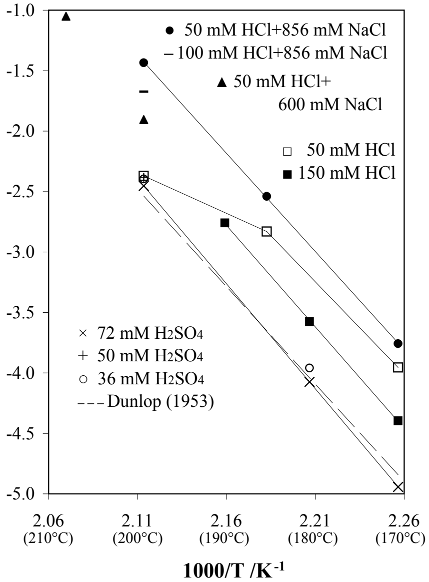


Figure 4.5: $ln(k_X/[H^+])$ plot against temperature.

the inverse of the absolute temperature, in order to show the rate of reaction of xylose excluding the effect of acid concentration.

The bottom line in Figure (4.5) shows the H_2SO_4 catalyzed reaction, i.e. the well known H^+ catalyzed route, where formation of **2** through reaction (I) is the rate limiting step according to the scheme in Figure (4.4). The linear relationship between k_X and $[H^+]$ can clearly be observed, accordingly the points for different H_2SO_4 concentrations are reasonably aligned in the plot in Figure (4.5). This results are also in very good agreement with the know kinetics provided in previous works [8] for the same range of acid concentration and temperature.

When a relatively large Cl^- concentration is present, $k_X/[H^+]$ values are larger, and accordingly they shift up in the Arrhenius plot. Such shift can be explained with a switch in the rate limiting step, namely from reaction (I), which is bypassed due to the Cl^- catalyzed formation of **2**, to the subsequent H^+ catalyzed dehydration reaction (III). The 50mM HCl curved line is particularly revealing the transition: at the higher temperatures it tends to the H^+ catalyzed mechanism (I); lowering the temperature the Cl^- catalyzed reaction (II) becomes faster, having seemingly a lower activation energy, leading to a switch to reaction (III) becoming therefore limiting step.

When reaction (III) is the rate limiting step, the kinetic parameter k_X should be directly proportional to $[H^+]$, as previously shown, and indirectly to $[Cl^-]$ through **2** formation. Contrary to this no linearity is evident between k_X and

$[Cl^-]$ or $[H^+]$, the data showing a marked less than proportional relationship. It can be analytically demonstrated, and it is also qualitatively intuitive, that such relationship indicates reaction (II) to be reversible, contrary to (I), being the equilibrium between **1** and **2** only partly attained. This means that the rates of reaction (II) and (III) are comparable, thus concentration of **2** varies accordingly. Due to this, an increased acidity at fixed $[Cl^-]$ would cause reaction (III) to be faster, at the same time lowering to some extent the mean concentration of **2**, and resulting in a less than proportional observed increase of xylose reaction rate. In the same way, an increase of $[Cl^-]$ at fixed $[H^+]$ would tend to increase the average concentration of **2**, resulting again in only a less than proportional observed increase of furfural rate of formation because of the combined effect of reaction (III) and (II). In this way the 150 mM HCl straight line intermediate position in the Arrhenius plot can also be explained.

For these conditions the competing side reactions also become more complex, involving **1**, **2** and possibly **3**, being ketopentoses very reactive also at lower acid concentrations as mentioned before.

The peculiar Cl^- behavior in this reaction is particularly interesting by itself. As it has been shown, there is good reason to believe Cl^- ions to act as a catalyst in the enolization reaction of xylose, which is normally catalyzed in basic environment even at lower temperatures. Alternatively the Cl^- ions could be considered to favor the presence of the 1,2-enediol with respect to both the aldose and ketose by a stabilizing effect, thus favoring the subsequent dehydration reactions starting from such form. Anyway, based on the results presented in this work, the 1,2-enediol promoting effect induced by the Cl^- remains a hypothesis consistent with the reaction kinetics of xylose to furfural, although no ultimate evidence is provided in support of this theory.

As far as the peculiar effect of $FeCl_3$ is concerned, it shows a significantly more vigorous action on xylose than H^+. Although, in a first instance, Fe^{3+} ions in water were believed to have a direct influence on xylose reaction, as it will be explained in chapter 6, such action may be ascribed to the indirect formation of HCl as a consequence of iron oxides precipitation at higher temperatures.

4.4 CATALYTIC REQUIREMENTS IN FURFURAL PRODUCTION

Contrary to the dehydration reactions yielding furfural from pentoses and HMF from hexoses, which require strong acids, aldoses isomerization is normally favored by basic conditions [132, 159], and proved to proceed through the 1,2-enediol formation [160]. Moreover, in the past, it was also observed that furfural formation from pentoses was not a simple dehydration reaction, since only poor furfural yields were obtained when xylose was reacted with dehydrating catalysts like pure $ZnCl_2$ or phosphorous pentoxide, whereas, when an aqueous solution of $ZnCl_2$ was employed, furfural yield approached that obtained using strong acids solutions [161]. Thus a discrepancy in terms of "catalytic requirements" becomes evident in the process of furfural formation from pentoses, presenting, in turn, an enolization followed by three dehydration reactions, being the two reactions normally favored by different catalysts.

Thus, when thinking at industrial furfural production, it should be borne in mind that the high severity normally required in terms of acid concentration and temperature is mainly needed to overcome the first enolization step, as this is normally not favored by acid. Whereas an acid catalyst is required for the following dehydration steps. Thus, in order to achieve better furfural yields under milder conditions and in a greener manner, the combination of two different catalysts, having in turn basic and acidic character, would be probably the key. On a similar observation a recent remarkable work is based[67, 162] where the combined use of acid and basic solid catalysts in a one-pot reaction allowed for good HMF and furfural yields, although improvements are still needed.

In the present work it has been shown that such double catalytic effect can seemingly be achieved by the addition of metal chlorides to aqueous acidic solutions, allowing for high furfural yields and relatively high xylose reaction rates.

In terms of furfural yield maximization an optimum for H^+ and Cl^- concentrations exists, also in relation with the loss reactions, involving a relatively large Cl^- excess and a relatively low acid concentration. Noteworthy seawater typical composition with the addition of a small amount of strong acid could be a suitable solvent for furfural production.

4.5 CONCLUSIONS

Chloride salts were shown to enhance the reaction of xylose to furfural in aqueous acidic solution at temperatures between 170 and 200 °C. Experimental results indicated the Cl^- ions to promote the formation of the 1,2-enediol from the acyclic form of the aldose, which undergoes subsequent acid catalyzed dehydration reactions to furfural.

The effect caused by the chloride salts addition to aqueous acid solutions was studied under various conditions. Significant improvements were observed with respect to the H_2SO_4-based case, furfural yield and selectivity respectively increasing by 18% and 28%, selectivity in particular attaining 90%. At the same time a 4-fold xylose reaction rate increase was possible by 1.7 M NaCl addition keeping the acid concentration as low as 50 mM (0.18 wt% HCl), and initial sugar concentration 33.3 mM.

5

THE USE OF DIFFERENT HALIDES IN DILUTE AQUEOUS ACIDIC SOLUTIONS ALLOWS FOR EXCEPTIONALLY HIGH FURFURAL YIELDS

Starting from the results discussed in the previous chapter on the effects of Cl$^-$ ions on furfural formation in aqueous acid solution, the general effect of different halides is addressed. Experimental results show the halides to influence at least two distinct steps in the reaction leading from D*-xylose to furfural under acidic conditions,* via *different mechanisms. The nucleophilicity of the halides appears to be critical for the dehydration, but not for the initial enolization reaction. By combining different halides synergic effects become evident resulting in very high selectivities and furfural yields.*

The contents of this chapter have been adapted from:

Marcotullio, G. and de Jong, W. Furfural formation from D-xylose: the use of different halides in dilute aqueous acidic solutions allows for exceptionally high yields, *Carbohydr. Res.*, 2011, 346, 1291-1293

5.1 INTRODUCTION

The influence of halides on the dehydration reaction of sugars to furfurals has been increasingly addressed, with particular attention regarding the selection of different ionic liquids showing optimal characteristics for this reaction [154, 163, 164]. The simultaneous use of solid basic and acidic catalysts has also been explored in order to foster the isomerization of glucose to fructose and the subsequent dehydration to 5-hydroxymethyl furfural [162]. In the previous chapter the peculiar influence of Cl^- ions on the formation of furfural from D-xylose in aqueous acidic solutions was shown, reporting very high yields and selectivities. It has been postulated that the Cl^- ions promote the formation of the 1,2-enediol from the acyclic form of the aldose, favoring thus the subsequent acid-catalyzed dehydration. Nonetheless, the experimental evidence is based on reaction rates studies, and thus insufficient to unravel the mechanism involving Cl^- in this reaction.

In order to further clarify these aspects, a systematic study has been carried out observing the variations in the kinetics of D-xylose reaction in acid solution brought about by adding different potassium halides. In particular KCl, KBr and KI were used, whereas KF was not included in the series due to the relevant difference of HF Brønsted acidity compared to the rest of the hydrogen halides. Using KF in acidic solution would decrease considerably the acidity of the solution making it impossible to compare the effect of this salt with the others on similar basis.

5.2 EXPERIMENTAL RESULTS AND DISCUSSION

For consistency with the results shown in the previous chapter, initial xylose concentration was kept at 33.3 mM. Experimental results summarized in Table 5.1 exhibit two distinct and competing effects when adding in turn KCl, KBr and KI to aqueous acidic solutions: on the one hand xylose reaction rate increases after the addition of all potassium halides, but to a different extent depending on the halide, and in particular following the order $Cl^- > Br^- > I^-$; on the other hand, selectivity, and thus furfural yield, are also improved by all potassium halides, but following the opposite order $I^- > Br^- > Cl^-$. Moreover a synergic effect becomes evident, in terms of selectivity towards furfural, when combining the halides at the two extremes of the series, *i.e.* Cl^- and I^-, Figure 5.1. Accordingly the reaction rate of xylose when adding KI and KCl salts in equal molar amount (Table 5.1, entry 6), approaches the average reaction rate when using only KCl or KI at the same total concentration (Table 5.1, entries 2 and 4), but, on the other hand, it clearly displays higher selectivity and yield. In particular, the highest selectivity and furfural yield - 95.3% and 87.5% respectively - was measured when using a combination of KCl and KI, with the concentration of

Table 5.1: Results from kinetic experiments, all reaction were carried out at 200 °C.

Entry	Acid[a] /mM	Salt(s)	Salt(s) /mM	k_X /10^{-4} [s^{-1}]	k_1 /10^{-4} [s^{-1}]	k_2 /10^{-4} [s^{-1}]	k_3 /10^{-4} [s^{-1}]	k_1/k_2 [-]	Selectivity [%]	Max. yield[b] [%]
1	50	-	-	43.2	34.5	8.7	1.9	4.0	79.7	69.1
2	50	KCl	500	73.9	62.8	11.1	1.7	5.7	85.0	77.7
3	50	KBr	500	63.0	55.4	7.7	1.4	7.2	87.8	80.6
4	50	KI	500	60.0	53.6	6.5	1.2	8.2	89.2	82.6
5	50	$KHSO_4$	500	57.7	47.2	10.5	2.1	4.5	81.8	72.2
6	50	KI-KCl	250-250	67.6	61.9	5.7	2.0	10.6	91.6	82.4
7	50	KI-KCl	500-250	70.3	64.6	5.7	1.5	11.3	91.8	84.4
8	50	KI-KCl	250-500	78.2	74.6	3.7	1.7	20.2	95.3	87.5
9	50	KI-KCl	500-500	82.3	75.9	6.4	1.6	11.9	92.2	85.4
10	50	KBr	750	66.9	62.1	4.9	1.9	12.7	92.7	83.4

[a] H_2SO_4 was employed in every experiment. The pH at room conditions was constant for every solution (1.25), and it was controlled before salts addition.

[b] Calculated based on eq. (3.3).

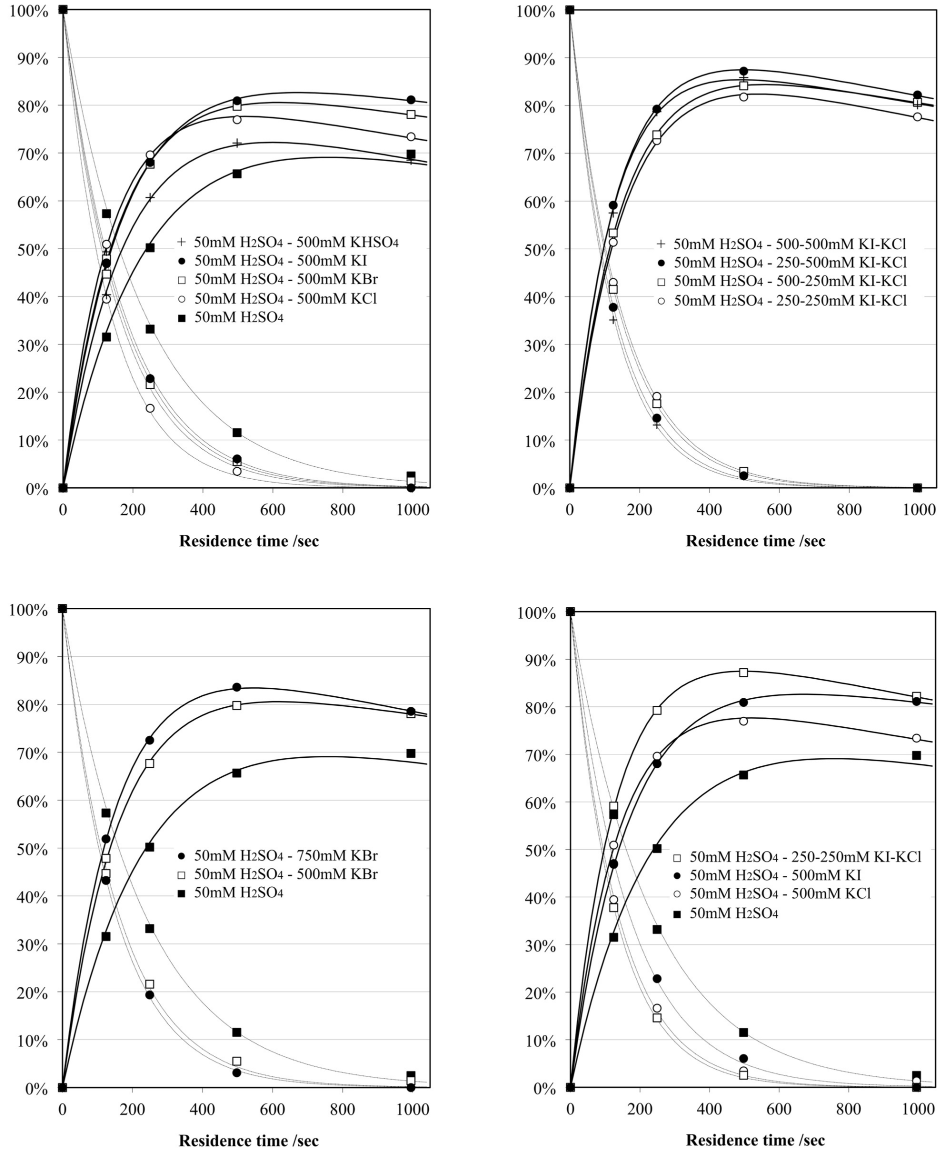


Figure 5.1: Effect of different halides salts on xylose reaction rate and furfural yield. Xylose (dotted line) and furfural dimensionless concentration (solid line) as from equation 3.2 after fitting to the experimental results.

KCl being double the KI concentration (Table 5.1, entry 8). This synergic effect of I^- and Cl^-, besides allowing for remarkable furfural yields, offers the ground for a deeper comprehension of the underlying mechanism of reaction.

Potassium bisulphate $KHSO_4$ was also tested in addition to the potassium halides. Adding $KHSO_4$ caused an increase in the xylose reaction rate, but only minor effects on furfural selectivity and yield if compared to no salts addition. The minor change of the selectivity to furfural compared to the change of k_X, suggests that the residual acidity of the HSO_4^- ion, or its capacity to donate the proton, is responsible for the increase of all of the reactions rates k_1, k_2 and k_3, leading thus to only a minor selectivity improvement. This confirms that not all the anions show the same effect on this reaction, and that the halides in particular show exceptional properties.

Analyzing the results it appears clear that the halides in acidic solution play a role in at least two different and consecutive steps in the reaction leading from xylose to furfural. In the scheme depicted in Figure 5.2 a reaction mechanism is proposed based on the results presented in this chapter and those of previous works [135, 165]. In this mechanism more than one option for side reactions is assumed, whereas the formation of furfural (**F**) entails a distinctive sequence of one enolization followed by three dehydration reactions, always started by protonation at specific positions. Noteworthy, the kinetics for such mechanism can still be described with very good accuracy by the scheme in Figure 3.1, considering k_2 as the sum of the possible side reactions, and considering the intermediates to occur in very low concentrations. As far as the role of halides is concerned, in first instance they tend to promote the formation of the 1,2-enediol **2** from the protonated acyclic xylose (**X**), secondly they act promoting the first and second dehydration steps forming **5** and **6**, and the last intramolecular dehydration and ring closure leading to **F**. The first enolization step is considered rate limiting, as discussed before in this dissertation [165], and thus every change in xylose reaction rate, and especially in k_1, can be ascribed to a rate enhancing action on this particular reaction. Adding Cl^- shows here the most pronounced effect, followed by Br^- and I^- in the last place; thus electronegativity, and/or the smaller size of the ion, or the - least weak - basicity in water, appear to be the driving forces favoring the formation of **2**. Regarding the mechanistic aspects of this reaction, C-2-C-1 intramolecular hydrogen transfer has been proven the prevailing mechanism for glucose dehydration in 1 M aqueous H_2SO_4, although of minor importance at lower acid concentration [132]. Considering the relatively low acid concentration and the significant presence of halides, the mechanism proposed in scheme depicted in Figure 5.2 seems more realistic under the conditions employed in this work. In such scheme the halides act as weak bases assisting the enolization reaction via proton transfer, hence with a decreasing efficacy in the order $Cl^- > Br^- > I^-$. Nevertheless, this specific aspect may be clarified only with further mechanistic studies under similar conditions, maybe using isotope-exchange techniques.

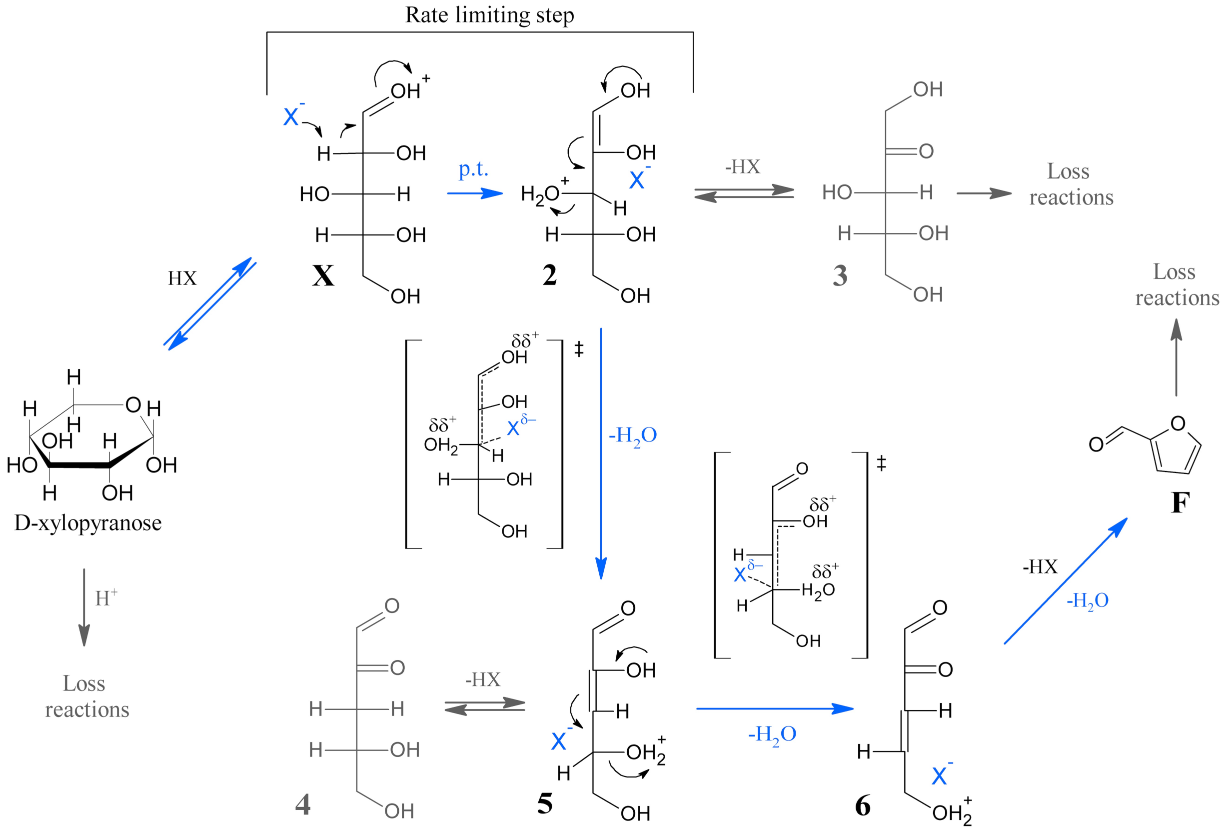


Figure 5.2: Reaction mechanism leading from D-xylose to furfural in acidic solutions. Aqueous halides are indicated as X^-.

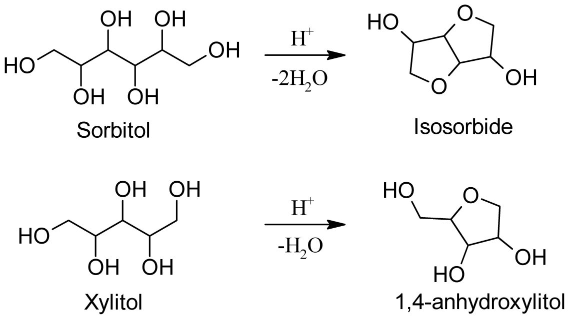


Figure 5.3: Main products from the acid catalyzed dehydration of sugar alcohols at high temperature.

After the enolization reaction, three dehydration steps are required to yield **F**, in particular at C-3 and C-4, followed by the final ring closure and intramolecular dehydration. Analyzing the results in Table 5.1, the selectivity to **F** is not only improved as a result of the increased k_1, as it was noticed earlier for Cl^- [165], but also because of a reduction in the side reactions rate k_2. This becomes evident especially when using I^-, followed by Br^- and lastly Cl^-, denoting a correlation with the nucleophilicity of the halides in aqueous solution, which derives from their size, solvation and polarizability. In view of these results, as illustrated in Figure 5.2, the halides are suggested to assist the dehydration reactions by stabilizing the transition states leading to **5** and **6**, where I^- results more effective because more polarizable and less strongly solvated than Br^- and lastly Cl^-. The dehydration reactions are not rate limiting, thus they do not influence the xylose overall rate of reaction. The mechanism proposed in Figure 5.2 finds also confirmation in the synergic effect evidenced when using KCl and KI in combination. These two halides have been shown to have their major effects respectively in the first enolization step, and in the following dehydrations, and consequently, combining the two, leads to the higher selectivities and yields.

5.2.1 *The analogy with sugar alcohols dehydration*

As far as the dehydrations steps are concerned, the presence of an adjacent electron-rich enol function at **2** and **5** is also relevant for understanding this mechanism. In this respect it is clarifying to consider the acid-catalyzed dehydration of sugar alcohols, and to remind that the dehydration rate of different pentoses in acidic solution can be directly related to their acyclic proportion in aqueous solution [135]. The dehydration of sorbitol and xylitol, despite the fact that they exist only in acyclic form, requires more severe conditions to take place compared to glucose and xylose, and they do not yield the corresponding furfuryl-alcohols as one could wrongly expect. Their reaction in acid solution is normally initiated with protonation at C-1 leading to 1,4 cyclization and intramolecular dehydration, yielding relatively stable products [166–168], see Figure 5.3. Sorbitol in particular can undergo a further dehydration and cyclization yielding a commercially valuable bio-based diol commonly known as isosorbide (1,2:3,6-dihydrosorbitol) [169, 170].

The incomplete dehydration of sugar alcohols, and their relative reluctance to such reaction, is indicative of the importance of the enol function present at **2** and **5** for the dehydrations to **F**. An enol is a very good electron donor, favoring in this case the elimination of water molecules as depicted in Figure 5.2. The nucleophilic character of the halides, especially of I^-, make them good candidates for providing similar assistance further promoting the selective dehydration to **F**.

5.3 CONCLUSIONS

Halides salts were shown to enhance the reaction of xylose to furfural in aqueous acidic solution by two distinct and consecutive effects. The formation of the 1,2-enediol from the acyclic form of the aldose was preferably catalyzed by the halides in the order $Cl^->Br^->I^-$, whereas selective dehydration to furfural is assisted by the halides in the opposite order $I^->Br^->Cl^-$. Synergic effects are also evident when using a combination of I^- and Cl^- ions, with selectivity of reaction attaining 95.3% and furfural yield 87.5%.

6

PRODUCTION OF HEMICELLULOSE-DERIVED CARBOHYDRATES FROM WHEAT STRAW *VIA* DILUTE-ACID HYDROLYSIS

In the present chapter the combined production of hemicellulose-derived carbohydrates and an upgraded solid residue from wheat straw using a dilute-acid pretreatment at mild temperature is exposed. Dilute aqueous HCl solutions were studied at temperatures of 100 and 120 °C, and they were compared to dilute $FeCl_3$ *under the same conditions. Comparable yields of soluble sugars and acetic acid were obtained, affording an almost complete removal of pentoses when using 200 mM aqueous solutions at 120 °C. The solid residues of pretreatment were characterized showing a preserved crystallinity of the cellulose, and a almost complete removal of ash forming matter other than Si. Results showed upgraded characteristic of the residues for thermal conversion applications compared to the untreated wheat straw.*

The contents of this chapter have been adapted from:

Marcotullio, G., Krisanti, E., Giuntoli, J. and de Jong, W. Selective production of hemicellulose-derived carbohydrates from wheat straw using dilute HCl or $FeCl_3$ solutions under mild conditions. X-ray and thermo-gravimetric analysis of the solid residues, *Biores. Tech.*, 2011, 102, 5917-5923.

6.1 INTRODUCTION

Hemicelluloses, together with cellulose and lignin, represent one of the three main constituents of lignocellulosic biomass, making up for about 30% of its structure. The predominant form of hemicelluloses are the xylans, i.e. the wide range of polysaccharides that have a β-(1→4)-D-xylopyranose backbone with a variety of side chains [52]. D-Xylose, the main monomeric component of such polysaccharides, is an industrially valuable feedstock for the production of xylitol, and it is gaining interest as additional feedstock, combined with glucose, for the production of bio-ethanol via fermentation.

As largely recalled in this dissertation, although mostly as an intermediate of reaction, xylose is the main feedstock for the production of furfural, mainly from corncobs and sugarcane bagasse. In the view of the development of novel solutions for the production of furfural, a particular attention is devoted to the optimized production of xylose and arabinose from lignocellulosic biomass.

Beside xylose, acetic acid, an industrially largely employed chemical, can be directly obtained by the hydrolysis of the hemicelluloses acetyl groups, which can account up to a few weight percent on the initial dry biomass.

6.1.1 *Hemicellulose dilute-acid hydrolysis*

Hemicelluloses, due to their amorphous structure, are comparatively easily hydrolyzed and dissolved in water. Both cellulose hydrolysis and furfurals formation require in fact more severe conditions to take place appreciably, and they are normally hindered at low temperatures [171, 172]. In xylose production patent literature temperatures between 100-150 °C are reported to be a preferred option, see [173], and in a recently published work an optimal temperature of 130 °C was indicated for xylose production from rice husks under similar conditions [174]. Dilute-acid pretreatment of biomass has been extensively studied, although mostly within the context of cellulosic bio-ethanol production via fermentation [175–177], resulting among the best options in terms of economic viability [178, 179]. In these cases relatively high temperatures of pretreatment were normally preferred resulting in a reduction of the cellulose crystallinity and, consequently, in an improved digestibility of the solid residue. On the other hand the reported hemicellulose recovery was not always remarkable. Only a minority of the available studies dealing with dilute-acid biomass pretreatment focused on the production of xylose, and nearly all of them explored a relatively low range of temperatures, [172–174, 180–183].

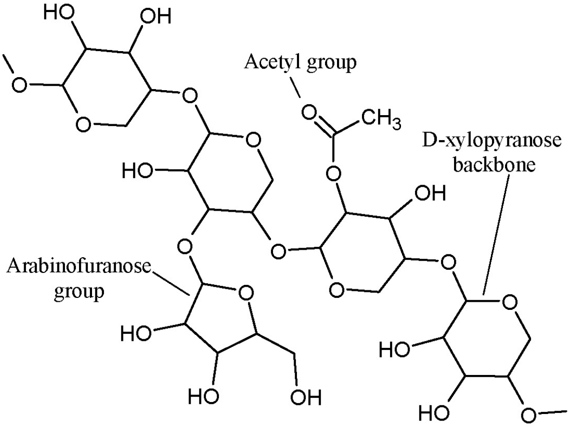


Figure 6.1: Representation of a portion of xylopyranose polymer, including acetyl and arabinofuranose substituents.

6.1.2 *Dilute-$FeCl_3$ for biomass hydrolysis*

In previous works and in chapter 4 it has been shown that $FeCl_3$ catalyzes the hydrolysis of carbohydrates and also the dehydration of monomeric sugars into furfurals [136, 147, 165]. Aqueous solutions of $FeCl_3$ present a Brønsted acid character due to the hydrolysis of Fe^{3+} resulting in the formation of different kinds of complexes. The main reactions taking place in this range of dilution are [184]:

$$[Fe(H_2O)_6]^{3+} \leftrightarrows H^+ + [Fe(OH)(H_2O)_5]^{2+}$$

$$2\,[Fe(OH)(H_2O)_5]^{2+} \leftrightarrows [(H_2O)_5FeOFe(H_2O)_5]^{4+} + H_2O$$

The equilibrium of these reactions is obviously influenced by pH and by the initial iron concentration. Hence, the H^+ molar concentration of a 100 mM $FeCl_3$ aqueous solution at ambient conditions is about 17 mM, i.e. 17% of an equimolar HCl solution. Even then, in previous works it has been reported that the effect of aqueous $FeCl_3$ on carbohydrates goes beyond its H^+ production at room temperature, and that the Fe^{3+} ion itself could play an important catalytic role [136].

6.1.3 *Characterization of the residues*

The use of biomass residues, including agricultural residues such as wheat straw, has great potential for thermal conversion, but it is nowadays still hindered by some issues: the heterogeneous nature of many such fuels [185], the unknown release chemistry of pollutants such as fuel-bound nitrogen and sulfur [186], and the quantity and quality of ash forming matter. The presence of high concentrations of alkali metals combined with Si, Cl and sulfur in agricultural residues is known to favor the formation of alkali silicates and alkali sulfates with melting points lower than most thermal conversion applications. The presence of a molten phase, then, gives rise to several problems such as slagging, fouling, corrosion and loss of fluidization [187]. In a previous work from our group [185] we have shown how a simple water leaching pretreatment could have beneficial effects for the pyrolysis of wheat straw in terms of the quantity and quality of ash forming matter but also showing a higher reactivity and lower char production. In this respect, the solid residues of acid hydrolysis retain a high potential for thermal conversion applications due to an expected reduced inorganic content and a partially degraded structure which could facilitate pyrolytic decomposition.

In view of what exposed above, this research aims at investigating the combined production of hemicellulose-derived carbohydrates and an upgraded solid residue from wheat straw using a dilute-acid pretreatment. Mild temperatures are explored in order to minimize sugars degradation reactions. Dilute solutions of HCl are used as representative for strong monoprotic acids, and these are compared to equimolar solutions of $FeCl_3$ as an interesting option for acid replacement [148]. Enzymatic degradability of the residues of dilute-acid hydrolysis has been extensively studied in literature, for this reason the residues of pretreatment are analyzed in this work using X-ray and thermo-gravimetric analysis in order to characterize their crystallinity, minerals content and their behavior under thermal conversion conditions.

6.2 HEMICELLULOSE HYDROLYSIS AND SOLUBLE CARBOHYDRATES RECOVERY

In this work wheat straw was treated in $FeCl_3$ or HCl dilute solutions for 120 min at 100 and 120 °C, refer to chapter 2 for a more detailed description of the experimental methods. As a result of these treatments, increasing fractions of biomass could be dissolved with increasing severity of reaction, reaching more than 37 wt% at 120 °C in 200 mM HCl or $FeCl_3$, (Table 6.2). A large part of the dissolved material was recovered in the filtrates as hemicellulose derived carbohydrates, the rest being mainly unidentified extractives and partly minerals. We report surprisingly high yields of pentoses when treating wheat straw for 120 min at 120 °C in 200 mM HCl or $FeCl_3$, respectively accounting for 26.5 and 26.0 wt% d.b. of the initial wheat straw, i.e. about 99% and 97% of the potential. More than 85% of this fraction is represented by monomeric sugars. Analyzing the effect of temperature, at 100 °C the fraction of sugars recovered in monomeric form is always less if compared to the treatments at 120 °C, figure 6.2, and treating wheat straw at 120 °C and 100 mM HCl or $FeCl_3$ produced similar

		[wt% d.b.]
Lignin	ASL	1.0±0.0
	All	15.1±0.1
Hemicellulose	Arabinan	2.1±0.1
	Xylan	21.5±0.7
	Mannan	0.2±0.1
	Galactan	0.5±0.0
Cellulose	Glucan	34.6±1.0
Extractives	H_2O	11.2±1.2
	EtOH	2.0±0.0

Table 6.1: Biochemical composition of the untreated wheat straw, data from [13].

amounts of total sugars but much more monomeric sugars than at 100 °C in 200 mM solutions, Table 6.2. Hence catalyst concentration can be well compensated by temperature in this range, also affording a significantly higher production of monomers. Using pure water under the same conditions of temperature leads to hardly any carbohydrates recovery in the liquid filtrate, so the presence of a strong acid, even at relatively low concentrations, is crucial to hemicellulose hydrolysis under such mild conditions.

The yield of arabinose, glucose and acetic acid is almost constant after all the treatments, and immediately evident even after the treatments under milder conditions. Evidently the α-L-arabinofuranoside or ester-linked acetyl group substituents are readily hydrolyzed yielding monomeric arabinose or acetic acid, whereas the depolymerization of the longer xylopyranose needs longer reaction times, [171, 182]. Wheat straw hemicellulose is known to contain glucose in the form of galactoglucomannans and/or β-glucans substituents, accordingly galactose and mannose are reported in minor amounts in the composition of the wheat straw employed in this work [13]. Results presented in Table 6.2 show the concentration of glucose to follow a trend very similar to arabinose and acetic acid, *i.e.* less depending on reaction severity than xylose. Moreover, as it will be shown below, the crystallinity of the solid residues, besides their TGA results, indicate that cellulose is hardly affected by the pretreatments. From these indications, it can be derived that the glucose present in the hydrolysates might mainly originate from hemicellulose side groups hydrolysis, although a partial hydrolysis of cellulose cannot be entirely excluded. Galactose and mannose detection and quantification might partly clarify this aspect, but, unfortunately, they could not be measured in this work due to the insufficient resolution of the analytical method employed. The use of sugars-specific HPLC configuration may be suggested for this purpose.

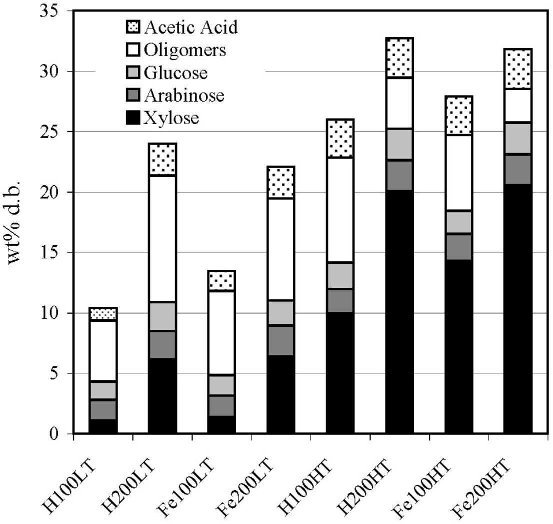


Figure 6.2: Soluble carbohydrates production from wheat straw. In the sample codes notations H and Fe indicate respectively dilute HCl and $FeCl_3$, and the following number their concentration in mM; LT and HT indicate the temperature of pretreatment, respectively 100 and 120°C.

The exceptionally high yields of pentoses obtained in this work are in fact hardly reported in literature when higher temperatures or much higher acid concentrations are employed [182, 188], mainly because of sugar reactions to furfurals and/or other degradation products. The use of mild temperatures at nearly atmospheric pressure, although for longer residence times, is thus a realistic option for the pentoses production oriented biomass pretreatments, provided that the larger size of the equipments can be economically outbalanced by better selectivity of reaction, process simplification and energy savings. Besides, higher temperatures of reaction, even if attractive for the shorter residence times and reduced equipment size, present scale-up issues regarding biomass continuous feeding at high pressures, material resistance and thus investment costs.

It is clearly shown in this work that equimolar aqueous solutions of HCl and $FeCl_3$ catalyze the hydrolysis of hemicellulose in a comparable way. The only relevant difference appears at the lower concentrations (100 mM) more evidently at 100 °C than at 120 °C, where $FeCl_3$ seems more active than HCl. It is also remarkable that the pH of the filtrates after the dilute $FeCl_3$ treatments are unexpectedly lower than after the HCl treatments at the same concentration. The explanation for this result relies on the peculiar chemistry of iron(III) salts in aqueous solutions. When a dilute aqueous solution of $FeCl_3$ is boiled at normal conditions a dark precipitate is formed, which consists mainly of iron oxides in

Table 6.2: Sugars recovery in the filtrate expressed as wt% d.b. of initial wheat straw.

[wt% d.b.]	100 °C					120 °C				
	Water	HCl		$FeCl_3$		Water	HCl		$FeCl_3$	
	-	100mM	200mM	100mM	200mM	-	100mM	200mM	100mM	200mM
pH filtrate [-][a]	5.96	2.46	1.81	2.25[a]	1.74[a]	5.59	2.32	1.80	2.25[a]	1.73[a]
Weight loss [%wt a.r.][b]	0.8	15.5	27.8	19.5	28.1	8.2	28.3	37.5	31.5	37.6
Tot. Xylose	0.8	5.3	15.0	7.3	14.2	0.9	17.2	23.3	20.0	22.9
Tot. Arabinose	0.4	2.0	3.1	2.2	2.8	0.4	2.8	3.2	2.8	3.1
Tot. Glucose	1.2	1.5	2.4	1.7	2.1	1.5	2.2	2.6	1.9	2.6
Tot. Acetic Acid	0.0	1.0	2.6	1.6	2.6	0.4	3.1	3.3	3.2	3.3
Monom. Xylose	0.1	1.1	6.1	1.4	6.4	0.1	10.0	20.1	14.3	20.6
Monom. Arabinose	0.0	1.7	2.4	1.7	2.6	0.2	2.0	2.6	2.2	2.6
Tot. Pentoses	1.2	7.3	18.1	9.5	17.0	1.3	20.0	26.5	22.8	26.0
Tot. Pentoses yield [%]	4.6	27.1	67.5	35.5	63.3	5.0	74.7	98.9	85.0	96.8

[a] As explained in the Methods, the pH of all the filtrates is measured at room temperature after dilution to 50ml. It is important to notice that, due to the equilibrium of Fe^{3+} hydrolysis reactions the H^+ concentration of a 5 times more concentrated solution would be less than 5 times larger. [b] Weight loss was measured on the basis of the initial weight a.r., after drying every pretreated sample for 24h at room temperature.

the form of α-Fe_2O_3 and β-FeOOH, as reported by Voigt and Göbler [189]. Consequently the H^+ concentration of the $FeCl_3$ liquid solution increases according to the simplified reaction:

$$3Fe^{3+} + 5H_2O \rightleftarrows 9H^+ + Fe_2O_3 \downarrow + FeOOH \downarrow$$

For these reasons aqueous $FeCl_3$, already at 100 °C, can be regarded as a source of HCl and iron oxides, lowering accordingly the pH of the solution. This is confirmed by the filtrates pH measurements (Table 6.2) and by the analysis of the inorganic elements distribution in the solid straw before and after the pretreatments, Table 6.3. Clearly Cl and Fe are not completely removed from the solids with washing, but the Fe/Cl weight ratio in the $FeCl_3$ pretreated wheat straw is clearly exceeding that of the pure salt. Although the presence of Cl can be mainly ascribed to the incomplete washing, the higher Fe proportion is due to its precipitation in solid forms.

Crossing the filtrates pH with the pentoses yield at constant temperature (Table 6.2), a relation is evident between the H^+ final concentration and the extent of hemicellulose hydrolysis, whereas, contrary to what was reported before, the effect of the Fe^{3+} ions results to be mainly indirect and referable to the H^+ production. Hence, treating biomass with $FeCl_3$ or HCl solutions is not really different from the catalytic point of view. The opportunity of using dilute $FeCl_3$ as an alternative to dilute HCl should be evaluated in a broader perspective, carefully evaluating environmental and economic benefits and costs. On the one hand the use of $FeCl_3$ might be less harmful than HCl, moreover, due to its equilibrium reactions in hot water, it presents a pH buffer effect partially mitigating the neutralizing capacity of agricultural residues like straw. On the other hand, $FeCl_3$ contains three times as much Cl compared to HCl on a molar basis, and the deposition of fine iron oxide particles on the biomass residues, probably also containing Cl, may have consequences in the downstream applications. In the second part of this work the effects of such Fe containing particles under thermal conversion conditions are reported, but their interaction with microorganisms or enzymes during biological conversions, e.g. in cellulosic ethanol production, should also be carefully evaluated.

6.2.1 *Crystallinity of the solid residues*

The residues treated at 120°C and 200mM HCl and $FeCl_3$ show a significantly higher crystallinity index than untreated wheat straw, Table 6.4. The CrI is a relative measure of the intensity of diffraction in the crystalline region compared to the amorphous region, thus the treated samples show an increased proportion of crystalline cellulose compared to amorphous cellulose and, more importantly, hemicellulose. A significantly increased CrI is not a common feature to all pretreatments aimed at the fractionation of biomass, as shown by Kumar et al. [127], and it may be considered a relevant aspect of this particular pretreatment. The increased CrI not only indicates an extensive hemicellulose removal, which is clear from the filtrates analysis, but also shows the limited effect of such pretreatment on the crystalline structure of cellulose, which can be attributed to the relatively mild conditions employed. The cellulose content of the residues of pretreatment was not directly measured, although, considering the glucose concentration in the filtrates and the samples weight loss reported in Table 6.2, it is expected to be markedly higher compared to the untreated wheat straw. Based on all these observations, it will be interesting for future research to test a pretreatment of this kind, possibly followed by a lignin separation/solubilization step, for the selective production of cellulose fibers, lignin and hemicellulose-derived carbohydrates. In particular it may be suggested to test a uncatalyzed organosolv type of treatment for the residues of dilute-acid hydrolysis, preferably using ethanol as solvent in the same range of temperature, aimed at recovering large fractions of the water-insoluble lignin, leaving a clean, cellulose-rich residue with high crystallinity.

6.3 RESULTS OF XRF AND THERMO-GRAVIMETRIC ANALYSIS OF THE RESIDUES OF PRETREATMENT

From the distribution of inorganics in all the pretreated samples compared to the untreated wheat straw (Table 6.3), silica (SiO_2) appears to be present in significantly larger amounts compared to all other elements. Silica is insoluble in water and thus cannot be expected to be removed in appreciable amounts during these kind of pretreatments. This is not true for potassium (K), which is the compound with the largest concentration in the untreated straw, and it is largely removed after all pretreatments. The extent of K removal is around 90% (K_2O basis) already after the pure water pretreatment, and seems to increase slightly with severity of reaction reaching more than 97% in some cases, Table 6.3. Calcium (Ca) was also largely removed during all treatments, apart from those using pure water, where only about 50% was removed. Evidently Calcium compounds show acid preferred solubility, in agreement with the general low water solubility of calcium alkaline salts like CaO, $Ca(OH)_2$ and $CaCO_3$. Magnesium (Mg) shows a behavior similar to that of Ca, but with much lower concentrations. Chlorine (Cl) was removed thoroughly (98%) when using pure water, although being present in all the other pretreated samples as a result of HCl or $FeCl_3$ incomplete washing. Looking at the little Cl residues left when using pure water, it can be expected to be removed thoroughly also when employing acids not containing Cl. Iron (Fe), and similarly Aluminum (Al), are removed to a much lesser extent probably because of the limited solubility of their oxides. Accordingly, the large Fe containing residues in the samples treated with $FeCl_3$ is explained because of the mentioned precipitation of Fe oxides. The presence of

Cl in the solid Fe precipitates is also not to be excluded. Phosphorus (P), detected as phosphates, and especially Sulphur (S), present as sulfides, are also removed, but less than other compounds. They seem to be more difficult to remove both with pure water and acidic pretreatments, also not showing any clear relation with the reaction severity. A fraction of P and S could in fact be included in more complex organic compounds beside soluble salts, similarly to what reported in a previous work [126]. Anyway the presence of P and S is of minor importance being less than 1 wt% of the total inorganics.

The results for thermo-gravimetric analysis (see Table 6.4) show that all the pretreated samples displayed a reduction of both the char residue at 550 °C and the ash residue if compared to the untreated wheat straw, as it could be expected mainly as a result of the reduced alkaline minerals content [185, 190, 191]. The total amount of volatiles released also increased for all the pretreated samples if compared to the untreated straw (68.7 wt% d.b.), approaching values around 80 wt% d.b., (Table 6.4). Such results have to be evaluated also considering that, in some cases, the pretreated straw was deprived of significant fractions of its main constituents. In fact the hemicellulose fraction, which is known to undergo devolatilization at lower temperatures [190], is removed to significant extents for all the samples apart from those treated with pure water or under milder conditions (namely 100mM of HCl and $FeCl_3$ at 100 °C).

In general, looking at the differential thermogravimetric plots (DTG), fig. 6.3, it is evident that the large presence of alkalies in the untreated wheat straw catalyzes the reactions of devolatilization, presenting a broad peak of reaction rate occurring at 323 °C, quite common for wheat straw [185, 190]. In the water treated samples two peaks become more evident, the first occurring at temperatures slightly lower than 300 °C and the second in the range of 350 °C. Here two different reactivities for the hemicellulose and cellulose fractions of the straw become evident due to the leaching of the alkaline minerals, as discussed in previous works [185]. The dilute HCl pretreated samples show in general highest-temperature peaks, reaching a maximum of 361 °C for the sample treated at 120 °C in 200 mM HCl. In these cases the increasing removal of hemicellulose, together with the alkaline minerals, displays a behavior slightly resembling pure cellulose [190, 192]. All samples treated in $FeCl_3$ present reaction rate peaks at lower temperatures if compared to the corresponding HCl treated samples. Besides, opposite to the HCl case, increasing $FeCl_3$ concentration appears to lower such temperature, thus denoting an improved devolatilization, even considering that larger fractions of hemicellulose have been removed. As anticipated before, the Fe deposits on the solid residues can be considered to be responsible for this catalytic effect. Thus, if on the one hand the removal of alkalies and of large part of the hemicellulose shifts the devolatilization reaction rate towards higher temperatures (in the range of pure cellulose), the presence of iron deposits on the residues acts as catalyst for the devolatilization reactions. At the same time the amount of fixed carbon at 550 °C is also increasing for the $FeCl_3$ treated residues,

Table 6.3: ash composition distribution in wt% of the most important elements making up for >99 wt% of the total inorganics. C, H, O, and N are excluded. Values in italic indicate the amount left compared to the untreated wheat straw. These values are calculated on SiO_2 basis, assuming that no SiO_2 is removed after pretreatments. This is a conservative hypothesis and thus these values represent rather an upper limit of the residual compounds rather than the actual residue.

		100 °C					120 °C				
	Untreated	Water	HCl		$FeCl_3$		Water	HCl		$FeCl_3$	
[wt%]	Wheat Straw	-	100mM	200mM	100mM	200mM	-	100mM	200mM	100mM	200mM
SiO_2	54.8	86.0	89.2	93.3	71.0	80.5	87.5	89.8	92.1	87.7	80.5
	100%	*100%*	*100%*	*100%*	*100%*	*100%*	*100%*	*100%*	*100%*	*100%*	*100%*
K_2O	28.0	4.9	2.8	1.2	3.0	1.1	3.7	3.0	2.3	1.2	1.4
	100%	*11.1%*	*6.2%*	*2.5%*	*8.3%*	*2.6%*	*8.2%*	*6.5%*	*5.0%*	*2.7%*	*3.4%*
Cl	5.7	0.2	2.6	2.4	9.5	6.1	0.1	3.1	2.0	3.7	6.9
	100%	*1.7%*	*27.6%*	*25.2%*	*128.8%*	*73.1%*	*1.6%*	*32.8%*	*21.0%*	*40.6%*	*82.1%*
Fe_2O_3	0.5	0.7	0.7	0.3	13.2	9.8	0.6	0.4	0.2	4.7	8.7
	100%	*78.5%*	*76.4%*	*36.9%*	*1855.5%*	*1223.4%*	*65.7%*	*39.7%*	*24.4%*	*539.3%*	*1083.2%*
CaO	7.0	5.4	1.5	0.4	0.8	0.3	5.4	0.9	0.6	0.3	0.3
	100%	*48.9%*	*13.1%*	*3.5%*	*8.6%*	*3.0%*	*47.8%*	*8.0%*	*5.4%*	*2.6%*	*3.3%*
Al_2O_3	0.4	0.5	0.5	0.4	0.3	0.5	0.5	0.4	0.5	0.5	0.4
	100%	*95.7%*	*89.7%*	*62.1%*	*64.2%*	*91.9%*	*83.5%*	*61.7%*	*77.0%*	*82.6%*	*84.1%*
MgO	1.0	0.6	0.3	0.1	0.2	0.2	0.6	0.3	0.4	0.2	0.2
	100%	*37.5%*	*16.1%*	*4.6%*	*14.6%*	*10.0%*	*36.3%*	*17.8%*	*21.4%*	*10.7%*	*14.5%*
P_2O_5	0.3	0.6	0.8	0.7	1.0	0.5	0.7	0.7	0.8	0.6	0.4
	100%	*27.0%*	*35.4%*	*29.0%*	*60.2%*	*26.9%*	*31.5%*	*32.4%*	*34.8%*	*29.8%*	*21.8%*
S	0.8	0.5	0.8	0.8	0.6	0.6	0.6	0.9	0.8	0.6	0.5
	100%	*52%*	*62.8%*	*55.3%*	*58.4%*	*52.6%*	*47.5%*	*68.4%*	*61.0%*	*48.7%*	*43.6%*

Table 6.4: Thermo-Gravimetric Analysis of the solid residues.

[wt% d.b.]	Wheat Straw	100°C					120°C				
	(Untreated)	Water	HCl		$FeCl_3$		Water	HCl		$FeCl_3$	
		-	100mM	200mM	100mM	200mM	-	100mM	200mM	100mM	200mM
Moisture [wt% a.r.]	5.42	6.3	6.3	3.4	5.5	5.9	8.5	4.7	5.0	4.0	5.5
Chars 550°C	30.3	22.9	19.4	22.3	23.8	23.3	20.9	22.6	23.8	23.8	24.2
Volatiles 550°C	68.7	77.1	80.6	77.7	76.2	76.7	79.1	77.4	76.2	76.2	75.8
Fixed carbon 550°C	21.8	15.8	13.5	14.2	17.3	16.9	16.8	13.5	14.1	14.6	17.2
Ash	9.5	7.2	5.9	8.0	6.5	6.3	4.1	9.1	9.6	9.2	7.0
Ash on initial [%][a]	100	74.7	52.5	61.0	55.0	48.0	39.8	68.5	63.4	66.5	46.1
Peak Temp. [°C]	323.3	354.8	355.3	358.1	349.6	345.3	354.7	359.7	361.2	353.7	348.8
Crystallinity Index	47.6	-	-	-	-	-	54.8	-	59.5	-	59.5
I_{002} (Crystalline)	1360	-	-	-	-	-	1234	-	1946	-	1809

[a] Ash present in the residue divided by the initial ash in the untreated wheat straw taking into account the weight loss after the pretreatment.

and this can also be ascribed to the presence of Fe deposits. Similar conclusions on cellulose reactivity were reported by Varhegyi et al. [192] as a consequence of the addition of $FeSO_4$ besides other inorganic salts.

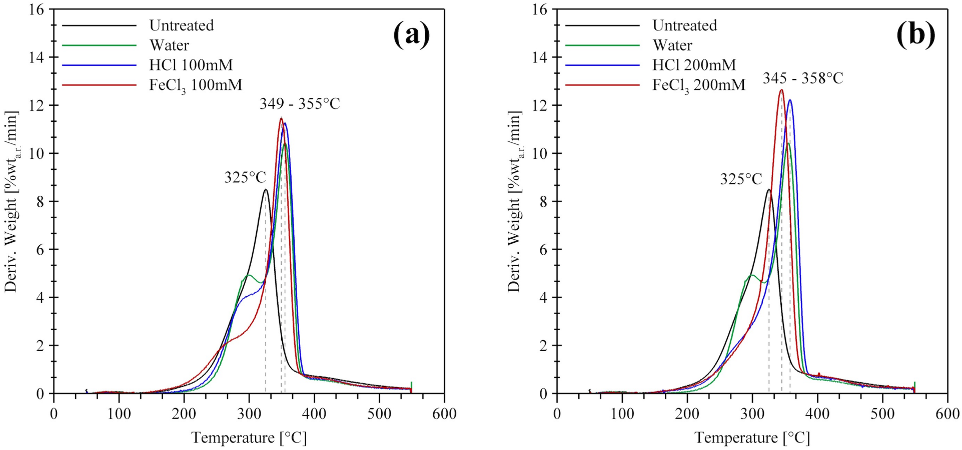
Due to the nearly total removal of unwanted alkaline materials like K and Cl, the residues of pretreatments present generally upgraded characteristics as solid fuel for combustion or gasification. The benefits from alkaline material removal are a reduced char production, as far as the the primary reactions are concerned, but also significant improvements in terms of equipment operation. The potential for slagging and fouling, equipment corrosion and fluidised bed agglomeration is in fact significantly reduced, becoming comparable to that relative to higher quality woody biomass [187, 193, 194]. As a matter of facts the high alkaline minerals content of agricultural residues, and their consequent ash behavior, is among the main reasons to hinder their use in large scale thermal applications despite their large availability and relatively low cost. An upgrading in this sense could increase the value of the residue itself making it attractive for use in large scale heat and power units in combination, or replacing, solid fossil fuels.

A thorough removal of alkaline minerals contained in wheat straw is also afforded by dilute $FeCl_3$, although accompanied by solid iron oxide particles deposition on the biomass residue, affecting the devolatilization reaction. The effect of such micro particles on secondary gasification reactions, for instance in fluidized bed reactors, would be worth further investigation, considering that iron containing minerals, like olivine, have been successfully tested as bed material for their positive catalytic effects on tars decomposition reactions [195]. Nevertheless, the opportunity of using iron containing salts for the pretreatment of biomass as an alternative to mineral acids, should be evaluated in a broader perspective, carefully balancing economic and environmental benefits and costs.

6.4 CONCLUSIONS

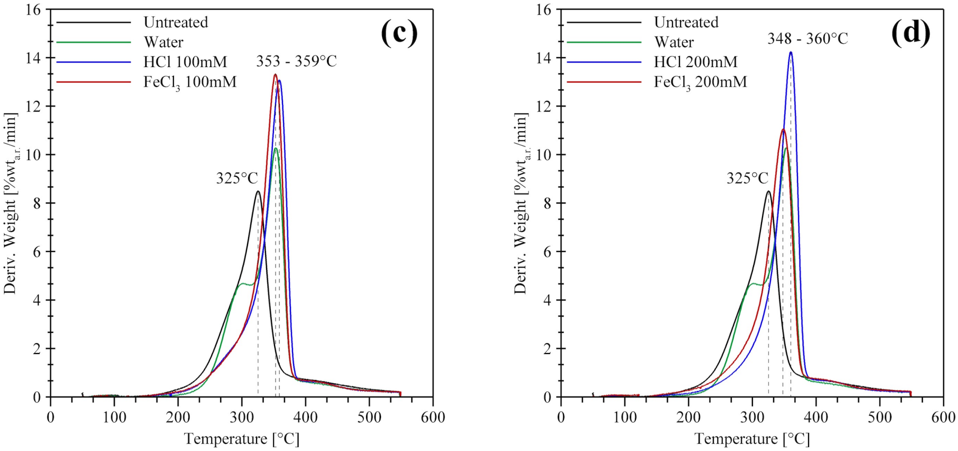
It was shown that minor concentrations of hydrochloric acid in water can be effective for hemicellulose hydrolysis already at temperatures between 100 and 120 °C. Recovery of hemicellulose derived carbohydrates, mainly considering xylose and arabinose, approached 100% under specific conditions. Dilute solutions of $FeCl_3$ were confirmed to be an option for mineral acid replacement, even though the Fe^{3+} ions were proved to act only indirectly on the hydrolysis of hemicellulose via their partial precipitation to iron oxides and consequent formation of HCl.

The residues of pretreatment showed upgraded characteristics with respect to the untreated wheat straw, presenting improved crystallinity and a significant reduction of alkaline minerals with direct consequences on their behavior under thermal conversion conditions.



(a) Wheat straw untreated and pretreated at 100°C for 120 min.

(b) Wheat straw untreated and pretreated at 100°C for 120 min.



(c) Wheat straw untreated and pretreated at 120°C for 120 min.

(d) Wheat straw untreated and pretreated at 120°C for 120 min.

Figure 6.3: DTG plots of wheat straw residues of pretreatments compared to the untreated, at 10 °C/min under nitrogen.

7

A NOVEL PROCESS FOR MAKING FURFURAL

Make things as simple as possible, but not simpler - Albert Einstein

The majority of current production is still based on more or less modified versions of the original Quaker Oats process (1921). For reasons that can be related to their limited technological evolution, the production processes in use today generally suffer from low yields (around 50%), besides significant economical and environmental concerns. All these reasons hindered the expansion and modernization of the furfural industry below its actual potential. A profound technological development is a priority in order to upgrade furfural to a large-volume bio-based commodity. The integrated production of furfural within modern biorefineries is a big opportunity, and it will most probably represent the next cornerstone in the development of furfural industry. In this chapter an innovative process concept is described, aimed at an economically viable and environmentally sound furfural production from biomass, with reduced energy and chemicals consumption.

The contents of this chapter have been adapted from the patent application:
Marcotullio, G. and de Jong, W., Process for the production of Furfural from pentoses, patent application PCT/NL2011/050730; October 2010.

7.1 CURRENT FURFURAL PRODUCTION PROCESSES

A variety of processes for the production of furfural from biomass have been studied and applied across last century. The concept behind all such processes is impregnating the raw solid biomass feedstock with an acidic solution (normally consisting of aqueous sulfuric acid), and reacting it at temperatures ranging from 150 to 250 °C. High pressure steam is passed through the reactants in order to keep them at reaction temperature and to strip out the furfural formed. Furfural is always recovered in the aqueous distillate at concentrations not exceeding 6% by weight.

Sulfuric acid use is substantial, up to a rate of 2.2 wt% on initial dry weight of biomass, therefore the discharged solids can be very acidic. In some process configurations acid usage is reduced, and the consequent loss of furfural yield is compensated by the use of higher temperatures and possibly larger amounts of steam.

A thorough review of existing process concepts was reported by Zeitsch [7], whereas more recent developments were reported by de Jong and Marcotullio [55].

7.1.1 *Operations of existing furfural production processes*

Processes industrially employed nowadays are not very different from the original Quaker Oats process dating back to the 1920s, see Figures 7.1 and 7.2. These processes are described more in details in literature [7, 41] from where some key figures can be drawn.

Reported furfural yield is about 11% on dry initial weight of biomass, which corresponds roughly to 50% of the theoretical yield. Oat hulls, which were originally employed, are quite rich of pentosans, thus furfural mass yield might even be lower when considering a different feedstock. For sugarcane bagasse, another common feedstock used for furfural production, the yield of furfural is normally between 9 and 10 % on initial dry matter.

The sulfuric acid usage is 2.2 wt% on initial dry biomass, and thus in the order of 20 wt% on recovered furfural basis.

Steam consumption for furfural production is remarkable. Furfural is recovered in a 5.8 wt% solution in water, thus 16.2 kg of steam per kg of furfural recovered are employed. In the original Quaker Oats process the operating temperature is 153°C with a residence time of 5 hours. Under these conditions the theoretical energy need for the production of saturated steam is 2.64 MJ/kg, resulting in a specific energy consumption of 42.9 GJ per metric ton of furfural produced.

The follow-up furfural distillation is also energy intensive, even though, in more integrated designs, it relies completely on large amounts of heat recovered

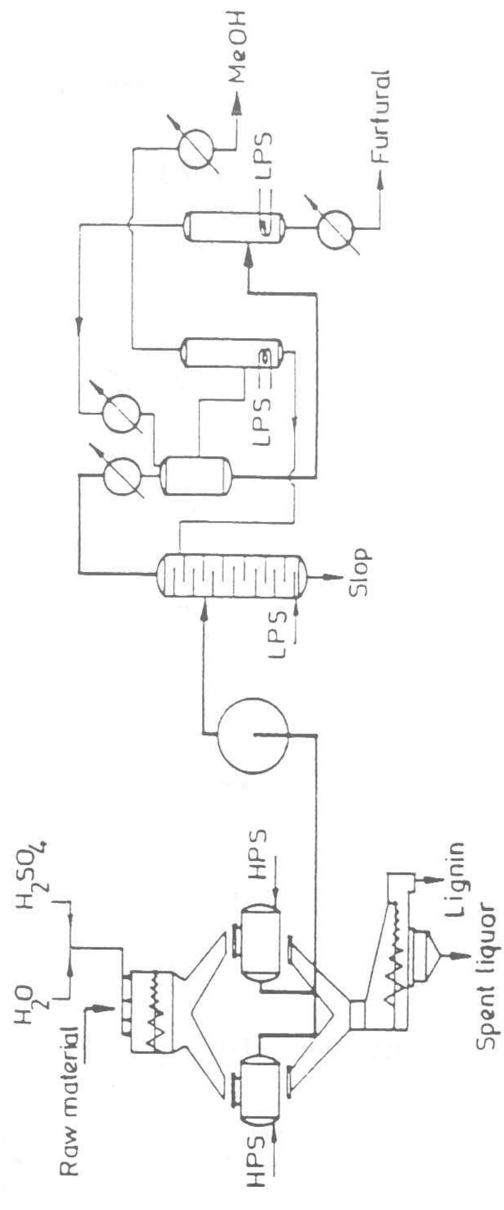


Figure 7.1: Schematic of the batch Quacker Oats process, adapted from [7]. HPS, LPS: High and Low Pressure Steam.

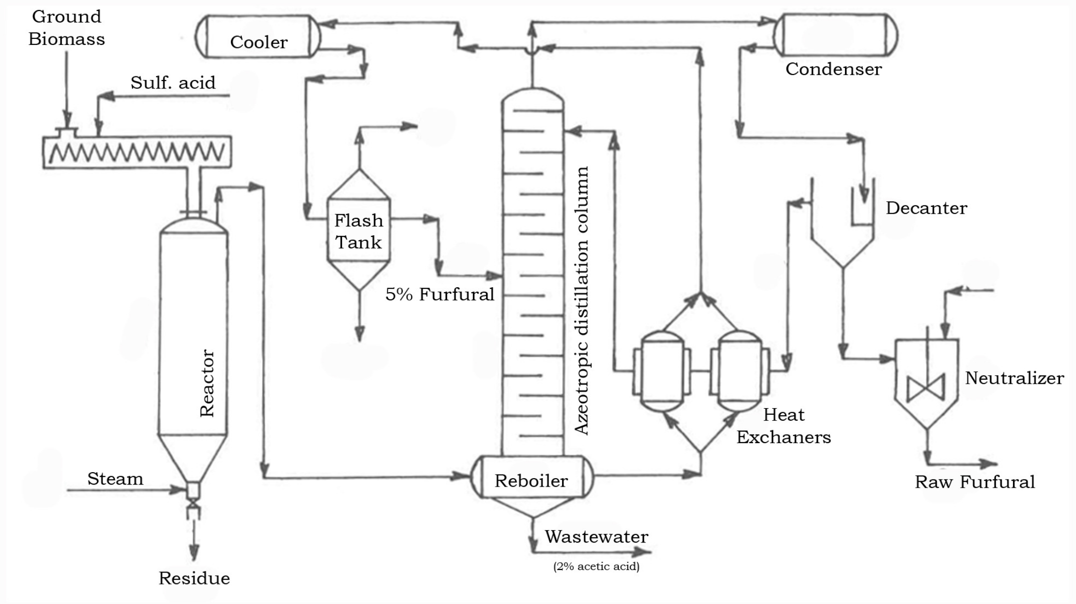


Figure 7.2: Schematic of a Chinese furfural plant with capacity of 2.5 kton/y (6 reactors), adapted from [7].

from the condensation of the high-pressure vapors emerging from the main reactor(s). Considering the schematic of an average batch process used in China, Figure 7.2, the production of high-pressure steam for the reactor is the main energy input to the process. Hence, it is not surprising that a strong correlation emerges between furfural prices (strongly influenced by Chinese producers) and asian coal prices [90].

7.2 THE OPPORTUNITY OF FURFURAL PRODUCTION WITHIN INTEGRATED BIOREFINERIES

Furfural production is normally carried out in dedicated plants, which, despite being based on residual feedstock like sugarcane bagasse or corncobs, do not really comply with the requisites of a modern and integrated biorefinery as described in Chapter 1. The solid residues of furfural production are normally not further valorized except from incineration.

In a modern lignocellulosic biorefinery, every fraction of the biomass should be used possibly for added value productions, minimizing the wastes and the environmental footprint. In the majority of biorefinery concepts cellulose is addressed as the most valuable constituent of biomass, and for this reason many biomass pretreatment processes aim at separating cellulose from hemicellulose and lignin. On the other hand, the hemicellulose fraction of biomass is of interest for furfural production.

As shown in chapter 6, among the main biomass constituents, hemicellulose is relatively hydrophilic and, moreover, readily accessible and fast hydrolyzing. Opposite to hemicellulose, lignin is only marginally soluble in water, and cellulose has a crystalline structure significantly more difficult to hydrolyze than the amorphous structure of hemicellulose. Because of these characteristics, in many biomass fractionation processes of interest for the biorefinery industry, somehow involving the use of water either as solvent or as anti-solvent, hemicellulose-derived carbohydrates normally end up in an aqueous stream together with other water-soluble impurities.

In view of this, two avenues can be foreseen for furfural production within modern biorefineries:

1. Furfural production via traditional processes as an integrated biomass pretreatment process: simultaneously converting pentosans into furfural and modifying the structure of the solid biomass residue in order to prepare it for further processing.

2. Furfural production as a follow-up of biomass pretreatment and fractionation: where a pentosan-containing aqueous stream is directed to a dedicated furfural production facility.

In the first case, due to the severity of reaction normally employed for furfural production, the structure of the residue is significantly modified compared to the raw biomass, and it should be assessed for further conversions and/or separations. In this perspective the limitations associated to traditional furfural production would remain basically unsolved, although advantages might result from system integration. When considering this option it is also important to remember that the biomass residue might still contain furfural(s) in amounts incompatible with further biological treatments due to enzymes inhibition (furfural(s) are well-known enzymes inhibitors).

In the second case soluble pentosans contained in a liquid aqueous stream, potentially arising from a variety of pretreatment technologies, may be used for furfural production. The idea of producing furfural via a two-steps process was already explored in the past, but the solutions proposed never reached commercial scale mainly because of the additional costs associated to the production of xylose [7]. Higher investment cost is the main limitation to such approach, although future perspectives might be promising considering the innovation efforts towards the development of new integrated biorefineries and new biomass pretreatment technologies.

In particular, cellulosic ethanol refineries being set-up in many countries, represent potentially an enormous source of pentosans, mainly available in side streams. In this view the current paradigm for furfural production could be shifted towards innovative, possibly more efficient, processes involving only liquid and vapor streams.

7.3 AN INNOVATIVE CONCEPT FOR FURFURAL PRODUCTION WITH HIGH YIELD AND LOW ENERGY CONSUMPTION

In view of the reasons mentioned above, and based on the results discussed in the previous chapters, a novel process concept has been developed at Delft University of Technology, which is schematically depicted in Figure 7.4. The process consists of feeding an aqueous solution containing pentoses at the top of a reactive distillation column, where furfural production takes place. The liquid downflow is under optimal conditions for the conversion of monomeric pentoses to furfural, which, once formed, is readily transferred to the upflow vapor stream. Needless to say, soluble pentosans, if present, will be rapidly hydrolyzed to monomeric pentoses under the conditions required for the formation of furfural.

As depicted in Figure 7.4, vapor recompression is the key solution opted for energizing the column with minimal energy consumption. Due to the peculiar furfural-water thermodynamics in the dilute region (Figure 7.3), the temperature difference between the top and the bottom of such column is expected to be in the order of 2 °C or lower. For this reason the work required for vapor compres-

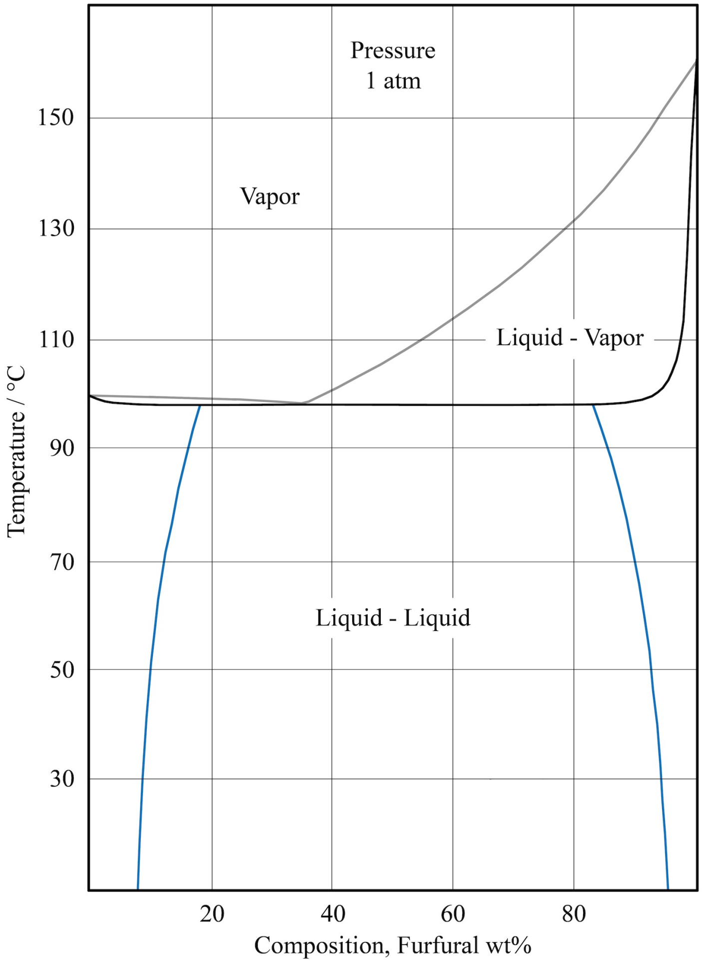


Figure 7.3: Furfural-Water T-x diagram at 1 atm., adapted from [8]

sion can be extremely low, allowing for remarkable energy savings compared to the existing processes.

Vapor compression is also proposed for the azeotropic distillation of furfural, with the aim of minimizing the energy consumption, and thus the operating costs. As it will be shown below, encouraging preliminary simulation results make this process concept an interesting option for furfural production from very dilute solutions of pentosans. Remarkably, raw biomass hydrolysates emerging from many biomass pretreatment technologies can be directly fed to such kind of process without further purification or concentration.

7.4 CATALYST CHOICE

In principle this process could be operated with or without the use of an acid catalyst, as furfural is also formed at neutral pH although in minor amounts. Nevertheless, in order to achieve optimal yields, the use of a strong acid catalyst is desirable. This may be a mineral or organic acid dissolved in the aqueous liquid downflow, but also a solid acid of the kind described in Chapter 1 bound to the column packing.

The use of suitable solid acids is certainly a preferred choice in the medium-long term, although many issues regarding the catalyst fouling, deactivation and regeneration should be carefully evaluated. Moreover, dissolved monovalent and divalent alkalis like K, Na, Ca and Mg are always present in biomass hydrolysates and, unless completely removed, they may likely poison the catalyst by cation exchange with H^+ at the acid sites [66].

7.4.1 *Homogeneous catalysis and recirculation*

In the near term homogeneous catalysis may be considered a viable option for this process due to its simplicity, no need for regeneration and low cost, provided that acid use is minimized, and only a part of the equipment is exposed to corrosive environment. To this aim, the acid containing column bottoms are recirculated within the process. By doing so, the downsides associated to homogeneous acid catalysis like acid consumption, neutralization and disposal of the spent salts are significantly limited.

On the other hand, recirculation requires dealing with impurities buildup, mainly represented by unwanted organics present in the feed, beside the products of side reactions. In order to control the composition of the recirculation stream, it should be partly diverted and replenished with a “clean” solution. A treatment for organic carbon removal at this stage allows for both limiting the concentration of impurities in the recirculation stream, and recycling the mineral acid catalyst. Such purification step could be based on existing wastewater treatment technologies, like adsorption or oxidation, or even on upcoming tech-

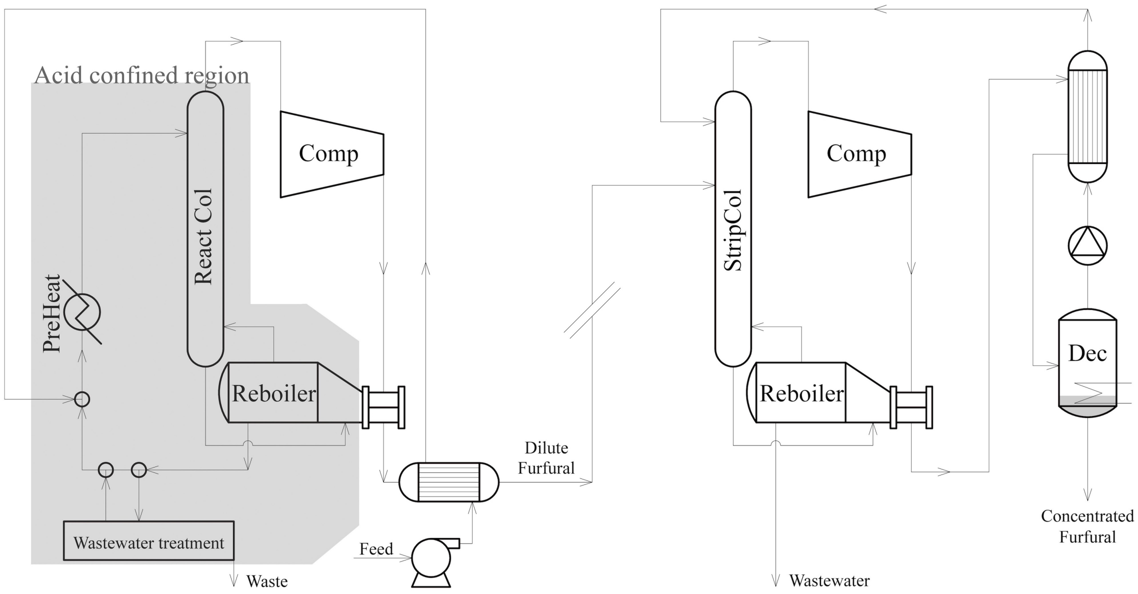


Figure 7.4: Process sketch. The grey shaded region includes the equipment parts exposed to a particularly corrosive environment, requiring thus appropriate corrosion-resistant construction materials.

nologies like aqueous phase reforming, or supercritical-water gasification, where the dissolved organic carbon is converted to a valuable syngas.

As a consequence of recirculation the dissolved acid will stay confined to a limited portion of the process and continuously recycled, with no need for replacement. It is noteworthy that, by doing so, very limited or no acid net consumption would be associated to furfural production.

7.4.2 *Halides addition for optimal yields and separation*

According to the results shown in Chapters 4 and 5, the use of inexpensive alkali or earth alkali halides, such as NaCl, in dilute-acid solution is a simple option to achieve optimal furfural selectivity and yields. Such practice would perfectly suite this process design, allowing for reaction selectivities up to 95%, Table 5.1.

Beside the mentioned effect on reaction catalysis, the use of dissolved salts is also expected to enhance the separation of furfural by salting-out effect, further reducing both furfural losses and energy requirements. Such salting-out effect is known since the earliest experiments on furfural formation [8], and experimental evidence was provided on the effects of salts on furfural-water mutual solubility and miscibility temperature [9]. Moreover NaCl has been recently used to enhance furfural production and separation via solvent extraction using THF [72].

Although the salting-out effect on vapor-liquid equilibrium was never quantified, it is expected to be relevant for the separation of furfural via steam stripping.

7.5 PROCESS SIMULATION

In order to evaluate the performance of the process both in terms of furfural yield and mass and energy balances, a model was created using the commercial process simulation software Aspen Plus^{TM} V7.0 from Aspen Technology Inc. Reaction kinetics relative to furfural formation from pentoses, as well as side reactions and furfural loss reactions, were implemented in the model based on the results exposed Chapter 3.

The knowledge of the thermodynamics of the binary system furfural-water is also critical for the modeling to be satisfactory, and to this aim a literature survey was carried out in order to asses the best models available [8, 9, 196–199]. The furfural-water system is well known, and experimental data for vapor-liquid equilibrium have been reported by several authors, especially in the temperature range between 40 and 170°C. Mutual solubility of furfural and water is also well known at 1 atm [9, 200].

The highly non-ideal behavior of such mixture requires a careful evaluation of the models to employ for the simulations. Especially when modeling vapor

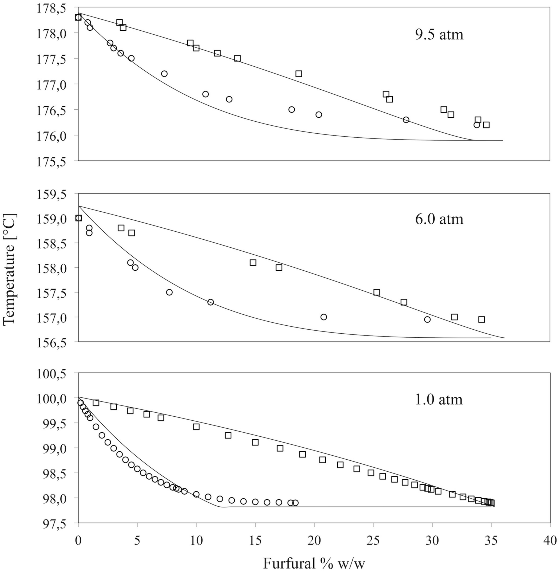


Figure 7.5: Furfural-water vapor liquid equilibrium in the dilute region. Measurement points for vapor (squares) and liquid (circles) composition against the NRTL model (solid line) at 1, 6 and 9.5 atm. Experimental data from [8, 9].

recompression, simulation results are particularly dependent on the precise estimation of the temperature at the bubble and dew point of the mixture, besides furfural vapor-liquid partition coefficients. Suitable thermodynamic models have been recently suggested in literature. Both NRTL and UNIQUAC binary correlation parameters were provided for estimating the liquid-phase activity coefficients, NRTL showing somewhat more satisfactory results. After a careful comparison with the available experimental data, especially in the dilute region, the NRTL model was chosen for the estimation of the liquid activity coefficients, whereas the Redlich-Kwong equation of state was used for the estimation of the vapor-phase fugacity coefficients.

Experimental data in the dilute region are compared to the model between 1 and 9.5 atm, see Figure 7.5, showing satisfactory results. The azeotrope temperature is slightly underestimated at the higher pressures, but it does not represent a problem for the scopes of this work as the uncertainty is in the order of 0.5 °C. On the other hand, furfural vapor-liquid partition coefficient is reasonably well described, especially within the solubility region (8.3 wt% furfural at 20°C), which is the region of interest for furfural-water distillation, Figure 7.6. For engineering purposes such model can be considered satisfactory across the whole temperature range.

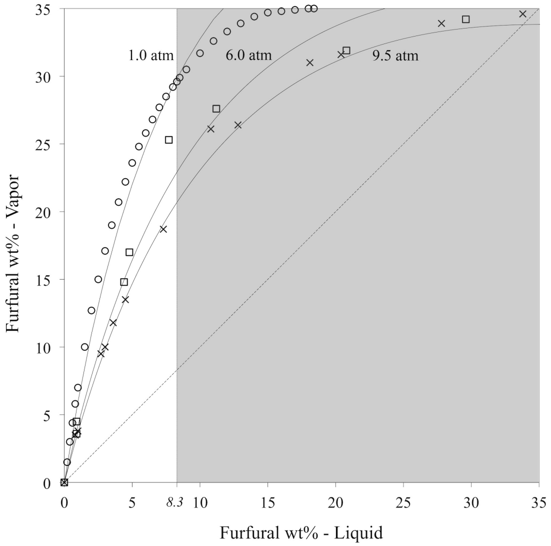


Figure 7.6: Furfural partition coefficient in dilute furfural-water mixtures. Experimental data compared to the model. The grey shaded region includes data of minor interest for furfural distillation.

7.5.1 *Results for a relevant process configuration*

The process described here is an intellectual property of TU Delft, and a patent application has been filed to both the Dutch and US patent office and it is at the moment under examination. In order not to interfere with the patenting procedures, and because of confidentiality issues, only partial information about the process conditions may be disclosed here as resulting from preliminary studies.

In Figure 7.7 main information regarding a relevant process configuration are depicted, including mass rate, pressure, temperature, besides stream composition limited to pentoses and furfural concentration. The targeted capacity is about 2.7 ton/h furfural, similarly to current furfural production plants.

The feed solution contains 5 wt% pentoses, and is further diluted after mixing with the recycle stream. The recycle stream carries specific amounts of an acid catalyst, in order to obtain optimal furfural yields. The rate of furfural-containing distillate equals the feed rate, so to maintain a constant rate of recirculation. As already mentioned, the wastewater treatment is intended for the removal of unwanted organic impurities, leaving the catalytic mixture unchanged.

Furfural separation and concentration is based on the traditional azeotropic-distillation, although integrated with the vapor recompression in analogy with

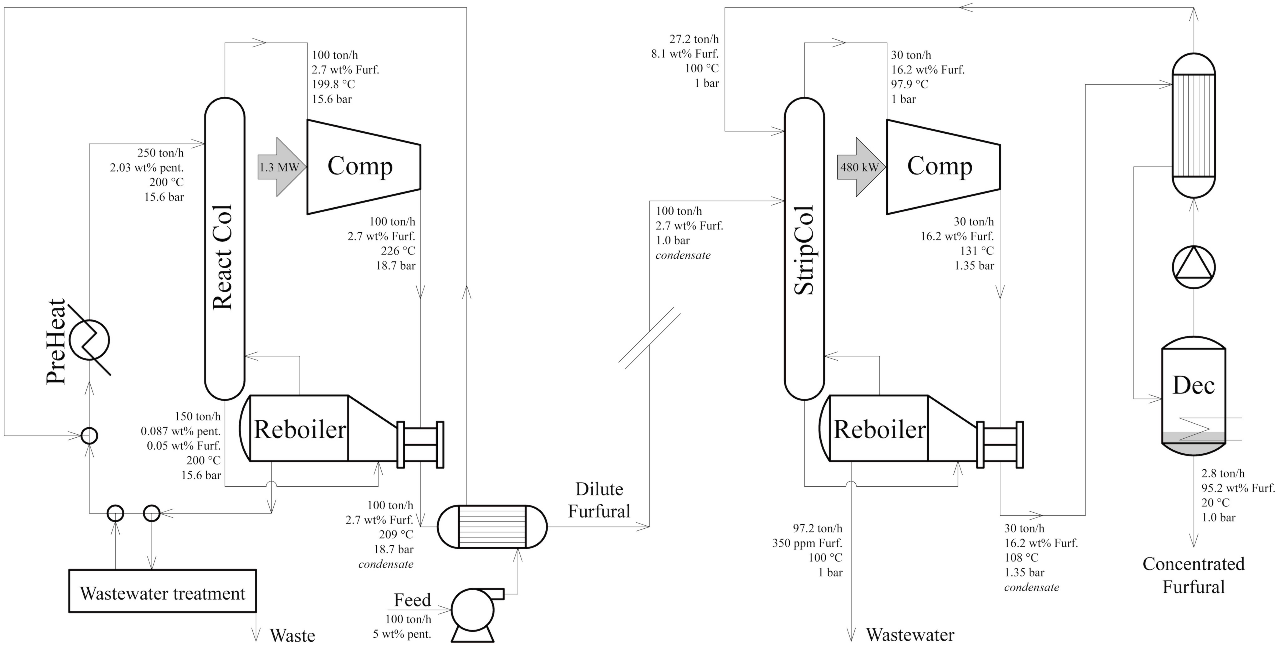


Figure 7.7: Main process streams of a relevant process configuration. Negligible pressure drop over the columns and heat exchangers is assumed at this stage.

the main reactor. An additional furfural purification column may be also added on the basis of the traditional furfural distillation as described by Zeitsch [7].

As it can be calculated from the main streams composition shown in Figure 7.7 furfural molar yield from pentoses is 83%. Even if the composition of the catalyst containing streams is not indicated, such yield is in line with the results exposed in chapters 4 and 5. Because the chemistry of furfural formation has been largely discussed in the previous chapters, this aspect is not further exposed here, preferring to focus on process design issues.

ASPECTS RELATED TO VAPOR RECOMPRESSION Vapor recompression represents the key aspect of the process as far as the energy consumption is concerned, especially addressing the costly steam stripping of furfural. Mechanical vapor compression is a known technique largely employed in seawater desalination for its relatively low cost, compact installation and low energy consumption. Raising the condensation temperature of the distillate vapor above the reboiler operating temperature enables heat transfer between the condensing distillate and the boiling bottoms, making the distillation process practically self-sustaining. This is accomplished at the expense of the top vapor compression. Hence, the energy required for vapor compression is the main energy input to the process and, in analogy with heat pumps, the closer the top and bottom temperatures, the lower will be the work input. Therefore, when dealing with close boiling-point mixtures the benefits brought about by this technique may be substantial.

As already shown, the furfural-water system, despite the significant difference between the normal boiling points of the pure components (161.7 and 100°C respectively), presents peculiar mixture behavior due to the hydrophobic character of furfural. Especially in the dilute region, up to the azeotropic composition (35 wt% furfural), this mixture shows very little variation of boiling temperature, resulting particularly suitable for vapor compression distillation. Moreover, due to the limited liquid solubility of furfural in water (8.3 wt% at 20 °C), concentrated furfural spontaneously separates from the condensed distillate, see Figure 7.7. For these reasons the overall furfural-water separation process is particularly simple and economical compared to most of the biomass derived chemicals.

7.6 PROCESS ECONOMICS

From the analysis of the streams depicted in Figure 7.7 it is evident that the direct energy use for producing and separating one ton of furfural starting from an aqueous stream containing 5 wt% pentoses is 0.67 MWh_e, representing a significant improvement compared to the 42.9 GJ_{th} per ton of furfural needed only for steam production in a traditional process. Even considering a reasonably wide variation of the country-dependent overall thermal conversion efficiency in power production (from 35 to 50%), the savings in terms of primary energy

Table 7.1: Summary of installed equipment cost

Equipment	Main characteristics	Material	kUS $ (2010)
Reactor system[a]	Heat exchange area = 4326 m^2, hold-up volume = 35 m^3	Titanium	6509
Vapor compressor #1	Installed power 1300 kW[b]	CS	1195
Heat recovery system #1	Hydrolysate feed/boiler discharge. Heat exchange area = 2250 m^2	SS304	1398
Process water treatment and replenishment	Based on activated carbon adsorption, wastewater rate = 30 ton/h	Titanium	2900
Stripping column	D = 2.5 m; 30 trays, [7]	SS304	725
Reboiler #2	Heat exchange area = 1335 m^2	SS304	977
Vapor compressor #2	Installed power 500 kW[b]	CS	464
Decanter	Volume 40 m^3, includes cooling coil	CS	94
Heat recovery system #2	Decanter inlet/outlet, heat exchange area = 675 m^2	SS304	601
Total installed equipment cost			14862

[a] Including reboiler and mass transfer equipment.

[b] It includes drive, gear mounting, base plate, and normal auxiliaries equipment.

are between 84.0 and 88.7%. It can reasonably be assumed that energy costs per ton of furfural would be reduced to a similar extent, and so it would the environmental footprint and CO2 emissions.

A higher initial concentration of pentoses in the feed stream may be considered in order to reduce both the variable and fixed costs, although care must be taken considering the consequent increase of the yield-reducing second-order loss reactions briefly discussed in chapter 3.

7.6.1 *Total cost of production estimate*

In order to fully evaluate the economic profitability of the process, a comprehensive cost-of-production estimate has been performed using both suitable cost-engineering models [201, 202], and real cost indications of actual furfural process equipment provided by experts in the field [90].

The cost model is based on the process configuration depicted in Figure 7.7, and on the following assumptions:

Table 7.2: Breakdown of Fixed Capital Investment (FCI)[a]

Investment item	Factor	Cost kUS$	% of FCI
Installed equipment	1.47	14862	35 %
Piping	0.66	6673	16 %
Instrumentation and control	0.18	1820	4 %
Electrical	0.11	1112	3 %
Buildings	0.18	1820	4 %
Yard Improvement	0.10	1011	2 %
Service facilities	0.70	7077	17 %
Total Direct costs		*34374*	*81 %*
Engineering and supervision	0.33	3336	8 %
Construction and fee	0.41	4145	10 %
Contingency	0.07	708	2 %
Total indirect costs		*8189*	*19 %*
Total Fixed Capital Investment (FCI)		*42564*	*100 %*

[a] Estimated using the Peters and Timmerhaus factors [201, 202]

- All costs and revenues are expressed in US$, which is the currency globally adopted in the furfural market.
- Pentoses are available in a liquid hydrolysate at a relatively low concentration of 5 wt%, at price of 130 US $/ton, dry basis [72].
- The plant is operated for 8150 hours per year, assuming that furfural production is integrated within a non-seasonal industry, such as pulp mills or perennial-crop based biorefinery.
- The total furfural capacity is 22 kton/y.

In Tables 7.1, 7.2 and 7.3, a summary of estimated installed equipment cost, total fixed capital investment (FCI), and total cost of production are reported.

Investment cost are relatively high for this process. The FCI of 42 M$ is more than double with respect to a traditional process with equivalent capacity [90]. This is to be expected as the whole process concept is designed with the aim of reducing variable costs, especially for energy, raw material and chemicals, at the expense of higher capital investment. The main titanium-made reactor system, with a significant heat exchange area needed for reducing the direct cost of vapor compression, represents alone about 44% of the installed equipment cost. Significant costs are also associated to the process-water purification and recycling system, needed to nearly eliminate the consumption of chemicals, in particular of strong acids. Various heat recovery systems also contribute to the installed equipment cost, to the benefit of a variable cost abatement.

Even considering the high FCI, the most important cost item in the annual production-cost is raw material, similarly to existing processes. The raw material cost depends directly on the cost of pentoses divided by the relatively low furfural mass yield - 54% in this case -, making pentoses cost the most critical variable in furfural production. On the other hand, the cost for utilities is significantly reduced compared to existing processes, accounting for 11.4% of the final furfural production cost of 833 $/ton.

It is evident from this analysis that the access to inexpensive pentoses streams is the most important issue in furfural production using this process.

The abatement of the FCI, and thus of the related cost items, is also critical, and could be pursued by the integration to an existing biorefinery facility, preferably non-seasonal, such as pulp mills, and by upscaling to a significantly higher capacity, in the order of 100 kton/y.

By carefully selecting an appropriate source for raw material, and an optimal production capacity, the unit cost of production might easily drop in the range of 650 US$/ton.

7.7 CONCLUSIONS

Furfural production paradigm should be revised in order to reduce the energy consumption, increase the yields and better fit within modern biorefineries. The process described in this chapter is a result of the entire research effort reported in this dissertation, and it tends towards this aim. In particular it addresses the following key aspects regarding furfural production:

- The significant reduction of direct costs related to steam (and thus energy) consumption, leading to improved economics and a reduced environmental footprint.

- The consideration of the latest findings on the mechanism of furfural formation in dilute acid/halides solutions allowing for optimal yields and separation.

- The drastic reduction of the specific acid consumption by virtue of the continuous recirculation of the catalyst-containing solution. The use of suitable solid acids is also foreseen in the medium term.

- The possibility of feeding the process with a dilute aqueous stream containing pentoses, opening up various opportunities for process integration within modern biorefineries.

Table 7.3: Summary of annual production cost

Cost item	Factor	kUS$/y	% of total	Unit cost US$/ton
Raw material	Pentoses cost = 130 US$/ton	5298	28.9 %	241
Utilities	Compressors + 20% for auxiliaries (120 US$/MWh$_e$)	2090	11.4 %	95
Process water treatment	35% water treatment investment	888	4.8 %	40
Maintenance	4% of FCI	1703	9.3 %	77
Supply	0.6 of FCI	255	1.4 %	12
Royalties	3% cost of production	660	3.6 %	30
Total variable cost		*10894*	*59.4 %*	*495*
Direct labor	45 employee-hours/day	517	2.8 %	23
Supervision	20% of direct labor	103	0.6 %	5
Lab cost	15% of direct labor	77	0.4 %	4
Taxes and insurance	3% of FCI	1277	7.0 %	58
S.A.R.E.[a]	2.5% of revenue	660	3.6 %	30
Overheads	72% of labor + 2.4% of FCI	1394	7.6 %	63
Interest	8% of FCI	3405	18.6 %	155
Total fixed cost		*7433*	*40.6 %*	*338*
Total annual cost		*18327*	*100 %*	*833*
Annual revenue	*Furfural unit price 1200 US$*	*26406*		
Gross earnings		*8079*		

[a] Sales, Administration, Research and Engineering

- Encouraging results from cost analysis, with a predicted cost of production significantly lower than average furfural exchange prices.

Although encouraging preliminary results have been achieved, several remaining issues are still to be addressed. In particular a more detailed process analysis is required including several by-products typical of furfural production, such as 5-methyl furfural, acetic and formic acids, and methanol among others. Especially when considering a woody feedstock the rate of formation of such by-products may be very important, and by choosing appropriate solutions they might bring significant benefits to the process, as recently reported by Xing et al. [72].

Furthermore, only after a more detailed analysis of the process, including a careful estimation of pressure drops and heat losses, and a detailed analysis of the process water treatment and recycling, it will be possible to better evaluate many aspects regarding the technical feasibility, materials choice, equipment sizing - especially regarding heat-exchange areas -, and process conditions optimization based on total cost minimization.

8

CONCLUDING REMARKS

This final chapter summarizes the conclusions drawn in this dissertation in view of the scopes of the research stated in chapter 1. Furthermore, suggestions and recommendations are given for future research .

8.1 CONCLUSIONS

In line with the scope of this research as stated in chapter 1, the main findings contained in this dissertation may be summarized as follows:

1. By carefully studying the reaction behavior of D-xylose and furfural in the selected range of conditions, new kinetic models have been proposed, presenting a good agreement with the measured reaction rates. The kinetic constants have been related to the acid concentration via the ion activity $a_{H_3O^+}$ to better account for the thermodynamics of the electrolytes in solution, which may be accurately modeled by means of the eNRTL model. The influence of temperature on the main rate constants showed a clear agreement with the Arrhenius law, furthermore, from the transition state theory, and from a careful literature review, a strong indication emerges of ring opening being involved in the activated state of xylose reaction to furfural. In this sense Cl^- ions were shown to promote the formation of the 1,2-enediol from the acyclic form of D-xylose, and thus the subsequent acid catalyzed dehydration to furfural.

2. Significant improvements were observed with respect to the H2SO4-based case in terms of furfural yield and selectivity from xylose when adding NaCl to a dilute-acid solution. A 4-fold xylose reaction rate increase was possible by 1.7 M NaCl addition keeping the acid concentration as low as 50 mM (0.18 wt% HCl), and initial sugar concentration 33.3 mM. General acid-base catalysis, rather than specific acid catalysis, is involved in the formation of furfural. In particular, a discrepancy in terms of "catalytic requirements" becomes evident in the process of furfural formation from pentoses, which involves an enolization followed by three dehydration reactions, two types of reactions favored by basic and acid conditions. Based on these results the "paradox of furfural yields" may be explained considering the complex chemistry of furfural formation in the presence of ionic species other than H^+ in aqueous solution. In this view, when thinking at industrial furfural production, it should be borne in mind that the high severity normally required is mainly needed to overcome the first enolization step, as this is not favored by acid. On the other hand the acid catalyst is indeed required in the following dehydration steps. Thus, in order to achieve better furfural yields under milder conditions and in a greener manner, the combination of two different catalysts, having in turn basic and acidic character, would be probably the key. Halides were shown to achieve this aim. In particular they were shown to enhance the reaction of xylose to furfural in aqueous acidic solution by two distinct and consecutive effects: the formation of the 1,2-enediol from the acyclic form of the aldose was preferably catalyzed by the halides in the order $Cl^- > Br^- > I^-$, whereas selective dehydration to furfural is assisted by the halides in the

opposite order $I^- > Br^- > Cl^-$. Synergic effects are also evident when using a combination of I^- and Cl^- ions, with selectivity of reaction attaining 95.3% and furfural yield 87.5%.

3. It was shown that minor concentrations of hydrochloric acid in water can be effective for hemicellulose hydrolysis already at temperatures between 100 and 120 °C. Recovery of hemicellulose derived carbohydrates, mainly considering xylose and arabinose, approached 100% under specific conditions. Dilute solutions of $FeCl3$ were confirmed to be an option for mineral acid replacement, even though the Fe^{3+} ions were proved to act only indirectly on the hydrolysis of hemicellulose via their partial precipitation to iron oxides and consequent formation of HCl. The residues of pretreatment showed upgraded characteristics with respect to the untreated wheat straw, presenting improved crystallinity and a significant reduction of alkaline minerals with direct consequences on their behavior under thermal conversion conditions.

4. The process exposed in chapter 7 is a result of the entire effort described in this research work. It addresses several issues regarding furfural production: 1. The significant reduction of direct costs related to steam (and thus energy) consumption, leading to improved economics and a reduced environmental footprint. 2. The inclusion of the latest findings on furfural mechanism of formation in dilute acid/halides solutions allowing for optimal yields and separation. 3. The drastic reduction of the specific acid consumption by virtue of the continuous recirculation of the catalyst-containing solution, besides the possibility of using suitable solid catalysts in the medium term. 4. The possibility of feeding the process with a dilute aqueous stream containing pentoses, opening up various opportunities for process integration within modern biorefineries. 5. Interesting economical outlook as resulting from cost analysis, with a predicted cost of production of 833 US$/ton, significantly lower than average furfural exchange prices.

8.2 RECOMMENDATIONS FOR FUTURE RESEARCH

The research work described in this dissertation left many open issues of interest for future research.

FURFURAL SALTING-OUT EFFECT As already mentioned in chapter 7, the addition of salts is expected to enhance furfural separation by salting-out effect. Future work in this sense is suggested in order to quantify the effect of salts on VLE of furfural-water-salts system. An attempt was made in this sense during this research work (results not shown), with the aim of determining the bubble point of water-salt-furfural systems by means of a Cailletet tube experimental setup. Regrettably, the results of such experimental campaign were unsatisfactory because of the occurrence of unacceptable systematic errors presumably due to furfural decomposition during the time required for the measurements. The release of minor amounts of volatiles consequent to furfural thermal decomposition gave rise to a slight pressure increase in the Cailletet tubes, the extent of which made the measured data unusable for VLE purposes. Such decomposition could not be prevented under the measurement conditions. For this reason it is recommended to use different methods than Cailletet tubes for VLE measurement involving water-salt-furfural systems, such as appropriate equilibrium apparatus enabling both vapor and liquid sampling under the target conditions.

SUGARS AND SUGAR DERIVATIVES HALIDE-ENHANCED DEHYDRATION The effect shown in this work concerning the use of halides salts on xylose dehydration is of general interest for the dehydration of sugars and also sugars derivatives. In the first place, a similar approach using different halides in aqueous solution is suggested for HMF production from hexoses. In this sense it would be interesting to study the different effect on glucose and fructose dehydration. Based on this same consideration it is also recommended to study the dehydration of sugar acids, such as gluconic acid, for the production of hydroxymethylfuroic acid (HMFA), or even the dehydration of galactaric (glucaric) acid into 2,5-furandicarboxylic acid (FDCA).

RAW BIOMASS PRETREATMENT Based on the observations exposed in chapter 6, it will be interesting for future research to test a pretreatment method involving a dilute-acid treatment of the raw biomass under mild conditions, followed by a lignin separation/solubilization step, for the selective production of cellulose fibers, lignin and hemicellulose-derived carbohydrates. In particular it is recommended to test an uncatalyzed organosolv type of treatment for the residues of dilute-acid hydrolysis, preferably using ethanol as solvent in the same range of temperature used in the dilute-acid treatment. By using a further treatment of this kind large fractions of the water-insoluble lignin are expected to be recovered, leaving a clean, cellulose-rich residue with high crystallinity. Such prehydrolysis and lignin removal could be of particular interest for the integrated furfural (and lignin) production within cellulose fibers industries.

The thorough removal of alkaline minerals contained in wheat straw afforded by dilute HCl and $FeCl_3$ may be of interest for biomass gasification. If the effect of a reduced alkaline minerals content has been already discussed, the effect of the iron containing micro particles on the biomass residues treated with dilute $FeCl_3$ on secondary gasification reactions, for instance in fluidized bed reactors, would be worth further investigation. In fact, iron containing minerals, like olivine, have been successfully tested as bed material for their positive catalytic effects on tars decomposition reactions. Hence, it is recommended to test dilute-$FeCl_3$ pretreated agricultural residues for gasification, with a particular attention to slagging, fouling, bed agglomeration, and tar decomposition. Nevertheless, the opportunity of using iron containing salts for the pretreatment of biomass as an alternative to mineral acids, should be evaluated in a broader perspective, carefully balancing economic and environmental benefits and costs.

FURFURAL CATALYSIS Regarding the development of suitable solid catalysts for the production of furfural (and furan compounds in general) it is recommended to take into account the discussion on the catalytic requirements for furfural production exposed in chapters 4 and 5. It is important for the catalyst to enhance the enolization reaction, next to the subsequent dehydrations. The purely acidic character given by the H^+ moiety has often been proven not sufficient to this aim. The simultaneous use of acid and basic solid catalysts is also not sufficient due to mass transfer limitations and to the instability of the intermediates of reaction. A single catalyst bearing a double function could be an interesting solution, as well as a combination of solid acids and soluble bases/salts in aqueous solutions. Further research is recommended in this direction.

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