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Removal Utilization/Separation of Tars from Syngas

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Removal, Utilization and Separation of Tars from Syngas

By

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ABSTRACT

Synthesis gas, or syngas, is among the most common products of biomass gasification and pyrolysis process. Syngas is produced by various fuels such as coal, biomass and any other hydrocarbon material. The principal use of syngas is in gas turbines as a fuel. It may also be used as the constructive material in other applications, such as methanol synthesis or biodiesel. Syngas is a mixture of gases, primarily with compounds of Hydrogen and Carbon Monoxide.

During gasification, other substances are created which can cause problems for the system machinery, and consequently create problems in the production of a final product. Harmful substances created in gasifiers include; nitrogen-based substance, sulfur-based substances, particulate matter, alkali metal, halides and tar compounds. These substances pose a threat to the system and may cause a series of problems at a further stage in the process. As gasification process is still under development, many case studies look at how different gas cleaning systems can eliminate or convert those contaminants from the syngas flows. Tar contaminants are the smallest product of the gasification process, however, they are consistently associated with malfunctions, such as pipe and filter blocking and deactivation of catalyst's particles. The term "tar" includes all the hydrocarbon compounds with molecular weight above benzene. Tar cleaning systems continue to cause major technical barriers to gas cleaning systems due to their complexity, and the diversity between the compounds in tar.

In order to save time and optimize the system's operation conditions, the establishment of a computer program is essential. The use of this program in an operation could save time, may minimize the energy consumption, and lower the economic cost of the system. Tar cleaning systems are separated into two main categories; dry and wet methods. Dry methods are carried out using heat and catalyst particles to convert the heavy hydrocarbon compounds to useful and non - harmful light compounds. On the other hand, wet methods commonly use cooling and liquid agents in order to condense or absorb the tar compounds into secondary flows.

To create the optimal computer program for this process, an extensive literature review exploring the existing cleaning systems and tar classification was carried out. The purpose of the literature review was to obtain a comprehensive understanding of the systems at work, including the contaminants. The literature review allowed for a deeper understanding of the cleaning principles and the properties of the tar contaminants. Consequently, a program was

designed which could estimate conditions such as; flow rates, temperatures and pressure in order to have the most sustainable arrangement. Further to the literature review, ASPEN Plus was chosen as the program to simulate the gas cleaning scheme. The program was based on the wet-model theories. Due to the high complexity and the lack of detailed data of the chemical reactions and kinetics occurring in dry models, an extended description was given for the second cleaning method with two simulations based in some of the main reactions that are taking place in a commercialized reformer and an ideal simulation with an RGIBBS module. To draw comparison between the two systems, data from literature on established implementations which use dry cleaning systems were compared with the results from AspenPlus used in this study. In addition, a small review for organic agent regeneration systems was carried out, as biodiesel was chosen as the absorber agent in the system.

In the presented study, two validation experiments were tested in order to prove that AspenPlus software works under the correct principles, and the results given are in line with those used in previous studies. At the second stage, data from two gasifiers were tested with the software in order to evaluate the optimum operation conditions needed to achieve tar concentration 0.1 mg/Nm3; the minimum limit for methanol synthesis. This study investigates the efficiency of an absorber column unit by using biodiesel. Methyl-palmitate oil was chosen to replace biodiesel as the organic agent in scrubber based on the liquid's similarities and sustainability as liquids. Due to the lack of data surrounding solubility and absorption, correlating tars in biodiesel or MPO, a simulation was carried out to predict the theoretical solubility of those compounds in the liquid.

Finally, the designed wet model was tested with the data of two pilot/commercialized plants; Synvalor and Guessing. The simulations results were compared with results from the plants cleaning systems.

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Abbreviations

"OLG"A	*Oil based Gas Washer*
AFR	*Air Fuel Ratio*
Aspen	*Advanced System for Process Engineering*
CFB	*Circulating Fluidized Bed*
CGS	*Cold Gas Cleaning*
CSTR	*Continuous Stirred Reactor*
DES	*Deep Eutectic Solvent*
DMEA	*Di-methyl ethanol amine*
ECN	*Energy Centre in Netherlands*
EOS	*Equation of State*
ES(ESP)	*Electrostatic Separator*
FC	*Fuel Cell*
FCC	*Fluidized Catalytic Cracking*
FT	*Fisher-Tropsch*
HGC	*Hot Gas Cleaning*
HHV	*High Heating Value*
IC	*Internal Combustion*
LHV	*Low Heating Value*
LHHW	*Langmuir – Hinshelwood – Hougen –Watson*
MDEA	*Methyl-diethanol-amine*
MEA	*Mono-Ethanol Amine*
NPV	*Net Present Value*
NREL	*National Renewable Energy Laboratory*
PAHs	*Poly-aromatic Hydrocarbons*
ppm	*Parts per million*
PR	*Peng Robinson*
RME	*Rapeseed Oil Methyl Ester*
RPS	*Rotation particle Separator*
RTIL	*Room Temperature Ionic Liquids*
SBR	*Steam to Biomass Ratio*
SCR	*Selective catalytic Reduction*
SPA	*Solid Phase Adsorption*
SNCR	*Selective non-catalytic Reduction*
SNG	*Synthetic Natural Gas*
SRK	*Soave-Redlich-Kwong*
TUD	*Technological University Of Delft*
WESP	*Wet electrostatic Separation*
WGS	*Warm Gas Cleaning*

1. Introduction

In recent years a number of new technologies have been developed in order to reduce the greenhouse effect, to sustain a more environmental future, and to stop further fossil fuel depletion. Engineers have developed a number of methods such as photovoltaic panels and wind turbines in order to reduce these harmful effects. In the last decade, biomass systems have become one of the most important energy carriers by which solid, liquid and gaseous fuels can be produced in a more environmental manner. Biomass fuels have proven to be a reliable energy source which produces up to 13% of the world's energy supply (Laksmono, et al., 2012).

One of the main products from biomass treatment is syngas. Syngas is a mixture of light hydrocarbon gases, mainly carbon monoxide (CO) and hydrogen (H_2), and may be used to produce products like synthetic natural gas (SNG), ammonia (NH_3+), methanol etc. (figure.1) (Beychok, 1975). The potential effective usage of syngas, and the sustainability provided by a neutral Carbon Dioxide source can have major impacts in advocating a more sustainable way of living. Biomass is not infallible, however, as the lack of a 100% efficient process and the produced undesirable byproducts affects the advancement, treatment, and usage of biomass fuels (Woolcock & Brown, 2013).

Based on the above, extra handling is undoubtedly needed to separate biomass byproducts which can be further used for other procedures, or disposed of in a safe way. The main concerns about the purity of the syngas are related to the efficiency of the whole procedure, as well as problems related with fouling, catalyst deactivation, environmental pollution, health concerns, pipeline blockages, the clogging of filters, choking of valves and metallic corrosion. (Asadullah, 2014). Contaminants related to such issues are mainly dust, tars, nitrogen-based compounds (e.g. NH_3, HCN) sulfur based compounds (e.g. H_2S, COS), hydrogen halides (e.g. HCl, HF) and trace metals (e.g. Na, K). (Nourredine, et al., 2015)

$$biomass + O_2(or\ H_2O) \rightarrow CO + CO_2 + H_2O + H_2 + CH_4 + other\ hydrocarbons$$
$$\rightarrow ash + char + tars$$
$$\rightarrow HCN + NH_3 + HCl + H_2O + other\ impurities$$
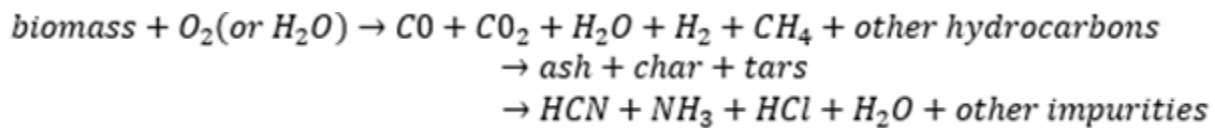
Figure 1 Biomass Gasification Products

The concentrations of those components can vary in the produced gas. According to Rabou et al., (2009) the parameters that affect the fraction of the contaminants in the product are the composition of the fuel, the process that is taking place, the temperature in the reactor, the residence time of the gas in the hot zone and the possible addition of a catalyst in the reactor. Table 1 below is representing the minimum gas concentrations limits of the above impurities at the final product for power production and methanol synthesis. The presented research will focus on tar removal, and provide a short discussion surrounding the available cleaning technologies and their effectiveness on a number of contaminants.

Table 1 Gas Quality Requirements (Ph. Hasler, 1998) (Hofbauer, et al., 2007)

		IC Engine	Gas Turbine	Methanol Synthesis	SNG Synthesis
Particles	mg/Nm^3	<50	<30	<0.2	0
Particles size	μm	<10	<5		
Tar	mg/Nm^3	<100		<0.1	below dewpoint
Alkali metals	mg/Nm^3		0.2		< 10 ppbV
NH$_3$	mg/Nm^3			<0.1	< 1 ppmV
S components	mg/Nm^3			<1	< 1 ppmV
Cl components	mg/Nm^3			<0.1	< 10 ppbV
CO$_2$	Vol.%	n.l.	n.l.	<12	

As mentioned above, contaminants formed during the production procedure may lead unwanted complications in further applications, (blockages in piping, clogging of filters, choking of valves, corrosion on turbines blades etc.), unwanted equipment processes, and, in order to follow the European restrictions of the produced fuel, in an abundance of extra costs. Various methods of treatment were tested recently in order to attempt to reduce and collect these contaminants. Cleaning technologies have been applied both inside and outside the process reactors (Gasifiers or Pyrolysis reactors), providing different removal efficiencies. Some of these can be used for the removal of several contaminants while others may be used for the separation of specific chemical compounds in the formed gas. These gas cleaning technologies can be separated into three main subcategories, according to the operating temperature; Hot gas Cleanup (HGC), Cold gas cleanup (CGC) and warm gas cleanup (WGC) (Woolcock & Brown, 2013). It may be apparent from the names of the cleaning categories that CGC are procedures which are established near ambient conditions and at Temperatures below the boiling point of water (T<100°C). HGC technologies are techniques that are treating gas in temperatures higher than the condensation point of ammonium chloride (~520 °C) and to nearest conditions of the downstream of the gasifier. At last WGC are techniques which operate between the temperature gap of the above two (100<T<300) and combine techniques from both (Nourredine, et al., 2015) (Woolcock & Brown, 2013). Cold technologies are more established and have been proven to produce high efficiencies, however, hot technologies are more attractive due to the avoidance of syngas cooling (Luc P. L. M. Rabou, 2009).

1.1.   Project Statement

The main goal of the present project is to further the evidence based on tar removal technologies by using AspenPlus simulations. In order to create models with realistic outcomes, validations models were built initially to test the program's operation conditions and results. Every model was tested with real data obtained from industrial and experimental gasifiers. Some of the designed simulations were programed with optimization codes in order to give the optimum operation conditions of the procedures which will utilize the energy and economic consumption of the

cleaning system. Finally, several sub-questions arose which needed to be fulfilled in order to achieve the primary goals of this project. These questions were as follows;

- Are dry cleaning methods more promising than the already developed wet cleaning methods?
- Can AspenPlus results be accurate enough in order for the program to be used for the design of an optimal cleaning system?
- Which conditions effect final product's tar concentration in a cleaning system and how?
- How can water consumption and waste water streams be reduced?
- Can a high purity organic liquid be separated from tars?
- How efficient is tar absorption in organic liquids?

1.2.   Thesis Outline

This study includes seven chapters which are sequentially organized.

Chapter two contains the theoretical background of tar compounds, production of tars, as well as outlining the cleaning methods that are currently used for tars removal. In addition, a brief literature explanation on tar collection and measurement methods is described at the end of chapter two. The described technologies and cleaning methods are essential for the simulations in the next chapters.

Chapter 3 describes another literature review for oil recovering methods from the absorbed tars. Additionally, based on the studied recovering methods, a brief economic analysis of potential usage of tar compounds is made in order to reveal the benefits of separating tars from the organic liquids.

Chapter 4 outlines the methodology and the steps carried out in the design the AspenPlus models. The background design of the models as well as the assumptions and laws taken into account in its use are also discussed. The targets of the designed models are outlined in Chapter 4.

Chapter 5 and 6 detail the modelling, simulation and the results of the Tar Removal Models. The suggested models as well as simulations corresponding to real gasifier flows were carried out on AspenPlus software. Initially, validation simulations for the wet model were completed in order to compare the software results with real data derived from experimental existing cleaning systems. Following that, simulations for both Dry and Wet methods were carried out, as well as simulations based on existing cleaning systems comparing their results with the results from the suggested configurations. In Chapter 5 and 6 comparisons are made between the models, and the details surrounding their operation discussed.

Finally, chapter 7 provides a conclusion of the project; the two systems and the two different methods of eliminating tars from syngas. Consequently, few recommendations for further research are given.

2. Tar impurities Definition and Properties

Tar is a mixture of organic compounds varying from primary oxygenated carbons to heavier deoxygenated hydrocarbons and polycyclic aromatic hydrocarbons (PAHs). The complexity and the number (400 components) of different species that exist in the produced gas create an obstacle for selective subtraction (Chunshan & Kenzi, 2010). They are usually formed as a product of secondary reactions during the gasification process which are taking place mainly on the pyrolysis stage (Hannula & Kurkela, 2011). A number of definitions have been provided to explain the behavior of these contaminants. Some researchers define tars as organic compounds produced under thermal or partial oxidation which are assumed aromatic while others define them as a mixture of condensable hydrocarbons which include single ring aromatics to PAHs (Anis & Zainal, 2011). The acceptable characterization was derived from the Directorate General for Energy of the European Commission during the meeting of the IEA Bioenergy Gasification Task, where they defined tars as hydrocarbons with molecular weight higher than benzene (C_6H_6, MWbenz= 78.11 g/mol), with benzene not to be considered as a tar (Bergman, et al., 2002).

In order to better understand their properties and find ways to optimally utilize these tars, different classifications are given to separate these compounds into groups with similar properties and characteristics. For example, according to Milne et al. (1998) tars can be classified under three main categories; primary, secondary and tertiary tars (Appendix. A). Primary tars are the tars which are developed directly from biomass constituents; cellulose, hemicellulose, and lignin. These are commonly heavier hydrocarbons, highly oxygenated and soluble in water. Secondary and tertiary tars are both products that form after primary tars cracking. It is usually hard to distinguish between the three, however secondary tars are characterized as phenolic and olefin compounds, and tertiary as methyl and PAHs derivatives of aromatic compounds. An alternative and highly regarded classification based on tar characteristics was composed by the Energy Research Centre (ECN) of the Netherlands during a biomass gasification conference in 2012. ECN separates tars into six categories, according their physical and chemical behavior (table. 2) (Rabou, et al., 2009).

The formation of these compounds occurs after a series of complex reactions and their composition in the product gas is a function of biomass feedstock, the type of gasifier used, and gas carrier, with some of these being more significant than others.

Mixed Oxygenates	Phenolic Ethers	Alkyl Phenolics	Heterocyclic Ethers	PAH	Larger PAH
400 °C	500 °C	600 °C	700 °C	800 °C	900 °C
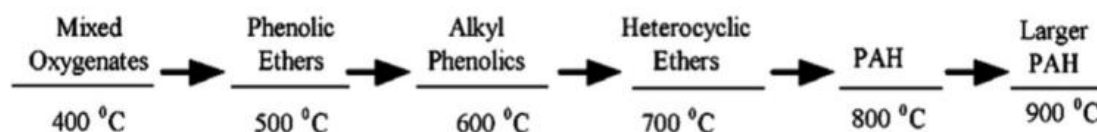
Figure 2 Tars Transformation (Milne, Evans, & Abatzoglou, 1998)

Table 2 Tar Classes (Bergman, Paasen, & Boerrigter, 2002)

Class	Type	Examples
1	GC undetectable tars.	Biomass fragments, heavier tars (pitch)
2	Heterocyclic compounds. These are components that generally exhibit high water solubility.	Phenol, cresol, quinoline, pyridine
3	Aromatic components. Light hydrocarbons, which are important from the point of view of tar reaction	Toluene, xylenes, ethylbenzene (excluding benzene)
4	Light polycyclic aromatic hydrocarbons (2-3 rings PAHs). These components condense at relatively high concentrations and intermediate temperatures.	Naphthalene, indene, biphenyl, anthracene
5	Heavy polycyclic aromatic hydrocarbons (>4-rings PAHs). These components condense at relatively high temperature and low concentrations.	Fluoranthene, pyrene, crysene
6	GC detectable, not identified compounds.	unknowns

For example, dry fuel composition and moisture content in fuels do not have a significant effect on the amount of tar produced. On the other hand, the type of gasifier, the operating temperature and the type of gas carrier (oxygen or nitrogen) have significant effects on tar concentration (Li & Suzuki, 2008). Their concentrations can be varied from 1 to 20wt% of dry fuel feed (Baker, et al., 1988). Increasing the reaction temperature results into the transformation of tars from light hydrocarbons to aromatics, oxygenates, olefins and finally heavy polycyclic aromatic hydrocarbons (Milne, et al., 1998). Previous research has shown the significant effect of process temperature in tar concentration. According to Anis & Zainal, (2011) at elevated temperatures (above 1000°C) - usually used in entrained bed reactors - tars concentration can plummet to as little as 1mg/mn$^3_{dry}$. Table.3 and figure.3 provide an example of product gas composition from different gasifiers with woody biomass feedstock, which were analyzed at different temperature profiles respectively.

		Fixed bed concurrent gasifier	Fixed bed countercurrent gasifier	CFB gasifier
Fuel moisture	%mf	6-25	n.d.	13-20
Particles	mg/Nm3	100-8000	100-3000	8000-100000
Tars	mg/Nm3	10-6000	10000-150000	2000-30000
LHV	MJ/Nm3	4.0-5.6	3.7-5.1	3.6-5.9
H_2	Vol.%	15-21	10-14	15-22
CO	Vol.%	10-22	15-20	13-15
CO_2	Vol.%	11-13	8-10	13-15
CH_4	Vol.%	1-5	2-3	2-4
C_nH_m	Vol.%	0.5-2	n.d.	0.1-1.2
N_2	Vol.%	rest	rest	Rest
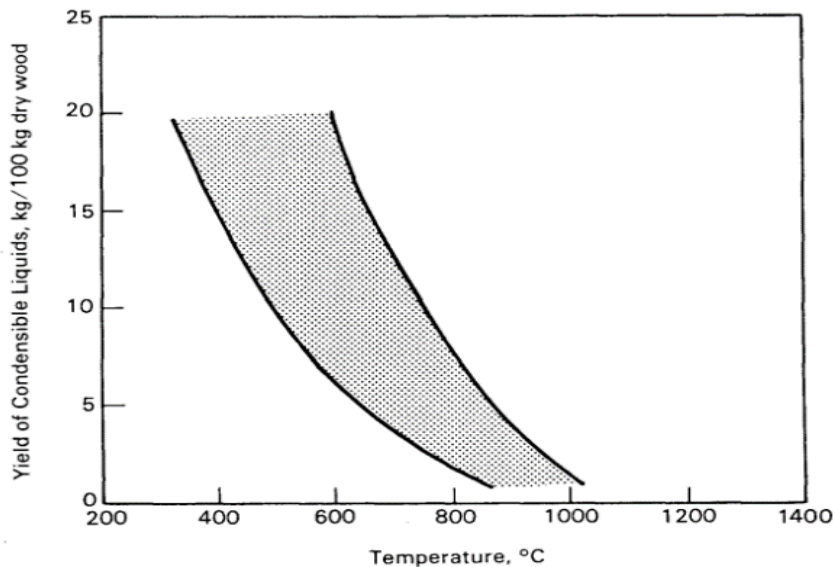
Figure 3 Tars Concentration from Woody Biomass (Anis & Zainal, 2011)

Although useful, tars also pose many problems in industry. The main triggering problem of tars is their condensation point. Downstream of gasifiers, tars exist in vapor phase due to the high process temperature. However, due to the cleaning treatment technologies and due to further processing, the produced gas needs to be cooled or pressurized, causing tar condensation. Condensed tars are characterized as very "sticky" and poisoning. They tend to stick on surfaces, causing fouling of catalysts, fragmenting of pipelines and pressure drops, resulting in operational interruptions and high maintenance costs (Vreugdenhil & Zwart, 2009). In the following figure.4 by ECN, the influence of tar concentration in the dew point of the tars is shown. Classes one and six are not illustrated, as they present tars that are either in very low concentrations which don't affect the procedure, or are unknown hydrocarbons, with unknown characteristics that vary between production procedures. As can be seen in the graph, class three tars have the lowest

dew point of all. The temperature regime in which these tars are condensing is not used in any advanced process, suggesting that they are unlikely to create complications in the system as a whole (Bergman, et al., 2002). Nevertheless, the crack of these tars to lighter carbon compounds such as CO, H_2 and CH_4 is supportive for the upsurge of gas calorific value and also for the volumetric increase of useful gas which can be then further utilized. Apart from this, class five tars are the most likely to condense in a high temperature regime, posing a threat to the production line. A similar trend can be found in classes two and four, which may also liquefy, though at lower temperatures. Despite their lower condensation temperatures, class two and four tars are still between the temperature limits of wet cleaning technologies. Classes two, four and five tars need more careful consideration for elimination in order to minimize problems arising during the production, cleaning or treatment of syngas (Milne, et al., 1998).
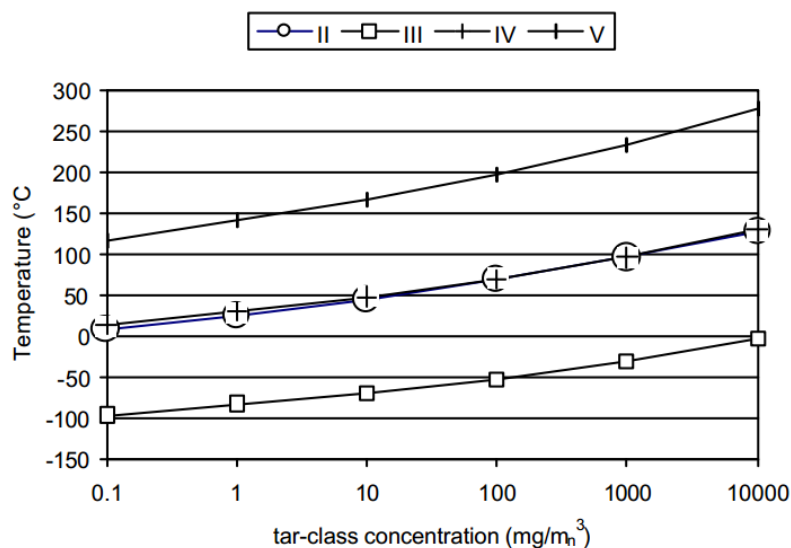
Figure 4 Tars Dew Point (Milne, Evans, & Abatzoglou, 1998)

Cleaning methods for tar removal can be characterized as primary and secondary. Primary methods include the technologies that are taking place inside the gasifier chamber, reducing tar concentration before the downstream cleaning units. Usually, these methods are not very effective so they have to be combined with secondary methods (Anis & Zainal, 2011). Secondary methods further separate into dry and wet techniques. Dry techniques include catalytic cracking, thermal cracking and plasma cracking (Nourredine, et al., 2015). Wet methods focus primarily on the absorption of tars into liquid scrubbers, and physical separation. Unlike other contaminants, not all tars are highly soluble in water. Soluble tars are difficult to separate from water, creating large amounts of waste streams either untreatable or difficult to utilize. Due to this, other components, such as organic liquids, are introduced to absorb the majority of tars, which subsequently contribute to an easier wastewater treatment later (Paethanom, et al., 2012) (Phuphuakrat, et al., 2010). An extended description of the cleaning methods will follow in the next sub-chapters.

2.1. Primary Cleaning Methods of Tars

Tar is formed during the incomplete conversion of biomass feedstock. One way to overcome this limitation is by enhancing the chemical reactivity directly in the gasifier's bed. These methods are called primary methods, and incorporate single or mix types of catalysts/additives directly in the hearth zone of the gasifier (Chiranjeevaraoseela, et al., 2015). Due to the high temperatures, few additives materials are capable and economically appropriate to be used. Various studies show that the use of dolomite, olivine, charcoal and calcined based catalyst are more optimal in biomass. The following figure illustrates the effect of some catalyst materials in tar conversion. However, usually the conversion rates are not high enough for total tar elimination, so a secondary method should always be considered (Guan, et al., 2014).
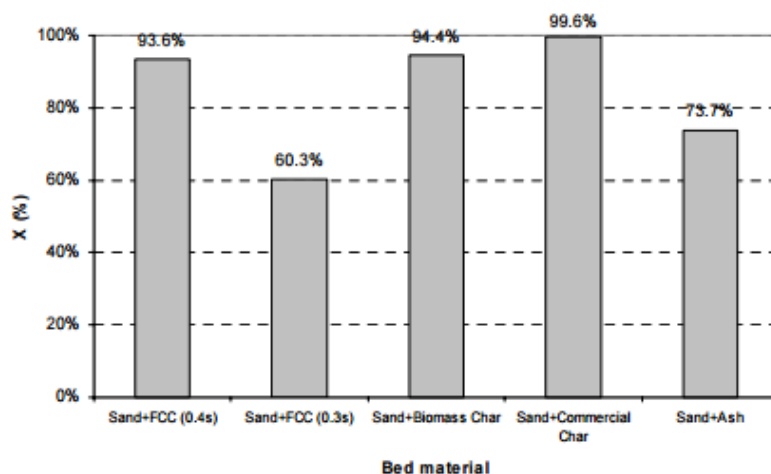
Figure 5 Effect of catalyst bed material on Conversion of the Model tar Component. Bed temperature 900 o C, 90 g/Nm3 initial tar concentration, 1 atm and 0.3-0.4 s residence time (El-Rub, et al., 2003)

Apart from catalytic cracking, different gasifier's designs can also offer tar reduction. For example, the use of smaller scale gasifiers helps the distribution of the oxidizing agent in the combustion zone and the removal of carbon dioxide from the gasification zone. This achieves a more effective conversion into products instead of tars (Singh, et al., 2014). Additionally, another widely used method, is the design of a double bed within the same gasifier. Finally, a simpler solution to reduce tar content is by applying higher temperatures (Neubauer, 2011). However, by using high-temperature gasifiers, information about catalyst stability is still unavailable. Additionally, by using vapor as gas medium, the produced gas has a low CO unsuitable for FT synthesis. (Jong & Ommen, 2015)

As previously mentioned, all of the primary cleaning methods do not achieve satisfactory low tar levels in the produced gas and there is always the need of combination either with a pilot filter (a type of filter coated with catalyst material which can be placed inside the gasifier), or more commonly with a secondary downdraft cleaning system. Nevertheless, the choice of a bed-catalyst is essential as it will affect the smooth operation of the gasifier in later stages as it will affect the $CO:H_2$ ratio of the product syngas and will also reduce adequate tar concentration.

2.2. Secondary Cleaning Methods of Tars

Secondary methods take place at the downstream of the gasifier. These combine wet and dry techniques and can eliminate tar content from syngas.

2.2.1. Dry Cleaning Methods

As outlined in the introduction of this study, dry or HGC technologies operate at high temperatures. An obvious advantage of dry cleaning methods is that cooling of the syngas is not required, hence greater process efficiency can be obtained. For example, by using HGC, filtration is increasing the overall efficiency around 13% (Heidenreich & Steffen, 2012). The extreme environments present cause difficulties in choosing materials and change the configuration of the cleaning technologies (Allegue & Hinge, 2012). Scrubber agents cannot be used due to the high temperatures. The use of HGC technologies has proven to improve the efficiency, the product quality and the economics of a system, as they offer complete breakdown of large PAHs without creating waste streams (Heidenreich & Steffen, 2012).

Dry cleaning methods for tar removal focus on eliminating tar content in the produced gas by cracking the heavy hydrocarbon molecules in the gas phase, rather than absorbing them in a liquid agent or separating them by liquefying them initially. The dry cleaning methods can be categorized into Catalytic, Thermal and Plasma Cracking (Laurence & Ashenafi, 2002). The figure below (figure 6) illustrates the multiple cracking reactions that take place inside a catalytic reactor.
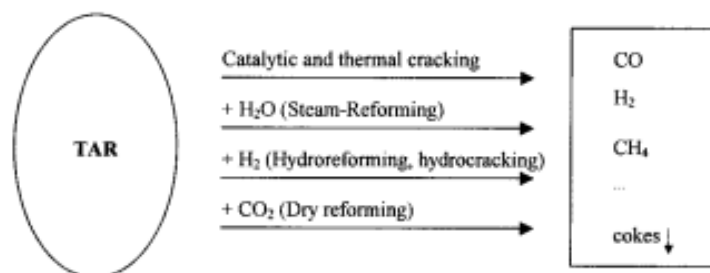
Figure 6 Dry model for Tar Elimination of Syngas Derived from Biomass (Corella, Toledo, & Aznar, 2002)

An array of relevant articles were studied for this literature review, based on tar dry cleaning modelling in AspenPlus. The majority of the studies are based on catalytic treatment. The studies mostly focus on one to three tars species for ease of the study, as a high number of reactions occur in the reformer. Due to this, a number of the studies assumed equilibrium conditions. For example, Kam, et al., (2009), investigated Biomass Integrated Gasification Combined Cycle. In this project, tars were modeled as phenol only. Tar catalytic treatment was modeled with an RGIBBS module in AspenPlus. RGIBBS model is responsible for estimating treated gas by minimizing the Gibbs energy of the mixture. Consequently, in the study by Kam, et al. (2009), reactions were not mentioned. Hannula & Kurkela (2011), and François, et al. (2013), modeled a cleaning system, consinsting of a cyclone, tar reformer, bag filter and a water scrubber. The seperation efficiencies of the technologies of all the species were taken from elsewhere in the literature (Rabou, et al., 2009) (Ahmed, et al., 2015). Tar reformer performance was modeled by

an RYield reactor. Equations regarding each tar species conversion rate were introduced by FORTAN coding. The conversion rate equations were based on empirical data from experiments.Other articles/projects described reactions and kinetics that were taken into consideration in the design of their project, however, no detailed description of the reactor was provided.

Furthermore, articles studying the partial oxidation of tars were studied. Damartzis, et al., (2012) modeled thermal oxidation cracking of three tar compounds; naphthalene, toluene and benzene. The tar compounds were assumed to be 20%w/w conversion of the initial biomass feedstock. Tar decomposition was model in a RCSTR module in AspenPlus. The RCSTR reactor required an extensive description of the reactions conditions (pressure, temperature) as well as stochiometry and kinetic information of the reactions. Finally, detailed reactions, kinetics as well as mass yields, equations of permanent gases, water, ten tar species over char an in-situ gasification process were studied by Abdelouahed, et al., (2012). The information given by Abdelouahed, et al., (2012) can be used for thermal cracking modelling.

2.2.1.1. Thermal Cracking

A more traditional way to drive tar cracking reactions is by providing the hydrocarbons with the required amount of heat so the reactions can be driven by themselves. During the thermal cracking process, raw gas is heated at temperatures above 1000 °C in order for tar to crack into smaller hydrocarbon molecules, flammable gases and steam (Søren, et al., 2005). In this technique, conversion effectiveness is strongly related to the temperature and the residence time of the raw gas in the heating zone. (Zhang, et al., 2009)

Thermal cracking can be achieved both inside and outside of the primary reactor. Heat is the primary reason that tar content has always been lower in entrained bed reactors than in other reactors. Additionally, the efficiency of this technique can be increased by adding air or oxygen (oxidation) directly to the heating zone. This method is called partial oxidation and is used to produce more carbon monoxide as it causes further cracking of the hydrocarbons in even smaller molecules (Allegue & Hinge, 2012). In order to increase the conversion rate during thermal cracking, three things can be done; firstly, increase the temperature of the furnace, secondly, increase the ratio of the oxidizing agent that is entering with the raw gas and finally, decrease the feed rate of the gas. However, high temperatures and high oxidant-gas ratio can increase the energy input while slower feed rates can slow down the whole procedure. For this reason, optimization of the operation conditions is performed in order to maximize the conversion and at the same time keep the minimum energy input (Mohammad, et al., 2003). The main disadvantage of this method is that tar components have varying temperature regimes that crack efficiently, and therefore extra heat is usually needed in order to achieve the desired temperatures (Anis & Zainal, 2011). A good example of thermal cracking can be seen in Figure.7. Figure.7, represents Naphthalene's concentration at different reactor's temperatures over time. As seen, at higher temperatures Naphthalene's concentration is being plumed in faster rates than lower temperatures. Shorter residence time of the treated syngas in the reactor concludes smaller reactor's size, yet, higher heat demands.
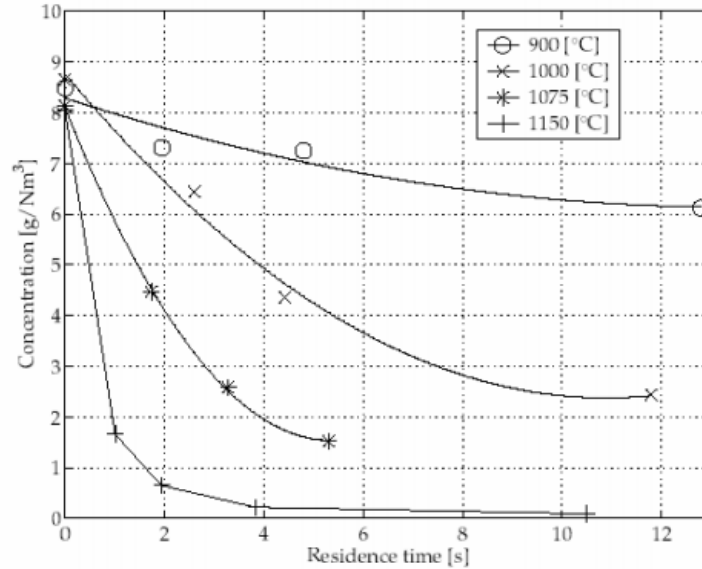
Figure 7 Naphthalene's Concentration over time in different reactor temperatures (Søren, Jesper, Birk, & Benny, 2005)

2.2.1.2.   Catalytic Cracking

Catalytic cracking is an endothermic reaction which needs large amounts of heat to be provided. Activation energy of a non-catalytic reaction (e.g. reactions 2.1 and 2.2) is usually high in the order of magnitude of 250-350KJ/mol, which means the operation temperature must exceed 900 °C. By using catalysts, the activation energy of the below reactions can drop to 56-123KJ/mol and hence, temperatures can be reduced to as low as 650 °C (Guan, et al., 2014). Reaction time may also be reduced.

$$Cracking\ Reactions:\ C_nH_m \rightleftharpoons \frac{m}{4}CH_4 + \left(n - \frac{m}{4}\right)C \qquad \text{(Reaction.2.1)}$$

$$\&\ pC_nH_m \rightleftharpoons qC_mH_x + rH_2 \qquad \text{(Reaction.2.2)}$$
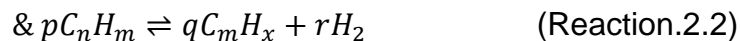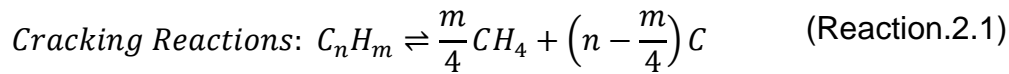
As seen in reaction 2.1, carbon (coke) is formed which can cause fouling on the catalyst active sites. To avoid this, catalytic reactors are commonly used to drive the following two reactions to eradicate and control the products from cracking tar compounds (Filippisa, et al., 2015). In commercial catalysts, coke formation, dust and sulfur are primary concerns related to catalysts deactivation.

$$stream\ reforming:\ C_nH_m + nH_2O \rightleftharpoons nCO + \left(n + \frac{m}{2}\right)H_2 \qquad \text{(Reaction.2.3)}$$

$$Boudouard\ reaction:\ C + CO_2 \rightleftharpoons 2CO \qquad \text{(Reaction.2.4)}$$

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$$Water-gas\ shift\ reaction{:}\ CO\ +\ H2O\ \rightleftharpoons\ CO2\ +\ H2$$

(Reaction.2.5)
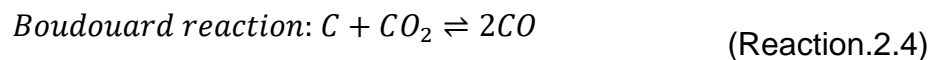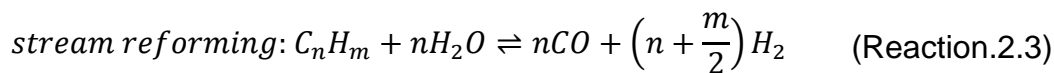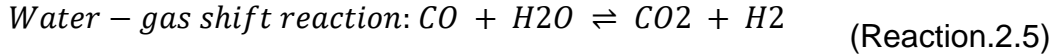
Furthermore, for this kind of application, a catalyst must be effective and stable in various temperatures and pressures. A good catalyst must be stable in order to have resistance to chemisorption, fouling, and aging, so it can be easily regenerated inexpensively (Guan, et al., 2014).

Tar cracking catalysts are separated into two main categories; Mineral and Synthetic (Zwart, 2009). Synthetic catalysts are more frequently used as they offer flexibility on the design and characteristics of the catalyst. Synthetic catalysts consist of an active element (where the reaction takes place), a promoter material which increases the stability and the activity of the catalyst and a support which gives a high surface area, durability and coke resistance (Anis & Zainal, 2011). The most common synthetic catalysts are nickel-based. These catalysts are often used in the petrochemical industry, through which they were found to be a key element in cleaning processes. Commercial Nickel catalysts can offer cleaning efficiencies up to 99%. Their greatest advantage is that, apart from reducing tars, they are also used for reducing ammonia, hence offering large hydrogen yields in the produced gas that could be desirable for liquid fuel synthesis. The following table provides an optimal example of tar conversion after a nickel based catalytic reactor (Morf, et al., 2002).

Table 4 Example of Syngas Nickel Steam Reforming Treatment (Wang, et al., 2010)

Produced Gas Component	Before the reactor	After the reactor
Hydrogen, H_2	0.01432 kg/m^3	0.0377 kg/m^3
Carbon monoxide, CO	0.1513 kg/m^3	0.063 kg/m^3
Methane, CH_4	0.1077 kg/m^3	0.0245 kg/m^3
Carbon dioxide, CO_2	0.4312 kg/m^3	0.4930 kg/m^3
Ethylbenzene, $C_6H_5CH_2CH_3$	112.24 µg/m^3	5.668 µg/m^3
Styrene, $C_6H_5CH{=}CH_2$	1.772 mg/m^3	80.84 µg/m^3
Naphthalene, $C_{10}H_8$	67.66 µg/m^3	0
2-methyl-phenol, $C_6H_4(OH)CH_3$	10.69 µg/m^3	0

Furthermore, nickel catalysts are able to drive the water-gas shift reaction (Reaction.2.5) in order to reduce the water content (Dayton, 2002). Based on the materials that are used as promoters and supports different tars conversion rates can be observed. For instance, by using a metal oxide as a promoter, greater effectiveness can be gained. Alumina offers high activity, but low stability, zeolites are referred as the best for naphthalene conversion and a combination of dolomites or olivine can lower the cost, increase the stability but can decrease the efficiency. Another example, nickel in the presence of sulfuric acid is known to be weak. By increasing the Molybdenium (Mo) concentration the deactivation effects of sulfur can be reduced, however it decreases its effectiveness on tar conversion. The choice of the right catalyst for each application is based on the needs of the producer and the techno-economic study that is made (Anis & Zainal, 2011). In

general, Nickel catalysts are quickly deactivated in the presence of sulfur contaminants, gas must be in relative high temperature in the entrance of the catalytic bed and are relative expensive. (Carlsson, 2008)

Other common catalysts that are used are from the mineral category. These include dolomites and olivine. These are both low cost and abundant materials that can be used to reduce tar content in both primary and secondary cleaning processes. Dolomite ($CaMg(CO_3)_2$) is a porous material, which must be calcined in order to become active. Its activity is a function of its porous size and Fe2O3 content (Orı, et al., 1997). Olivine is consisted mainly of MgO, Fe_2O_3 and SiO_2. It's a non-porous material with greater stability but lower effectiveness than dolomite. In low tar contents, these can have a large effect. Moreover, they show greater selectivity to heavier hydrocarbons and both materials are less effective than Nickel catalysts (Sundac, 2007).

Another important catalyst category is the 'non-nickel catalysts', in which both -metal oxides and alkali metals are included. Oxidized metal catalysts show greater performance than nickel based ones, but are more expensive to utilize. Metals like Rh, Pt, Pd and Ru show the highest efficiencies. Apart from high tar conversion, those catalysts are contributing to the production of high Hydrogen purity, however, are very vulnerable to sulfide, carbonyl sulfide, tar, carbon monoxide, chloride and ammonia where nickel catalyst does not face any of these problems (Xu, et al., 2015). Alkali metals catalysts show considerable effectiveness in the decomposition of primary tar components coming directly from cellulose and hemicellulose decomposition. Similar effectiveness is observed with carbon dioxide. The most effective elements are K, Na, Ca, Fe and Mg, respectively (Anis & Zainal, 2011). They can be added directly in the gasifier bed to enhance biomass reactions, however, they also enhance char and ash formation. Alkali metals in the gasifier bed are 6-8 times more active than dolomite, reducing not only tar components, but also sulfur and nitrogen impurities (Kumar, et al., 2009). The main disadvantage of alkali metals is their decomposition in the gasifier bed, which causes high ash and char content as well as difficulties for the ash disposal. Other disadvantages of alkali metals as in-situ catalyst particles in high temperature reactors (>900°C) are lost of their activity due to particle agglomeration and melting. (El-Rub, 2008).

Finally, another inexpensive catalyst material is carbon. Carbon materials used for syngas cleaning include activated carbons, chars, and black coke. Those materials are very effective in volatile adsorption and also for ammonia decomposition. Their high porosity enhances the transport of the reactant particles to the internal interface for better conversion (El-Rub, 2008). Activated carbon can be obtained by pretreatment of carbon granules. Both carbon materials can be obtained directly from the gasifier's bed, as they are by-products of the gasification process. According to Kadam, (2009) these carbon materials can reach cleaning efficiencies up to 95-99%. Their absorption capacity is strongly related with the particle and porous size. Apart from the above mentioned catalysts, there are other materials that can provide good catalytic activity for tar components. Acid catalysts like zeolites and silica alumina can provide good decomposition efficiencies, but are still in research point. Table 4 outlines the advantages and disadvantages of various catalysts used in syngas.

Table 4 Characteristics of Various Catalysts (Zwart R. , 2009)

Catalyst	Advantages	Disadvantages
Calcined rocks	. Inexpensive and abundant . Attain high tar conversion -95% conversion with dolomite . Often used as guards for expensive catalyst . Most popular for tar reduction	Fragile materials and quickly eroded from fluidized beds
Olivine	. Inexpensive . High attrition resistance	Lower catalytic activity than dolomite
Clay minerals	. Inexpensive and abundant . Less disposal problems	. Lower catalytic activity than dolomite . Most natural clays do not support the high temperatures (>800ºC) needed for tar reduction (lose pore structure)
Iron ores	. Inexpensive . Abundant	. Rapidly deactivated in absence of Hydrogen . Lower catalytic activity than dolomite
Char	. Inexpensive . Natural production inside the gasifier . High tar conversion comparable to dolomite	. Consumption because of gasification reactions . Biomass char properties not fixed and depends on biomass type and process conditions
FCC	. Relative cheap but not cheaper than the above . More knowledge is known about it from the experience with FCC unit	. Quick deactivation by coke . Lower catalytic activity than dolomite
Alkali metals	. Natural production in the gasifier . Reduce ash handling problem when used as a catalyst	. Particle agglomeration at high temperature . Lower catalytic activity than dolomite
Activated alumina	High tar conversion comparable to dolomite	. Quick deactivation by coke
Transition metals	. Able to attain complete tar reduction at 900ºC . Increase the yield of CO and H_2 .Ni-based 8-10 times more active than dolomite	.Rapid deactivation because of sulfur and high tar content in the feed . Relatively expensive

2.2.1.3. Plasma Cracking

The final hot gas cleaning method involves plasma cracking. Plasma cracking is an alternative method that uses an electrostatic-plasma beam to rise raw gas temperature without using any extra materials (e.g. catalysts) or producing polluted gas fumes. Technologies currently available include pulsed corona, dielectric barrier discharges, DC corona discharges, RF plasma, and microwave plasma. Pulsed corona is typically the most commonly used technique (Anis & Zainal, 2011). By using plasma technology, microwave irradiation is being transmitted into gas molecules

providing energy into it. This energy has the same effect as heat rises the gas temperature and crack hydrocarbon molecules. The main advantage of this technology is that is placed vertical with flow and offer more control and uniform escalation of the temperature (Bosmans, et al., 2013). Nevertheless, this technology combines more complex machinery and the cost of installation and operation is higher than thermal cracking technology (Wnukowski, 2014).

2.2.2. Wet Cleaning Methods

Cold or wet cleaning technologies are the most effective, and are hence more developed than the HGC methods. These methods have been used in industry for a longer period of time, as they provide easier ways to treat contaminants in the produced syngas, using mainly scrubbers and absorbing liquid for cleaning. The necessity for syngas cooling is a big disadvantage, as it reduces the energy efficiency for the whole production of a clean syngas flow. A further concern is the treatment of the generated waste streams, as they cannot be abended or tossed into the environment. Cold methods are useful in removing various contaminants with just a single technology. The most common use of the liquid agent is the removal of particulate matter, water soluble chemicals like sulfur dioxide (SO_2), Hydrochloric acid (HCl), Hydrofluoric acid (HF) and Ammonia (NH_3) and, tars (Carlsson, 2008).

In these methods, tar molecules are first liquefied and separated by physical methods, or are absorbed in liquid agents. The dew point of tar components and the solubility play an important role in the efficiency of such systems. Furthermore, there is no risk of catalyst deactivation and there is no need for heat supply when using wet cleaning methods. The production of waste streams is the only limiting barrier in wet cleaning procedures as the modern ways must minimize the production of waste water downstream.

After extensive research, no relevant literature was found based on wet cleaning modelling in AspenPlus. Projects were presented by Hannula & Kurkela (2011), and François, et al. (2013), which provided some relevant information. Both articles developed a model for catalytic reforming of hydrocarbons in AspenPlus. In both project designs, a model of a water absorber is illustrated after the tar reformer. The modeled water scrubber was designed to absorb tars as well as other species, based on empirical absorption efficiencies obtained in other studies.

2.2.2.1. Separation Equipment

To separate tar molecules from the gaseous stream, two procedures must first be carried out; gaseous tar molecules need to be converted to liquid by decreasing the temperature or increasing pressure, or by absorbing tars in a liquid. Both mechanisms create a double phase flow with gas and liquid molecules. When stand-alone systems are used, the dry gas temperature needs to be from 20 to 60°C in order for tar categories 2, 4 and 5 to be condensed. Mechanical technologies can be used without the use of any liquid agent and only by the use of liquefaction of tars into droplets. Mechanical methods include Inertia separation, Barrier Filtration, Electrostatic separation, turbulent flow precipitation, Rotational particle Separator (RPS) and etc. Inertia separation cleaning is commonly using cyclones, impact separators, and dust agglomerates. Cyclones are considered as the widest used method for solid or liquid materials from gases. They

can combine with all the below technologies as final collectors for particle diameters larger than 5µm (Leith & Metha, 1972).

Electric Separators technology is based on the different electrical properties of solid particles from gas. A tube type or a parallel plate configuration commonly takes place for this procedure. (Woolcock & Brown, 2013) A high electric field is applied between the two sides charging the solid particles (dipolar forces). Following this, a single stage electrostatic electrode that generates corona discharge is used to attract particles by the electric difference, so solids stick on the surface with the different voltage. (Bologa, et al., 2009) Characteristics that affect this procedure are density, viscosity, and resistivity. (I.J Lin, 1982). Rotating particle separators are other devices that can be used for tar removal. These mechanical devices are designed to coalesce condensed tar droplets by using centrifugal flow on the gas flow. A rotating curved plate (pyramidal) is placed vertical to the flow so droplets can hit and consequently separate by the rotating forces (Bosmans, et al., 2013). An illustration of the operation, ESP and RPS can be seen in the following figure.8.
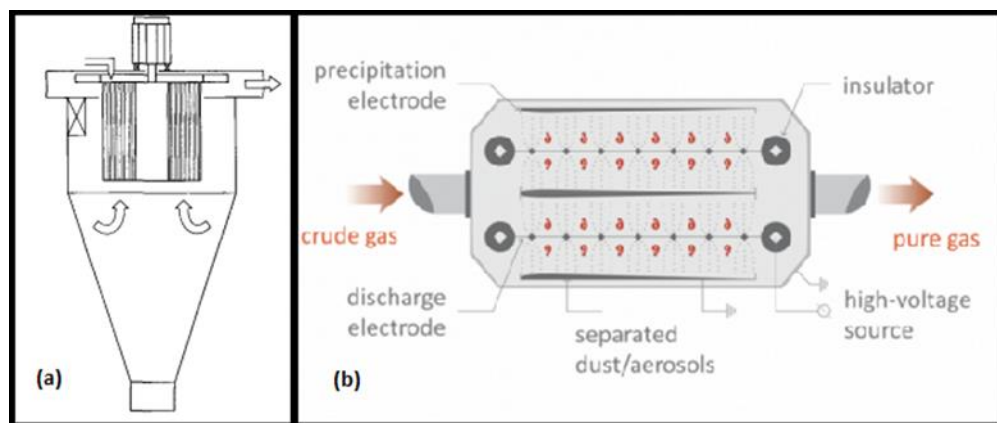
Figure 8 (a): RPS-(b): ESP (Hasler & Nussbaumer, 1999) (saveenergy.ch, 2016)

Physical methods used for phase separation combine machineries using centrifugal forces- cyclone, increasing velocities- venture scrubbers, electro-static fields- (ESP) and porous pathways- filters. Wet scrubbing technologies commonly used are; spray scrubbers, wet dynamic scrubbers, cyclonic spray scrubbers, impactor scrubbers, venturi scrubbers, and electrostatic scrubbers. These provide an effective separation method for particles smaller than 3µm. For greater separation performance electrostatic methods, higher temperatures and higher velocities are available, but these methods are typically more energy consuming and so are not as favorable. (Woolcock & Brown, 2013) Figure.9 illustrates a schematic of the above mentioned technologies.
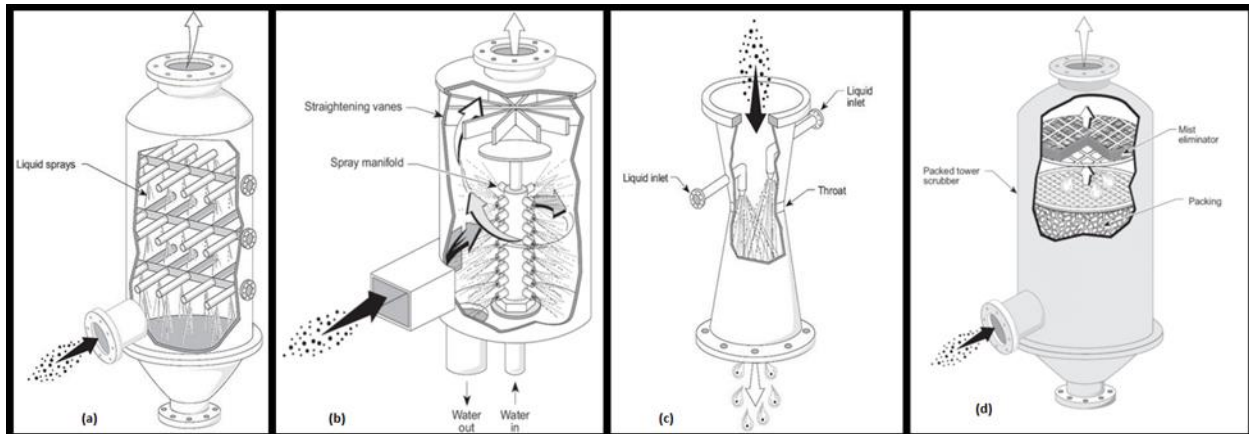
Figure 9 (a): Spray tower-(b): Cyclone Spray Chamber-(c): Venturi scrubber-(d): Packed bed scrubber (IHS Engineering360, 2016)

As seen in figure.10 below, by using different equipment materials varying efficiencies may be obtained for different particle sizes. For instance, cyclone is more efficient in removing larger particles and are usually used as secondary systems (Chiranjeevaraoseela, et al., 2015). Electrostatic precipitators are highly efficient in a large diversity of sizes, and their efficiency and selectivity is prejudiced by many parameters such as voltage, temperature, gas or liquid velocity, composition etc. By combining this method with a spray tower at the inlet, the cleaning efficiency is increased, sometimes offering up to 100% heavy tar elimination and close to 80% for light and heterocyclic tars (Paasen, et al., 2004). Barrier filters with fixed or loose material can provide highest efficiencies, however, recovering and cleaning are obstacles for this technology. Condensed and absorbed tar molecules may create a sticky substance on the filter material, creating the need for intense cleaning because blocking may be caused (Balas, et al., 2014). Granules bed is preferable due to the recirculation of the bed material with sand, lignite coke, sawdust and char to are the main granules materials. Fabric bag and ceramic hot gas filters are insufficient when used alone unless they are coated with catalyst material (Zwart, 2009).
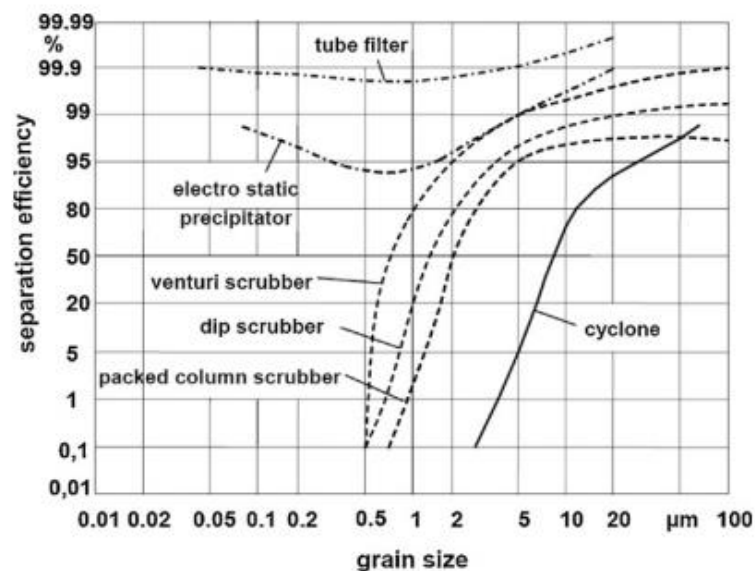
Figure 10 Physical Methods Effectiveness (Anis & Zainal, 2011)

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Venturi scrubber is another effective technology for tar elimination. In this cleaning technology the absorbing liquid can be sprayed on the gas flow before the gas enters the scrubber, as well as inside or at the exit of the scrubber. The droplets separate from the turbulent flow by passing through a cyclone or a mist eliminator (Chiranjeevaraoseela, et al., 2015). Table.5 indicates the effectiveness of each of these methods, for tars but also for other contaminants.

Table 5 Reduction Efficiencies (Ph. Hasler, 1998)

	Temp (^{O}C)	Particle reduction	Tar reduction	NH_3 reduction	HCl reduction	H_2S reduction
Catalytic tar cracker	900		>95%			
Fabric filter	App. 200	60-85%	25-0%			
Sand bed filter	10-20	70-95%	60-95%	>95%	90%	80-95%
Rotational wash tower	50-60	70-90%	10-25%			
Venturi Scrubber			50-90%			
Rotational atomizer	<100	95-99%			90%	>95%
Wet electrostatic Precipitator (ESP)	40-50	>99%	0-60%			

Finally, the most favored wet technology for tar removal is the use of scrubbers. Packed columns, spray towers and impingement scrubbers are some the most popular technologies that are used. Organic liquids or water are the scrubber agents that are used to absorb tars and other contaminants (Woolcock & Brown, 2013). Spray towers are the simplest method. Spray towers consist of an empty cylindrical vessel with nozzles, out of which liquid spray is ejected. These spray towers have the lowest efficiency, but are much cheaper from other similar technologies. Packed columns consist of vessel with packing material providing a large area for the gas to come in contact with the liquid that recirculates inside (Kolmetz, et al., 2014). Impinge columns offer the highest efficiencies from these technologies. In this technology, pretreated gas is directed from the top of a cylindrical vessel through a pipe in the liquid which covers approximately half the volume of the cylinder. Their efficiency can reach up to 95% at the beginning of the operation (Anis & Zainal, 2011). The operation of the described spray towers, cyclone, packed columns as well as venturi scrubbers can be visualized in the above figure.9.

Many current gas cleaning applications combine physical separation methods with absorbent liquids. A prime example is "OLGA"-oil based gas washer, ECN's project. In the OLGA method, firstly the temperature of the exhaust gas is dropped just above the dew point of water in order to liquefy heavy tar molecules, next these molecules are separated by a cyclone, and finally by using an oil scrubber tower, the remaining lighter tar molecules are absorbed and recycled back to the gasifier as feed or treated by a secondary recovering system which will be described into the next chapters (Bergman, et al., 2002).

Wet methods offer a more reliable and more effective solution for tar and other contaminant elimination, however, they are more energy consuming and more expensive to operate. The effectiveness of wet methods is strongly related with the combination of technologies and the scrubbing agent that are used.

2.2.2.2. Scrubber's Agents

Wet methods use liquids to absorb tars. Up until recently water was the most commonly used fluid agent to absorb tars, due to its availability and low cost. However, the use of water as tar absorber leads to the generation of large wastewater streams. Due to newly developed environmental regulations and the difficulties that are faced in wastewater treatment new absorbing liquids have been introduced. Water is no longer considered as the main scrubber agent for these cleaning technologies (Rabou, et al., 2009).

As previously discussed, "new" scrubber liquids include organic fluids such as vegetable oil, engine oil, diesel oil, acid methyl esters, biodiesel etc. These oils are now widely considered as adequate replacements to water. Water has low effectiveness in tar absorption. Water is adequate in only absorbing hydrophilic and light tar compounds such as phenols due to their polarity. On the other hand, organic liquids, due to their density and viscosity, are more effective in tar absorption.

 On the contrary, oily materials show great effectiveness in absorbing all tar classes. Different types of oil lead to different cleaning efficiencies. Diesel oil and vegetable oil have been shown to be the most effective, with diesel oil achieving efficiencies close to 99% for all tar classes except light tars. According to Paethanom, et al., (2012) oil performance revealed diesel> vegetable oil> biodiesel> engine oil respectively in order of effectiveness. Phuphuakrat, et al., (2010) argue, however, that because of diesel's high price and its evaporation at temperatures close to 100oC, vegetable oil is the best choice for tar absorption. (Paethanom, et al., 2012) (Phuphuakrat, et al., 2010)

Additionally, the method by which the absorbing agent is used in the cleaning devices is crucial for the overall efficiency of the system. For example, a common technique is passing the gas by a stirred vessel through which the organic agent is being recirculated. The mixing speed as well as the temperature plays an important role in the absorption of tars. With the increase of the mixing speed and the decrease of the temperature the absorbance of the oil is increased, resulting in more tars being absorbed in the organic agent. However, there is a point where, with a further increase in speed and decrease in temperature, the absorbance is decreased. The primary reason for this is that the gap created between the liquid and the impeller pushes liquid to the wall surface of the reactor. Apart from that, new technologies combine solid particles inside the organic liquid either in rows or columns (before or after) in order to adsorb the rest of the unabsorbed molecules in the gas stream (Anchan, et al., 2011). Finally, for the utilization of the waste liquids, two methods are most commonly used in industry; First, burning the waste stream to provide heat to the gasifier or for thermal cracking and second, recirculating the waste stream at the gasifier so it will produce more syngas (Rabou, et al., 2009). This project will also explore alternative

methods to separate the scrubbing-oil from tar, in order to reuse the oil and valorize tars into chemicals.

2.3.   Methods of Collecting Tars

Due to the complexity and the varying nature of tar compounds it was essential for analysis methods to be discovered and implemented for these substances. During the previous decades, several trials have been established to develop a universal tool for measuring the concentration of tars inside syngas at the exit of the gasifier or the exit of the cleaning unit.

The methods that have been developed are divided in two main categories the off-line and on-line methods and are;

- Off-line methods
    - Esplin method
    - European tar protocol
    - Solid Phase Adsorption (SPA) method
- On-line methods
    - Flame Ionization Detection method
    - Photo spectroscopy
    - Laser spectroscopy
    - Light Emitting Diode Spectroscopy

An extended description of these methods was written by Svensson (2003). A description of the European tar protocol and SPA are provided in this project, as these are the two methods that were used to obtain the data for the further models.

2.3.1.   European Tar Protocol

European Tar protocol is now one of the most common sampling methods that is used to analyze tar compounds within syngas. It was first appeared at the 10th European Biomass conference in Wurzburg as two different protocols which in April 2000 were combined to create the European Tar protocol (ETP). (Neeft, et al., 2000) ETP is allowing a broad analysis of produced syngas flows under different conditions such us;

- Different gasifier types
- Temperature regimes from 0 to 900oC
- Pressure regimes from 0.9 to 60 bar
- And concentrations from 1mg/Nm3 to 100g/Nm3 (Kiel, 2003)

The system contains six cylindrical impinger bottles placed in series. The first four bottles are placed in a water bath at 20oC and the last two in a cold water bath at -20oC. The whole technique is based on the absorption of the tar compounds within the liquids inside the bottles. In order to overcome restrictions of temperature and evaporation the first five bottles are filled with a non-toxic, unexpansive organic solvent with high boiling point. For these reasons the most common

used solvent that is used is isopropanol. The last bottle is always without any liquid. A typical arrangement of the analysis method can be seen at the next figure.
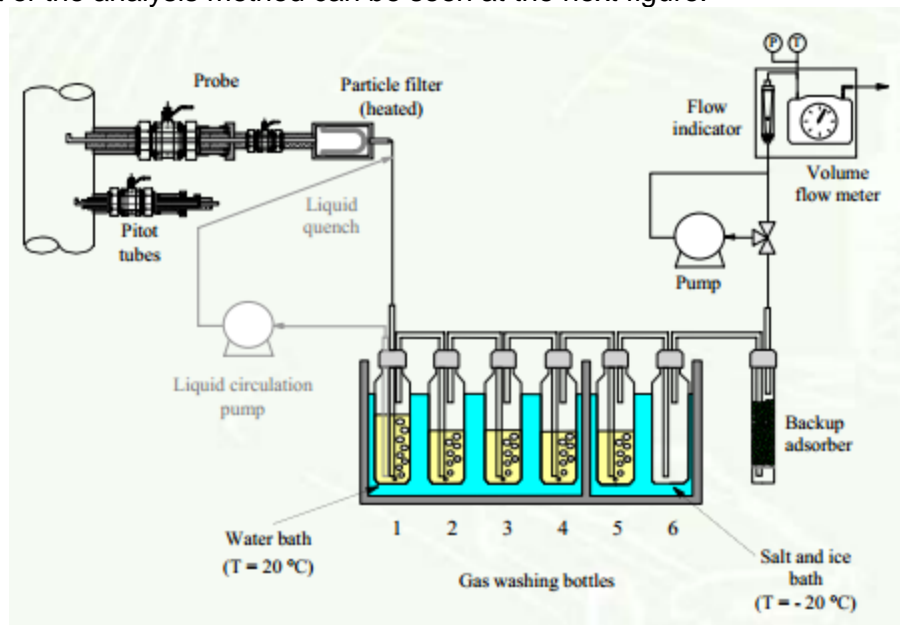
Figure 11 European Tar Protocol layout (Biomass Technology Group., 2016)

The bottles are placed in such way in order to reduce the gas temperature to -20 oC. The first bottle is used mainly for moisture collection however, part of tars are being absorbed there too. The next four are used for tar absorption and the last one just to ensure that no solvent has evaporated from the system. (Romar, et al., 2010)   This procedure is offering a clear overview of the tar concentration inside produced syngas steams. Nevertheless, two weaknesses of this method that need to be improved are the time that is needed to take measurements and that always an operator is needed to be present. (Svensson, 2013)

2.3.2.   Solid Phase Adsorption (SPA)

Solid-Phase Adsorption is another common offline tar analysis method that is used. Compared with ETP, SPA method first appeared in 1997 KTH in Sweden by Barge and then improved and established by ECN in 1998. (Grootjes, 2011)

Compared to ETP, SPA is quicker in measuring tar concentration in syngas streams (less than a minute). Conversely, SPA is facing other limitations. These limitations are mainly related with the operation conditions of the flow and the type of compounds that exist within the syngas. In brief, SPA can measure tars under the below conditions;

- Tar compounds should have Molecular Weight (MW) from 104(styrene)-300(coronen) g/mol
- The gasification must take place at temperatures over 700ºC
- And tar concentration should be between 0.05 and 10 mg/ml (Svensson, 2013)

As seen from the restrictions above SPA is unable to measure heavy tars.

The procedure for SPA analysis is starting by sampling 100ml of syngas directly from the flow. The 100ml vapor sample is then injected to a Solid Phase Extraction tube where a polypropylene column is already packed with a solid absorber. The absorber is always a silica based amino phase. By ejecting the gas into that column the tars are being absorbed by the absorber. Phenolic compounds are strongly bonded with the absorber with the rest of the tars to remain in the gas phase. Following the collection, the column is eluted with appropriate amounts of dichlomehtane and isopropanol in order to collect the aromatic and phenolic compounds respectively in the tube. Nitrogen gas is commonly used to separate the two fractions of tars inside the tube. Further to this the eluted mixture runs through a Gas Chromatographer-GC (Mass Spectrometer-MS or Flame Ionization Detector-FID) or High-performance liquid chromatography-HPLC which are technologies that are identifying the tar compounds in the particular flow (Verdant Chemical Technologies, 2016). Figure.12 below is illustrating the arrangement of the SPA method.

1 = to syringe or electrical pump; 2 = adapter (polypropylene);
3 = sample reservoir; 4 = sorbent tube (polypropylene, 1.3 OD x 7.5 cm);
5 = fritted disc (20 mm polyethylene); 6 = amino-phase sorbent;
7 = rubber/silicone septum; 8 = septum nut (polypropene);
9 = "Tee"-adapter (glass); 10 = hypodermic needle (stainless steel);
11 = product gas inlet; 12. = heating tape
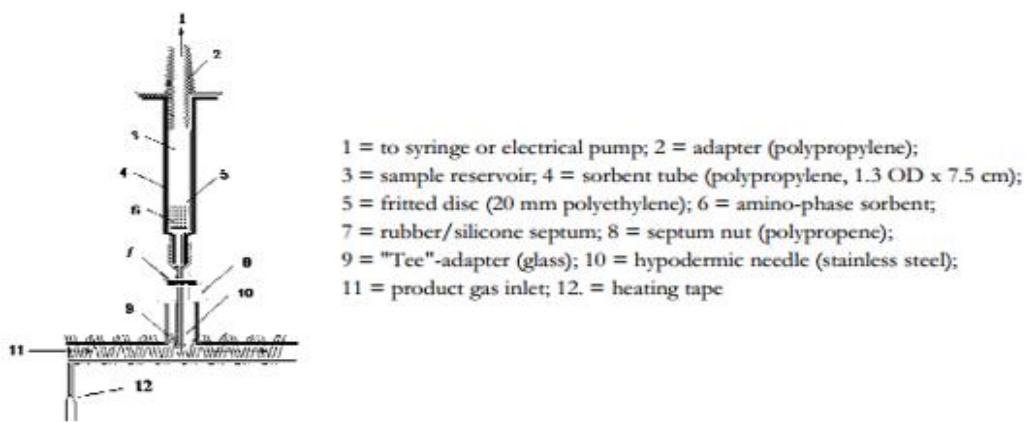
Figure 12 SPA layout (Svensson, 2013)

3. Review of Oil Recovery Technologies from Absorbed Tar Compounds

Regeneration of the scrubber oil would be an essential addition for a more effective and cleaner tar separation technology. It could also serve as a secondary system that can separate specific tar compounds of interest for further use. Oil agents have been proven to be more efficient absorbents than water, and also have lower impacts on environmental scale as they can be recovered easier than water and can also serve as fuel into gasifiers. Their usage has become more desirable in recent times as more liquids are showing improved efficiencies through experiments. Regeneration systems on an industrial scale are still underdeveloped, with the majority of the existing new technologies to be still in controlled lab scale (Mwandila, 2010).

Various methods of oil recovery systems have been studied over the years, with the majority based on light tars-oil solutions. Lighter tars as phenols are more soluble in water than organic agents and therefore are more difficult to be separated. The majority of these methods are not scaled up yet, as they are not economically feasible due to their high energy consumption. Filho et al. (2010) briefly describes three of the classic methods that have already been investigated yet never applied in industrial scale. In short, these methods are:

- Clay-acid treatment: This method is carried out by using sulfuric acid as a solvent to attract polar compounds. Initially the solution passes through a polymeric filter to attach the carbonic compounds. After filtration, the solution is progressed to a vacuum distillation in order to separate the scrubber agent and at the end is exposed in clay treatment to recover the acid that is used.
- Propane treatment: Propane is used to attract asphalt particles and other insoluble compounds. Subsequently, atmospheric or vacuum distillation with thermal treatment combination is applied to remove heavy PAHs and water.
- Hydrogenation-Distillation: This method can be carried out at atmospheric or vacuum distillation. Hydrogen is used to eliminate sulfur, nitrogen and oxygen compounds from the oil. (Filho, et al., 2010)

In order to reduce the cost of these technologies, other methods were also explored. The majority of the present studies are based on separation technologies with solvents. The studied solvents are used to absorb the impurities from the waste oil, creating a biphasic solution which can then be easily separated. This biphasic solution can also retain the organic liquid that was initially used. The above description is illustrated in figure.13. Two compounds categories have been extensively studied for the Solvent Recovery Process (SRP) ; Deep Eutectic Solvents (DES) and ionic liquids at room temperature (RTIL).
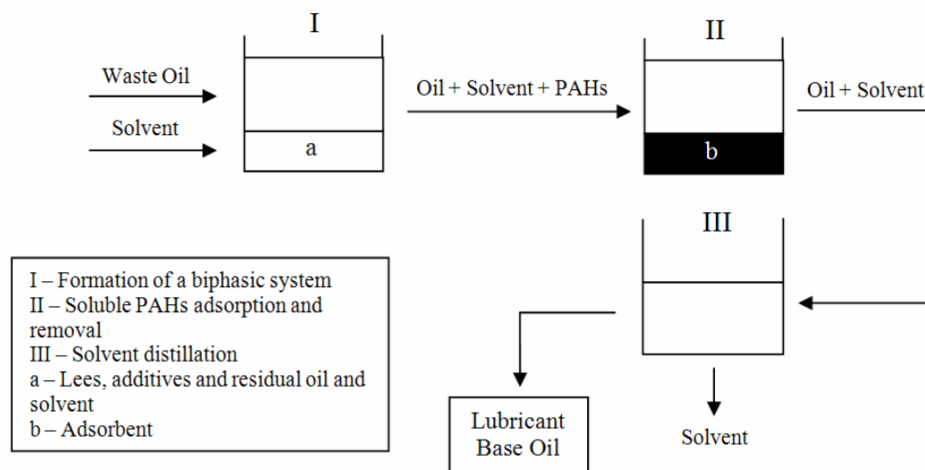
Figure 13 Solvent Recovery Process (Filho, Moura, & Ramos, 2010)

DES are solvent solutions which are mainly created by the combination of two or three compounds. The mixture can be formed by Lewis or Brønsted acids and bases which are sharing hydrogen bonds (e.g. $AlCl_3$ + 1-Ethyl-3-methylimidazolium chloride) (Smith, et al., 2014). DES are commonly used for the separation of phenols from organic solvents. The DES process is as following; Initially, the solvent is being mixed with the waste oil stream in order for a biphasic solution to be formed. After the biphasic solution is being formed, the oil can be recovered as is consisting the one of the two phases of the mixture. The recovered oil can be extracted by distillation. Following that, water is added into the rest of the solution (tars&solvent) in order to create a second two phase system; one phase being the solvent which is soluble in water and the other one the extracted phenols. Finally, water can be separated from the solvent by thermal treating at 333.15K under atmospheric pressure. The application of DES for solvent recovery takes place at 110°C for 30 minutes (Tiantian Jiao, et al., 2014). Some examples of DES solvents include: choline chloride($C_5H_{14}ClNO$), triethylamine hydrochloride($(C_2H_5)_3NHCl$) and ethylamine hydrochloride($C_2H_5NH_2HCl$). DES method has been tested and has successfully been shown to remove phenols and cresols, however, this procedure is producing small amounts of waste water (Pang, et al., 2012). Based on the same principle, RTIL technologies are able to extract phenols as well as aromatic amines. Similar to DES solvents, RTILs have negligible vapor pressure and high thermal stability, which are needed in order to minimize contamination through evaporation and to keep stability in a wide range of temperatures. RTILs are more complicated compounds than DES but they offer higher separation efficiencies. Depending on the organic solvent used, RTILs can be fully or partially miscible with polar liquids (e.g. methanol, acetone etc.) or they create two phase system with oil of low polarity (e.g. hexane, toluene etc.) (Poole & Poole, 2009). RTILs can adjust the selectivity of the extraction by influencing the pH of the solution. Moreover, using ionic liquids gives the operator the potential to extract other compounds than phenols, such as alcohols, carboxylic acids, metal ions, PAHs and sulfur compounds that are usually absorbed by organic liquids. (Egorov, et al., 2008)

Another method for oil separation from tars is employing solid acid particles as catalyst/adsorbents that have the specialty to adsorb aromatic hydrocarbons on their surface. This method is again combined with thermal treatment, as with increase in temperature the rate of absorption is increased but the absorption capacity is decreasing. Examples of materials that can drive this technology are; silica alumina($SiO_2.nAl_2O_3.xH_2O$), NH_4-mordenite (NH_4 (Ca, Na_2, K_2)$Al_2Si10O_24 7H_2O$) and γ-alumina(γ-Al_2O_3). The regeneration of the adsorbent particles can be done by burning the adsorbed compounds or by washing (Wu, et al., 2000).

Furthermore, several new technologies aim for a complete removal of tar compounds from oil scrubbers instead of selective procedures. The simpler procedures use heat alone for separation. Such procedure is "Air stripping" technology which was applied by ECN as part of the OLGA tar removal technology. In this procedure, waste oil is placed in a reactor where a hot air stream (180-220 °C) is passing through the base of the reactor causing recirculation of the liquid and increase of its temperature (figure.14). With this method, tar compounds are being volatized and are escaping from the reactor with the hot air which is then further cooled in order for tars to be collected (Zwart, et al., 2010).
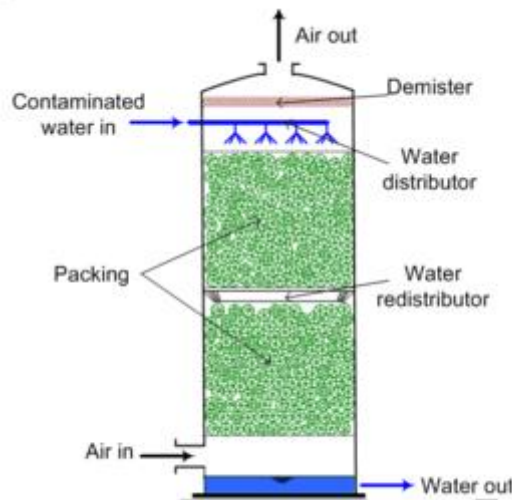
Figure 14 Air Stripping Technology for water treatment

Chevron company has also developed a system with the same skepticism as ECN. The system's waste oil is being pumped through a furnace which is increasing the solution temperature in the pipes. Afterwards, the waste stream enters a distillation unit where the lightest compounds (phenols, cresols) are rising to the top, medium molecular weight compounds are condensed in the middle and heavy tars are lying at the bottom (Chevron Corporation, 2016). Moreover, there is the potential in combining thermal treatment systems with catalytic cracking directly on the waste oil streams in order to convert tars to liquid oil. This method has been tested on a lab-scale by Laksmomo, et al. (2012) and has given encouraging results. The majority of the characteristics of the recovered oil such as; density, LHV and the acidic value of the recover oil flow rate after the conversion, are close to a diesel oil and are under the European and American standards. Only viscosity is rising slightly above the permissible limits for some catalysts. This method is at the moment driven in batch reactors where the catalyst is preferably in direct contact with the

waste oil (placed free into the reactor). In the batch reactor an impeller is mixing the liquid and at the same time an external heater is raising the temperature of the liquid, causing the solution to evaporate. After the mixture has evaporated, is being collected in a separate vessel and allowed to cool at room temperature. Consequently, the oil is ready to be re-used. Laksmono, et al., (2012) have tested three different catalysts (ZSM-5, MgO and Al_2O_3,) for their performance. It was shown that a combination of heat and a zeolite catalyst gave the best results with 73% recovery in 10mins at 350ºC. The rest of the waste oil, with the unconverted tars and the catalyst were left at the bottom of the reactor. (Laksmono, et al., 2012)

Finally, the only commercial method used for oil-tars extraction is the centrifugation method. This method is carried out using a continuous stirred reactor (CSTR) with a helical impeller at the center where it is rotating and heating the incoming fluid in order to separate the tars. The temperature in this method does not exceed 90ºC and the residence time is around 10 minutes. From the centrifugation and heating the liquid in the reactor creates three zones. The upper zone is the recovered phase of oil which is collected by an exit at the top of the reactor. The intermediate is the un-recovered oil and at the bottom lies the separated tars that are being extracted by second exit at the bottom of the reactor. This method is highly dependent on the kind of oil scrubber that is being used. Organic liquids with higher viscosities show decreased efficiencies. On the other hand, liquids with low viscosities like diesel and RME have a higher separation efficiency (Malek, et al., 2015). Pall's Corporation Centrifugal Discharge Filter System, seen in the figure.15, is commercially available and often uses filters as additional holders of tars.
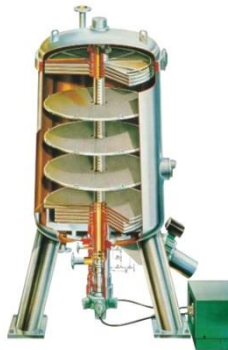
Figure 15Pall's Corporation Centrifugal Discharge Filter System (Pall Corpoaration, 2013)

3.1. Potential Usage of Tar Compounds

As previously mentioned, an innovative oil regeneration process would not only serve as a more sustainable technology but would also increase the economic benefits of the system as a whole. Tar compounds are utilized across a wide variety of industries and have many applications. For example, the majority of tar compounds are used in the production of plastics, bitumen and fuels. More specifically, the compound naphthalene is used in the production of mothballs, phenols for the production of lubricants and toluene for the production of paints and glues etc. The majority of these substances are however harmful to human health so EU introduced a series of regulations in order to monitor the usage and concentrations of these compounds in foods and other products. A brief description of these regulations can be found in the tables.A.2 & A.3 in Appendix A. The oil recovery systems outlined in this chapter focus on the separation of certain

organic oil solvents from tars, instead of visioning of all the compounds in their pure form. Individual PAHs are very difficult to separate when they exist in the same solution due to the high degree of overlap in their physical properties such as vapor pressure, boiling point, solubility, molecular weight etc. (Manzano, et al., 2012). The table A.4 in Appendix A. provides a review of the prices of a selection of the tar compounds that are studied in this project. Tar concentrations from the oil's waste streams of the two tested models, with data from the TUD and Synvalor gasifiers, are also provided. The prices have been taken from the SIGMA-ALDRICH company as this is the sole company that provides prices for all the outlined products. SIGMA-ALDRICH is responsible for selling high purity solutions of these compounds for mainly experimental purposes (SIGMA-ALDRICH, 2016). The actual market value of these compounds is less than the prices that are presented, however, in order to check that market, you are required to be an authorized organization registered in the stock market.

This subchapter outlines a brief economic analysis based on the flows from TU Delft's gasifier and the Guessing plant. For reasons of simplification, it will be assumed 20% efficiency of the secondary system to separate all the tar compounds in their pure form. Last two columns of the table A.4 (Appendix A) represent the profits obtained if the above assumption is taken into account. As seen, the profits are $0.35 €/m^3_{syngasin}$ and $12.23 €/m^3_{syngasin}$ from TUD and Guessing tar recovery respectively. The elevated profits from Guessing gasifier simulation are related to the tar compound of Benz[a]anthrene which is only exists in Guessing's syngas flow. According to the Sigma-Aldrich website is very expensive compared to other substances. The profits are presented in the form of currency per syngas cubic meter produced by the gasifier.

The profitable flows may allow for a more economical system, however, the separation and the production of the tar compounds in their pure form requires the establishment of more efficient hydrocarbon separation technologies. To establish the economic background of the system and to determine if the production of by-products will be beneficial, a complete economic analysis must be carried out. This will outline if the purchase of equipment and its maintenance (initial cost) will contribute to positively to the overall economic prospective of the system.

4. Methodology of Project Models

The main aim of this research is to compare a dry with a wet method for the removal of tars from syngas as well as recommending new configurations and operation conditions which will try to optimize the existing cleaning technology both economically and energetically. Chapter 2 provided detailed descriptions of both technologies. The function of these extensive descriptions is to provide clarity in the choice between the two systems, which will be presented in the following chapters. The comparison between the two methods will be based on simulations by the Advanced System for Process Engineering (ASPEN) PLUS programming performance analysis. AspenPlus is a favorable tool for modeling numerous processes, such as gas cleaning systems, and is accurate in predicting the upcoming results. The experimental data tested in the models were derived from the Technological University of Delft (TUD) gasifier as well as from the pilot plants of Synvalor and Guessing which will be described in detail in the following chapters. The data from TUD and Synvalor were provided by the project supervisor, while the data for the Guessing gasifier were taken from the literature. A model for a tar cleaning system that fits well with experimental data will be useful in order to evaluate trends of tar conversion, and scaling up to an industrial scale system. Moreover, this model would be beneficial as it could simulate system's efficiency and behavior under different operating conditions in a continuous process.

Several modelling studies are neglecting tars in biomass gasification or syngas cleaning models due to their low concentration (Hannula & Kurkela, 2011). As outlined in this research neglecting tars in biomass gasification or syngas cleaning may be a crucial mistake, leading to inaccurate results and serious problems. The designs of models presented in this project were based on the obtained data from TUD's gasifier. Later, they were tested with data from Synvalor and Guessing gasifiers in order to create a comparison with pilot cleaning systems that are already in operation. Guessing gasifier uses a catalytic reactor for eliminating tars, therefore, it was chosen to create a comparison of the designed wet model of this project with a tested dry technology. In the same manner Synvalor's gasifier data were tested on the models, as Synvalor cleaning technology is based on scrubbers filled with biodiesel and water and thus it could provide a comparison between the models predictions and experimental results.

4.1. Targets and Assumptions of Project Models

As mentioned previously, "OLGA" technology from ECN is presented as the most promising way to treat syngas. "OLGA" offers the highest cleaning efficiency and the highest conversion rates as the mixture of the absorbed tars and the organic scrubber agent is being recirculated back to the gasifier for further conversion of the heavy hydrocarbons into useful lighter hydrocarbon products. The target of this study is to suggest and create two models which are as efficient and sustainable competitive as the OLGA project. Both models have to meet certain requirements in order to be reflected as pioneer and well established. These requirements are as follows:
- Minimize (or eradicate) the production of waste-water down-streams
- Reduce the amount of power needed for cleaning

- Decrease the cost of the process by minimizing the energy consumption, or by producing useful by-products.

In order to simulate both models, two different approaches were followed. For the wet model - as the model is based on the physical properties of the compounds - the precise concentrations of all the different tar compounds were taken into account. However, in the dry model, only benzene, naphthalene and toluene were modeled due to the high number of different reactions that occur on the catalyst and the limited published information about the individual kinetics of these reactions. The overall inlet tar concentration remained constant, as in the wet model, by increasing the flow rate of the three hydrocarbons.

For both models the following assumptions were made:
- Models are operating at steady state;
- The conversion of tar concentration from $\frac{g}{m^3}$ to $\frac{mg}{Nm^3}$ was based on the ideal's gas law;
- Pressure drops at the components of the system were taken from literature or assumed to be zero;
- The reaction rates expressions for the tar cracking reactions were based on the power law and   Langmuir – Hinshelwood – Hougen –Watson (LHHW) models;
- The Arrhenius coefficients, as well as the reaction order and the kinetics of the reactions, were taken from the literature.

According to AspenPlus Method Assistant tool; as both models outline gas processing, the best fitting method for the simulations is the use of a cubic equation of state-based property method such as Peng-Robinson (PR), or Soave-Redlich-Kwong (SRK) equations of state (EOS). Conversely, for these simulations the Redlich-Kwong-Soave (RK-Soave) EOS was chosen as, according to Twu et al. (1998), this is slightly better as a tool for gas condensation (Twu, et al., 1998). A description of the formulas of the above mentioned assumptions and the EOS is presented in the following table.6.

Table 6 Modelling formulas that are used by AspenPlus

Law's	Formulas	Definitions
Ideal's Gas Law	$P * V = n * R * T$ (Eq.4.1)	. P: Pressure (Pa) . V: Volume (m³) . n: number of moles (mol) . T: Temperature (K) . R: Gas constant (KJ mo⁻¹ K⁻¹)
Power Law	$-r_a = k * C_A^a * C_B^b$ (Eq.4.2)	. C_A: Concentration of compound A (g/m³) . C_B: Concentration of compound B (g/m³) . a: order in A . b: order in B . r_a: Reaction rate
Arrhenius Equation	$k = A * e^{\frac{E_a}{R*T}}$ (Eq.4.3)	. k: specific reaction rate . A: pre-exponential factor (s⁻¹) . Ea: Activation Energy (KJ mol⁻¹)
RK-SOAVE EOS	$P = \dfrac{RT}{V_m - b} - \dfrac{a}{\sqrt{T}V_m(V_m + b)}$ (Eq.4.4) $a = \dfrac{0.42748R^2T_C^{2.5}}{P_c}$ (Eq.4.5) $b = \dfrac{0.08664RT_c}{P_c}$ (Eq.4.6)	. V_m: molar volume (m³/mol) $(V_m = \dfrac{V}{n})$. P_c: pressure at the critical point (Pa) . T_c: Temperature at the critical point (K)

The main aim of this study was to deliver two models that separate or convert tars from syngas in order to reach the boundary limits for methanol synthesis. The analysis and the comparison of which method is better was based on the energy efficiency of the system.

5. Wet Method Model & Simulation

In order to build an effective wet model for a certain gas flow, various configurations were tested. These configurations were used to check the altered responses of the system under different conditions. The wet method model created in this project targeted the provision of a product of high purity, as well as the design of an effective recovery system for the absorbing agent used to absorb the tars. Biodiesel oil was chosen as scrubber agent as it reduces the usage of clean water, minimize the waste water down-streams and can be recovered more easily than water itself. Additionally, as was mentioned in Chapter 2.2.2 biodiesel is more effective for absorbing tar compounds than water.

5.1. AspenPlus Validation

Prior to the building of these models, there was the need to validate the selected compounds for every model. Furthermore, there was a need to ensure that AspenPlus is running smoothly and the upcoming results are logical and accurate. Results from two scientific papers, where various liquids were tested for tar absorption, were used, in order to compare the correspondences of the modelling results. Methyl-palmitate oil with chemical formula $C_{17}H_{34}O_2$ and boiling point 417°C was used as the scrubber absorber substance in the models. Methyl-palmitate was chosen because of its similarities with biodiesel and its existence in an excessive fraction in most of biodiesel products (Orificia, et al., 2013). The use of an organic liquid as an aqueous scrubber is very effective at removing tar compounds, ammonia and acid impurities. Additionally, a liquid of a high boiling point is enhancing the solubility of tars due to the low vapor pressure of the liquid. (Zwart, 2009)

The first experimental results used for the validation of the model were by Paethanom et al. (2012). Paethanom et al. (2012) described an experiment which was built to measure absorption and adsorption of tars through oil liquids and rice husk char, respectively. The syngas flow rate consisted of 93.7 g_{tar}/m^3 of tars, from a total syngas flow of 1,5 l/min and Nitrogen as a gas carrier. The main gaseous species such as H_2, CO, CO_2 etc. as well as the individuial tar species concentrations were not given by the authors, so in order to approach the experiment the following assumptions were taken into account:
- The main compounds concentrations were assumed to be similar to those produed from TU Delft's gasifier without any water vapor in the syngas.
- The individual tar species concentrations were given in the second stage of the study where the adsorption of tars on rice husk was measured. Graphs were produced to show the inlet and outlet concentration of tars at the reformer. The given inlet concentration was not illustrating the initial concentration of tars in the system but rather the concentration after absorption through an oil scrubber. In order to create a more realistic model based on the experiment, the particular tar concentrations at the reformer's inlet has been increased in order to meet the overall tar concentration before the scrubber. By using the overall conversion rate of tars through the absorber, the given tar concentrations at the reformer's inlet were increased in order to meet

the overall concentration of tars at the systems inlet. For example, the measured overall tar concentration at the reformer's inlet was calculated as 9.772 g_{tar}/m^3 by adding all individual concentrations of tars from the given graphs. According to the article Paethanom et al. (2012) the initial tar concetration in sygas was 93.7 g_{tar}/m^3. Based on this data, tar conversion at the oil absorber was calculated at 89.5%. By dividing each individual tar concentration (provided for the inlet of the reformer) by the tar conversion rate a relatively strong result is produced regarding the initial tar concentration of each compound.

The overall concentrations as well as the operation conditions and flow rates are presented under Appendix B in table B.1.The absorption experiment described by Paethanom et al. (2012) used an oil containing static vessel, where syngas was allowed to pass through for a given amount of time. 500ml of oil were used for each experiment, with two different oils tested; vegetable oil and waste cooking oil (their density and viscosities were provided). The sampling time for each simulation was 48 minutes. As AspenPlus modelling is based on steady state operations, to model a dynamic operation an approach called "snaphtots" of steady state was established. According to Gruber, (2004), steady state images of time can create a dynamic simulation by placing them one after the other. This occurres by multiplying the gas flow, or by placing absorbers in a row letting the scrubber liquid to pass from one scrubber to the other by using a constant oil flow, which is equal to the volume of the oil that is used int the container. The first approach is considered to be easier, as with a multiplication box in AspenPlus and a sensitivity analysis tool, the software can vary the inlet syngas fowrate and use the results for each varience. By multiplying syngas inflow by 2,3,4 etc. is corresponding for steady state snapshots in time. For instance, by multiplying the flow by 2, it illustrates the conditions of the gas and the oil at the second minute of the simulation.

Figure.16 illustrates the AspenPlus flow sheet used to simulate the experimental conditions. As seen, a RadFrac column is used with only two stages and is chosen to operate as an absorber column. The multiplication box B1 is set to 48 in order to obtain the results for the 48th minute as the experiment. The two different oil liquids were introduced to the program as pseudo-compounds. Methyl-Palmitate oil was chosen as the absorbing liquid while its properties such as density, viscosity and molecular weight were altered according to the properties of the oils used in the article (vegetable oil and waste cooking oil).
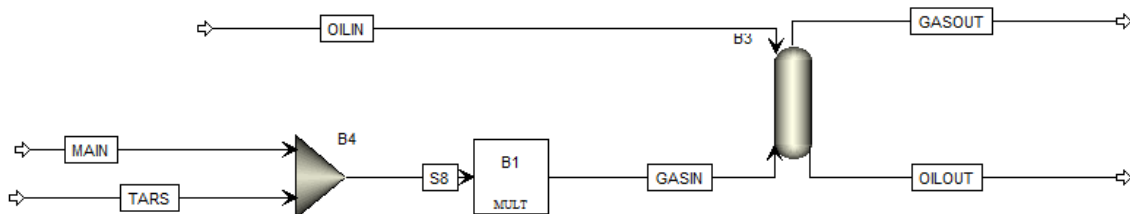
Figure 16 AspenPlus configuration for the validation models

The bar charts displayed in figure.17 illustrate the experimental results by Paethanom et al. (2012) (A) and AspenPlus simulation results (B). As seen in the charts, simulation results for 48 minutes sampling time match the experimental ones. The two vertical charts illustrate the tar concentration after the scrubber while the horizontal graphs represent the efficiency of gravimetric tar removal or tar conversion rate. Experimental results showed 63.6% and 56.4% gravimetric tar removal by the vegetable oil and the waste cooking oil, respectively, in comparison with 61.2% and 56.5% that were obtained by the model. Simulation results include an additional bar (yellow bar) representing the tar removal efficiency by using biodiesel in the form of pure methyl-palmitate oil. This was done in order not only to validate the simulation results, but to also indicate the greater efficiencies that can be obtained by using biodiesel oil. The tested methyl-palmitate oil achieved gravimetric tar removal close to 90% showing the greater ability to absorb tars compared to the other tested oils. Results obtained by AspenPlus were similar to the results obtained from the real experiment signifying that AspenPlus is a reliable and robust software for simulating tar absorption.
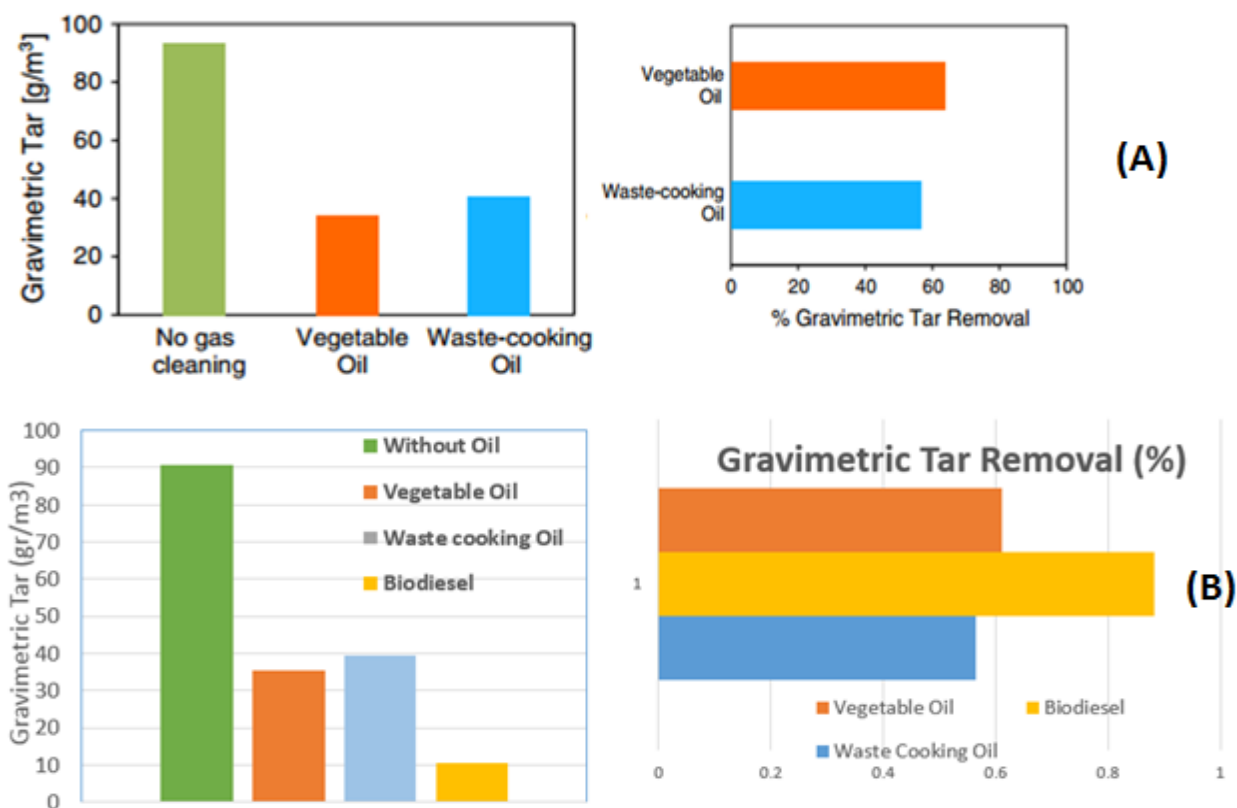
Figure 17 Results from (A) Paethanom et al. (2012) (B) AspenPlus model

In order to further check the validity of the model, a second set of experimental data, obtained by Phuphuakrat et al. (2010), were tested. In this study four different oils (diesel, biodiesel, engine oil and vegetable oil) and water were tested for their tar absorption efficiency. For validation purposes only biodiesel and water were modeled in order to check the simulation results as well as to check the effects of using Methyl-Palmitate oil instead of an actual biodiesel liquid.The

methodology used by the study of Phuphuakrat et al. (2010) was similar with the previous study, with the main difference being that there was on-line monitoring for the change of tar concentration in the outflow gas. The individual tar species concentrations were given but they were varying with time as excpected. For the model purposes each tar compound concentration was assumed stable as a mean value of the measured concentrations in the article by Phuphuakrat et al. (2010). Table.B.2 in appendix B shows a review of the operating conditions as well as the concnetrations of both tars and main gaseous species. The layout that it was used for this model is the same as in figure.16. The only difference was that in this case a sensitivity analysis was used in order to take the results for every minute of the gas inside the liquid scrubber.

Figures 18 and 19 illustrate simulation results from the experimental data and the actual experimental data, respectively. As seen in the six tar graphs, simulation results are in agreement with the results of the experiment itself. From these tar species, benzene is the only one with a significant change over the experimental time (both in simulations and experiments). The increase in concentration in the outlet can be explained due to the high concentration of benzene and toluene at the inlet of the vessel which are higher comparison to other tar species. Therefore, the two species are absorbed by the biodiesel at a faster rate than other tars. The elevated difference in concentration leads to a greater diffusive flux of those elements to the biodiesel. The diffusive flux is further decreased due to the increased concentration of the same compounds in the biodiesel causing the slight increase of benzene and toluene concentration at the absorber's outlet. The experimental concentrations of benzene and toluene at the absorber vessel outlet were approximately 4.9 and 0.1 g/m^3, respectively. From the simulated model, 5.1 and 0.08 g/m^3 were obtained for benzene and toluene correspondingly. The concentration of the additional tar species was constantly close to zero at the outlet of the scrubber. The accuracy of the model results with the experimental results allow for the use of Methyl-Palmitate oil as a substitute for actual biodiesel.

Figure 18 AspenPlus model results using Phuphuakrat et al. (2010) article's data with biodiesel as absorption agent
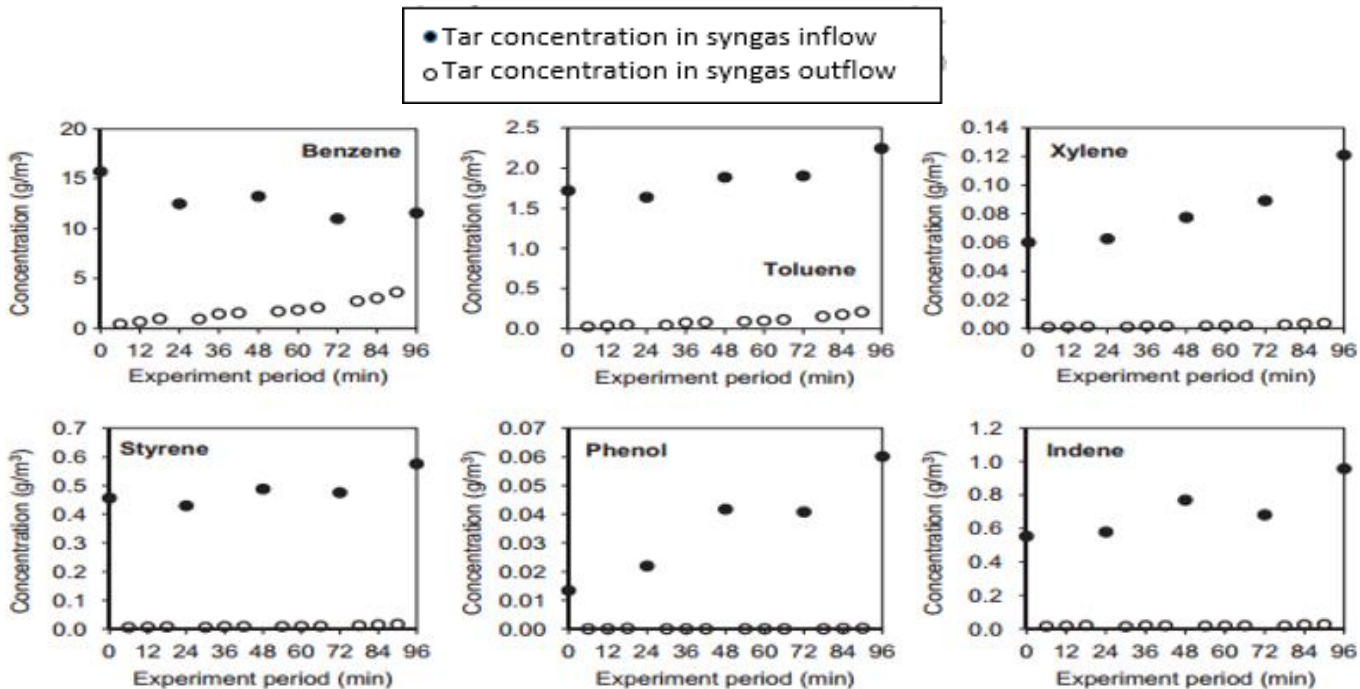
Figure 19 Phuphuakrat et al. (2010) results with biodiesel as absorption agent

An additional simulation with water as the liquid scrubber agent was made in order for a better clarity and better comparison of the model's results with the experimental. Figures 20 and 21 illustrate the result after water was used in the model and at the experiment respectively. Again as in the biodiesel case it can be seen with clarity that AspenPlus is approaching the experimental results very closely. From the results it can be seen that, with an exception of phenolic compounds, other tar species are not soluble in water. The differences in tar concentration from the inlet to the outlet are very small which was expected as water can only absorb polar compounds. According to the author, the small differences at the outlet of the absorber can be can be attributed to condensation. In the case of phenol, as seen both by the model and by the experimental data, it is fully dissolved in water only up to the end when the concentration of phenols at the exit of the treated gas is slightly increasing. In both experimental and simulation results the concertation of phenols is seen to have increased at the exit of the vessel during the final moments of the experiment at less than $0.01g/m^3$. The slight increase of phenols at the exit of the system can be explained due to the high solubility of phenols into the water. As in the experiment described above the high solubility of phenols leads to the rapid increase in the water's concentration of phenols. Therefore, with the increase in the concentration of phenols in the water during the final moments of the simulation, the mass transfer is being decreased mostly due to the smaller concentration difference and thus the slight increase of phenols concentration into the water is noticed.

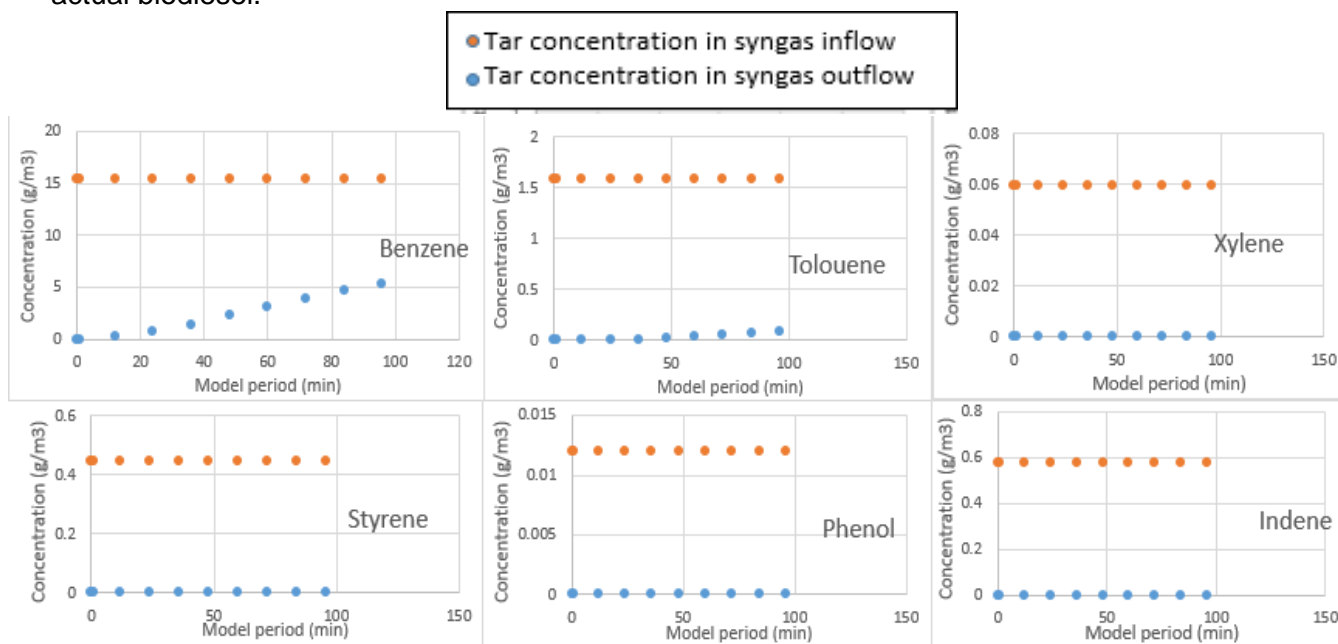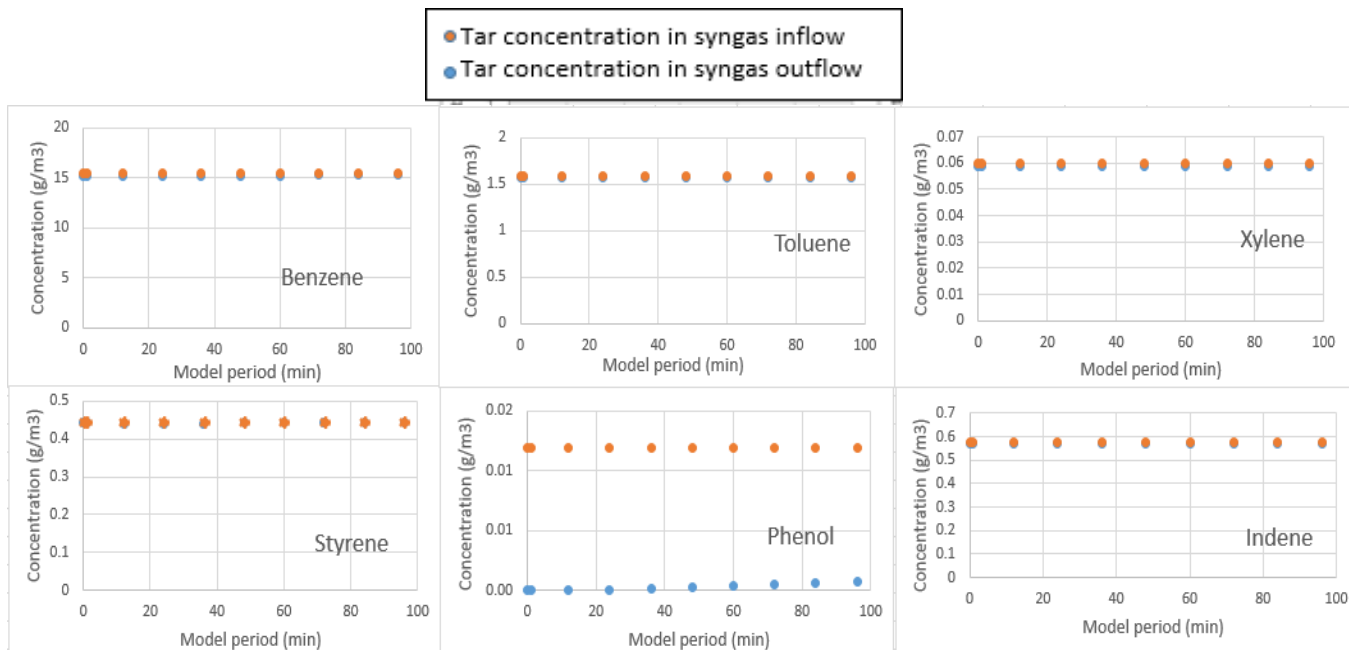*Figure 20 AspenPlus® results using Phuphuakrat et al. (2010) article's data with water as absorption agent*
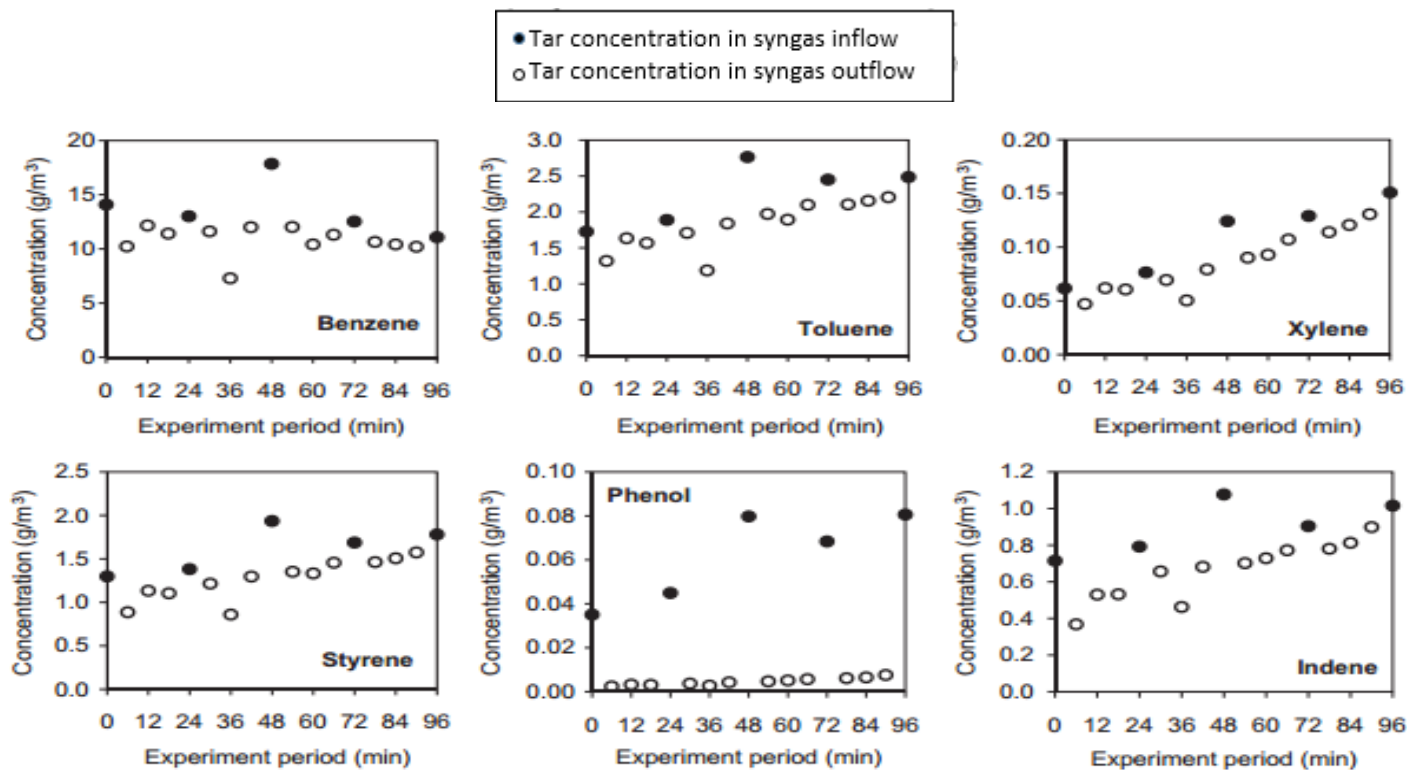
Figure 21 Phuphuakrat et al. (2010) results with water as absorption agent

From the above simulations two things could be concluded. Firstly, AspenPlus is a powerful tool to be used for tar absorption tests and secondly, methyl-palmitate oil can be used as an accurate substitute for biodiesel.

5.2. Wet Model's Design Process and Results

The design of the wet model for syngas cleaning was based on data obtained from TUD gasifier. The inlet data was taken from TUD's circulating fluidized bed (CFB) gasifier with air fuel ratio (AFR) λ=0.31Kg$_{air}$/Kg$_{fuel}$ and steam to biomass ratio (SBR) SBR=1 as mentioned. Wood pellets were used as biomass feedstock and M85 as fluidization medium. The dry wood's composition and the produced raw gas composition as well as tar's composition are presented in the Appendix B in tables B.3, B.4 and B.5, respectively. The syngas downstream flow was in average 30.2m³/h and, for the purpose of the model, was assumed to be constant. The temperature and the pressure of the produced raw gas were assumed the same inside and at the exit of the gasifier at 845°C and 1.25 bar, respectively. As seen from the data and table.1 the composition of raw syngas is unsuitable for FT, IC or methanol synthesis. Moreover, since steam is used as the gasification agent, water in the syngas must be separated. Hence a proper gas cleaning unit should be designed. For this case study, syngas composition with tars under the limits for methanol synthesis (<0.1mg/Nm³) was considered acceptable. Lastly, the main target was to eliminate tar contaminants from the raw gas. The evaluation of the system's efficiency was based on the equation below:

$$n_{cln} = 1 - \frac{C_{tarsout}}{C_{tarsin}} \qquad \text{(Eq.5.1)}$$

Where n_{cln} is the cleaning efficiency (%)/conversion rate or removal efficiency, $C_{tarsout}$ is the tars concentration at the outlet of the system and C_{tarsin} the concentration of tars at the inlet of the system.

5.2.1. Design and Simulations

Initially, a test to estimate the dew point of tars contaminants in the particular flow (TUD gasifier data) was made from the ECN webpage, via their online tool (ECN-E&S, 2016). The test was established in order to have an image of tars characteristics in the certain gas flow as well as to set a system schematic of the machinery topology as the temperature effect is substantial in the system. Tar concentrations were converted to normal units of volume in order to be placed on the online tool. Table B.5 in Appendix B2. illustrate the concentrations of the individual tar species for the test flow outlined in this project as they were inputted into the online tool in normal volume units. The conversion in normal volume was based in the ideal gas law:

$$V_N = V * \left(\frac{P_a}{P_{ref}}\right) * \left(\frac{T_{ref}}{T_a}\right) \qquad \text{(Eq.5.2)}$$

Where P_a, T_a are the pressure and the temperature of the sample when was taken and T_{ref} (273.15K) and P_{ref} (1atm) the reference pressure and temperature.

The online tool revealed a dew point of 86.4°C for the given tar composition. The low dew point of the tars provides the system with the opportunity to remove the majority of the water-vapor within the raw gas flow at an early stage of the system. This is done in order to ensure the removed water- vapor is in high purity. This can be done by cooling the gas at a temperature close to 90°C and, at the same time, passing it through a gas-liquid separator such as scrubber as discussed under sub-chapter 2.2.2.1. The condensed water will be removed from the syngas avoiding further procedures of cleaning or any water recovery process. Later in the process, the free water or low water content gas will pass through the oil scrubber with the biodiesel as agent, for the reasons that were discussed above. The oil will utilize the gas flow by absorbing the tars at low temperatures without consequence of oil evaporation. The absorbing towers will be operating with constant oil flow. The used oil downstream will be recovered by a secondary system as was mentioned in Chapter 3. By using an oil recovery system, the system will attain the recirculation of the majority of the used oil minimizing the operation cost of using new oil. In addition, tars could be produced as a by-product offering the possibility of valorization into chemicals in order to improve the overall economics of gas cleaning. However, the target of this case study, was to treat a variety of different syngas streams, therefore a standard tar cleaning configuration was established without taking into account the tar dew point. This configuration was built with an optimization program to recover the operating conditions that are needed to clean to the desired target limit all streams with the least economic and energetic consumption.

Consequently, a standard configuration with minor operation changes for the wet model was modeled in AspenPlus. Figure.22 illustrates all the components and their position in the designed system. To create the gasifier's downstream flow two streams were combined at the beginning. The flow with name "MAIN" refers to the non-condensable gaseous species in the syngas (such as H_2, CO, CO_2, etc.) and the secondary flow stream "TARS" which includes the contaminants (tars in this occasion). Combining the two streams with a "MIXER" tool was carried out as it makes it easier for the user to introduce the concentrations for a given flow.
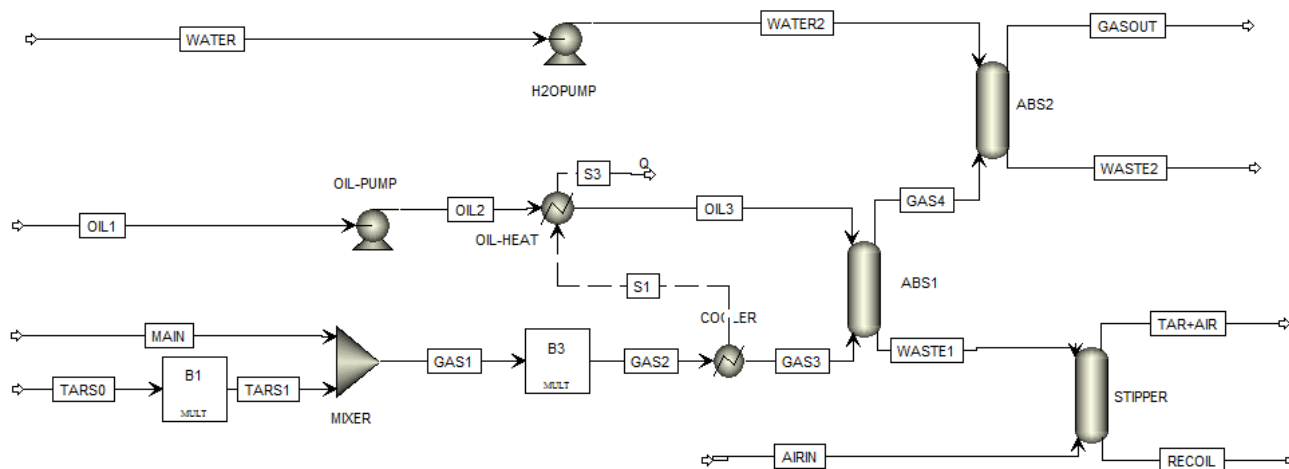
Figure 22 AspenPlus Wet Model Configuration

As seen in Figure.23 the tested syngas flow is first being cooled at the COOLER. The dashed line that connects the COOLER with the OIL-HEAT (Heater) was used for the program to use the amount of heat extracted from the syngas, to heat the biodiesel flow. Later, the cooled syngas flow passes through an oil- absorber (ABS1). There the majority of tars are being absorbed by the oil, utilizing the syngas flow. Finally, a water-absorber (ABS2) is being used to absorb remain light tars and cool the syngas temperature around 25°C.

Separately from the main cleaning system, an oil regeneration model was introduced. In the bottom right of figure 22, a RadFrac column with two stages illustrates the air-stripper technology that was introduced by ECN (described in Chapter 3). Since AspenPlus works under steady state conditions, the results could not be compared with a dynamic performance where the regenerated oil is mixed with new oil in order to be used for tar absorbing.

The manipulated conditions that can be controlled in this system are;
- Gas Temperature, both before and after the absorption tower
- Oil Pressure and Temperature before the absorber
- "Clean" syngas temperature at the outlet of the system
- Air inlet temperature

The main difference in the design of this model from the system described in Chapter 5.1. is that the oil agent does not stay in a vessel but is recirculating or renewed by using a secondary oil recovery system. Consequently, the oil flow in the absorber is constantly new or recovered oil liquid. The second water absorber used is mainly for cooling of the syngas flow, and not for absorption; however, is expected to absorb some tar species. A brief explanation and description of each module operation are provided in table.C.1 in Appendix C. The water and the oil were initially assumed to be both at room temperature and atmospheric pressure.

In the first phase of the design the number of stages of the oil absorber needed to be estimated, as with a higher number of stages the residence time of oil and gas in the absorber is greater. This means longer time for the oil to be kept in contact with the gas molecules and hence the higher absorbance of gaseous species until it reaches to its saturation point. A RadFrac column was chosen from AspenPlus modules to model the absorption column. RadFrac was chosen as it is a Rate-Based model that can perform calculations in non-equilibrium conditions, and simulate real packed columns instead of idealized such as Flash separators modules. RadFrac columns treats absorption as a mass and heat based transfer process (Witzøe, 2015). The degree of absorption is highly affected by several parameters and it can be determined by using the particulate column.

The use of reboiler or a condenser, tray sizing and rating and packing sizing, type and rating are some of the parameters that affect absorption efficiency of the column. In this project none of the above parameters were studied. The project emphasized the number of stages of the RadFrac column and how these effect the tar concentration. The rest of the columns parameters remain the same as they are provided by the system. According to AspenPlus, the columns diameter was 0.3048m and the height of a single stage 0.6069m. RadFrac stages can be represented as layers inside the column where the liquid and the gas pass through in order to reach the exit of the

absorber. On the other hand, the water absorber was designed with only two stages as it was designed to operate as a simple scrubber. The reason for testing the absorber stages is because it is decisive for the economical part of the system. To decide the optimum number of stages, a secondary system was designed. The method used to obtain the results was trial and error.

The system in figure 23 it was used to estimate the optimum number of absorber stages. In order to do so two targets had to be fulfilled;

- Tar concentration at the outlet of the absorber to be less or equal to 0.1 mg/Nm^3
- Minimize the initial and operation cost of the absorber.

Initially, syngas is cooled to 90ºC in order to condense the majority of the water vapor. Later a separator module is used to separate the condensed liquid from the stream. After, the separation of the liquefied vapor from the system, syngas is being reheated at 110ºC as well as the biodiesel flow. The purpose of heating the two streams at 110 ºC, was because in the primary wet model the syngas outlet from the oil absorber had to be at a temperature higher that the water condensation temperature in order to avoid its condensation in the oil absorber.
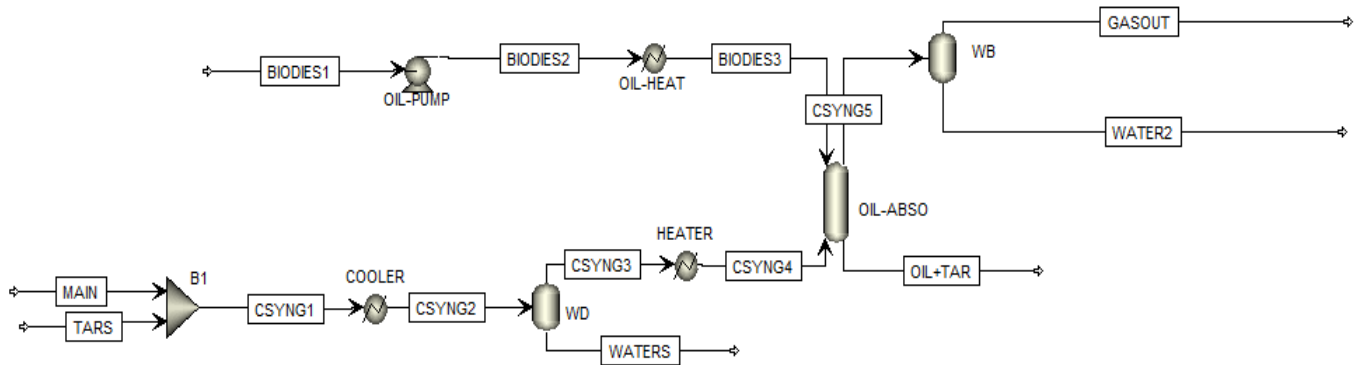
Figure 23 AspenPlus Model for Absorber design

For the economical part, the economic model of "Net Present Value" was used (Zivot, 2010). The specific economic model can be described by the equation.5.3.

$$NPV = -I_o - \frac{C_1}{(1+r)^n} - A_1\left[\frac{1}{r-g_1}\left(1-\left(\frac{1+g_1}{1+r}\right)^n\right)\right]*\frac{1}{(1+r)^n} - A_2\left[\frac{1}{r-g_2}\left(1-\left(\frac{1+g_2}{1+r}\right)^n\right)\right]*\frac{1}{(1+r)^n} + \frac{A_3((1+r)^n-1)}{r*(1+r)^n}$$

(Eq.5.3)

Where; NPV: Net Present Value, Io: Initial Investment (absorber cost), A1: fuel (biodiesel) price, C1: First maintenance, n: number of operation years, A2: maintenance price per year, A3: profit (syngas value), g1: fuel inflationist, g2: maintenance inflationist and r: interest rate. The absorber tower cost was assumed to be 2834$+1063$/number of stages according to (Anon., 2014), maintenance costs were neglected, fuel price was assumed at 729.044$/m^3 by (Lamers, 2011), years of operation were assumed 20 and the average profits from the produced syngas are assumed to be 550$/m^3 according to (Boerrigter, 2006). The interest rate was taken from the European Central Bank for corporations at 2.53% (EUROSYTEM, 2016) and the inflation rate for

biodiesel was assumed according to (DIGITAR.NET, 2012) at 9.09%. The above prices may not be the ideal indicators but they are very close to reality, and so they serve to approach the optimum selection. The highest NPV in this case will give the best possible choice for the absorber stages that have to be selected.

Based on the dew point that was calculated on ECN website, an initial cooler was used to cool the gas close to 90°C. The purpose of the initial cooling was to extract the majority of the water vapor from the syngas stream without condensation of the tar species. Several simulations were run for absorber stages between 4 and 100, with the constrain of syngas outflow being within the limits for methanol synthesis. The two graphs below were obtained from the above simulations.
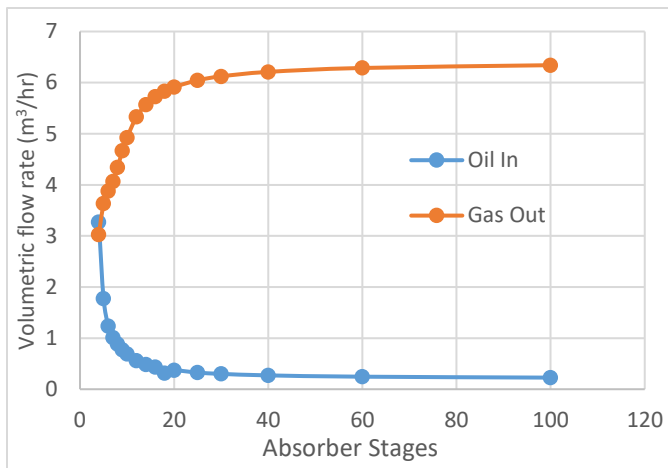
Figure 24 Flow changes with different absorber stages
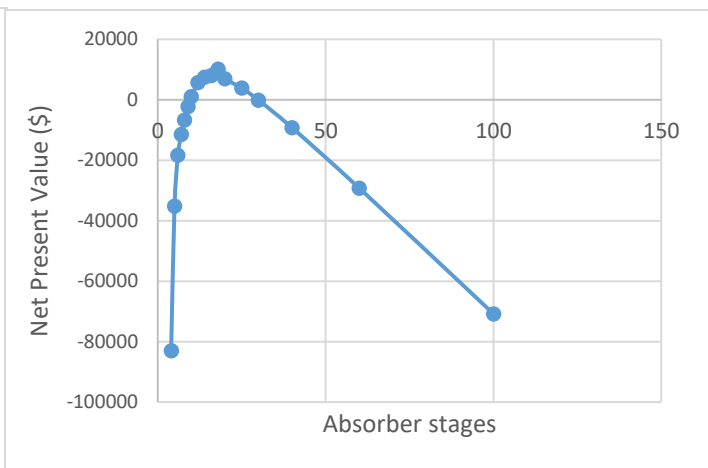
Figure 25 NPV with different absorber stages

As seen in figure.24, with the increasing number of stages the required oil volumetric flow is decreasing up to a point around 30 stages where is reaching a constant value. This is due to the time that is needed for the oil to absorb the tar species. Less stages are corresponding to a decreased volume of the absorber and therefore, more oil is needed to be provided in order to absorb the same amount of tars. However, due to mainly concentration's differences (Fick's law) other species such as H_2 have also been absorbed by the oil. For larger number of absorber stages less oil is needed due to the increased time the oil is in contact with the gas flow. In this occasion the same oil can absorb more tars than before. In the same way other gaseous species in the main gas flow are reaching their saturation point in the oil earlier than before so a higher volumetric flow of gas outlet is being observed. The increased gas outflow and the decreased oil inflow are decisive for the NPV model(figure.25) as they represent the profits and the costs of the system, respectively.

The graph in figure.25 shows the NPV of the system with the increasing number of stages. With the increase number of stages, a bell shape graph is obtained which means that for very low or very high number of stages the system will be economically infeasible. The reason of this shape occurs for two reasons:

- First, for low number of stages. greater volumes of biodiesel are needed for the system to fulfill the requirements, leading to an increase in the operational cost of the system;
- and for larger amount of stages the initial cost is increased in terms that the system cannot be repaid by itself.

For these reasons, the number of stages for the designed system was chosen to be equal with 18 as it was shown to give the best NPV and is close to the point where the flows of oil and produced syngas are stabilized.

By using an absorber with 18 stages which approximately translates into 0.3m diameter and 11m height, the system in figure.23 was modeled in order to determine the operation conditions that are needed, to satisfy the targets of the system. An optimization code was used in order for AspenPlus to estimate the optimal operating conditions where the system should work. By using an optimization code, the particular model could be also used to estimate the optimum operating conditions for different syngas streams as the configuration that was chosen was for a general system.

The main target of the optimization code was to minimize the operation costs of the system. The equation was introduced in AspenPlus through FORTAN coding and was a function of five main conditions;

- Cooling Energy at the syngas cooler before the absorber (KW)
- Heat Energy at the oil heater before the absorber (KW)
- The oil flow that is needed to treat the particulate flow (Kg hr^{-1})
- The amount of air that is needed to regenerate the oil (m^3 hr^{-1})
- And the heat that is needed to be added to air (KW)

The FORTAN function was responsible for estimating the above conditions. The above mentioned conditions should be minimized in order to reduce the operation cost of system.

In order for the program to estimate the optimal operation conditions, certain specifications were required. These were as follow:

- Tar concentration at the GASOUT stream to be less or equal to 0.1 mg/Nm^3;
- Syngas temperature at the GAS4 stream to be higher or equal to 110°C
- Syngas temperature at the GASOUT stream to be equal to 25±5 °C so it can be used directly for further processes;
- the mole fraction of Methyl-palmitate Oil in the recovered oil stream to be greater or equal to 0.99

The temperature at the GAS4 stream was chosen to be higher than 110 °C in order to avoid water condensation. According to water's thermodynamic tables at 1.25 bar water condenses at 106 °C (Reynolds, 1979). As it was already mentioned the system is aiming to minimize waste water streams by removing the majority of the water at the water washer (cooler) at the exit of the system. The condensation of water in the oil absorber will also cause a biphasic solution (as water is immiscible with oil). This will lead to the need of further treatment in order to prevent corrosion in the oil recovery machinery as well as extra treatment.

5.2.2. Results and Discussion

Table 7 shows the results of the wet cleaning method simulation for the TUD gasifier outlet syngas stream.

Table 7 Results of the 1st AspenPlus Wet Model Optimization Code with TUD data

Variable	Stream	Result
Manipulated Variables		
Oil Pressure (bar)	Oil 3	1.254
Oil Temperature (°C)	Oil 3	108.34
Syngas Temperature (°C)	Gas 3	110
Oil flow rate (m³/hr)	Oil 1,2&3	0.667
Air Temperature (°C)	AIRIN	180
Air flow rate(m³/hr)	AIRIN	56.585
Ponded Variables		
Syngas Temperature (°C)	Gas 4	110.01
Waste-Oil Temperature (°C)	Waste 1	109.99
Water flow rate (m³/hr)	Water 1,2	0.101
" Clean" Syngas Temperature (°C)	Gas Out	25.75
"Clean" Syngas flow rate (m³/hr)	Gas Out	4.096
Waste Water Temperature (°C)	Waste 2	38.6
" Clean" Syngas Tars concentration (mg/Nm³)	Gas Out	0.099785

As seen all the requirements were satisfied under the given conditions. The net consumed energy by the oil-heater and syngas cooler was estimated at 21.16KW. 3.25KW of heat must be absorbed by the syngas, while 24.53KW of heat must be provided to the oil-heater. Furthermore, according to AspenPlus the operational costs were minimized. A significant difference is noticed from the absorber design simulation at figure.24. For the 18 stages absorber the oil flow needed to treat the specific syngas flow is 0.2 m³/hr higher than the previous. The main reason why this occurring is mainly the presence of water vapor in the syngas flow which makes it more difficult for the oil flow to absorb tars as it is also absorbing a fraction of vapor molecules. In particular, 40%(mass based) of syngas water vapor escapes within the waste water stream. The absorption of water by oil cannot be avoided in this model as the model was designed to treat all the possible syngas flows. However, the elevated temperature decreases the fraction of water absorbed in the biodiesel. The pressure of the oil is similar to the gas pressure as was expected, in order not to have any flooding or turbulence in the absorber. The outlet temperatures of both waste oil and clean syngas are similar as they are reaching a thermal steady state condition at the outlet. The air temperature at the inlet of the air-stripper column was estimated 180 °C which was the lowest possible temperature for the optimization program. That was due to the fact that the program was aiming at minimizing the energy consumption. The air flow was hence increased instead. The simulated oil regeneration system was found to work effectively achieving 99% (molar-based) recovered oil. The overall conversion rate of all the species in model can be seen in the table D.1 in Appendix. D.

Table.8 illustrates the removing efficiencies (molar-based) of the air-stripper for every compound that was absorbed in the oil absorber. As seen, the regeneration system is extremely effective

(close to 100%) for all the syngas non-condensable gaseous compounds (H_2, CO, etc.), as well as removing benzene, toluene and in lower scales ethylbenzene, xylene and Styrene. The result from AspenPlus suggests greater removal efficiencies for lower molecular weight compounds which are more volatile and which can be easier vaporized from the organic liquid. Light and heavy polycyclic aromatic hydrocarbons such as; naphthalene, anthracene, as well as heterocyclic compounds such as phenols are highly soluble in organic liquid and thus showed smaller removal efficiencies form the air-stripper technology.

Table 8 Removal Efficiency of compounds from AspenPlus simulations of the Air-stripper model

Compound	Removal Efficiency (%)	Compound	Removal Efficiency (%)
H_2	0.99	Naphthalene	0.06
CH_4	0.999	Ethylbenzene	0.40
CO	0.99	Xylene	0.37
CO_2	0.99	Acenaphthalene	0.01
N_2	0.99	1-CH_3- Naphthalene	0.027
H_2O	0.99	2-CH_3- Naphthalene	0.026
Benzene	0.87	Acenaphthene	0.0082
Phenol	0.27	Fluorene	0.0041
Toluene	0.63	Phenanthrene	0.001
Styrene	0.34	Anthracene	0.0008
Indene	0.14	Methyl-Palmitate Oil	0.0002

In addition, this model was designed to create sensitivity analysis curves for the operational parameters, to identify how their change effects tar concentration at the outlet. In order to create these curves a single operation condition was varying by keeping the rest stable. The tested conditions were; Biodiesel's flow, pressure and temperature as well as syngas temperature at the inlet of the oil absorber. In each simulation, the stable conditions were set as the optimal conditions (given in the simulation above). The results obtained are shown in figure 26.

These curves illustrate the effect of the main operation conditions on the overall tar concentration in the scrubber's gas outlet in g/m^3. As seen in the graphs, significant effect on the outlet tar concentration is only a function of the oil flow and temperature. Both oil pressure and syngas temperature at the inlet of the absorber are playing minor role at the corresponded outlet. The particulate outcome was expected as the main parameters that effect the absorption coefficient are the amount of oil present to absorb the tar species as well as the temperature of the absorption agent which is the main parameter influencing the viscosity of the oil agent.
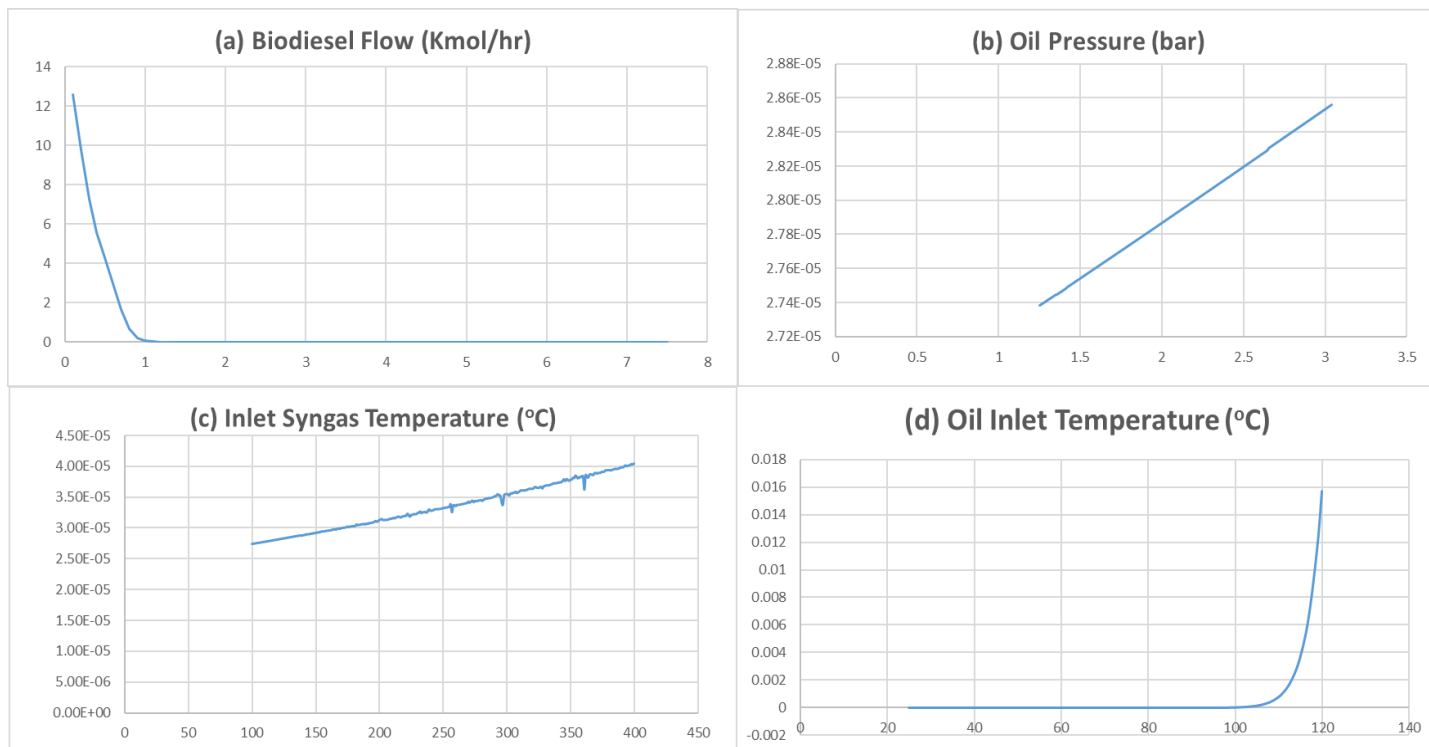
Figure 26 *AspenPlus Wet Models Sensitivity Analysis Results for tar concentration at the water absorber outlet by manipulating (a) Biodiesel Flow rate (b) Biodiesel Pressure (c) Biodiesel Temperature (d) Syngas Temperature at the oil absorber*

As discussed in Chapter 2.2.2 absorption of tars in a liquid agent is strongly connected with the amount of liquid, its' viscosity and the liquid's chemical bonds. The addition of a greater quantity of the liquid agent drives Fick's law, and absorbs more compounds until both liquids reach a steady state condition. In figure a, an exponential decrease of tars with the increasing liquid flow can be seen. As also seen in figure d, with decreasing the oil temperature the liquid is becoming increasingly viscous and is hence more efficient to absorb tars. Tar concentration at the outlet decreases as the temperature of the biodiesel increases.

5.3. Saturation Point of Tars in Oil

For further investigation, AspenPlus Plus was used as a tool to estimate the saturation point of each individual tar compound biodiesel liquid. The flowsheet configuration that was used was the same with the one used for model validations (figure.16 in sub-chapter 5.1) with TUD gasifier data. In this simulation, individual tar concentrations as well as the overall tar concentration was measured for a time regime between 0 and 200 hours. The reason of this simulation was to estimate the maximum fraction of tars that could be absorbed in biodiesel from the given syngas flow. The oil flow for this simulation was set at 10 l/hr at the same pressure and temperature as the syngas inflow in the absorber (1.25 bar and 110°C, respectively). Simulation results for total and individual tar concentration in biodiesel over time are shown in figures 27 and 28, respectively.
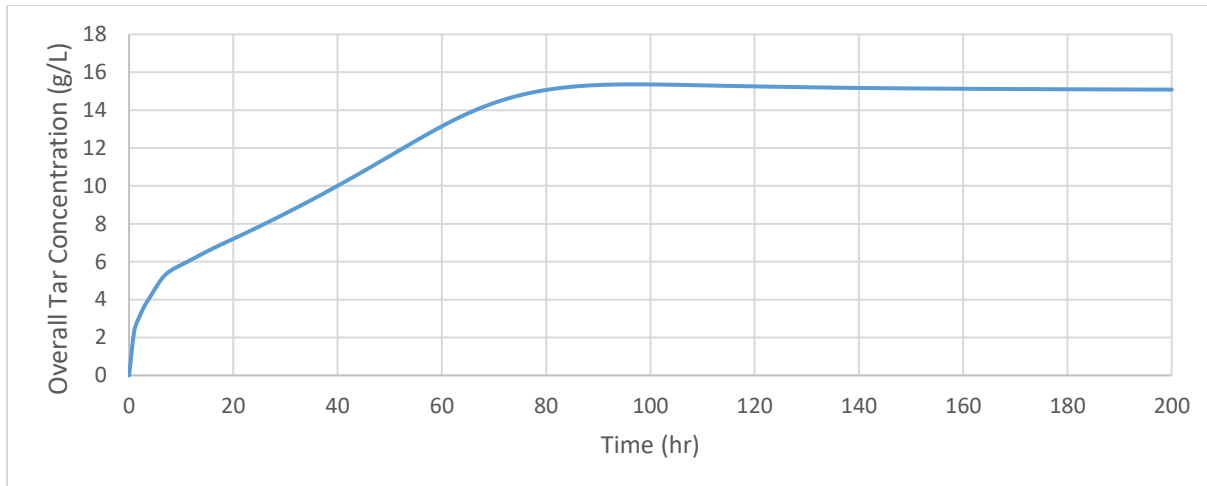
Figure 27 AspenPlus results for the overall Tar concentration in Biodiesel at the absorber's Outlet over time
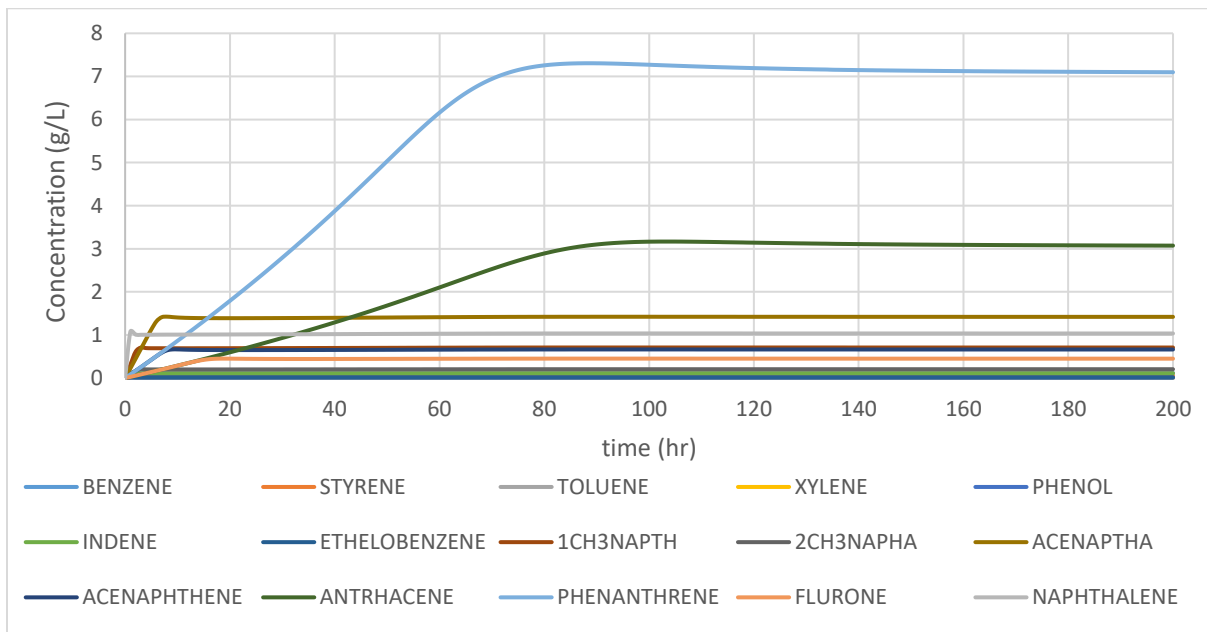
Figure 28 AspenPlus results for individual Tar Concentration in Biodiesel at the absorber's outlet over time

As seen in the graphs above (Figure.27 & Figure.28), tar concentration in the biodiesel follows an exponential behavior respective to time according to the following equation:

$$C_i(t) = C_o(1 - \exp(-kt)) \qquad \text{(Eq.5.4)}$$

Equation 5.4 follows an exponential increase of the tars concentration in the biodiesel agent over time. C_o represents the saturation concentration and k follows as time constant. Based on the results of figure.28 the saturation concentration of each species can be determined by the constant value that every tar compound reaches after a certain amount of time and is presented in the Table.9. It can be clearly seen that, with the exception of phenanthrene and anthracene,

the tar components reach their saturation point in biodiesel early (less than 20 hours) in smaller concentrations (less than 2g/L). The saturation concentrations for each compound from this simulation are depicted in Figure.28. The exponential increase of tars concentration in biodiesel after the 50th hour is mainly due to phenanthrene and anthracene. Phenanthrene, as well as its linear isomer anthracene, are insoluble in water, however they are highly soluble in low polarity organic solvents like Methyl-Palmitate Oil that was used in this case study *(Anon., 2010)*. According to Acree, (2013), phenanthrene's solubility in organic solvents is in average $0.038L/L_{solvent}$. According to AspenPlus results, the obtained value for phenanthrene's saturation concentration was $7.097 g/m^3$ or $0.006 \cdot 10^{-6} L_{phenanthrene}/L_{oil}$. The huge difference between the two values will be explained in the following paragraph.
.

Table 9 AspenPlus results for the Saturation Point and Solubility of tars in Biodiesel Oil

Tars	Saturation Concentration of tars in the oil (g/L) Co	Solubility (gr$_{tar}$/gr$_{oil}$)	Saturation Concentration of pure compound (g/L) at 100ºC
Benzene	0.119	1.675E-04	1.526
Styrene	0.055	7.84E-05	9.542
Toluene	0.114	1.62 E-04	3.825
Xylene	0.004	5.98E-06	9.518
Phenol	0.006	8.69E-06	13.196
Indene	0.110	1.62 E-04	27.983
Ethylbenzene	0.019	2.73E-05	7.882
1CH3-Naphthalene	0.709	4.33 E-04	-
2CH3-Naphthalene	0.205	1.18 E-04	-
Acenaphthylene	1.420	3.15 E-04	-
Acenaphthene	0.663	1.18 E-04	-
Anthracene	3.073	3.94E-05	-
Phenanthrene	7.097	1.181 E-04	-
Fluorene	0.450	3.94E-05	-
Naphthalene	1.03	15.154 E-04	69.799
Total	15.074	0.003927324	

This simulation results may be useful only for the particulate syngas flow tested. This is because syngas is acting as a miscible mixture of all the different tar compounds and in no way the results are representative for these compounds' actual solubility in biodiesel. In order to estimate the solubility of each compound in different solvents, the compounds need to be present in their pure form and under controlled conditions such as atmospheric pressure and room temperature. Nevertheless, AspenPlus can be used as a tool to estimate the saturation concentration of tar compounds in any kind of solvent and for any kind of flow like in this case. For instance, the fourth column of table.9 is representing simulation results for the saturation concentration of tar

compounds in their pure form in biodiesel. This simulation was run at 100°C, so some of the compounds were neglected in the simulation as they were already in their liquid phase. Higher temperatures caused the vaporization of the absorbing agent, creating errors in AspenPlus simulations. Consequently, 100°C was chosen as the maximum temperature for the simulation. For the simulations a gaseous stream with only one tar compound (each time) and nitrogen were passing through the oil absorber. The program was designed in order to save the concentration of each compound at the oil absorbers outlet. As seen in Table.9, the saturation concentrations of the tar species in column four are largely different from the values in the first column. This difference occurs due to the absorption of different species, in the organic liquid during the first simulation in comparison to the selective absorption of individual compounds during the second simulation. As mentioned in Chapter.5.2.1 RadFrac column treats the absorption of tars as a mass and heat based transfer process. During these simulations temperature was kept constant for both syngas and oil stream. Therefore, the absorption process was mainly based on mass transfer processes. Consequently, by absorbing multiple species, the mixture was expected to develop different physical properties changing the absorption efficiency of the oil. By absorbing various species inside one solution different phases will be developed based on the physical properties of each specie. The different phases of the new mixture will contribute to a change in the physical properties of the organic liquid such as vapor pressure, boiling point, and solubility. According to Rogers, (2015.) solubility of a substance in solvent is not only depended on the intermolecular forces between the solvent and the solute but also on the excess or deficiency of common species in the solution. By simulating the selective absorption of individual species, the organic liquid develops a single phase mixture (as tars are miscible in organic liquids) with two consisted compounds (oil + specie). The absorption coefficient of this mixture is relatively higher than a multiple phase oil mixture.

Additionally, conditions such as fluid pressure and temperature are significant factors, affecting the saturation point. Increased pressure and temperatures can increase the saturation concentration point. The given results were obtained from the waste oil stream. In real case scenarios when tar compounds are liquefied and have been absorbed by organic solvents, miscible mixtures are created with either one or more phases. In order to measure the actual saturation, point of hydrocarbons in oil, the mixture has to be left for a time period until it reaches steady state conditions and the immiscible phases can then be separated. The tar concentration in the oil phase will be at it the saturated concentration of the particulate compound in the solvent. Seidell, (1919) has studied the saturation concentration of various hydrocarbons in several organic liquids. Based on his book, the saturated concentration of Napthalene in different solvents is presented in the following table.10.

Table 10 Saturation concentration of Naphthalene in various organic liquids (Seidell, 1919)

Solvent	Concentration of Naphthalene ($gC_{10}H_8/100g_{solvent}$) at 70°C
Chloroform ($CHCl_3$)	87.2
Carbon Tetra Chloride	80
Carbon Di Sulphide	90.3
Benzene	88
Chlor Benzene	85
Hexane	78.8
Toluene	97.5
Tested Methyl-Palmitate Oil (simulations)	99.8

To compare the referred by Seidell, (1919) values with the obtained AspenPluns results, an extra simulation was performed. The simulation tested Naphthalene's saturated concentration in Methyl-Palmitate oil under the suggested conditions by Seidell, (1919). The result that was obtained by this simulation is provided in the last row of Table.10. As seen from the results, the saturation concentration in Methyl-Palmitate oil is slightly higher than other organic solutions. The slight increase in the Naphthalene concentration into the Methyl-Palmitate oil can be justified by the larger viscosity of the Methyl-Palmitate oil compared to other organic solutions. According to Pratas, et al., (2011), Metyl-Palmitate viscosity was estimated 5.36 cP at 20°C this is ten times larger than toluene's viscosity at the same temperature, which came to 0.59 cP.

Additionally, simulations testing the non-condensable gases solubility in biodiesel were performed. The tested configuration for these simulations was the same as in the above simulations for tars solubility. The following Figure.29 and Figure.30 present the results from AspenPlus simulations. Figure.29 presents the molar fraction of each gas that was absorbed in the biodiesel by increasing the biodiesel flow. The measured absorbed percentage was calculated according to Equation 5.5.

$$\%(molar)Absorption = \frac{F_{i_{in}} - F_{i_{out}}}{F_{i_{in}}} \qquad \text{(Eq.5.5)}$$

Where F_{in} and F_{out} are molar flow rates at the entrance and the exit of the absorber respectively. Figure 30 illustrates the saturation point of these gaseous species in biodiesel.

As seen in Figure.29 the absorption of the non-condensable gases by the oil agent is much lower than tar absorption. This result was expected. This result can be attributed to the low condensation point of the non-condensable gases as well as the more stable structure of the compounds. The resulting combinations does not allow unfavorable kind of chemical bounds to be developed between the gas molecules and the organic liquid.
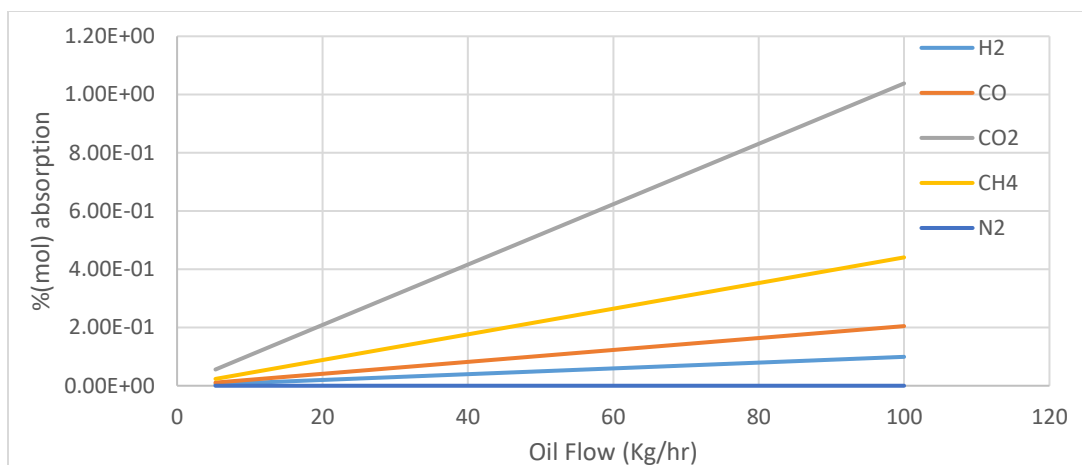
Figure 29 Non-condensable gases absorption efficiency

Additionally, the concentration of the non-condensable compounds was measured at the oil absorber's outlet as in the previous simulations. Figure.30 is showing the response of the system for 10 hours. As seen from the graph three conclusions can be made:

- Non-condensable gases are reaching their saturation point in the oil sooner than tar compounds;
- the achieved saturated concentrations are lower than the ones of the tar compounds;
- apart from CO_2 the rest of the gases can be stated as insoluble as their concentration in the oil is lower than 0.0002 g/mL
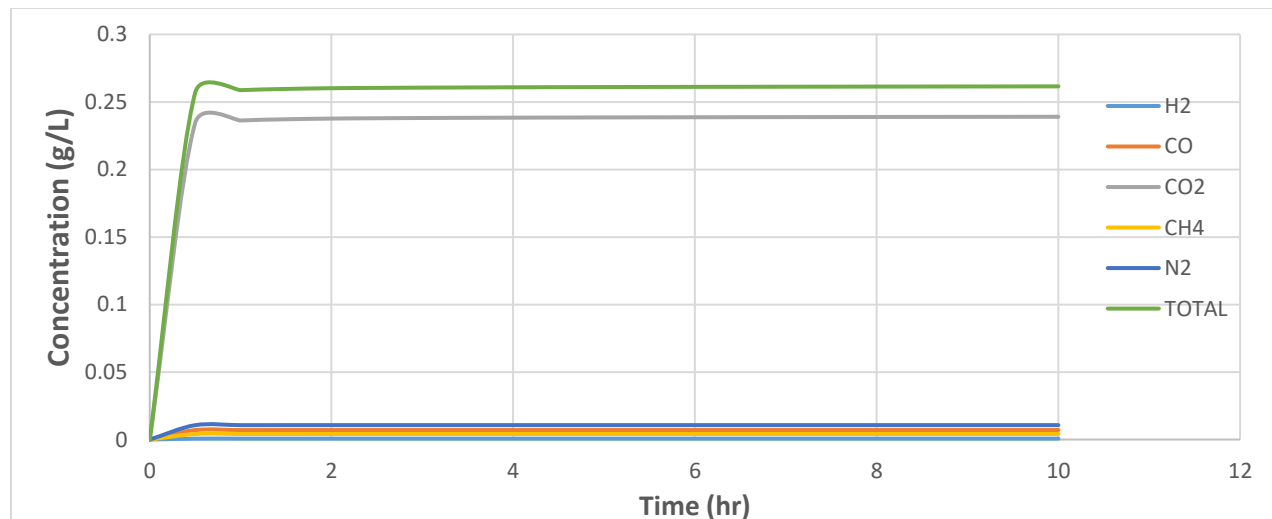
Figure 30 Non-condensable gases Concentration in the Biodiesel at the absorber outlet

5.3.1. Air-Stripper Recovery Efficiency using tars Saturated Concentrations in Biodiesel

As tested in Chapters 5.2.1 and 5.2.2 air-stripper technology, was efficient in the delivery of 99% molar purity recovered oil stream. The waste oil treated with the air-stripper technology (outlined in Chapters 5.2.1 and 5.2.2) initially consisted of 96.2% methyl-palmitate oil. Therefore, the simulation was able to remove only the 2.8% of tar impurities in order the oil flow to fulfill the 99% molar purity constrain. Following the examination of the saturation point of tars in the biodiesel an

extra air-stripper model was built to observe the air-stripper model's performance when tars are present in greater fractions in biodiesel. The design model used for this simulation is illustrated in the following Figure.31. The oil's flow rate as well as its temperature and pressure were taken from the waste oil stream results of the wet model's simulation.
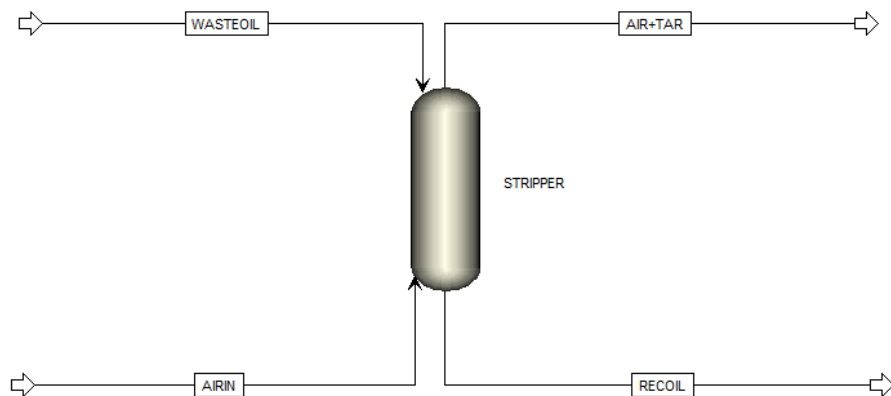
Figure 31 AspenPlus Air-Stripper Configuration

In this oil-recovery simulation the used waste-oil stream (WASTEOIL) is entering the air-stripper column with 90% molar purity. As in the wet model's simulation, an optimization code was used in order to decrease the air heating requirements and achieve 99% molar purity of methyl-palmitate oil at the oil's outlet (RECOIL). After simulating the model, a 16.67 m^3/hr air flow at 250°C was found to be needed in order to fulfill the requirements of the optimization code. Compared, with the results of the wet model with TUD data, the air flow for this simulation was decreased by approximately 40 m^3/hr and, the temperature was increased by 70°C. The reason of having elevated temperature in this model, is the higher concentration of heavier tar species in the treated oil flow. As it was shown initially at the wet model's air stripper results, non-condensable gases and lighter tar compounds are easier to get volatized compared to heavier PAH's. The obtained removal efficiencies from this simulation are illustrated in the following table.11. As seen in the table.11 heavier tar compounds have lower removal efficiencies as are more soluble in the organic agent and more heat is needed to volatize them. Moreover, under the resulting air conditions 9% of the initial methyl-palmitate oil is volatized and escaping the absorber within the air flow.

Compound	Removal Efficiency	Compound	Removal Efficiency
H_2	100%	Naphthalene	99.9%
CH_4	100%	Ethylbenzene	100%
CO	100%	Xylene	100%
CO_2	100%	Acenaphthalene	98.7%
N_2	100%	1-CH_3- Naphthalene	99.6%
H_2O	100%	2-CH_3- Naphthalene	99.6%
Benzene	100%	Acenaphthene	98.4%
Phenol	100%	Fluorene	95.6%
Toluene	100%	Phenanthrene	71.4%
Styrene	100%	Anthracene	65.3%
Indene	100%	Methyl-Palmitate Oil	8.99%

According to AspenPlus results for this simulation, 91.12% (mass-based) of waste oil was recovered after the air-stripper model. The remaining 8.88% of the waste oil flow has been volatized and escaped the system with the hot air outlet. Conclusively, to remove high weight hydrocarbons greater heat requirements are needed. Moreover, the use of an organic liquid with high boiling point will minimize the volatized fraction of the oil escaping with the hot air.

5.4. Models and Simulations of Synvalor's Gasifier

Synvalor gasifier was established by the Synvalor B.V company, in collaboration with a TUD research team. It is a pioneer reactor concept that does not use any bed material within the gasifier. The main characteristics of this innovative concept are the small volume of the installment and the low maintenance and operation costs that are needed during its operation. The small volume of the gasifier is mainly caused by the multiple tangent gas inlet slots that are used to create fluidization inside the reactor. Its design and experiments were primarily based with softwood as fuel, and with a target to achieve 2.2MWth capacity (Anastasakis, et al., 2016).

The aim of this subchapter is to model Synvalor Gasifier's tar cleaning system in AspenPlus configuration as well as to compare the results of the plant with the simulation results of this project. A simplified diagram of the cleaning system with the operating temperatures can be seen in the figure.32. The syngas flow concentrations as well as the analysis results of tar concentration both in the organic liquid and the syngas from the real experiments can be found under appendix B.3 in the tables B.7, B.8 and B.9. In tables.B.7 and B.8 tar concentrations in the particulate produced syngas, from four SPA samplings can be observed before and after the cleaning system, respectively. Moreover, as the system is operating with two 600L packed columns, table.B.9 is illustrating the concentration of the absorbed tars in the first biodiesel scrubber.
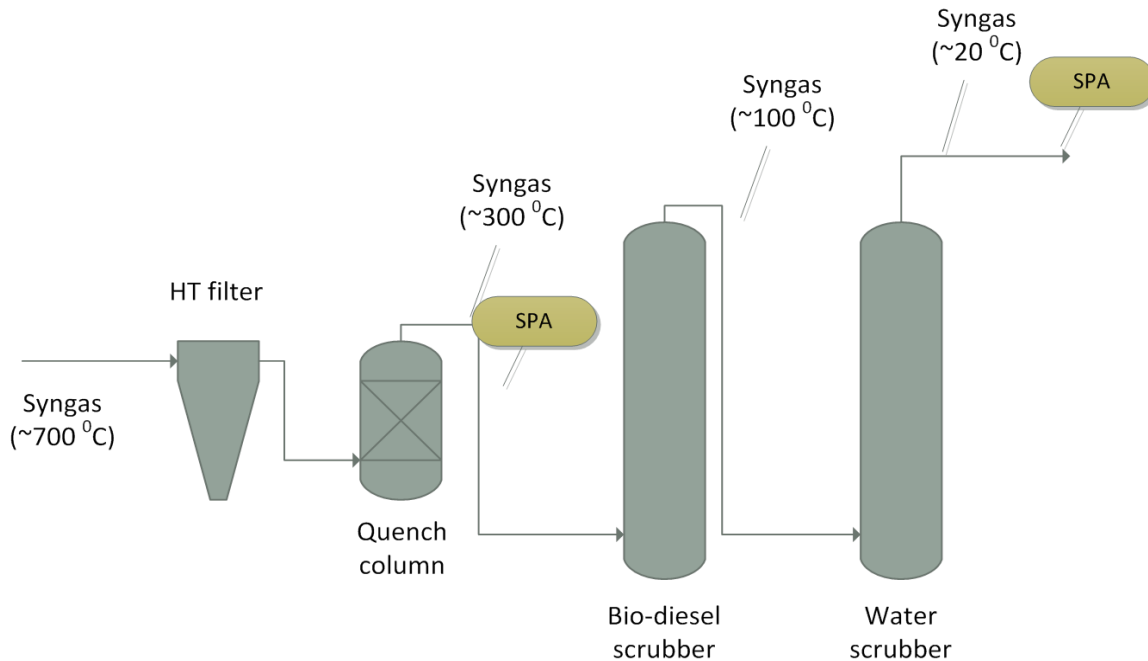
Figure 32 Synvator gasifier's simplified syngas cleaning system (Anastasakis, et al., 2016)

Firstly, the concentrations and the flow rates had to be determined. As AspenPlus operates under steady state conditions and not as a dynamic process, an overall average flow rate was estimated by using the amount of syngas that passed through the scrubber; after the two measurements that were taken in the two days of the experiments. A 2.54m³/min volumetric syngas flow rate was estimated as the mean value of the two days (Table.B9). The average tar concertation was estimated in the same way by calculating the mean value of the measured concentrations before the scrubber from the four measurements that were taken (Tabe.B.7). However, AspenPlus database does not include the following heavier hydrocarbon molecules in its database; Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Dibenzo(a.h)anthracene, Benzo(g.h.i)perylene and Indeno (1.2.3-cd)pyrene. Initially, it was tried to introduced these compounds manually by adding their properties into AspenPlus database. Due to lack of literature surrounding these compounds it was impossible to calculate all the asked properties such as Enthalpy of formation, Gibbs free energy, and specific gravity. In order to overcome this obstacle, the mass flow rate of these species was divided into the remaining tar compounds included in AspenPlus libraries.

The model that was created in AspenPlus is illustrated in figure.33. To create a realistic module for the two packed columns that were used in the real cleaning system, RadFrac modules were chosen from AspenPlus. RadFrac columns were designed to have 2 stages, and selected tray and packing sizing to emphasize the 600 liters of each column's capacity. By using trial and error method, the flows of oil and water were estimated to meet the temperature regimes of the operation, as presented in figure 32. The estimated flows were 1.6 l/min and 9.01l/min for oil and water, respectively. To set the used oil's physical properties, methyl-palmitate oil was chosen and it was set as a pseudo-component in order to introduce given characteristics of the actual oil such as boiling point, flash point and viscosity of the particulate oil. The characteristics of the biodiesel

that was used in the real experiment can be seen in table B.10 in Appendix.B.3. The reason of doing that was to create a more realistic outcome. Additionally, -16.85KW of power was estimated to be needed to reduce the temperature of Synvalor's syngas from 700ºC to 300ºC (the minus sign indicates absorption of heat). From the above estimated flows the following conversion rates were obtained, which are presented in table.12.
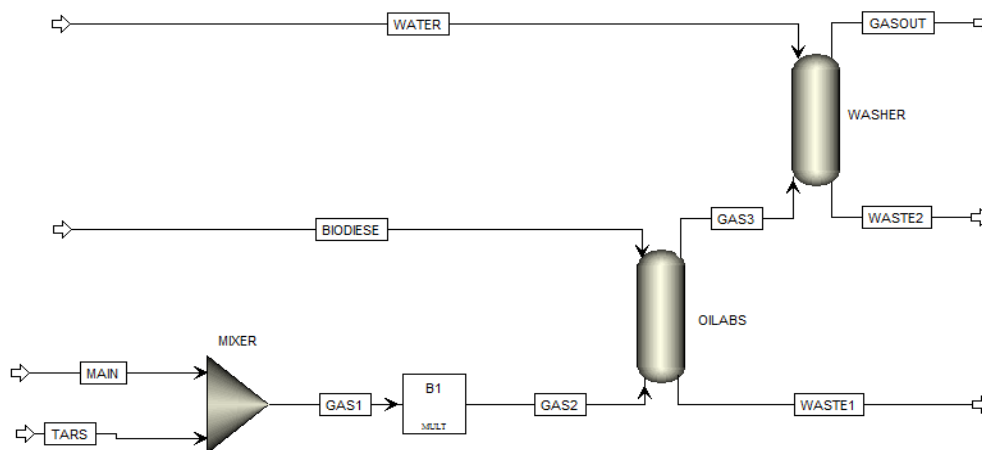
Figure 33 Synvator AspenPlus layout

5.4.1. Results and Discussion of Synvalor's Gasifier Models

As it can be seen in the results of the table.12, the conversion rates that were obtained from the modeled simulation were found very similar with measured ones through the experiments. The difference between the two conversion values can be explained by the use of a similar oil instead of the actual organic liquid, and the fact that AspenPlus libraries did not have all the tar compounds of the tested flow.

Table 12 AspenPlus Results from Synvalor validation model

Substance	Tested Conversion-Rate	Model Conversion-Rate
Naphthalene	0.973	0.959
Acenapthylene	0.956	0.895
Fluorene	0.910	0.979
Phenanthrene	0.988	0.998
Anthracene	0.989	0.998
Fluoranthene	0.998	0.999
Pyrene	0.999	0.999
Benoz(a)antracene	1	0.999
Chrysene	1	0.999

Nevertheless, the values that were obtained from the simulation were close to the average conversion rates from the actual experiment which presents the capability of AspenPlus programming to model and simulate wet syngas cleaning systems with high accuracy.

Furthermore, the collected data from Synvator gasifier were used as inputs in the previously designed wet model of this project. After simulating the designed system under Synvator's data the below results (table.13) were obtained.

As seen in the results presented in table.13, it can be concluded that in order to eliminate tars from Synvator's gasifier product gas, a continuous 175.5l/hr oil is needed. This is approximately double in comparison with the 98L/hr that were estimated for the real model. The net energy requirements of the designed model were estimated at -17.65KW. The minus sign indicates cooling energy (absorbing heat). The cooling requirements are elevated by 0.8KW from the Synvalor's "validation" model, however, the designed model achieves tar elimination at the methanol synthesis limits. TUD wet model simulation revealed the need of heat to be introduced into the system as the heating requirements were higher from cooling. Synvalor's validation model as well as Synvalor's designed model simulation shown the need for cooling. It was estimated that 24.11KW of heat must be absorbed by the syngas cooler in order to cool syngas from 700 to 110°C. This is in comparison to 3.25KW of cooling requirements from TUD wet model simulation, which reduces the temperature of the flow from 845°C to 110 °C. The big difference in the two obtained values can be explained by the difference in the flow rates and the composition of the two produced gases. As previously assumed, Synvalor's syngas flow rate is approximately double than the tested flow of TUD. Additionally, the gas produced by Synvalor's gasifier has a lower concentration of tars ($1.3g/m^3$) in comparison with TUD syngas ($3.02g/m^3$). The specific capacity of a gas mixture can be calculated by the summation of each specie specific heat (Cp_i) multiplied by the molar fraction (n_i) in the mixture. (Eq.5.6) Therefore, as tar's specific heat is lower in comparison with water, and the two produced gases are rich in water vapor, the specific heat of Synvalor's gas flow is expected to be higher.

$$C_{P\,Gas\,Mixture} = \sum n_i * Cp_i \qquad\qquad \text{(Eq.5.6)}$$

Furthermore, an estimated 6.46KW must be provided to the oil heater to increase oil's temperature from 25 to 108°C at Synvalor simulation, in comparison to 24.53KW in TUD wet model simulation for the same change in temperature. The greatest difference in the heating requirements of the two simulations can be seen in the elevated oil flow rate of TUD simulation (660L/hr), in comparison with the oil flow of Synvalor simulation (175L/hr). The surplus of heat extracted from both Synvalor's simulations can be used to heat the air at the air-stripper module.

Table 13 AspenPlus Results from the designed wet model by using Synvalor data

Variable	Stream	Result
Manipulated Variables		
Oil Pressure (bar)	Oil 3	1.252
Oil Temperature (^{o}C)	Oil 3	108.421
Syngas Temperature (^{o}C)	Gas 3	125.922
Oil flow rate (m^3/hr)	Oil 1,2&3	0.17593
Air Temperature (^{o}C)	AIRIN	180
Air flow rate(m^3/hr)	AIRIN	15.593
Ponded Variables		
Syngas Temperature (^{o}C)	Gas 4	109.878
Waste-Oil Temperature (^{o}C)	Waste 1	116.565
Water flow rate (m^3/hr)	Water 1,2	0.25
" Clean" Syngas Temperature (^{o}C)	Gas Out	25.75
"Clean" Syngas flow rate (m^3/hr)	Gas Out	4.096
Waste Water Temperature (^{o}C)	Waste 2	38.6
" Clean" Syngas Tars concentration (mg/Nm^3)	Gas Out	0.09979

The particulate biodiesel flow can be reused as the air-stripper column recovers biodiesel oil with 99% molar purity. According to AspenPlus results air-stripper can recover 99% (mass base) of the waste oil flow. By using this technology, the operation cost will be minimized by reducing biodiesel usage as well as the energy consumption of the system as the energy requirements are utilized. The results according to the compounds conversion rate can be found in the Table D.2 in Appendix D.

6. Dry Method Model & Simulation

6.1. Design and Description of Primary Dry Model

A different approach was adopted with the dry method than the one that was undertaken with the wet method. As mentioned in Ch.2.4.1.2 nickel catalyst reformers have the ability to reduce tars from syngas with effectiveness up to 100% (depending on the support and promoter materials). In accordance with above, a nickel based catalyst was decided to be used in one stage of conversion process in the dry model. A nickel based catalyst is one of the most reliable and effective existing methods for petrochemicals compounds to be used at this stage. (Vivanpatarakij, et al., 2014) Support and promoter materials were neglected due to the difficulty to draw reliable data about certain reactions under a specific type of catalyst and at similar operation conditions of tested syngas. The high syngas temperature at the gasifier's exit will help increase the speed of the reforming reactions on the surface of the catalyst. According to Pfeifer & Hofbauer, (2008) the reactions occurring on Nickel catalyst, it is expected CO_2 and H_2 fractions to be increased in the treated gas stream, causing a decrease in the LHV of the gas, but an increase in the chemical energy of the product The data for the kinetics and thermodynamics of the reactions were taken from the literature where the based-catalyst element was Nickel. Due to the high number of reactions and the luck of data concerning their kinetics and thermodynamics, the model design was based on, benzene, naphthalene and toluene compounds which present in great fraction in the particulate TUD gasifier's tested flow. (figure.34)

Benzene   Toluene   Naphthalene
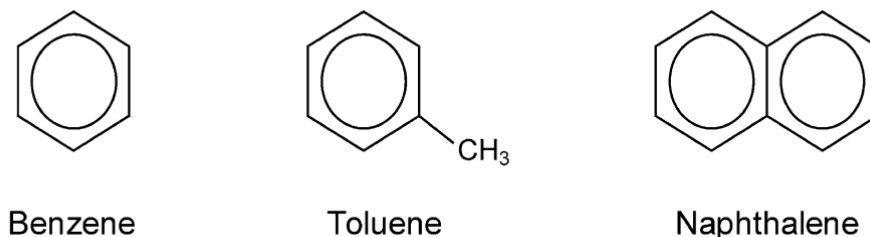
Figure 34 Skeletal formula of the tested tars in the dry model(WIKI,2016)

The use of a designed catalyst in a reactor can drive several reactions to occur at faster rates and also at lower temperatures. For hydrocarbon compounds, nickel catalyst is commonly used and, according to many case studies that can drive the bellow reactions effectively. (Corella, et al., 2002)

- Carbon forming - $C_nH_x \leftrightarrow nC + \frac{x}{2}H_2$
- Steam re-forming - $C_nH_m + nH_2O \leftrightarrow nCO + \left(n + \frac{m}{2}\right)H_2$
- Hydrogenations
- Dry reforming - $C_nH_x + nCO_2 \leftrightarrow \frac{x}{2}H_2 + 2nCO$
- And Catalytic or thermal Cracking $- pC_nH_m \leftrightarrow qC_mH_i + rH_2$

The reactions are further complex and specific when it comes to heavy hydrocarbon compounds such as tars. In order to obtain the above reactions with regards to tars, an extensive literature review was carried out to obtain available information upon the chemical occurring reactions with

data on their kinetics and thermodynamics. The equations that were found are presented in the table E.3 at Appendix E, with a brief description of their kinetics and thermodynamics. However, all these reactions could not be used in AspenPlus due to the varying conditions under which they had been tested. (pressure, temperature, gas medium, catalyst structure, flow rates and syngas composition) As seen in table E.3 the referred reactions were obtained from experiments from different gas agents. Temperatures, Pressures regimes, catalyst particles (Nickel was always the based material) and Consequently, in order to simulate a dry model in AspenPlus the reactions with the closest operation conditions to the TUD syngas flow were used into the program. The purpose of choosing reactions that were tested in conditions similar to the TUD flow was to avoid any pre-heating or pre-cooling of the flow and minimize the energy requirements of the system. The following Table.14 gives a more detailed description of the modeled reactions.

Table 14 Modelled Reactions with their kinetics parameters

According to Article	Stoichiometry	Kinetics	Tested Temperature	Tested Pressure	Catalyst Material	Residence Time/ Catalyst
(Depner & Jess, 1999)	$C_6H_6 + 6H_2O \rightarrow 9H_2 + 6CO$ $C_{10}H_8 + 10H_2O \rightarrow 14H_2 + 10CO$	$r_j = \dfrac{k_{m0j} * \exp\left(-\dfrac{E_a}{RT}\right) * c_j}{1 + K_{oj} * \exp\left(\dfrac{C_j}{T_R}\right) * c_j}$ 		Naphthalene	Benzene		450-1125 °C	160KPa	Ni-MgO	0.1s / -

Table 14 Modelled Reactions with their kinetics parameters

According to Article	Stoichiometry	Kinetics	Tested Temperature	Tested Pressure	Catalyst Material	Residence Time/ Catalyst
(Depner & Jess, 1999)	$C_6H_6 + 6H_2O \rightarrow 9H_2 + 6CO$ $C_{10}H_8 + 10H_2O \rightarrow 14H_2 + 10CO$	$r_j = \dfrac{k_{m0j} * \exp\left(-\dfrac{E_a}{RT}\right) * c_j}{1 + K_{oj} * \exp\left(\dfrac{C_j}{T_R}\right) * c_j}$ (see sub-table A)	450-1125 °C	160KPa	Ni-MgO	0.1s / -
(Caprariis, et al., 2014)	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$ $C_6H_6 + 6CO_2 \rightarrow 12CO + 3H_2$	$r_j = -k_{app} * c_j$ $k_{app} = A * \exp\left(\dfrac{E_a}{RT}\right)$ (see sub-table B)	750-800 °C	-	Ni-Co/Ce Al2O3	0.6s / 2g
(Swierczynski, et al., 2007)	$C_7H_8 + 7H_2O \rightarrow 7CO + 4H_2$ $C_7H_8 + 14H_2O \rightarrow 7CO_2 + 18H_2$	$r_t = -k(T) * c_t * c_{H_2O}$ $K(T) = A * \exp\left(-\dfrac{E_a}{RT}\right)$ $A = 3.14 * 10^{13}\ m^3\ kg^{-1}h^{-1}$ $E_a = 196\ Kj/mol$	800 °C	-	Ni/olivine	- / 5–300 mg
(Hacarliog lu, 2007)	$(1) CH_4 + H_2O \rightarrow CO + 3H_2$ $(2) CO + H_2O \rightarrow CO_2 + H_2$	*APPENDIX.E*	873-923K	1-20atm	Ni/MgAl2O4	0.2s / 0.05g

Sub-table A (Depner & Jess kinetics parameters):

	Naphthalene	Benzene
k_{moj} (m³Kg⁻¹s⁻¹)	$1.4*10^6$	6.2
E_a (Kj mol⁻¹)	149	34
K_{oj}	$1.5*10^{-3}$	$1.3*10^{-3}$
C_j (K)	11800	9400

Sub-table B (Caprariis kinetics parameters):

	Methane	Benzene
$A (s^{-1})$	22471	608
E_a (Kj/mol)	76	57

As seen in Table.14 the kinetics of modeled reactions were measured on different catalyst particles and temperature profiles. The above reactions were considered acceptable for this simulation as the catalyst based metal was Nickel and the tested temperatures were similar to the TUD gasifier syngas flow. In order to model the above reactions, the below AspenPlus layout (Figure.35) was designed. Peng Robinson (EOS) was chosen as the solver method as according to (aspentech, 2011) this property is particularly suitable for gas treatment in high temperatures. Both reactors were designed with 0.3g of catalyst loading and 0.05s residence time of the gas inside the reactor. The amount of catalyst and the residence time that were introduced into the simulation were set up based on obtained literature.
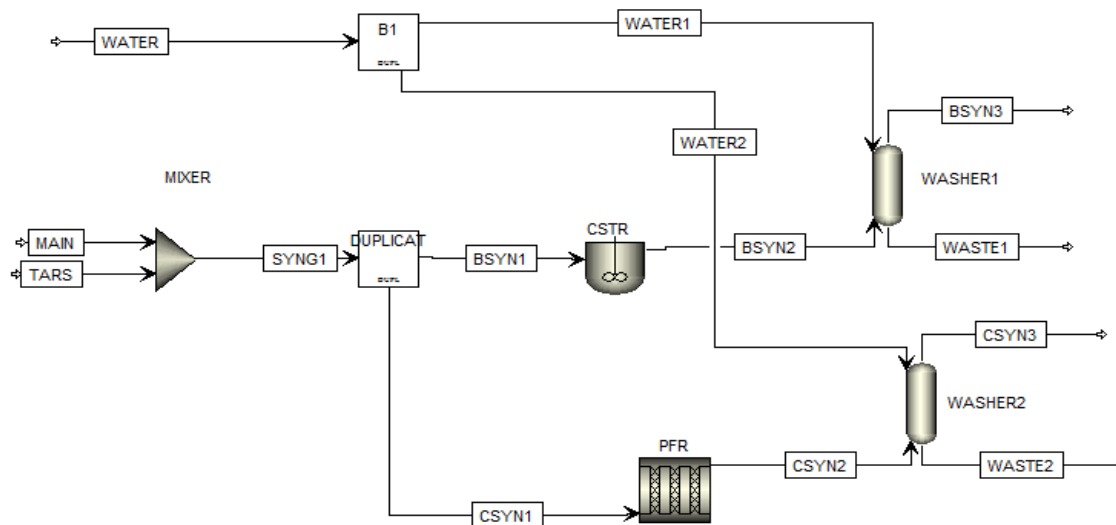
Figure 35 AspenPlus Dry's Model Configuration

Two reactors operations were tested; constant reactor's temperature (845°C) and adiabatic operation (figure.35). The pressure in the reactors was chosen to remain constant as the pressure of the inflow. Due to overlapping of some reactions and fully consumption of some of the compounds during the constant temperature operation PFR rector was indicating warnings related to consumed compounds. As seen in Figure.35 two RadFrac columns were used after the two reactors. As in the wet cleaning model, the two RadFrac columns were used as water washers to decrease the temperature of the produced syngas streams from the reactors. RCSTR and RPFR reactors were chosen for this simulation, due to their ability to simulate conversion of species based on detailed information on the species reactions and kinetics. As the project's aim was to deliver two models with accurate and realistic outcomes, the CSTR and PFR reactors were considered more suitable, due to their ability to perform simulations under specific conditions. (pressure, temperature, kinetics, etc.)

6.1.1. Results and Discussion of Primary Dry Model

After simulating both operations the below results were obtained. Table.15 indicates the molar conversion of compounds after the reactors. Equation 5.1 was used for the estimation of the

species conversion rates. Due to this, the conversion rates that are indicating with a minus sign represent the compounds that their yield was increased.

As seen from the results (Table.15) of both operations, the conversion rates from both reactors are similar, with PFR showing higher conversion rates. As proven by Wijayarathne and Wasalathilake, (2014), in order to achieve the same conversion rate between a CSTR and PFR, the CSTR volume has to be 3.5 times the PFR volume. At adiabatic conditions all of the non-condensable gases yields are increasing with the exception of methane, which is almost entirely consumed. As expected, Hydrogen showed the highest increase. Toluene was nearly eliminated, yet benzene and naphthalene showed a slight change. The temperature of the streams at the outlet were 745 °C and 738°C for CSTR and PFR, respectively.

Table 15 AspenPlus Conversion Rates results for Dry Model's Simulation

	Constant Temperature		Adiabatic Operation	
	CSTR	PFR	PFR	CSTR
H_2	-0.9250	-0.9555	-0.8730	-0.821
CO	0.0699	0.0732	-0.01786	-0.0061
CO_2	-0.18545	-0.1936	-0.15858	-0.1503
CH_4	0.995	1	1	0.9447
N_2	0	0	0	0
$H2O$	0.105	0.1098	0.0953	0.0897
C_6H_6	0.4324	0.5182	0.39588	0.3368
C_7H_8	0.992	0.9999	0.9999	0.9507
$C_{10}H_8$	0.3958	0.4802	0.1307	0.1254

The decreased temperature indicates the endothermic nature of the reactions. On the other hand, by keeping reactor's temperature constant, tar conversion is increasing due to the higher temperature of the reactor. However, carbon monoxide yield is decreasing from its initial amount. To keep the reactors temperature at 845°C, 0.52 and 0.53KW of heat are needed for CSTR and PFR respectively according to AspenPlus. Results from the two simulations are not representative of a real reformer as the reactions that were modeled were based on different catalyst particles and so different conditions are needed in order to optimize tar conversion. Toluene was found to be totally consumed, with the other two contaminants (benzene and naphthalene) were still in high concentrations in the outflow stream. This result can be justified by the lack of reactions that involved benzene and naphthalene. PFR showed slightly higher conversion efficiency than CSTR under the same conditions. Nevertheless, a noticeable effect of temperature and heat on the conversion of tar compounds to useful compounds in the stream was shown. By applying additional heat to the reactor the conversion rate is increased. In this case to keep the temperature constant the amount of energy is minute in comparison to the energetic consumption observed in the wet model.

6.2. Secondary Dry Model Using RGIBBS reactor

In addition to the above model, an ideal reactor was simulated in AspenPlus. RGIBBS reactor was used in a Temperature regime from 845 to 1200ºC. Figure.36 illustrates the layout that was designed for the RGIBBS model in AspenPlus. In this model the syngas stream, is being treated in the RGIBBS reactor and later it is being cooled in a water absorber. RGIBBS reactor module in AspenPlus provides reaction calculations based on chemical and phase equilibrium conditions by minimizing Gibbs energy of the system. In the particulate experiment RGIBBS reactor all the system components were considered products. The main advantage of RGIBBS reactor is that it can run through the simulations without the need of kinetics, thermodynamics, yields and stoichiometry data for the reactions. It primarily illustrates the optimum reactor performance under ideal conditions. An optimization code was used in this simulation in order to estimate the optimum heat requirements which the reactor need to eliminate the tar compounds. The optimization code in this case had targeted to minimize the amount of heat of the reactor by manipulating temperature regime inside the reactor with target to reduce tar concentration at the same limits as in the wet models.
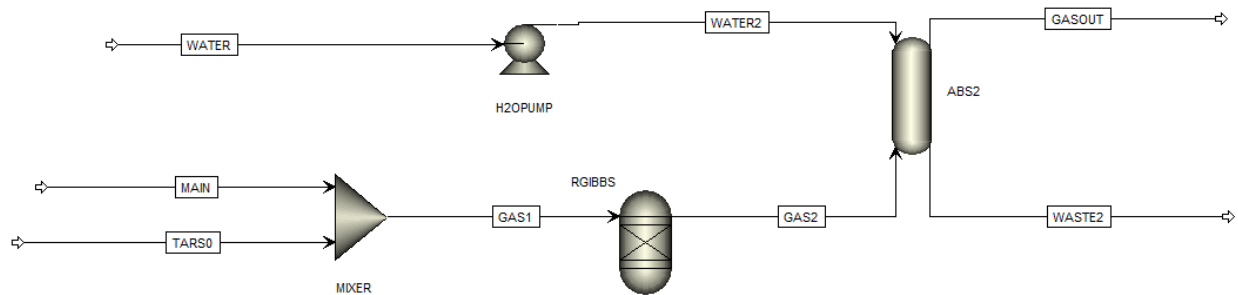
Figure 36 AspenPlus "RGIBBS" Dry's model Configuration

6.2.1. Results and Discussion of Secondary Dry Model

After simulating the above illustrated dry model, RGIBBS reactor eliminated all tar compounds from the tested syngas flow with 100% efficiency. According to AspenPlus, the reactions took place at 845ºC with overall heat requirements 0.72KW. The results are not representative of a real case reformer as the amounts of heat are usually higher than in this ideal case. The results are referring to an optimum case of gas treating. From the obtained results, however, the way that the yields of non-condensable gases are changing under ideal treatment can be noticed. For example, in this simulation, the outlet stream does not contain tar compounds as they are eliminated in the reactor. Hydrogen, CO and CO_2 yields increased by 79%, 73% and 3.5% respectively. CH_4 and H_2O yields were decreased by 99% and 7.4%, respectively. Initially, the LHV value of tested TUD syngas flow was estimated at 2.472 MJ/Nm^3. After RGIBBS treatment, LHV of the treated was increased to 3.1342 MJ/Nm^3. The LHV of the treated gas was increased 21.12% of the initial value due to the increased yields of Hydrogen and Carbon Monoxide. The LHV value of the two products was estimated by the equation 6.1. Based on these results it can be concluded that - after development and research - during an ideal catalytic method of cleaning the non-condensable gases yield will more likely follow the behavior discussed above.

$$LHV\left(\frac{MJ}{Nm^3}\right) = ([H_2] * 0.10798 + [CO] * 0.12636 + [CH_4] * 0.35818 + [C_2H_2] * 0.056)$$

<div align="right">(Eq.6.1) (Mohammad, et al., 2003)</div>

To create a realistic model for tar cracking on a Nickel catalyst various experiments must take place. An optimal example of a catalytic treatment experiment was made by University of Vienna for the Guessing Gasifier which will be described more extended in the next chapter. Nevertheless, even with actual experiment taking place, the engineering team of the University of Vienna were not able to collect and find all the reactions which are occurring in the reformer. Due to this, they based their model on toluene.

6.3. Model and Simulations of Guessing Gasifier

One of the biggest and highly representative gasifiers in the world is established in Guessing, Austria. An 8MW cogeneration plant is established in the area and is fully supplied by the operating gasifier. The plant under operation since 2007 and is one of the most innovative, commercialized plants worldwide (Simader, 2004).

Figure 37 Biomass CHP Plant Güssing (AER, 2007)

An admirable innovation of this plant is the successful catalytic tar destruction reformer which can operate more than 12 hours without catalyst deactivation and achieves tar outlet concentrations lower than 0.02 g/Nm^3 (Pfeifer & Hofbauer, 2008).

The plant operates a dual fluidized bed steam gasifier with mainly biomass feedstock wood pellets. It is developed by the University of Vienna and the local district heating company (Kaushal, et al., 2007). Guessing, cogeneration plant is a perfect example of a well-designed and well established, catalytic tar reformer in a commercial scale plant. However, throughout this work and

all preparation there are still great deal of unknowns about the chemical reactions occurring inside the reformer as it was designed mainly on toluene steam reforming reactions (Pfeifer, 2012) (Pfeifer & Hofbauer, 2008). A small review of the plant's product and operation conditions can be found in Appendix B4 in table B.12.

This sub-chapter will study the response of the previously designed wet cleaning system with the particular gas flow from Gussing Gasifier. The measured 0.02 g/Nm^3 outlet tar concentration of the Gussing cleaning system is just only unsuitable for methanol synthesis so to obtain the values for the same amount of cleaning efficiency the optimization code was changed to meet the same expectations as the plant. Additionally, as the given outlet tar concentration from Gussing reformer was given in dry gas composition the optimization code was changed to neglect the vapor content at the outlet of the water scrubber. For the further, 6% of the tar fraction that was not indicated in the experimental results and is probably referring to heavy PAHs, benzanthracene was chosen as the replacing compound.

6.3.1. Results and Discussion of Guessing Model

By simulating the previously mentioned data in the designed wet model of this study the following results (table.16) were obtained.

Table 16 AspenPlus results from Wet model simulation with Guessing's data

Variable	Stream	Result
Manipulated Variables		
Oil Pressure (bar)	Oil 2&3	3.718
Oil Temperature (ºC)	Oil 3	104.8
Syngas Temperature (ºC)	Gas 3	114.862
Oil flow rate (m^3/hr)	Oil 1,2&3	0.0351859
Ponded Variables		
Syngas Temperature (ºC)	Gas 4	106.1
Waste-Oil Temperature (ºC)	Waste 1	106.46
Water flow rate (m^3/hr)	Water 1,2	0.8
" Clean" Syngas Temperature (ºC)	Gas Out	25.11
"Clean" Syngas flow rate (m^3/hr)	Gas Out	0.2905
Waste Water Temperature (ºC)	Waste 2	25.18
" Clean" Syngas Tars concentration (mg/Nm^3)	Gas Out	19.98
Conversion of Tars		
Total Conversion Rate	100%	
Naphthalene conversion rate	99.99%	
Acenaphtylene conversion rate	100%	
Indene conversion rate	100%	
Phenanthrene conversion rate	100%	
Styrene conversion rate	99.9%	
Anthracene conversion rate	100%	
Benzanthracene conversion rate	100%	

As seen, the overall conversion of tars in this case is slightly higher than the conversion of the plant. From the designed system 1.06kW of Net energy is needed to reduce the temperature of the particular syngas flow from 850°C to 110°C and to subsequently heat the oil flow from 25°C to 108.46°C. At Gussing catalytic system, the temperature is increased from 850°C to 900°C. However, the Gussing's syngas flow is initially cooled down to 160-180°C to remove dust from the flow by passing the gas through filters. According to that, the Net energy needed to cool and then heat the particulate gas flow is only 2.3kW which is approximately twice higher than the one needed in the wet model. Nonetheless, the catalytic reformer of Gussing's plant needs extra energy for pretreatment before the 12-hour operation until the catalyst deactivates. That pretreatment includes preheat of the reformer at 850°C by a constant helium flow (20ml/min) as well as a 1 to 2-hour constant hydrogen flow to increase the selectivity of the reformer. Additionally, during the reformer's operation an extra vapor stream is needed to drive the steam reforming reactions and decrease the formation of carbon at the catalyst pellets. (Pfeifer & Hofbauer, 2008) These data were not provided in the literature and could not be used in further comparison. The heating requirements of Guessing's experiment and simulation cannot be compared to the previous designed models as the tested syngas flow for this model was lower than the ones of TUD and Synvalor. As proven by the designed system simulation, the heat requirements for the Guessing's produced gas are lower than the presented experiment. This primarily occurs due to the decrease of the syngas temperature initially at the experiment in order to pass through filter. If hot filtration was used in the experiment, the heat requirements of the dry method would be less than the model's.

For the designed wet model 35.2L of pure biodiesel were found to be needed for every hour in order to clean syngas to the desired tar levels. As was mentioned in Chapter.3, oil recovery systems can offer 73% of oil recovery. Consequently, only 9.5L/h of fresh biodiesel could be needed to achieve the desired gas cleaning. Subsequently, for a 12-hour operation biodiesel consumption would cost approximately 7.00$. On the contrary, Gussing's reformer uses 400mg of Ex 3256 catalyst every 12 hours of operation which costs around 0.33$. A brief economical estimation suggests that, Gussing's dry cleaning system operational costs are inexpensive in comparison to the model in this project, as expected. However, the potential of producing chemicals as by-products, as mentioned on the Chapter 3.1 and the extra cost of pretreatment (which could not be calculated) may change the overall perspective of the two models. Additionally, more traditional methods recommend, using waste oil streams as feed to the gasifier as biomass fuel or by burning it in order to provide heat to the process. Both of these methods are able to decrease the economic impact of using organic liquids as absorber agents. In order to build an objective comparison between the two models, detailed economical models for the system's operational cost must be carried out to visualized the economic influence of these methods.

7. Conclusions and Discussion

Syngas cleaning systems are reasonably complex systems, yet have been proven to be vital in providing a high purity product which will not cause any further complications in the usage of the product gas. Tar impurities may be the smallest fragment of contaminants in the produced syngas flow, however, as demonstrated in commercialized gasifiers, where the production is continuous, the problems caused by these compounds indicate the need to eliminate them. The primary aim of this project was to deliver two realistic/accurate models in AspenPlus software for tar treatment. The models were created to draw comparison between the two main tar treatment methods; dry and wet. The target of the project was to create these models in order to provide realistic outcome of the syngas outflow. The dry model was generated unsuccessfully due to lack of data in the literature based on the occurring reactions in a catalytic reformer. On the contrary, a wet model was designed successfully. The wet model was designed in order to estimate the optimum operation conditions of the system which minimize the energy and mass consumption.

Five questions were outlined in the introduction of this project. In this final chapter, these questions are answered according to the obtained results from the simulations as well as the literature review.

- Are dry cleaning methods more promising than the already developed wet cleaning methods?
  - According to the literature review carried out in Chapter.2, dry cleaning technologies are more promising in terms of energy saving, environmental impact and economical costs. However, this is not true for all dry technologies, as thermal and plasma cracking methods are more energy consuming than traditional wet methods. Additionally, the potential use of an oil recovery technology, recirculation of the oil's waste stream back to the gasifier for further gasification or use as a fuel to provide heat to the gasifier, will make wet cleaning technologies more neutral waste systems. This will minimize waste production and thus will make the wet system more environmental.
  - The dry simulation models designed in AspenPlus showed a reduction in energy demand when compared to the wet simulation. 0.53KW and 0.52KW were the estimated energy demands for the designed primary dry model at constant temperature by PFR and CSTR, respectively. The net energy consumption from the tested wet designed models were estimated 21.67KW for TUD simulation and - 17.65KW (cooling energy) for the Synvalor simulation, which were two gradients higher than the dry models. However, the results from the dry model were not realistic when compared with the wet model as the reactions that were modeled were taken from different experiments. Toluene concentration was effectively eliminated from the tested TUD's syngas flow, yet the dry model did not meet the initial targets of the project (tar concentration for methanol synthesis). Additionally, the consumption of biodiesel in the wet model was minimized due to the designed air-stripper model.

More than 90% of the biodiesel flow was estimated to be recovered in order to be reused. In the dry systems, the amount of catalyst that was used in the reformers was 0.3g for the designed primary dry model reformer. These amounts of catalyst were proven to operate for 12 hours, and even with 90% of oil recovery systems, the operational cost of a dry method was found less than those of a wet method. If an oil recovery system could operate with 100% recovery efficiency only then wet method would be more economical competitive than a catalytic reformer.

- Can AspenPlus results be accurate enough in order for the program to be used for the design of a real optimal cleaning system?

  - AspenPlus is an efficient tool for modelling numerous processes. This project proved that AspenPlus software can be used effectively for the design of experimental lab-scale cleaning systems to the design of industrial-scale cleaning systems. The two experimental articles found in Chapter 5.1, as well as the Synvalor's cleaning system, were simulated successfully with high precision on their results compared to the actual data. AspenPlus results from all the tested flows followed results of the experiments. The biggest deviation was measured at Synvalor's validation model, where the actual Acenapthylene conversion rate was by 6% lower than the result from the simulation.

- Which conditions affect final product's tar concentration in a cleaning system, and how?
  - Catalyst loading, reactor volume/residence time and heat are the main parameters that are significant in the catalytic cleaning method. Sensitivity analysis were not derived for the dry model due to overlapping of the modeled reactions and errors that occurred in AspenPlus. Based on results of the dry model's simulation, however, tar conversion was higher during the constant temperature operation than in adiabatic operation. From this it can be concluded that higher temperatures are optimizing the conversion of tars. The variance of temperature or heat is strongly depended on the chosen catalytic material and on the tar compounds contained within the syngas flow.
  - For the wet cleaning method; oil's flow rate, oil's temperature, syngas temperature and absorber design were found as the key parameters affecting tar removal. As was shown by the sensitive analysis simulations of the wat model calculated in Chapter 5.3, oil's volumetric/mass flow rate was the most crucial factor for tar absorbance in a continued process. In low flow rates oil is incapable of absorbing the required amount of tars, as the oil reaches its saturation point in tar concentration prematurely in the absorber. By increasing the oil's flow rate, tar concentration at the exit of the system is decreased exponentially, as more fresh oil is available to absorb tar compounds. Another significant condition was found to be the oil's temperature at the inlet of the absorber. During the simulations in this project, it was decided that the syngas temperature at the exit of the oil absorber would remain higher than 110°C in

order to keep the majority of water vapor in the syngas. This decision was made in order to remove the water content of syngas during the last water scrubber, with the decrease in the temperature serving to avoid the creation of waste water downstream. The proposal was carried out as expected, as the water at the exit of the water scrubber consisted only by traces of the non-condensable gases (CO, H_2, CH_4, CO_2), toluene, benzene and biodiesel that was evaporated during the oil absorber operation. However, oil at low temperature could absorb tars more efficiently. By increasing oil's temperature, it was revealed, that tar concentration in syngas at the outlet is being increased exponentially. The primary reason for this occurrence is related to the viscosity of the oil. According to literature and empirical experiments discussed in this project, low viscosity oil is more efficient in absorbing tar compounds from syngas (Tarnpradab, et al., 2016). Furthermore, syngas temperature is a significant factor in tar absorbance. As it was proven by the sensitivity analysis simulations of the wet model syngas temperature does not have a significant impact on the syngas tar concentration at the outlet of the absorber. However, if syngas temperature is high enough it will cause oil evaporation. Thus, oil liquid with high vapor pressure and boiling point can effectively serve as absorbing agent, as it can absorb tars in higher temperatures without evaporating.

The final parameter affecting tar absorption was found to be the absorber/scrubber column design. This parameter was not discussed in depth in the presented project, however, specifications such as vessel volume/absorber stages, tray size/type and packing size/size are some of the most important constraints for tar absorbing. As shown in this project smaller size reactors or columns offer lower efficiency in tar absorbing as the residence time of the absorbing agent and syngas inside the reactor is low for the organic agent to absorb the desired amount of tars.

- How can water consumption and waste water streams be reduced?
  A variety of different ways to decrease/eliminate waste water streams were described and discussed in this project. The designed wet model used biodiesel in high temperatures to absorb the majority of tars from the tested flows without contaminating the water in the water scrubber. Successfully, as revealed in the results, the water at the water scrubber's outlet had minor undetectable traces of tar compounds. From this, it can be concluded that the water stream may be reused for many cycles, if a secondary cooling system is available to cool the heated water at outlet of the water scrubber. Nonetheless, in real wet cleaning systems water scrubber technology is also responsible for absorbing other contaminants. Especially, Nitrogen based contaminants are very soluble in water. For syngas flows rich in polar tar compounds as well as other contaminants such as NH_3 and H_2S, water absorber is responsible for the absorption of those compounds. Another technique that is applied by many technologies is the use of oil as both an absorbing agent as well as a cooling agent. However, this approach neglects the water content of syngas stream which will condense and therefore extra waste oil treatment will be needed.

Additionally, if an oil-absorber will be designed successfully to absorb the desirable amount of tars, waste water streams will be reduced if air, refrigerant liquids, or heat exchangers are used for syngas cooling instead of water cooling systems. Finally, all the dry cleaning techniques should have zero waste water streams if t designed effectively.

- Can a high purity organic liquid be separated from tars?
  A series of oil recovery technologies were outlined in the literature review. From these technologies only two are commercially available; Air-stripper and the Centrifugal Discharge Filter System. These systems are primarily designed to recover other streams (e. g. water, oil from dust, etc.) however they are also effective in removing tars from organic liquids with relatively high efficiency. Other technologies are more adapt at removing certain tar classes from oil. For example, DES technology is focused on removing polar tar compounds from oil rather than heavy PAHs. Consequently, depending on the syngas tar composition the use of the discussed non-commercialized technologies may be more suited. Furthermore, a wet cleaning model was designed in order to illustrate air-stripper technology. Simulations showed that an oil stream with 99% oil molar purity could be recovered. Successfully, from the obtained results of the simulations, that were carried out for all the wet models, air-stripper model was able to recover more than 90% of the waste oil stream. Based on this result, it can be concluded that air-stripper technology is effective to deliver a high purity recovered oil stream in order to be reused for many cycles into the oil-absorber system. As was revealed, the separation efficiency of air-stripper technology is strongly related with the molecular weight of tars. According to the obtained results from the air-stripper models simulations (from the first wet model with TUD data and with saturated concentrations) the separation efficiency of the technology is decreased when working with heavier tar compounds. This will have a large impact on the technology's energy and economic consumption, as treating oil flows with larger fractions of heavier tar species, higher flows and temperatures of air will be needed. Additionally, as proven by the air-stripper simulation results in Chapter 5.3, at higher temperatures the fraction of recovered oil is being decreased. 96% of waste oil was recovered in the first wet model simulation using TUD data (Chapter 5.2.2), while 90% of oil recovery was obtained by the air-stripper model with tars saturated concentration (Chapter 5.3). It is expected if heavier tars are included in the produced syngas, (e.g. Synvalor syngas flow) air-stripper removal and recovery efficiency will be decreased in comparison with the tested simulations.

- How efficient is tar absorption in organic liquids?
  In this project organic liquids were shown to be effective in the absorption of tars. Individual models for estimating tars saturation point in the tested methyl-palmitate oil (biodiesel) were made. The saturation point of tars was found to differ when testing individual tar compounds with a mixture of tar compounds. According to the results

obtained from the simulation with TUD syngas flow, the tar compound with the highest saturation point was phenanthrene with saturation concentration at approximately 7 g/L. followed by its isomer anthracene with saturation concentration of 3g/L. The saturation concentration of the remaining tar compounds was found lower than 2 g/L. As previously mentioned, oil's temperature is a significant variable for tar absorption from organic streams. Organic liquids at lower temperatures are proven to be more efficient in absorbing tars than oils at higher temperatures. During the simulations of this project temperatures higher than the dew point of tars were used, as AspenPlus cannot distinguish between different phases of a mixture, and thus tar condensation needed to be avoided. The models were hence tested with both flows of biodiesel and syngas at 100°C, as in higher temperatures oil evaporation was noticed. In this temperature regime, many individual tar compounds were impossible to be tested due to their low dew point. From the tested compounds, Naphthalene was found to be the most soluble tar compound in biodiesel, with saturation concentration of 69 g/L. A model testing Naphthalene's saturation concentration in biodiesel at 70°C was also tested. The purpose of this simulation was to create a comparison with similar bibliographic data for Naphthalene saturation concentration in various organic liquids. As it was revealed, the obtained by the simulation result was slightly increased compared to the results obtained by Seidell (1919). According to Seidell (1919) the saturation concentration of Naphthalene in toluene liquid was found to be 97.5g/L, compared to 99.8g/L found in this project for Naphthalene's concentration in biodiesel. The increased Naphthalene's concentration in biodiesel can be justified by the more viscous behavior of biodiesel oil, compared to the organic liquids that were tested by Seidell (1919). Saturation concentration models also simulated the non-condensable gases present in syngas. It was found that tar compounds were exceedingly more soluble than permanent gases in the organic absorber. The maximum saturation concentration for the non-condensable gases was obtained for CO_2 at 0.25g/L.

Recommendations

In order to design an accurate catalytic cleaning method which delivers realistic results, experiments based on every tar compound must be carried out, to determine the kinetics of the reactions that occur on each compound under a given catalytic treatment. The experiments must be carried out under same conditions such as Pressure, temperature, flow and catalyst particle. A further study on catalyst material, design, occurring reactions of tar compounds on a catalyst is required, as dry systems are more sustainable and more economic than the wet systems. Furthermore, as AspenPlus was proven to be an accurate software in simulating wet cleaning technologies, it would be optimal to use the Aspen dynamic system to test the recirculation of the organic liquid through the absorbing column. By using dynamic analysis, the user would be able to observe the system's operation through time, offering information about the systems energy consumption, overall production, oil's tar concentration, as well as operation conditions such as temperature and pressure, at any stage of the process. Finally, detailed economic models based on the initial and operational cost of the wet systems must be carried out, in order to create a

better comparison between wet and the dry systems. Waste oil streams can be recovered by using an appropriate oil-recovery system, recirculate back to the gasifier as biomass fuel or be burned to provide heat to the system. Additionally, the possibility of separating recovered tars into chemical should be further study as it can affect the economic prosperity of a cleaning system. These methods can reduce a great fraction of the operational costs of the system, as biodiesel price is high compared to water or energy prices.

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Appendix A

Tars Classification, Regulations and Price

Table A. 1Classification of tar compounds Morf, Hasler, & Nussbauner, 2002)

Tar compound class	Compound type	Compound name
Primary tar compounds	Acids	Acetic acid
		Propionic acid
		Butyric acid
	Ketones	Acetol (1-hydroxy-2-propanone)
	Phenols	Phenol
		2,3-Dimethylphenol
		2,4/2,5-Dimethylphenol[a]
		2,6-Dimethylphenol
		3,4-Dimethylphenol
		3,5-Dimethylphenol
	Guaiacols	Guaiacol
		4-Methylguaiacol
	Furans	Furfural
		Furfural alcohol
		5-Methylfurfural
Secondary tar compounds	Phenols	Phenol
		o-Cresol
		p-Cresol
		m-Cresol
	Monoaromatic Hydrocarbons	p/m-Xylene[a]
		o-Xylene
Secondary/ tertiary tar[b]	Monoaromatic hydrocarbons	Benzene
		Ethylbenzene
		a-Methylstyrene
		3&2-Methylstyrene
		4-Methylstyrene
		3-Ethyltoluene
		4-Ethyltoluene
		2-Ethyltoluene
	Miscellaneous hydrocarbons	2,3-Benzofuran
		Dibenzofuran
		Biphenyl
		Indene
	Methyl derivatives of aromatics	2-Methylnaphthalene
		1-Methylnaphthalene
		Toluene
Tertiary tar compounds	PAH: 2-ring	Acenaphthylene
		Acenaphthene
		Fluorene
		Naphthalene
	3-ring	Phenanthrene
		Anthracene
		Fluoranthene
		Pyrene
	4-ring	Benz[a]anthracene
		Chrysene
		Benz[e]acephenanthrylene
		Benzo[k]fluoranthene
	5-ring	Benzo[a]pyrene
		Perylene
		Dibenzo[ah]anthracene
		Indeno[1,2,3-cd]pyrene
	6-ring	Benzo[ghi]perylene

Table A. 2 EU regulations for PAH's (Chemical Inspection and Regulation Service, 2012)
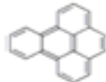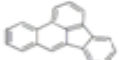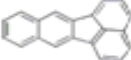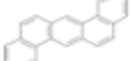
Name	CAS	Structure	Limits
Benzo[a]pyrene	50-32-8		1 mg/kg
Benzo[e]pyrene	192-97-2		
Benzo[a]anthracene	56-55-3		Sum of 8 PAHs < 10mg/kg
Chrysene	218-01-9		REACH has designated ISO 21461 as standard testing method for 8 PAHs in tyre.
Benzo[b]fluoranthene	205-99-2		For extender oil, IP346 is used.
Benzo[k]fluoranthene	207-08-9		According to the ISO 21461, tyres are compliant with the restriction on PAHs if the concentration of vulcanizates compound is not greater than 0.35% of Bay proton's limit.
Benzo[j]fluorant	205-82-3		
Dibenzo[a,h]anthrancene	53-70-3		

Table A. 3 EU limits for PAH's in Materials (Chemical Inspection and Regulation Service, 2012)

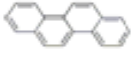| Parameter	Category 1	Category 2	Category 3
	Material in contact with foodstuff, or materials intended to be put in the mouth and toys for children age of < 36 months	Materials with foreseeable contact to skin for longer than 30 seconds (long-term skin contact) and toys not covered by category 1	Materials with foreseeable contact to skin up to 30 seconds (short term skin contact) or without skin contact
Benzo(a)pyrene mg/kg	Not detectable(< 0.2)	1	20
Sum 18 PAHs (EPA) mg/kg	Not detectable(< 0.2)	10	200

Table A. 4 Tars prices

Substance	grade	Price (€/g)	TUD's tar concentration in oil's waste stream ($g_{tar}/m^3_{syngasin}$)	Guessing's tar concentration in oil's waste stream ($g_{tar}/m^3_{syngasin}$)	TUD tar profits	Guessing tar profits
Benzene	>99.9%	0.06	1.47	0	0.02	0
Naphthalene	1	0.02	0.39	2.7	0	0.01
Phenol	1	0.29	0.01	0	0	0
Toluene	0.99	0.05	0.59	0	0.01	0
Styrene	0.99	0.01	0.12	0.19	0	0
Indene	0.98	13.04	0.09	0.38	0.23	0.99
Anthracene	0.99	1.31	0.01	0.19	0	0.05
Ethylbenzene	1	0.09	0.05	0	0	0
Xylenes	1	0.01	0.01	0	0	0
Acenapthylene	0.75	3.13	0.08	0	0.05	0
1-CH3-naphthalene	1	0.77	0.11	0	0.02	0

2-CH3-naphthalene	1	0.03	0.03	0	0	0
Acenaphtene	1	1.67	0.03	0.66	0.01	0.22
Fluorene	1	0.34	0.01	0	0	0
Phenanthrene	1	0.84	0.03	0.45	0.01	0.08
Benz[a]anthrene	1	109.5	0	0.5	0	10.88
Total			3.03	5.07	0.35	12.23

B.1 Wet Model's Validation Models

Table B. 1 Paethanom, et al, (2012) article's data

Oil flow rate		0.5 lt/min	
Oil Temperature		27 ºC	
Oil Pressure		0.0095 MPa	
Main flow rate		0.00149968 cum/min	
Main Temperature		65 ºC	
Main Pressure		0.0095 MPa	
Tar flow rate		0.14055 g/min	
Tar Temperature		65 ºC	
Tar Pressure		0.0095 MPa	
Tar flow compounds (Mass Fraction)		**Non-tars flow compounds (Mole Fraction)**	
Benzene	0.709	Hydrogen	0.1148
Phenol	0.00985	Carbon Monoxide	0.419
Toluene	0.11032	Carbon Dioxide	0.1744
Styrene	0.05516	Methane	0.0198
Indene	0.0433412	Nitrogen	0.6491
Naphthalene	0.063041		
Xylene	0.0059101		
Phenanthrene	0.003378		

Table B. 2 Phuphuakrat et al, (2010) article's data

Oil flow rate		0.5 lt/min	
Oil Temperature		28 ºC	
Oil Pressure		1 atm	
Main flow rate		0.0015 cum/min	
Main Temperature		32.5 ºC	
Main Pressure		1 atm	
Tar Temperature		32.5 ºC	
Tar Pressure		1 atm	
Tar flow compounds (Flow rate (gm/min))		**Non-tars flow compounds (Mole Fraction)**	
Benzene	0.02325	Hydrogen	0.1148
Phenol	0.000018	Carbon Monoxide	0.419
Toluene	0.0024	Carbon Dioxide	0.1744
Styrene	0.000675	Methane	0.0198
Indene	0.00087	Nitrogen	0.6491
Xylene	0.00009		

B.2 TU Delft's Gasifier Data

Table B. 3 TUD Dry wood pellet composition

Moisture (wt%)	Ash (wt%)	C (wt%)	H (wt%)	N (wt%)	S (wt%)	O (wt%)
6.48	2.29	48.77	5.98	0.19	0.76	42.01

Table B. 4 Raw Syngas Main Compounds Concentrations (at vol%) from TUD gasifier

H_2	CO	CO_2	CH_4	N	H_2O	Total
11.48	4.19	17.44	1.98	6.21	58.72	100.00

Table B. 5 Tar concentration into the TUD gasifier produced Syngas

Compound	Formula	Concentration(g/m³)
benzene	C_6H_6	1,47
phenol	C_6H_6O	0,01
toluene	C_7H_8	0,59
styrene	C_8H_8	0,12
indene	C_9H_8	0,09
naphthalene	$C_{10}H_8$	0,39
ethylbenzene	C_8H_{10}	0,05
xylenes	C_8H_{10}	0,01
acenaphthalene	$C_{12}H_8$	0,08
1-CH3-naphthalene	$C_{11}H_{10}$	0,11
2-CH3 naphthalene	$C_{12}H_{12}$	0,03
acenaphthene	$C_{12}H_{10}$	0,03
fluorene	$C_{13}H_{10}$	0,01
phenanthrene	$C_{14}H_{10}$	0,03
anthracene	$C_{14}H_{10}$	0,01
fluoranthene	$C_{16}H_{10}$	0,00
pyrene	$C_{16}H_{10}$	0,00
benzo(a)anthracene	$C_{18}H_{12}$	0,00
chrysene	$C_{18}H_{12}$	0,00
benzo(b)fluoranthene	$C_{20}H_{12}$	0,00
benzo(k)fluoranthene	$C_{20}H_{12}$	0,00
benzo(a)pyrene	$C_{20}H_{12}$	0,00
dibenzo(ah)anthracene	$C_{22}H_{14}$	0,00
benzo(ghi)perylene	$C_{22}H_{12}$	0,00
indeno(cd)pyrene	$C_{22}H_{12}$	0,00
Total		3,02

Table B. 6 ECN Online Tool- Dew Point Calculator for TUD syngas data (ECN-E&S, 2016)

Compound ○ ⬆ ⬇	Molecular Weight [g/mol] ⬆ ⬇	Concentration [mg/m$_n^3$]	
Benzene	78.11	5301.940834	5301.940834
Toluene	92.14	2127.989859	2127.989859
Ethylbenzene	106.17	180.3381236	180.3381236
m/p-Xylene	106.16	36.06762472	36.06762472
o-Xylene + Styrene	106.17	432.8114967	432.8114967
Phenol	94.11	36.06762472	36.06762472
Indene	116.16	324.6086225	324.6086225
Naphthalene	128.18	1406.637364	1406.637364
2-methylnaphthalene	142.2	108.2028742	108.2028742
1-methylnaphthalene	142.2	396.7438719	396.7438719
Acenaphtylene	152.19	288.5409978	288.5409978
Acenaphtene	154.21	108.2028742	108.2028742
Fluorene	166.23	36.06762472	36.06762472
Phenanthrene	178.24	108.2028742	108.2028742
Anthracene	178.24	36.06762472	36.06762472
		Clear	Remove
		Calculate	Load
Total			10928.49029098
Dew point (K)			359.6
Dew point (°C)			86.4
Name			TUD
Time			2016-03-10 22:20:14

B.3 Synvalor's Gasifier Data

B.4 Guessing's Gasifier Data
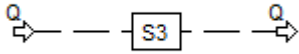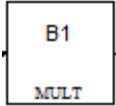
Table B. 7 Guessing's Gasifier Syngas-Plant Data

Operation Conditions	
Total Flow	100 Nm^3/hr
Bed Material	Olivine
Gasifier's outlet Temperature	850°C
Pressure	5 bar
Fuel	Wood Chips
Reformer Operation	
Residence time	0.8s
Temperature	900 ^{o}C
Diameter	50mm
length	100mm
Space Velocities	1100 [m$_N^3$/m^{3}h]
Catalyst load	400mg
Catalyst Composition	
NiO	40[wt.%]
Al2O3 and other oxides (SiO2, Na2O, K2O)	1.3 [wt.% K]
Main Gasses Composition	
Carbon Monoxide (CO)	13.23%
Carbon Dioxide (CO$_2$)	12.75%
Methane (CH$_4$)	6.21%
Hydrogen (H$_2$)	21.38%
Water (H$_2$O)	42.79%
Other	3.64%
Composition and concentration of compounds in Tars (before reformer)	
Overall Tar Concentration (dry gas)	8.5 (g/Nm^3)
Naphthalene	58%
Acenaphtylene	12%
Indene	9%
Phenanthrene	7%
Styrene	5%
Anthracene	3%
rest	6%
Composition and concentration of compounds in Tars (after reformer)	
Overall Tar Concentration (dry gas)	0.02 (g/Nm^3)
Total Conversion Rate	99.8%
Naphthalene conversion rate	99.9%
Acenaphtylene conversion rate	99.8%
Indene conversion rate	100%
Phenanthrene conversion rate	99.6%
Styrene conversion rate	99.7%
Rest conversion rate	99.6%

Produced Power	
Fuel power	8 MW
Electrical power	2 MW
Thermal power	4.5 MW

Table C. 1 AspenPlus modules

Module	Scheme	Operation	Operating Parameters	Comments
Mixer		Mixing two or more Streams	-	Was used mainly to mix the main gasifier's products with tars
Heater		Providing Heat to Streams	Temperature Pressure	Pressure drop was neglected
RadFrac		Serve us an absorber column	Number of Stages Heat or Cool provided	
Pump		Increase the pressure of the stream	Temperature Pressure	Pump efficiency was assumed 0.7
Heat		Heat line	Start – End Temperature or Duty	Carry heat in and out of the modules
Mult		Multiplying the conditions of an inner streams by factor	Multiplication factor	It was used for steady state "snapshots" in time
Material		Stream line	Temperature, Pressure, Flow rate and concentration	Carry material in and out of the modules

Conversion rates results from AspenPlus Simulations

Table D. 1 Conversion rate results from AspenPlus Wet Model using TUD data

Specie	Conversion Rate (%)
H_2	0.53%
CH_4	2.24%
CO	1.06%
CO_2	5.13%
N_2	1.09%
H_2O	98.32%
Benzene	100.00%
Phenol	100.00%
Toluene	100.00%
Styrene	100.00%
Indene	100.00%
Naphthalene	**100.00%**
Ethylbenzene	100.00%
Xylene	100.00%
Acenaphthalene	100.00%
1-CH3- Naphthalene	100.00%
2-CH3- Naphthalene	100.00%
Acenaphthene	100.00%
Fluorene	100.00%
Phenanthrene	100.00%
Anthracene	100.00%

Table D. 2 Conversion rate results from AspenPlus Wet Model using Synvalor's data

H_2	**0.01%**
CH_4	0.06%
CO	0.03%
CO_2	0.13%
N_2	0.03%
H_2O	31.49%
Naphthalene	99.99%
Acenapthylene	100.00%
Fluorene	100.00%
Anthracene	100.00%

Phenanthrene	100.00%
Fluoranthene	100.00%
Pyrene	100.00%
Benoz(a)antracene	100.00%
Chrysene	100.00%

- $C_6H_6 + 6H_2O \leftrightarrow 6CO + 9H_2$
- $C_6H_6 + 12H_2O \leftrightarrow 6CO_2 + 15H_2$
- $C_6H_6 + 6CO_2 \leftrightarrow 12CO + 3H_2$
- $C_6H_6 \leftrightarrow 6C + 3H_2$
- $C_7H_8 + 7H_2O \leftrightarrow 7CO + 11H_2$
- $C_7H_8 + 14H_2O \leftrightarrow 7CO_2 + 18H_2$
- $C_7H_8 + H_2O \leftrightarrow C_6H_6 + 2H_2 + CO$
- $C_7H_8 + 2H_2O \leftrightarrow C_6H_6 + 3H_2 + CO_2$
- $C_7H_8 + 10H_2 \leftrightarrow 7CH_4$
- $C_7H_8 + H_2 \leftrightarrow C_6H_6 + CH_4$
- $C_7H_8 + 7CO_2 \leftrightarrow 14CO + 4H_2$
- $C_7H_8 + 11CO_2 \leftrightarrow 18CO + 4H_2O$
- $C_7H_8 \leftrightarrow 7C + 4H_2$
- $C_{10}H_8 + 10H_2O \leftrightarrow 10CO + 14H_2$
- $C_{10}H_8 + 20H_2O \leftrightarrow 10CO_2 + 24H_2$
- $10H_8 + 10CO_2 \leftrightarrow 20CO + 4H_2$
- $C_{10}H_8 \leftrightarrow 10C + 4H_2$

Table E. 1 Methane Steam Reforming Kinetics for Chapter 6.1.. according to (Hacarlioglu, 2007)

		A (molPa$^{0.5}$Kg^{-1}$_{cat}$S^{-1})	E$_A$(KJmol^{-1})	K$_p$ (923K)
Reaction 1:	r_A $$= \dfrac{k_1\left(p_{CO}p_{H2O}p_{H_2}^{-2.5} - \dfrac{p_{CO}p_{H_2}^{0.5}}{K_{p1}}\right)}{(den)^2}$$	$3.71251*10^{17}$	240.1	2.649
Reaction 2:	$r_B = \dfrac{k_2\left(p_{CO}p_{H2O}p_{H_2}^{-1} - \dfrac{p_{CO_2}}{K_{p2}}\right)}{(den)^2}$	$17.17*10^7$	67.13	1.913
Reaction 3:	r_C $$= \dfrac{k_3\left(p_{CH_4}p_{H2O}^2 p_{H_2}^{-3.5} - \dfrac{p_{CO_2}p_{H_2}^{0.5}}{K_{p3}}\right)}{(den)^2}$$	$8.9587*10^{16}$	243.9	

$$DEN = 1 + K_{CO}P_{CO} + K_{H_2}P_{H_2} + K_{CH_4}P_{CH_4} + \frac{K_{H_2O}\left(P_{H_2O}\right)}{P_{H_2}}$$

$$k_j = A_j * \exp(-\frac{E_{A_j}}{RT}) \quad \& \quad K_J = B_j * \exp(-\frac{\Delta H_j}{RT})$$

Table E. 2 Pre-exponential factors and Enthalpies of formation for the steam reforming reactions

Species	B_j (Pa^{-1})	ΔH(KJ/mol)
CO	$8.23*10^{-10}$	-70.65
CH$_4$	$6.64*10^{-9}$	-38.28
H$_2$	$6.12*10^{-14}$	-82.9
H$_2$O	1.77	88.68

Table E. 3 Kinetics & Thermodynamics of various reactions

Reaction	Pre-exponential Factor A (s-1)	Activation Energy E_a (KJ/mol)	Enthalpy of formation ΔH^o (KJ/mol)	Reaction Rate expression	Reference
$CH_4 + H_2O \rightarrow CO + 3H_2$	7.26×10^6	75.6	206	$r_A = \dfrac{k\left(p_{CH4}^{0.5} p_{H2O}^{-1.25} p_{H_2}^{-1.25} - \dfrac{p_{CO} p_{H_2}^{1.75} p_{H_2O}^{-0.5}}{K_{p1}}\right)}{(den)^2}$	(Padban & Becher, 2005)
$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$	7.24×10^{10}	211.5	165	$r_A = \dfrac{k\left(p_{CH_4} p_{H_2O} p_{H_2}^{-0.5} - \dfrac{p_{CO_2} p_{H_2}^{2.25} p_{H_2O}^{-1}}{K_{p3}}\right)}{(den)^2}$	(Hoang, Chan, & Ding, 2005) (Liu, 2006)
$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	22471	76	247.3	*Assumed*	(Hoang, Chan, & Ding, 2005)
$C_6H_6 + 6H_2O \rightarrow 6CO + 9H_2$	2×10^{16}	443	-	$r_A = k * C_{C6H6}^{1.6}$	(Li & Suzuki, 2008)
$C_6H_6 + 6CO_2 \rightarrow 12CO + 3H_2$	608	57	-	*Assumed*	(Caprariis, et al., 2014)
$C_6H_6 \rightarrow 6C + 3H_2$	1.39×10^{12}	141	-82.88	$r_A = k * C_{C6H6}^{1.37}$	(Haghighi, Rahimpour, Raeissi, & Dehghani, 2013)
$C_6H_6 + H_2O \rightarrow CO + 3C + 2CH_4$	4×10^{16}	443	-	$r_A = k * C_{C6H6}^{1.3} * C_{H2}^{-0.4} * C_{H2O}^{0.2}$	(Abdelouahed, et al., 2012)
$C_7H_8 + 7H_2O \rightarrow 7CO + 11H_2$	3.3×10^{10}	247	869.97	$r_A = k * C_{C7H8}^1$	(Oliveira & Silva, 2013)
$C_7H_8 + 14H_2O \rightarrow 7CO_2 + 18H_2$	51.2×10^7	196	647	$r_A = k * C_{C7H8}^1 * C_{H2O}$	(Swierczynski, Courson, & Kiennemann, 2007) *(Li & Suzuki, 2008)*
$C_7H_8 + H_2 \rightarrow C_6H_6 + CH_4$	1×10^{12}	247	104	$r_A = k * C_{C7H8}^1 * C_{H2}^{0.5}$	(Jess, 1996) (Abdelouahed, et al., 2012)
$C_7H_8 + 7CO_2 \rightarrow 14CO + 4H_2$	608	57	-1163	*Assumed*	(Hoang, Chan, & Ding, 2005) (Simmell, Kurkela, Stahlberg, & Hepola, 1996)
$C_7H_8 \rightarrow 7C + 4H_2$	1.39×10^{12}	141	50.17	$r_A = k * C_{C7H8}^{1.37}$	(Haghighi, Rahimpour, Raeissi, & Dehghani, 2013)
$CO + H_2O \rightarrow CO_2 + H_2$	7.68×10^9	274.1	-41	$r_A = \dfrac{k\left(p_{C0} p_{H2O}^{0.5} p_{H_2}^{-0.5} - \dfrac{p_{CO_2} p_{H_2}^{2.25} p_{H_2O}^{-1}}{K_{p2}}\right)}{(den)^2}$	(Bustamante, et al., 2005)
$C_{10}H_8 + 10H_2O \rightarrow 10CO + 14H_2$	1.7×10^{14}	350	-	$r_A = k * C_{C10H8}^{1.3}$	(Li & Suzuki, 2008)
$C_{10}H_8 + 2H_2O \rightarrow 3CH_4 + 2CO + 5C$	1.7×10^{15}	350	-	$r_A = k * C_{C10H8}^{1.6} * C_{H2O}^{-0.5}$	(Jess, 1996)
$C_{10}H_8 \rightarrow 1/6 C_6H_6 + 3.5H_2 + 9C$	3.4×10^{14}	350	-	$r_A = k * C_{C10H8}^{1.6} C_{H2}^{-0.5}$	(Abdelouahed, et al., 2012)
$C + H_2O \rightarrow CO + H_2$	5.09×10^4	238	131.3	*Assumed*	(Alselaa & Elfghi, 2014)
$CO_2 + C \rightarrow 2CO$	1.12×10^8	245	173	$r_A = k * C_{CO2}^1 * C_C$	(Osakl & Mori, 2006) (Alselaa & Elfghi, 2014)
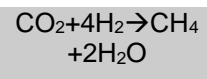
$CO_2+4H_2\rightarrow CH_4$ $+2H_2O$	$7.75*10^6$	69.06	-165	$r_A = k * C_{CO2}^{0.3} * C_{H2}^{1.2}$	(Richter, G.Benish, A.Mazyar, Green, & Howard, 2000) (Brooksa, Hua, Zhub, & Kee, 2007)