Final report

BIO-BASED FLEXIBLE PRODUCTION OF TRANSPORTATION FUELS IN A COMBINED PYROLYSIS-GASIFICATION PLANT (BIO FLEX)

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PREFACE

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SUMMARY

The sustainable society requires an efficient and selective energy system in which biofuels play an important role and thus, reliable, and efficient conversion routes for their production are required. Contrary to traditional routes for production of renewable transportation fuels from biomass, the production of highly valuable intermediates such as light olefins (C_2 - C_4) allow highly selective production of diesel and/or gasoline via the Mobil olefins to gasoline and distillates (MOGD) process. This process scheme is advantageous because can produce a very valuable intermediate (olefins) and therefore can benefit the chemical industry as well.

This report documents the assessment of the feasibility of making liquid transportation fuel (gasoline and diesel) precursors from biomass via thermochemical treatment (i.e., gasification and pyrolysis). More specifically, three different process schemes for production of lower olefins were considered: (i.) O₂ blown biomass gasification and olefins synthesis from the derived syngas; (ii.) integrated pyrolysis of biomass with O₂ gasification of char with combined production of olefins from pyrolysis vapours and syngas;(iii.) same as case (ii.) but with air as gasifying medium.

The synthesis of liquid fuel precursors proceeds via the production of light olefins (C_2 - C_4) and their subsequent conversion to liquid fuels via MOGD.

Given the logistics limitations of biomass, small to medium plant sizes were considered in the study (5-50 MW_{th} of biomass heating value). The production of carbon containing liquid fuel precursors is more efficient when the biomass is pyrolyzed and the produced char subsequently gasified achieving nearly 40% of carbon conversion compared to the direct gasification of biomass with O_2 which exhibits ~29% carbon efficiency. All the scenarios investigated were heat self-sufficient and flexible in adjusting the product composition according to fuel market demand by altering the operating conditions (temperature, pressure) of the oligomerization reactors (MOGD). Around 18-27% of the available carbon in biomass is lost to CO_2 while trying to adjust the syngas composition for olefins production. The carbon selectivity to olefins both from the biooil to olefins and the syngas to olefins processes are in the vicinity of 60% and advances in catalysis can further improve the overall carbon efficiency.

The requirement for pure O_2 in gasification step is capital intensive with costs for air separation and compression representing 10-13 % of the total capital investment. Therefore, considerable cost reduction can be achieved if other means of O_2 supply/generation are employed. In connection to the latter and the high carbon penalty paid in the syngas composition adjustment, synergies with renewable hydrogen production via electrolysis seem suitable to boost the overall carbon efficiency (theoretical carbon efficiencies >50% can be achieved) and at the same time provide pure oxygen supply for the gasification of char. The best-case scenario (biomass pyrolysis-air gasification of char) for a 50MWth plant indicated a capital investment of 1 700 000 SEK/bpd of liquid product is needed with a total production cost of 10.33 SEK/l.

Concluding, the integrated pyrolysis gasification with parallel upgrading of bio-oil and syngas to light olefins offers considerably higher carbon efficiencies when compared to stand alone gasification of biomass. Improvements in catalysis for syngas and bio-oil upgrading and direct CO_2 hydrogenation as well as synergies with renewable hydrogen technologies can benefit both the carbon conversion and the process economics.

SAMMANFATTNING

I ett samhälle med ett effektivt och flexibelt energisystem kommer bränslen framställda från biomassa att spela en framträdande roll. För produktionen behövs pålitliga och effektiva omvandlingsprocesser. Med hjälp av värdefulla kolinnehållande mellanprodukter, i detta fall specifikt s.k. lätta olefiner (C_2 - C_4), går det att uppnå en större selektivitet i bränsleproduktionen än vad traditionella produktionsprocesser från biomassa kan erbjuda. Det alternativa konceptet kallas oligomerisering, eller "Mobil olefins to gasoline and distillates" (MOGD). En fördel med MOGD är att den producerade mellanprodukten, olefiner, också kan användas i kemiindustrin.

Den här rapporten redovisar möjligheter att producera olefiner från biomassa via termokemisk behandling (förgasning och pyrolys), som kan användas för att framställa transportbränslen (bensin och diesel). Tre olika processkonfigurationer för olefinproduktion utvärderades:

- 1. Biomassaförgasning och syntes av olefiner från den producerade syntesgasen
- 2. Tvåstegsinteragerad termokemisk omvandling av biomassa (pyrolys och förgasning *med syrgas*), kombinerat med produktion av olefiner från både pyrolysångor och syntesgas
- 3. Tvåstegsinteragerad termokemisk omvandling av biomassa (pyrolys och förgasning *med luft*), kombinerat med produktion av olefiner från både pyrolysångor och syntesgas

Studien avgränsades till små till medelstora anläggningar (5–50 MW termisk biomassa, högt värmevärde) för att minska transportkostnaderna för biomassa.

Resultaten indikerar att produktionen av olefiner är effektivast processkonfiguration 3, pyrolysförgasning tillsammans med en parallell uppgradering av bioolja och syntesgas till lätta olefiner. Där uppnås en kolverkningsgrad på nära 40 %, vilket kan jämföras med kolverkningsgraden för fristående förgasning av biomassa, som är 29 %.

Scenarierna som undersöktes var självförsörjande på värme samt var flexibla i justeringen av driftsförhållandena (temperatur och tryck) i reaktorerna för MOGD för att kunna anpassa produktionen av olefiner till varierande förhållanden mellan bensin och diesel i den vidare drivmedelsproduktionen. 18-27 % av det tillgängliga kolet förloras som koldioxid när syntesgasens sammansättning justeras för olefinsyntesen. Kolselektiviteten för olefiner ligger i närheten av 60 % för båda processerna bioolja till olefiner och syngas till olefiner.

Förgasning kräver syrgas, och kostnaderna för luftseparation och kompression utgör 10–13% av den totala kapitalinvesteringen. Genom att utnyttja synergier med förnybar vätgasproduktion går det att göra både betydande kostnadsminskningar och producera syrgas, samtidigt som en teoretisk total kolverkningsgrad på över 50 % skulle kunna uppnås. Förbättringar av katalytiska processer för uppgradering av syntesgas och bioolja, liksom direkt koldioxidhydrogenering, skulle gynna både kolomvandlingen och processekonomin ytterligare.

Det mest lovande konceptet i utvärderingen indikerar en kapitalinvestering på 1,7 MSEK/fat per dag, och en total produktionskostnad på 10,33 SEK/liter av olefiner för en anläggning i storleksordningen 50 MW (termisk biomassa, högt värmevärde).

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LIST OF ABBREVIATIONS

AC	Annualized Cost or Activated Carbon
ANN	Artificial Neural Network
ASF	Anderson–Schulz–Flory
BOP	Balance Of Plant
bpd	Barrels-per-day
Ĉ CU	Carbon Capture and Utilization
CECPI	Chemical Engineering Plant Cost Index
daf	Dry ash-free
ETO	Ethanol-to-Olefins
FCC	Fluid Catalytic Cracking
FT	Fischer – Tropsch
FTO	Fischer – Tropsch-to-Olefins
GCC	Grand Composite Curve
GHSV	Gas Hourly Space Velocity
HHV	Higher Heating Value
HRSC	Heat Recovery Steam Cycle
HT-WGS	High Temperature Water Gas Shift
IC	Indirect Cost
IGCC	Integrated Grand Composite Curve or Integrated Gasification Combined Cycle
LHHW	Langmuir-Hinshelwood-Hougen-Watson
MOGD	Mobil's Olefins to Gasoline and Distillate
MTG	Methanol-to-Gasoline
MTO	Methanol-to-Olefins
PSA	Pressure Swing Adsorption
SE-WGS	Sorption Enhanced Water Gas Shift
TC	Total Cost
TDC	Total Direct Cost
VSA	Vacuum Swing Adsorption
WGS	Water Gas Shift
WHSV	Weight Hourly Space Velocity
ZSM-5	Zeolite Socony Mobil-5

1 INTRODUCTION

The strive to re-establish a suitable and long-standing environment in which human activity and nature thrive together passes through the sustainable development goals set by UN. The Agenda 2030 highlights the actions and targets that are needed to address environmental and social challenges to achieve the sustainable development goals [1]. Such challenges include among others the climate change, the depletion of natural resources, loss of bio-diversity, inequality and geopolitical instability [2]. A total of 169 goals has been set to guide the transition to a more sustainable society and economy by 2030 [3].

Bioenergy can support clean energy supply, local societal and economic growth, preserve the environment and the natural resources, and increase energy independence; thus, its role is pivotal in a sustainable society. Sweden has set a goal of reducing emissions from domestic transport by 70 % in 2030, compared to 2010 [4]. This has incentivized the need for transforming the production of transportation and new processes for bio-based transportation fuels are needed. The transformation will necessitate 5.5 Mm³ of bio-based transportation fuels in 2030 [5]. At the same time, changing demand of fuel type (gasoline or diesel) [6] require processes that could offer a flexible product composition, based on sustainable raw materials.

Biomass is the main source of renewable carbon, and processes allowing its efficient conversion to various valuable energy carriers, would help to reshape the transportation fuel market. Currently, there is a large theoretical potential of 4.5 Mm³ for sustainably produced lignocellulose-based liquid fuels in 2030 [5]. Thermochemical conversion of biomass (i.e. pyrolysis and gasification) is one of the known ways to convert renewable carbon into vapour/liquid and gaseous for the synthesis of transportation fuels, which could replace fossil fuels, utilizing the existing infrastructure and transportation fleet [7–9] (Figure 1).



Figure 1. Simplified representation of thermochemical route for biomass conversion to transportation fuels.

Several synthesis routes for production of transportation fuel from the thermochemical treatment of biomass have been developed and analysed with most of them suffering from low carbon

efficiencies, low flexibility, or unselective product distribution [12–14] that delimit the economical and operational margins of the standalone processes. Nevertheless, a higher carbon utilization can be achieved by integrating the pyrolysis and gasification and benefitting from the synergies between them [10]. This integrated system would require a shared synthesis route aiming at high carbon efficiency, as shown in Figure 2.



Figure 2. Conceptual synergetic thermochemical route for transportation production of transportation fuel from biomass.

Carbon efficiency (η_c) indicates the degree of carbon utilization within the boundaries of a system and is defined as the ratio of the useful carbon obtained from the process (carbon in desired product- in the context of this study, it the carbon in the transportation fuel) to the incoming carbon (the carbon contained in the biomass).

$$\eta_C = \frac{C \text{ in desired product(s)}}{Incoming \ C}$$

Given the different nature of the products obtained from pyrolysis and gasification, a shared fuel synthesis route would require a common precursor-intermediate (chemical carrier) deriving from the two different processes. Therefore, integration of pyrolysis and gasification should aim for efficient conversion to an intermediate-platform product that can be converted efficiently to liquid transportation fuels. This combined approach would add flexibility and improve efficiencies, especially with the advances in the field of catalytic treatment of both pyrolysis vapours (bio-oil) and gasification-derived gas (syngas) [11,12].

Such intermediate is the light, or lower, olefins (C_2 - C_4), a chemical commodity of great importance for the (petro)chemical industry [13], which has also been used for synthetic gasoline production through the Methanol-to-Olefins (MTO), Ethanol-to-Olefins (ETO) and Methanol -to-Gasoline (MTG) processes [14,15]. Hence, the production of lower olefins could potentially offer higher carbon efficiencies than catalytic deoxygenation of pyrolysis oil for production of liquid fuels precursors (see also section 2). The direct conversion of syngas to lower olefins can substantially improve carbon efficiency by being more selective than traditional synthetic routes (such as Fischer Tropsch) and thus achieving a higher overall carbon conversion [16]. The production of liquid hydrocarbons in the gasoline and diesel range can be materialized via the olefins oligomerization according to Mobil's olefins to gasoline and distillate process (MOGD) [14].

Light olefins (ethylene, propylene, and butylene) are also building blocks of pivotal importance in the chemical industry and their oligomerization can yield important feedstock for the chemical and manufacturing industries. In this fashion, production of light olefins from biomass is a pathway that could ensure local economic growth even after complete electrification of the transportation fleet.

This work aims at scrutinizing the technical and economic feasibility of an integrated pyrolysisgasification plant to produce liquid fuels via olefins intermediate in a try to achieve a more carbon efficient route for transportation fuels production from biomass.

Three different process schemes for production of lower olefins were considered:

- i. O₂ blown biomass gasification and olefins synthesis from the derived syngas.
- ii. Integrated pyrolysis of biomass with O₂ gasification of char with combined production of olefins from pyrolysis vapours and syngas.
- iii. Pyrolysis of biomass integrated with air gasification of char for combined production of light olefins.

The difference among the schemes lies in the thermochemical treatment that biomass undergoes, and the oxidizer used in the gasification section. The study of the first process scheme is used as a baseline for the standalone biomass treatment (gasification) scheme given that gas to liquids processes via gasification are well-established in commercial scale [17]. The standalone biomass gasification process scheme considers O_2 gasification of biomass in an entrained flow reactor due to the high carbon conversion that this type of reactor can achieve (for details see section 2). The integrated pyrolysis gasification process considers other types or reactors which are also described in section 2.

The production of liquid hydrocarbons for all process schemes is carried out by the MOGD process. The investigation includes the necessary alternation in process conditions (and thus the techno-economic outputs) to tailor the hydrocarbons mixtures to current and future gasoline to diesel ratios (G/D) for the Swedish market.

In the next section, the different processes and their characteristics are described. The selection of the technologies is justified and a rationale for conceptual process synthesis is presented. This includes any technical implications arising from their selection.

In section 3, modelling approaches for each individual process unit is presented. Parametric studies of the main unit operations are carried out in order to investigate the process conditions that maximize carbon conversion to desired products for each individual unit.

Section 4, details the integration of the individual process models and the obtained results for fuel mix (gasoline/diesel) for the years 2020 and 2030, together with technoeconomic analysis.

In the last section concluding remarks are made and recommendations for future research are presented.

2 BACKGROUND

In contrast to other renewable sources of energy, biomass is the only resource that could supply with liquid, gaseous and solid energy carriers, as well as commodity chemicals. Forest logging residues in Sweden have the energy potential of 24-98 PJ y⁻¹ [18,19] and together with the forest industry by-products, originating primarily from sawmills, have the potential to become an important actor for efficient biofuel production by converting biomass residues, to higher value fuels via thermochemical processes rather using it for combustion purposes [20–22] (Figure 3).



Figure 3. Wood flow for the forest industry. Taken from [23].

Thermochemical treatment of the lignocellulose residues provides a sustainable way to produce the renewable liquid fuels that the Swedish market requires [24]. The two main thermochemical processing techniques are pyrolysis and gasification.

Biomass pyrolysis (thermal decomposition in the absence of air) is a promising and versatile way to produce liquid feedstock that could potentially replace fossil-based transportation fuels. It takes place at temperatures of 400-500°C producing mainly a liquid product (also known as bio-oil), a solid carbon (char) and gaseous products. Their proportions depend on the pyrolysis conditions and feedstock [7]. Typically pyrolysis aims at maximizing the liquid product, nevertheless, the high water and oxygen content of the bio-oil give rise to undesired properties such as such as corrosiveness, chemical and thermal instability, high viscosity, and incompatibility with conventional fossil-based fuels [7,25]. Therefore, catalytic treatment of pyrolysis oil is needed which aims at reducing the oxygen content of the crude bio-oil (also known as bio-crude). Catalytic

pyrolysis is an upgrading route for producing more stable liquids to be used as a feedstock for fuel production in existing infrastructure [26]. This is realized using catalysts inside the biomass pyrolysis reactor to directly convert the newly formed unstable vapours to stabilized liquid hydrocarbons (Figure 4).



Figure 4. Catalytic pyrolysis concept for production of fuel compatible hydrocarbons. Taken from [27].

However, this in situ treatment results in low carbon efficiencies at commercial scale (KioR) [28]. Generally, the higher the deoxygenation degree, the higher is the stability and compatibility of the liquid with the fossil-based hydrocarbons. The effect of degree of deoxygenation on the carbon (and thus energy) efficiency of catalytic pyrolysis process is shown in Figure 5.



Figure 5. Degree of deoxygenation (ξ_0) vs carbon (η_c) and energy (η_E) efficiencies for catalytic pyrolysis using different catalysts. Taken from [28].

The high catalytic activity of deoxygenation catalysts results in formation of light gaseous hydrocarbons instead of liquid deoxygenated molecules. Thus, in lieu of catalytic pyrolysis, the development of a process able to convert the pyrolysis vapours to gaseous hydrocarbons which can be used for synthesizing liquid fuels could conceptually offer increased carbon efficiencies [12].

Gasification of biomass refers to another thermo-chemical conversion technique that allows the solid biomass (or any other carbonaceous material) to be converted to a mixture of combustible gases (also known as producer gas) containing mainly CO and H₂. The process takes place at elevated temperature, in excess of 700 °C, in the presence of a sub-stoichiometric amount of oxygen, to avoid complete combustion [29]. The composition of the producer gas is highly dependent on the type of feedstock, gasification reactor, process conditions such as temperature, pressure, or the oxidizing agent. Typically, the main goal of a gasification process is to convert the solid biomass to a gas mixture containing CO and H₂ that can be used for synthesis purposes, also known as syngas. Therefore, based on the carbon efficiency definition given above (section 1), a maximum carbon efficiency from gasification process is obtained when the carbon entering the gasifier is converted to carbon monoxide.

 $\eta_{C,gasfication} = \frac{amount \ of \ C \ in \ CO}{Incoming \ amount \ of \ C \ in \ the \ gasfier}$

Practically, this requires some steps of gas conditioning and composition adjustment after the gasification to obtain the syngas. The conversion of the synthesis gas to liquid transportation fuels

can be realized by a process discovered by Fischer and Tropsch and from a chemical perspective it is the production of long chain hydrocarbons by hydrogenation of carbon monoxide [30].

$$nCO + \frac{m+2n}{2}H_2 \rightarrow C_nH_m + nH_2O$$

The products of the FT process consist of several compounds which are mainly linear paraffins and α -olefins [31].

Biomass gasification integrated with Fischer-Tropsch (FT) synthesis is commonly investigated as route for production of renewable liquid fuels because it has the potential to convert biomass into liquid hydrocarbons that could match the market specifications of fossil-based transport fuel and therefore can be integrated into the existing infrastructure [32] (Figure 6).



Figure 6. Gasification-FT route for production of transportation fuels from biomass.

However, FT products follow the Anderson–Schulz–Flory (ASF) distribution, which is inherently wide and unselective [33] and limits the overall carbon conversion to specific products [10].

The ASF product distribution of the FT process is depicted in Figure 7, which shows the weight fraction (w) of the different products formed with different carbon numbers (C_n), and the probability (α) that a formed molecule will continue to react to form a longer chain molecule (chain growth probability) [34]. This probability depends on the catalyst and the operating conditions. The weight fraction of a certain chain length is determined by [35]:

$$w = n(1-\alpha)^2 \alpha^{n-1}$$

As shown, methane (C_1) will always be the largest single product; to avoid its formation (gasoline and diesel molecules have carbon numbers greater than C_6) chain growth probability should approach one. However, at α close to one the prevailing products have chain lengths of more than 20 carbon atoms, which exceeds the chain length for diesel fuel [36] and thus additional cracking of FT longer chain products is needed to obtain liquid transportation fuels [35].



Figure 7. ASF product distribution (w-weight fraction) as a function of chain growth probability (α) of FT process.

Overall, both the pyrolysis and the gasification-based routes to transportation fuel via bio-oil catalytic deoxygenation and FT suffer from low carbon efficiencies.

Another route frequently investigated for synthetic gasoline production is the conversion of biomass-derived syngas into methanol and its subsequent conversion to gasoline (via processes involving olefins conversion) is the methanol-to-gasoline process (MTG) developed by Mobil (now ExxonMobil) [37]. However, fuel mix demand which currently is shifted towards diesel fuels, with a significant demand for gasoline fuel still in place [38], necessitates the production of both gasoline and diesel.

Unlike the MTG process, which produces only gasoline range hydrocarbons, one of the most versatile ways to produce a mixture of synthetic gasoline and diesel is Mobil's Olefins-to-Gasoline and Distillate (MOGD) process. Originally, MOGD was designed to operate coupled to methanolto-olefins (MTO) process [14]. The requirement for converting syngas to methanol as an intermediate to generate olefins can be eliminated because recent developments show that direct synthesis of lower olefins from syngas could be achieved with high selectivity (more than 70 %) [11,39,40] without following the limiting ASF product distribution of the FT process. Typical effects of process parameters on the olefin selectivity of the current FT process are shown in Table 1.

Parameter	Chain length	Chain branching	Olefin selectivity	Alcohol selectivity	Carbon deposition	Methane selectivity
Temperature	\downarrow	\uparrow	*	\downarrow	\uparrow	\uparrow
Pressure	\uparrow	\downarrow	*	\uparrow	*	\downarrow
H_2/CO	\downarrow	\uparrow	\downarrow	\downarrow	\downarrow	\uparrow
Conversion	*	*	\downarrow	\downarrow	\uparrow	\uparrow
Space velocity	*	*	\uparrow	\uparrow	*	\downarrow
Alkali content iron catalyst	\uparrow	\downarrow	\uparrow	\uparrow	\uparrow	\downarrow

Table 1	. Selectivity	Control in	FT Process.	Taken from	[31].
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Note: Increase with increasing parameter: \uparrow . Decrease with increasing parameter: \downarrow . Complex relation: *.

The MOGD process achieves the oligomerization of the light olefins to form higher molecular weight olefins that fall into the gasoline, distillate/diesel, and even lubricant chain length range. The gasoline obtained is more olefinic and aromatic and of better quality with a higher motor octane number than typical fluid catalytic cracking (FCC) gasoline [41]. The distillate product is mainly iso-paraffinic and has a very high cetane number contrary to typical FT process product that contains low octane normal paraffins [42]. Boiling range, flash point and viscosity are similar as to conventional middle distillates. MOGD process could also produce jet fuel. The process is characterized by a very high flexibility towards selective production (selectivity is greater than 95 % [43]) of either gasoline or middle distillates of attractive quality (distillate/gasoline ratios of 0.2/100 to 90/10 for commercial plants), depending on market requirements [11,12]. MOGD is applicable to a wide range of processes and has been tested using commercially produced catalyst in refinery-scale equipment [12].

Therefore, the conversion of pyrolysis-derived oil into olefins rich gas, by taking advantage of the 'simplicity' of its generation coupled to char gasification to generate syngas that is transformed directly to olefins could offer a processing advantage to synthesize the required intermediate (olefins) for efficient carbon utilization to gasoline and diesel fuels. In section 2.1 the different processes required for such system are presented, analysed and a conceptual processing scheme is synthesized.

2.1 CONCEPTUAL PROCESS DESCRITPION AND SYNTHESIS

2.1.1 Pyrolysis

Pyrolysis refers to the thermal decomposition of biomass in the absence of any oxidizer. During pyrolysis, complex macromolecules of biomass break down into relatively smaller molecules producing: (i) a solid residue also known as char which mainly consists of carbon and ash; (ii) gases (mainly CO, CO₂, CH₄, H₂ and other light hydrocarbons); (iii) vapours/liquids known as bio-oil or bio-crude (mainly oxygenates, aromatics, water, products of low degree of polymerization, tars, etc.) [7]. The proportion of the different product depends on pyrolysis conditions and feed-stock properties.

Based on the operating conditions, pyrolysis can be classified into: (i) slow pyrolysis, (ii) intermediate pyrolysis, and (iii) fast/flash pyrolysis. Slow pyrolysis occurs under very slow heating rates $(0.1-1^{\circ}C/s)$ and very long residence time with the major product of the process being the solid char. Intermediate pyrolysis occurs at higher temperatures (300–700°C) at a fast heating rate, with residence time ranging from 10–30 s [44]. Fast pyrolysis occurs in a temperature range of 300– 750°C, with a fast-heating rate, and very short residence time (~1–2 s). In fast pyrolysis, biomass decomposes to generate vapors, aerosol, and some char [44]. After condensation of vapors, a brown mobile liquid is obtained (bio-oil). Bio-oil (or bio crude) production from biomass pyrolysis is typically carried out via fast pyrolysis. Reactors for realizing fast pyrolysis of biomass include fluidized bed reactors, cone reactors etc. [7].

Bio-oil is a complex multi-component mixture of molecules derived from depolymerization and fragmentation of biomass building blocks, namely: cellulose, hemicellulose, and lignin. It can be classified into the following generalized categories: hydroxy-aldehydes, hydroxyketones, sugars and dehydrosugars, carboxylic acids, and phenolic compounds [45]. Due to its high thermal and chemical instability, once condensed the bio-oil is difficult to vaporize because of polymerization reactions, leading to coke formation, that are accelerated upon heating. Therefore, direct hot treatment-conversion is preferable for most carbon efficient utilization of bio-oil [7].

2.1.2 Gasification

The gasification process is a complex phenomenon consisting of several reactions that happen in series and in parallel. Some of the reactions taking place in the gasifiers are:

$$\mathcal{C}_{(s)} + \frac{1}{2}\mathcal{O}_{2(g)} \rightleftharpoons \mathcal{C}\mathcal{O}_{(g)} \tag{1}$$

$$\mathcal{C}_{(s)} + \mathcal{O}_{2(g)} \rightleftharpoons \mathcal{C}\mathcal{O}_{2(g)} \tag{2}$$

$$C_{(s)} + CO_{2(a)} \rightleftharpoons 2CO_{(a)} \tag{3}$$

$$C_{(s)} + H_2 O_{(g)} \rightleftharpoons 2CO_{(g)} \tag{4}$$

$$C_{(s)} + 2H_{2(g)} \rightleftharpoons CH_{4(g)} \tag{5}$$

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$$
 (6)

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons CO_{2(g)} \tag{7}$$

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons H_2O_{(g)}$$
 (8)

$$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons 3H_{2(g)} + CO_{(g)}$$
 (9)

$$CH_{4(g)} + CO_{2(g)} \rightleftharpoons 2H_{2(g)} + 2CO_{(g)}$$
 (10)

Different types of gasification technologies have been developed during the years. They are typically classified into three categories: (i) moving bed, (ii) fluidized bed, and (iii) entrained-flow

reactors. The difference in these technologies is mainly based on tar¹ production and heat and mass transfer mechanisms, operating temperature, and pressure as well as residence time of solids and the gases.

While moving bed gasifiers are more suited towards the production of heat and power from small to medium scale, entrained flow and fluidized bed gasifiers have been used for synthesis applications.

Entrained flow gasifiers operate at temperatures higher than 1000°C and are flexible in feedstock tolerance (biomass, coal etc.). The requirements for fuel particle size are very strict and typically particles ≤ 0.15 mm are used [46]. Due to very high operating temperature the produced gas is very clean, almost methane and tar-free [47].





Fluidized bed gasifiers operate at temperatures lower than 1000°C (but higher than 750°C [49,50] see Figure 9) and they are more flexible in particle sizes as biomass particles of few mm in size can be used [46].

¹ "all organics boiling at temperatures above that of benzene should be considered as 'tar'."[51].



Figure 9. Temperature profile of fluidised bed gasifiers. Taken from [48].

The tar content in the produced gas of fluidized bed gasifiers is higher than the one in entrained flow reactors [46]. The tar mainly originates from thermal decomposition (pyrolysis/ devolatilization) of biomass biopolymers (cellulose, hemicellulose, and lignin) in the first steps of conversion of biomass, generating organic vapors (primary tars) (Figure 10). The generated vaporized fragments undergo secondary reactions at higher temperatures producing the so called 'secondary tars'. At higher operating temperatures the secondary tars transform into aromatic structures and become more refractory thus difficult to convert [51].



Figure 10. Reaction sequence and potential paths for gasification. Taken from [52].

There are several measures to reduce the produced tar in fluidized bed gasifiers. Of primary means for tar reduction is the utilization of bed materials with tar cracking properties (such as olivine) and the use of secondary oxidizer (air or O_2) at the freeboard to increase the temperature and allow tar conversion [53]. Selection of proper bed material can result in more than 70 % reduction of the

heavy fraction of tar [54], while temperature increase can decrease the concentration of light hydrocarbons to more than 80 % and the total tar content to more than 50 % [53].

The separation of pyrolysis and gasification steps offers several advantages:

- The vapours from biomass pyrolysis constituting the major source of tar formation are stripped from the solid char and thus an essentially 'tar-free' gas production can be achieved in the gasifier (volatile matter remaining in the char is one tenth of the initial volatile content of the initial biomass content). Gasifier concepts using staged char gasification have demonstrated production of a tar-free gas (tar concentrations of 1mg/Nm³ or less) [55–58].
- The char produced from fast pyrolysis processes is extremely reactive which allow for efficient gasification [59–61].
- The organic vapours formed in the pyrolysis reactor do not contain any inorganic compounds due to the low pyrolysis temperatures and thus poisoning of the subsequent catalytic systems for pyrolysis vapour upgrading can be avoided [59,62]. The deactivation of the zeolite catalysts used to convert pyrolysis vapours into olefins mainly originates from the formation of coke which can be removed by oxidation or even converted to syngas [63]. Sulfur poising of metal modified ZSM-5 catalysts has been reported and originates from the bulky S-compounds of heavy oil-feeds leading to acid sites blocking. However, such compounds are not found in biomass pyrolysis vapours and the temperatures employed in conversion to olefins are high enough to ensure that poising is inhibited (> 400°C [64]).

2.1.3 Gas Cleaning

Gas cleaning is the link between gasification and the final gas use and therefore is dependent both on gasifier's operation and downstream gas requirements. Gas impurities need to be removed from the gasification gas (producer gas) because they constitute poisons for the catalytic processes for the synthesis of the transportation fuels. Those include the organic tars mentioned above, sulfur, and nitrogen heteroatom species (e.g., thiophene, pyridine) and need to be removed or reduced to below ppmv levels. Inorganic constituents containing sulfur (hydrogen sulfide-H₂S, carbonyl sulfide-COS), chlorine (hydrogen chloride-HCl), nitrogen (ammonia-NH₃, hydrogen cyanide-HCN), and alkali metals are also found in the gasification gas.

Organic compounds, other than tar, commonly found in product gas of gasification processes operating at temperatures below 1000°C include mainly methane. Hydrocarbons generally do not constitute a poison for synthesis applications but can polymerizate on the surface of the catalysts blocking the access to reacting molecules. Albeit tar levels at the exit of the gasifier are expected to be in the range of few mg/Nm³ (see also 2.1.2), measures must be taken to protect potential harmful effects.

Dolomite beds operating at 650°C can provide removal of at least the heavy tars compounds [65] and serve as a guard beds for chlorine compounds protecting other equipment [66]. Alkalis can

condense at temperatures below 650°C, forming particulates ($<5 \mu m$) and their removal can be facilitated by barrier filters [66]. Filtration of gas at temperatures around 600°C results also in small reduction of tar load in the gas by ~10 % [67].

Removal of sulfur-containing compounds can be achieved by a variety of removal strategies/technologies. Generally, the cleaning processes can be categorized as absorption, (physical/chemical), hybrid processes, hot carbonate-based, and solid adsorbent-based processes.

The absorption processes can be distinguished to physical and chemical depending on whether the processes utilize the solubility differences among the components in a solvent or they are based on chemical reactions between the impurities and a selected absorbent.

Physical absorption processes require high operating pressures and high acid gas partial pressures at low operating temperatures to obtain economic solvent loading since the solvent loading capacity improves at higher acid gas partial pressures and lower operating temperatures. Thus, the capital and operating costs of the physical absorption processes are generally higher compared to those of the amine processes, contributed by the high-pressure equipment and the additional heat exchange equipment and refrigeration required to achieve reduced operating temperatures. Hydrocarbons are soluble in most organic solvents to some degree, and that makes physical absorption processes not economical when there are high concentrations of hydrocarbons in the raw gas [68].

In a chemical absorption process, the acid gas compounds undergo reactions with the solvent to form chemical bonds. The solvent can be regenerated by heating, stripping the absorbed gases. A classic example of chemical absorption is the amine process.

Generally, amine processes are suitable for applications with low to medium acid gas concentrations as the economic benefits of the process decline with increasing partial pressures of acid gases [68]. The economy of the process is largely dependent on the heat duty requirements of the solvent regenerator and the solvent circulation rate, which is dictated by the solution capacity as well as its concentration. High concentrations reduce the circulation rate but increase the corrosion resistance requirements for the equipment and thus installation costs. Therefore, there is a maximum allowable concentration of solvent in the recirculated solution [68].

The physical and chemical absorption processes can remarkably improve the syngas purity and reduce H_2S , CO_2 and NH_3 content. However, the challenge is to minimize impurities level in an economical manner. Moreover, a final purification step is still required to achieve the low sulfur contents required for FT-like processes [69]. Absorption processes are well developed and operate in several variations around the world. However, they operate at very low temperatures and high pressures lowering the overall thermal efficiency. Moreover, such processes are complex and have high investment costs [70]. Royalty costs are also a significant cost to consider and their use is favored at large scale due to the economy of scale [70].

The hot carbonate process is a type of chemical absorption process where instead of amine solutions a hot potassium or sodium carbonate solution is used. It is primarily used for CO_2 removal and secondary for H_2S removal. Organic sulfur compounds (COS, RSH and CS_2) can also be removed to some extent. The process can be single staged, double staged or split flow. One big problem for application of hot carbonate process to the syngas cleaning is the high concentration of CO which reacts with the carbonate to form acetates [68,71].

Adsorption is a suited method for desulfurization of raw syngas because of the temperature range that the process can operate at [72]. It can be divided in low and high temperature adsorption.

At low temperature (~ambient temperature) adsorption, physical adsorption is the prevailing mechanism which has limited sulfur capacity. A typical example is the use of activated carbon to remove H₂S from biogas. Numerous processes are available for low temperature adsorptive desulphurization. However, advantages in processing, notably energy conservation and capital savings, make high temperature desulphurization attractive. At high temperature adsorption, chemisorption (which involves reaction of the adsorbent with the gas H₂S) prevails and is also called reactive adsorption. Reactive adsorption is superior to ordinary physical adsorption because of the stronger interactions between the adsorbent and the sulfur compounds thus increasing the desulfurization efficiency [73]. Syngas hot gas cleaning offers higher efficiencies and cost advantages when compared to low temperature methods.

The materials used for adsorption of H_2S are based on metal oxides and metals that react with H_2S and produce the corresponding metal sulfides. The most common metals and metal oxides include zinc oxide, copper/copper oxide, manganese oxide, nickel/ nickel oxide, iron oxide, lead oxide.

ZnO is the most used oxide for sulfur removal. With regards to the desulfurization activity zinc is active up to 1150° C with ZnS as the sulfided form and ZnO as the stable form of excess zinc. Due to formation of zinc vapor upon reduction of the oxide to metallic form the operating limit for ZnO is calculated around 700°C. Experimental observations have confirmed the formation of zinc vapor in similar atmospheres [74]. It has also been found that the ZnS formed from ZnO is active for the conversion of COS to H₂S, and the equilibrium of the conversion of COS to H₂S is controlled by [75]:

$$2COS + H_2 + H_2O \rightleftharpoons 2H_2S + CO + CO_2$$

 H_2S though, reacts more easily with ZnO than with COS. Most of the COS is converted to H_2S by catalytic hydrolysis and then reacts with ZnO, although a part of the COS may react directly with ZnO. H_2 accelerates the conversion of COS to H_2S , and the water-gas shift reaction accelerates the reaction between COS and ZnO. CO_2 does not affect the reaction[75]. Therefore, the reactions that can be considered at equilibrium for gas cleaning are:

$$CO_{2(g)} + H_2S_{(g)} \rightleftharpoons H_2O_{(g)} + COS_{(g)}$$
$$ZnS_{(s)} + CO_{2(g)} \rightleftharpoons ZnO_{(s)} + COS_{(g)}$$

Experimental studies using ZnO bed showed that the performance is not affected by highly concentrated tarry gas (11 g/Nm³) despite carbon deposition on the particle surfaces [76], and sulfur levels can be reduced to 2ppmv (bulk removal). Sodium carbonate was found to optimally remove chlorides at an operating temperature of 450°C [77].

A 2nd lower temperature (300-350°C) ZnO bed can reduce sulfur concentration to ppbv levels (concentrations well below 300 ppbv [76–78]), and can also help in removal of alkali.

Warm gas cleaning has been demonstrated in industrial scale IGCC plants with removal efficiency of H_2S and COS >99.95 % [79].

2.1.4 Syngas Tailoring (Water Gas shift Reactor)

The adjustment of the H_2 to CO ratio to desired levels for synthesis of the light olefins (stoichiometrically a H_2 :CO of 2 is needed) can be achieved using a water gas shift (WGS) reactor. The WGS reaction is a reversible chemical reaction between carbon monoxide and steam to form carbon dioxide and hydrogen.

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$$

From a thermodynamic point of view, the WGS reaction is not affected by the reaction pressure, nevertheless, up to a point, total pressure positively affects the CO conversion because it increases the reaction rates [80]. Based on the temperature and the reaction environment the water-gas shift catalysts are categorized as high temperature (300-450°C), low WGS (150 to 250°C), sour (tolerant to sulfur presence in the gas) and sweet (non-tolerant to S species in the gas) WGS catalysts.

Typical sour shift catalysts can convert COS and other organic sulfur compounds into H₂S, which also helps in capturing H₂S since it is removed more easily than COS from the syngas [81]. Sour catalysts require sulfur presence to remain active; however, Co-Mo sulfided catalysts, which can be used both at high and low temperature conditions, are also active in the absence of sulfur in the gas [82]. Indeed, Hakkarainen et al. [83] used non-sulfided commercial CoMo/Al₂O₃ in the absence of sulfur in the feed, which can be the case in biomass processing, and found that the catalyst acts in the WGS reaction mainly as an oxide catalyst and thus can still be active for the reaction. Iron based HT-WGS offers also protection to syngas-to-olefins reactor (FTO) by adsorbing residual sulfur or chlorine containing compounds [84]. Typically, Fe-Cr catalysts are used for HT-WGS.

Low temperature catalysts include Cu-based as well as noble metal catalysts. The low temperature WGS Cu catalysts cannot tolerate even traces of sulfur [80,85], which can particularly important when considering low grade fuels for biomass gasification. Hence, sulfur tolerant catalysts with high activity and selectivity for the WGS reaction are more desirable [80] since this will minimize any chance of poisoning [86].

Nevertheless, to avoid any H₂S slip from the WGS reactor to FTO unit, an intermediate ZnO guard bed can be placed a to ensure sulfur concentrations below few ppb. ZnO adsorbent can provide sulfur removal which offers protection equal to 20 times the annual catalyst replacement cost [87].

No effects of ammonia presence in long running tests was found for both HT- and LT- WGS catalysts up to concentrations of 100 ppm [87]. Similarly, no effects of HCN presence on HT-WGS up to 10 ppmv has been noticed. HT-WGS Fe_3O_4 Cr_2O_3 catalysts have been reported tolerant to H_2S concentrations of 540 ppmv. The combination of NH₃ and H₂S in the syngas feed results in H₂S uptake by the catalyst until bed saturation, though very little decrease in CO conversion activity was observed [87].

HT-WGS catalysts showed no sign of carbon deposition when exposed to tar containing stream at concentrations of 11mg/Nm³ [88]. Nevertheless, a tar content of 500 mg/Nm³ affect the WGS catalysts performance with the -OH and COO- containing compounds being more prone to irreversibly deactivate the catalyst's active sites. Conversely, biomass-derived tar compounds such as phenol and fluorene lead to reversible effects [89].

Reduction in WGS activity but stable performance has been observed by Moud et al. when exposing a Fe-based WGS catalyst directly to gas stream with biomass pyrolysis vapours at 400-450°C. No FT activity was observed and the reduction in WGS was attributed to coverage of the catalyst surface by oxygenated groups of the pyrolysis vapours. Post mortem analysis revealed that even after several hours of exposure to heavily loaded tarry gas the catalyst maintained at least 30 % of its initial WGS activity [90].

Integrating WGS reactors with CO_2 adsorption process can enhance the performance of the reactor if WGS catalyst and CO_2 adsorbent are mixed in the reactor bed or placed in multi-bed arrangement. Capturing CO_2 inside the WGS reactor allows more efficient CO conversion leading to smaller reactor sizes and increased CO_2 capture [78]. Different materials have been tested for CO_2 sorption with results indicating more than 95 % of CO_2 capture [91–95].

Concluding, warm gas cleaning and tailoring systems have been demonstrated and verified through the continuous operation at industrial and pilot scales, coupled to poison-sensitive and insensitive catalysts located downstream from the cleaning system with simultaneous capture of CO₂.

The above-described arrangement (dolomite bed, candle filter, ZnO bed, sorption-enhanced WGS) can ensure the gas meets compositional requirements for conversion to olefins.

Gas separation is of great importance in a gas-to-liquid process as performance of conversion steps relies very much on suitable gas composition and purity. Pressure swing adsorption (PSA) technology is already a mature technology in air separation, drying, and hydrogen purification [96]. PSA or VSA (vacuum swing adsorption)-a variant of swing adsorption at sub atmospheric pressure, have been used for natural gas and methane steam reforming gas separation [97–99], syngas separation [100] as well as olefins recovery [101,102] for different processes and thus are of commercial availability. Typical sorbents used are zeolites and activated carbons with different surface modifications for more efficient separations. Separation takes place usually at ambient temperatures and increased pressures (<10 bar).

2.1.5 Bio oil to olefins process

The conversion of bio-oil to olefins has not been reported in the literature extensively and no commercial unit has been built.

The various oxygenates in the oil/vapors respond differently to the cracking conditions. The conversion of individual oxygenates over different types of catalysts has been investigated, however little information exists when it comes to conversion of bio-oil to light olefins. Studies have mainly focused on conversion of model compounds such as alcohols, phenols, aldehydes, ketones and acids etc., with varying results and conclusions depending on the catalyst formulation and experimental conditions applied [103–106].

Based on the model compound studies, it is difficult to deduct 'optimal' operating conditions given the broad spectrum and different behavior of the chemical functionalities found in the biooil. As an example, alcohols generate their corresponding olefins by dehydration at low temperatures with the rate of dehydration of iso-alcohols being higher than that of linear ones. However, at temperatures exceeding 250°C, these olefins are converted to higher C_{5+} olefins which are then converted to paraffins and aromatics at temperatures above 350°C. At temperatures higher than 400°C, cracking occurs and the paraffins and aromatics are converted back to ethylene, propylene and butenes [104]. On the other hand, the conversion of furans (product of sugars dehydration[107]) into olefins is subject to debate given the contradictory conclusions made by different researchers. Studies have reported that when normal and substituted furans react over HZSM-5 and 4 % Ga/HZSM-5 at temperatures higher than 500°C coke formation prevails [105] while Cheng et al. [106] indicate that olefins selectivity increases at 650°C over similar catalysts.

As it can be understood, the information on individual chemical moieties does not allow for generalizations and therefore process conditions will be selected based on published data of actual biooil conversions.

2.1.6 Direct syngas conversion to olefins

The direct conversion of syngas to olefins has been long desired as it provides advantages in olefins processing industries and allows the more efficient utilization of biomass derived syngas. The processing advantage of the direct conversion of syngas to olefins is shown in Figure 11 [108].

Iron is the most used catalyst due to its low cost and high availability. It can be present in the form of Fe-carbide, magnetite, or α -Fe, consequently affecting the product distribution. It has been shown that reduced iron catalysts are highly selective towards olefin production. Iron catalysts are considered unstable, which explains the incorporation of promoters to enhance the stability and activity. Mn-promoted iron catalyst is proved to inhibit the formation of magnetite state, preserving the stability during the reaction, and increasing light olefins selectivity while reducing methane formation. Bifunctional catalysts can selectively convert highly reactive intermediates responsible for catalyst fouling and they have been excessively tested to produce light olefins in Fischer-Tropsch process. Bifunctional catalysts were found to increase the olefins yields and selectivity while keeping the methane production to the minimum. Their dual functionality led to the modification of the ASF distribution previously discussed [39,108].



Figure 11. Different processes for olefins production from syngas. Taken from [108].

As shown in Figure 12, the highest selectivity for olefins is obtained using K-promoted catalysts.

For high CO conversions (>70 %) temperatures higher than 300°C are needed, however this may lead to excessive carbon laydown on catalyst surface and thus its deactivation [108].

Bifunctional catalysts have been found to lead to higher C2-C4 olefins selectivity (80%) [11].



Figure 12. Some of the unsupported catalysts used in FTO process. Taken from [108].

2.1.7 Olefins oligomerization process (MOGD)

The MOGD unit operates at moderate temperatures up to 400 °C and variable pressures, ranging from 1 bar utilizing low pressure steam generation to remove the exothermic heat of reaction within the unit [13].

The oligomerization of olefins refers to the preparation of molecules consisting of only a relatively few monomer units as opposed to polymerization which implies the production of high molecular weight products [109]. Mainly heterogeneous catalysts are used for oligomerization with the main focus being on acidic zeolites, even though other acidic catalysts have been used [109].

Alkene oligomerization over acid catalysts has been motivated primarily by the need to develop processes to convert the low molecular weight alkenes to distillate quality fuels, while Ni based catalyst are used as dimerization catalysts or for the synthesis of high-octane gasoline [109].

Zeolites are the main type of catalysts reported in the literature to be used in oligomerization of olefins and have successfully being used at industrial scale for liquid fuels production in the MOGD process developed by Mobil [110,111].

The MOGD process utilizes ZSM-5 type zeolite, typically with a SiO_2/Al_2O_3 molar ratio of 70 including 35 wt% alumina[109]. The process can operate in distillate and gasoline mode. Depending on the reaction conditions, the gasoline to distillate ratio in the product may be varied between 0.12 and above 100 [112].

In the distillate mode, fixed bed reactors are typically used at temperature of around 300°C and at a weight hourly space velocity (WHSV) of 0.5-1. At such conditions olefins are transformed into distillate fuel with a cetane number after hydrogenation of over 55 [109] (minimum cetane number according to EN590 standard is 51[113]). The product is essentially 100 % olefinic with approximately one methyl branch per five carbon atoms[114], while the degree of branching being is independent of the initial reactant [115]. The typical layout of the MOGD process is shown in Figure 13.



Figure 13. The MOGD process. Taken from [116].

When the process operates in gasoline mode minimum distillates are produced and the temperatures employed vary between 285-375°C and the pressure from 4 to 30 bar [109]. Olefinic gasoline with a research octane number of 92 is formed in good yield [109].

Table 2 shows typical product properties of the gasoline-range and diesel-range material. While ethene is relatively unreactive in the distillate mode, its conversion can be greatly enhanced at the higher temperatures and lower pressures employed in the gasoline mode [117].

	Distillate	
	Raw	Hydrotreated
Specific gravity at 15°C	0.79	0.78
Pour point (°C)	<-50	<-50
viscosity at 40 °C (cS)	-	2.5
Cetane Number	33	56
90% B.P. (°C)	333	343
	Gasoline	
Specific gravity at 15 °C	0.73	
RON	92	
MON	79	

Table 2. Typical product specification from the MOGD process [109].

2.2 CONSIDERATIONS OF THE STUDY

The study investigates the production of liquid feedstock for transportation fuel production via the synthesis of light olefins and their subsequent oligomerization to fuel-range hydrocarbon chains via the MOGD process. The yield as well as the composition of liquid is of interest as the product

should reflect current and future fuel mix demand. Chain lengths with carbon numbers from 7 to 11 will be considered as gasoline range hydrocarbons while carbon numbers from 12 to 20 refer to diesel range product [36].

The potential for costs reduction in production of biofuels is limited by logistics limitations that biomass impose on centralised facilities[108,118], and thus small to medium plant sizes (\leq 50 MW_{th}) will be considered in the study. The fuel mix demand for gasoline and diesel is based on historical data with linear projection for 2030. Even though the approach is quite simplistic and does not consider fleet electrification, it still reflects the future trend. The rate of decline in gasoline demand is expected to be faster than fossil-based diesel (and thus the G/D ratio). Gasoline powers the majority of passenger cars [119] with an average age of 10-11 years (median value 10 years) [120], while 97 % of heavy duty tracks diesel-fuelled [120]. The fuel mix for passenger cars changes faster than for heavy duty trucks [120], indicating a faster penetration rate of more modern technologies and thus a faster decline in gasoline fuel. It is important to note that the study considers a fuel mix (G/D) and not actual volumes (Figure 14).



Figure 14. Fossil-based fuel consumption in Sweden and projection of gasoline to diesel demand in 2030. Source [24].

The process scenarios analysed as mentioned above, are based on different processing schemes for biomass treatment. The first scenario considers direct gasification of biomass in entrained flow gasifiers using oxygen and steam as oxidizing agents followed by direct synthesis of olefins that are used in the MOGD process. The conceptualized block diagram is shown in Figure 15.



Figure 15. Simplified block diagram of process scheme 1.

This gasification technology allows for high operating temperatures (>1000°C) and thus high carbon efficiencies (CO production) in the gasification with minimum tar formation (see also 2.1.2).

The second biomass processing scenario is based on integrated pyrolysis-gasification (or staged gasification), where the biomass is pyrolyzed (aiming at maximum oil/vapours production) and the produced char is gasified to produce additional CO (Figure 16).



Figure 16. Simplified block diagram of process scheme 2.

That kind of process (pyrolysis of biomass and autothermal gasification of char) can be realised in a twin fluidised bed system like the GoBiGas plant [121] or the cone reactor concept from BTG [122] or similar technologies [123]. The operating temperature of the gasification in such system is less than 1000°C.

The third processing scenario is identical to the second one, but air is used as gasifying agent instead of O_2 (Figure 17).



Figure 17. Simplified block diagram of process scheme 3.

The battery limit is the processing plant only, with biomass being delivered, sized and at a moisture level that meets the plant's demands. Biomass drying and preparation were not considered. Typical biomass composition is shown in Table 3.

Table 3. Biomass composition considered in the study.

Moisture wt% af	5
C wt% daf	51.2
H wt% daf	6.24
O wt% daf	42.45
N wt% daf	0.1
S wt% daf	0.01

The gas cleaning system is comprised of a cyclone for ash and particulate removal (>5 μ m), guard bed with dolomite operating at 650°C, candle filter for alkali and fine particulate removal (<5 μ m) operating at 600°C, a HCl sorption guard bed together with ZnO for bulk sulfur removal operating at 450°C, a low temperature ZnO/zeolite bed at 350°C for polishing the S and reducing ammonia content and a sorption enhanced HT WGS reactor able to sorb 90 % f CO₂[77]. Any remaining HCN is considered to be knocked out in the water condenser after the WGS reactor [87]. Condensation of WGS effluent is followed by activated carbon/zeolite filter to eliminate any light hydrocarbons and trace contaminants before the syngas to olefins (FTO) unit.

The syngas to olefins section consists of a reactor-separation train of three reactors in series operating at CO conversions of 50 %. This configuration was selected in order to remove the water vapour from the product stream by condensation (Figure 18). Increased steam partial pressure in the reactor results in: (i) lower reactant (CO and H_2) partial pressures and thus slower reaction kinetics, and (ii) increased conversion of CO to CO_2 via the WGS reaction.



Figure 18. FTO reactor train considered for olefins synthesis from syngas.

All gases separation is performed with PSA units using different sorbents depending on the gases to be removed/ separated.

For air separation in the gasification step PSA-VSA is considered, producing O_2 with purity of 99.5 +% [124,125].

In the absence of any commercial biooil to olefins process and detailed operating data or other key information, data from literature were extracted and incorporated in the developed models. As such, the results obtained should be regarded as sample findings for a conceptual process and not representative of performance of commercial processes developed by any technology providers.

3 PROCESS MODELLING

All the process units have been simulated using inhouse developed MATLAB models. The choice and the modelling approach for each of the process units in the different scenarios is detailed below. Parametric studies to evaluate the effects of the different process variables to each of the units have also been carried out to determine optimum conditions for maximizing the carbon efficiency per unit operation. The carbon efficiency for each of the process units is defined in the corresponding section.

3.1 GASIFICATION

Gasification is a complex process involving various chemical reactions, heat, and mass transfer processes. It is crucial to maintain high carbon efficiencies in this processing step to achieve a high carbon efficiency in the overall processing scheme.

Mathematical models of the gasification process provide insights about the significance of the operating parameters affecting the gasifier performance [126]. Reactor conditions, feedstock composition and oxidizer composition determine greatly the output gas composition and thus the carbon efficiency of the process. The carbon efficiency of the gasification process was previously defined as the amount of feedstock carbon that is converted to useful (useable) carbon for synthesis purposes (i.e., CO):

 $\eta_{C,gasfication} = \frac{amount \ of \ C \ in \ CO}{Incoming \ amount \ of \ C \ in \ the \ gasfier}$

The simplest models consider mass and energy balances throughout all the reactor to predict the composition of the produced gas, not considering detailed processes and chemical reactions, which for process evaluation purposes is satisfactory. Approaches for mathematical modeling of gasification process could generally be categorized into (a) kinetic and (b) artificial neural network (ANN) and (c) thermodynamic equilibrium [126].

Kinetic models are accurate and detailed but technology specific since reactor geometry and hydrodynamics must be considered and computationally intensive. Such models are able to predict concentration of impurities (mainly tar) that are far from thermodynamic equilibrium.

Equilibrium models use mass and heat balances over the entire reactor (irrespective of the technology). Unlike the kinetic models, no information about the influence of the hydrodynamic and geometric parameters can be obtained. Thermodynamic equilibrium modelling is mainly based on methods where Gibbs free energy of the system is minimized. When the Gibbs free energy is minimized, the reacting system is at its most stable composition and thus in chemical equilibrium.

Equilibrium models assume that gasification reaction rates are fast enough, and residence time is long enough to reach the equilibrium state. However, it should be noted that thermodynamic equilibrium may not be reached for all processes within the gasifier. Formation of intermediate products is mainly due to the relatively low operation temperatures, with product gas outlet temperatures between 750 and 1000°C as in process schemes 2 and 3, or short residence time of the gases in the gasifier [127].

The problems associated with the low gasification temperature are the overestimation of H_2 and CO yields and the underestimation of CO₂, CH₄, tars and char [128]. To compensate for non-equilibrium effects or reactions, several approaches have been used. Non-corrected thermodynamic equilibrium modelling is a good approach only in case of a high enough temperature throughout the reactor. Generally, the temperature needs to be higher than 1000°C to use non-corrected equilibrium models [7,128–130].

Non-equilibrium effects are treated by adding constrains such as restricted equilibrium approach and correction from experimental data. These additional constraints are related to physical entities without material content such as extent of reactions, heat losses etc. In preliminary and process optimization studies, constrained equilibrium models are sufficient [131].

The non-stoichiometric version of the Gibbs minimization method needs, no specification of the reaction mechanisms to resolve the problem, only the elemental composition of the feedstock as input; hence, it is mostly suited for biomass modelling [6]. Moreover, thermal losses are considered in the heat balances. This heat loss is usually considered as a fixed percentage of the thermal power entering with the biomass (e.g. 1 % , 5-10 % [132–136]).

In this study a restricted equilibrium approach was used, which accounted for non-equilibrium effects for methane content in the gas as well as heat losses. The model did not consider any tar formation and the produced gas was assumed to consist of CO, $H_2 CO_2$, H_2O , CH_4 , HCN, H_2S , COS, NH_3 and N_2 in the case of air gasification.

For char gasification (<1000°C process schemes 2 and 3), the losses were assumed equal to 3 % of the HHV of biomass due to the lower operating temperatures of the gasifier. In the latter cases the heat for the pyrolysis reactions which is provided by the gasifier was also considered as an additional heat sink (Figure 20).

Non-linear constraints were required for the water-gas shift (reaction 6 in section 2.1.2) and methane reforming (reaction 9 in section 2.1.2), as the minimisation results would not show these reactions to be in equilibrium otherwise. The effects of pressure were accounted for by using Peng-Robinson equation of state.

The temperature approach for thermodynamic equilibrium of methane was tuned against operating data from Cortus Energy pilot plant in Köping, Sweden. The temperature of approach for thermodynamic equilibrium was varied in order to minimize the deviation in gas composition obtained from the gasifier.



Figure 19. Modelling approach for gasification unit in process scheme 1.


Figure 20. Modelling approach for gasification unit in process schemes 2 and 3.

As shown in Figure 21, a maximum of carbon efficiency is obtained depending on the operating conditions. Maximum η_C is obtained at temperature of approximately 1250°C, whereas further increase in temperature results in reduced efficiencies because the heat to increase the temperature is supplied by additional oxidation of CO to CO₂ (increased λ).

The introduction of steam in the system (increased S/B) would result in reforming of CH₄ to produce additional CO and thus increase the η_C . However, steam reforming reaction is endothermic and lowers the temperature of the gasifier. Hence, additional O₂ is added (increased λ), to maintain the high temperature, which reduces the η_C .



Figure 21. Parametric study of the effects of air (λ) and steam to biomass ratio (S/B) on carbon efficiency (top) and effect of pressure and temperature on carbon efficiency (bottom).

Even though the model shows that the addition of steam reduces the carbon efficiency, steam needs to be added for more realistic simulation. In entrained flow reactors the tar content is drastically reduced at temperatures above 1000°C with steam addition, mainly because of the enhanced tar reforming reactions. Moreover, steam addition helps to reduce soot formation which is observed at temperatures higher than 1000°C [137]. The addition of steam has been reported to produce fewer refractory tars, which are considered as soot precursors and are harder to convert at high temperatures [51].

3.2 PYROLYSIS

Given that biomass pyrolysis involves numerous and complex reactions to yield the bio-crude, an exact reaction mechanism and kinetic model is extremely difficult; hence, pyrolysis is typically described by lumped models containing conceptual or pseudo-reactions. Researchers have proposed different schemes, but it is difficult to develop a precise kinetic model considering all the affecting parameters. Lumped models involving one or more reactions are mainly used [138].

Single global reaction models are oversimplified, while models with parallel reactions distribute the products according to operating conditions and time but still fail to give a good description of the final pyrolysis output. Kinetic models with secondary reactions provide more reliable data and are more appropriate for process design and simulation [7].

Single particle models have limited predicting power, while product quality and composition cannot be predicted at all [139].

In this study, data from Garcia-Perez [140] were fitted as a function of temperature. The fitting can predict the yields and C, H, O composition of liquid gaseous and solid products. The gaseous products include CO₂, CO, CH₄, C₂H₄, C₃H₆, C₂H₆, C₃H₈, H₂ and H₂O. In the absence of any data in the study, sulfur was assumed to be retained in the char at the temperatures of interest.

The energy of the pyrolysis reactions was determined based on a global energy balance of the isothermal pyrolysis model. The energy for the pyrolysis reactions can be provided by hot bed material coming from the gasification of char and therefore the energy of pyrolysis was considered as a heat sink in the gasification section. The enthalpies of the different products in vapor phase (except for char) was determined based on Yang et al. who developed rigorous correlations for determining enthalpy of formation and enthalpy changes of gas phase bio-oil based on H/C and O/C ratios in the bio-oil [141].

In Figure 22 the carbon selectivity of the pyrolysis process is shown. As pyrolysis temperature increases more carbon is converted to gaseous products with significant production above 500°C. Maximum carbon selectivity to bio-oil occurs in the temperature range of ~ 475 to 510°C. The temperature is negatively correlated to carbon in solid char. Carbon efficiency (η_c) for pyrolysis is determined as the total useful carbon of the pyrolysis products to the incoming carbon of biomass. The carbon contained in the is considered useful if it can be theoretically converted to olefins (and thus liquid fuel). This includes the carbon in bio-oil/vapours, char (it can be gasified and produce CO), and the gaseous CO, C₂H₄, C₃H₆. CO₂, CH₄ and C₂₋₃ paraffins are considered as carbon losses.

 $\eta_{C,pyrolysis} = \frac{amount \ of \ C \ in \ (bio - oil, char, CO, C_{2-3} \ olefins)}{amount \ of \ C \ in \ biomass}$

At maximum conversion to bio-oil, which is the desired carbon conversion of the pyrolysis process, the theoretical available carbon for subsequent conversion to desired olefins accounts for almost 94% of the initial carbon (of which, almost 52 % is in the bio-oil, approximately 40 % in the char and the rest in the pyrolysis gases).



Figure 22. Carbon selectivity and theoretical maximum carbon efficiency of pyrolysis as a function of temperature.

3.3 SYNGAS TO OLEFINS PROCESS

Unlike for gasification which can accurately be simulated with the use of equilibrium models because of high temperatures, the reaction kinetics of the CO hydrogenation processes (or Fischer-Tropsch like processes), need to be incorporated into a reactor model. The kinetic models of FT process can be classified into three categories: (1) models for overall reactant consumption, (2) models for hydrocarbon product distribution (selectivity models) and (3) comprehensive, or detailed, kinetic models describing both the overall reactant consumption and hydrocarbon formation rates [142]. A typical modelling approach for FT process is simply to fit the ASF distribution; however, extra reactions are usually added to account for the deviations from the ASF distribution [143]. Another approach for accounting for olefins production is to modify the chain growth probabilities and tune them with experimental data [39]. In this study the kinetics model over potassium promoted iron catalyst described in Do et al. [144] has been used. The kinetic parameters follow a Langmuir-Hinshelwood-Hougen-Watson (LHHW) type kinetic expressions with kinetic parameters estimation deriving from experimental data using artificial bee colony and differential evolution algorithms as reported by Najari et al. [145]. Due to the high exothermicity of the reactions involved, the reactor was considered to operate at isothermal conditions with water/steam as coolant. The reactions considered in the model include water gas shift reaction, CO hydrogenation reaction (FT reactions), and the direct CO₂ hydrogenation reactions:

 $CO + H_2O \rightleftharpoons CO_2 + H_2$ $CO + 3H_2 \rightarrow CH_4 + H_2O$ $2CO + 4H_2 \rightarrow C_2H_4 + 2H_2O$ $2CO + 5H_2 \rightarrow C_2H_6 + 2H_2O$ $3CO + 6H_2 \rightarrow C_3H_6 + 3H_2O$ $3CO + 7H_2 \rightarrow C_3H_8 + 3H_2O$ $4CO + 8H_2 \rightarrow C_4H_8 + 4H_2O$ $4CO + 8H_2 \rightarrow C_4H_{10} + 4H_2O$ $nCO_2 + 3nH_2 \rightarrow (CH_2)_n + 2nH_2O$

The process parameters affecting the selectivity to C_2 to C_4 olefins are the gas composition, expressed as H_2/CO and CO_2/CO ratios as well as the temperature. As shown in Table 4, very small H_2/CO ratios results in very low selectivity to olefins because of promotion of water gas shift reaction (and thus generation of CO_2) to produce hydrogen for the hydrogenation reactions. As the H_2/CO increased close to theoretical stoichiometric requirement of 2, the selectivity to olefins increases and so does the selectivity to the corresponding paraffins because of more available H_2 for hydrogenation. Further increase to more than 2.25 does not have any effect on olefins selectivity, however shorter catalytic beds are needed to achieve a required CO conversion (GHSV increases).

As shown in Figure 23 high temperatures promote the selectivity to olefins as mentioned above, however the presence of CO_2 in the reacting gas results in a reduction in olefin selectivity because of the hydrogen consumption in direct CO_2 hydrogenation reactions and of the reduction of CO partial pressure.

Thus, H_2/CO ratios between 1.75 and 2.25 with minimum CO_2 presence are needed to maximize the olefins production.

H₂/CO	Carbon sele	ctivity (%)		GHSV	
	C1	C ₂ -C ₄ olefins	C ₂ -C ₄ paraffins	Olefins/Paraffins	(I _{gas} /kg _{cat} .h)
0.5	46.47	48.07	5.46	7.66	0.46
0.75	32.31	61.30	6.39	8.28	0.85
1	18.26	74.31	7.43	8.61	3.32
1.25	13.75	78.48	7.77	8.69	60.47
1.5	13.65	78.56	7.78	8.68	100.99
1.75	13.60	78.63	7.77	8.70	134.64
2	13.59	78.63	7.78	8.69	167.20
2.25	13.56	78.66	7.77	8.70	197.72
2.5	13.55	78.67	7.78	8.70	227.89
3	13.54	78.68	7.78	8.70	286.77
3.5	13.54	78.68	7.78	8.69	345.43
3.75	13.54	78.68	7.78	8.69	374.00
4	13.53	78.69	7.78	8.69	402.41

Table 4. Effect of H₂/CO on carbon selectivity at 50% CO conversion at 290 °C.



Figure 23. Effect of temperature and CO₂ presence in the gas on olefins selectivity.

3.4 BIO-OIL TO OLEFINS PROCESS

As described, there are no available models for predicting the olefins yield and selectivity from biooil and thus empirical correlations derived from experimental data to predict conversions are needed. Experimental data of biooil, instead of model compounds, can be used to predict olefins production from pyrolysis vapors. A quite comprehensive set of data on real bio oil conversion to olefins is reported by Gong et al. [12] and was used to predict yields and selectivity of the olefins.

As shown in Figure 24 there is an optimal temperature at which the selectivity to olefins is maximized. The operating temperature window for this reactor is between 550 and 600 °C with olefin selectivity approaching 60% of the incoming carbon; at these conditions almost complete conversion of bio-oil is achieved. A temperature increase favours the conversion of bio-oil with higher temperatures promoting the production of gases. The optimal temperature for bio-oil conversion is higher than the optimum pyrolysis temperature for maximum carbon selectivity to bio-oil (Figure 22), and thus in-situ catalytic pyrolysis cannot serve the purpose of maximum olefins selectivity. Moreover, extra energy input is needed to run the process.



Figure 24. Effect of temperature on product selectivity of biooil to olefins process.

3.5 OLIGOMERIZATION OF OLEFINS

In an olefins oligomerization reactor, chain polymerization and cracking reactions occur, and heavier olefins are produced over ZSM-5 zeolites. A detailed and accurate model of such process can be hugely complicated, due to the growing number of isomers with increasing carbon numbers. The thermodynamic modelling of olefins oligomerization faces difficulty in identifying all of the isomers involved, which have different thermodynamic properties, as well as due to the lack of thermodynamic data on olefins and each of their isomers [115].

Equilibrium calculations including each olefin isomer become impractical at higher carbon numbers. In order to understand the complexity of calculation it can be mentioned that only hexene has 18 possible isomers, decene 895, pentadecene (C_{15} =) has over 185000, and eicosene (C_{20} =) has over 46 million [115]! The isomer complexity can be simplified by the assumption that isomers are in equilibrium, which allows for development of lumped models.

Nevertheless, discrepancies have been observed between experimental and calculated data at high carbon numbers, and therefore experimental modified equilibrium has been established [146,147]. At relatively low pressure and temperatures higher than 350°C equilibrium constraints become important [114]. Combined kinetic modelling and thermodynamic equilibrium calculations elucidate the performance of the process in a satisfactory manner [148,149] with the additional constraint that some of the isomers would not form over the catalyst, due to their inability to pass through ZSM-5 pores, and therefore some species are discounted from the isomer groups [150]. This model is used as the basis of the oligomerization model that holds true for up to C_{20} olefins.

The mole fraction of each individual isomer in an isomer group in the reactor is determined by[151]:

$$\frac{y_i}{y_I} = e^{\left[\frac{\left(\Delta G_{f,I}^o - \Delta G_{f,i}^o\right)}{RT}\right]}$$

where *I* refers to isomer group and *i* is the individual isomer. Calculation of Gibbs free energies of formation of isomer groups between 2 and 8 by Alberty showed a linear dependency of Gibbs energy of formation, enthalpy, entropy, and heat capacity on carbon number of the isomer groups, with the slope and the intercept being also linearly related to temperature. This allows for the calculation of higher isomer groups by extrapolation [147,150]. Thus, thermodynamic properties of isomer groups can be estimated as a function of temperature.

The reactions scheme of the process can be represented by first order combination and cracking reactions of olefins with and to each other:

$$2C_2H_4 \rightleftharpoons C_4H_8$$

$$C_2H_4 + C_3H_6 \rightleftharpoons C_5H_{10}$$

$$2C_3H_6 \rightleftharpoons C_6H_{12}$$
...
$$C_8H_{16} + C_{12}H_{24} \rightleftharpoons C_{20}H_{40}$$

The extent, ξ , of kth reaction in equilibrium where olefins *n* and *m* produce olefin of size *m*+*n* is constant and thus can be written:

$$r_k = \frac{d_{\xi_k}}{dt} = k_f C_{n^o} C_{m^o} - k_b C_{n+m^o}$$

where $C_{n^o}, C_{m^o}, C_{n+m^o}$ are the concentrations of olefins of size *n*, *m*, and *m*+*n* respectively, and k_f and k_b are the reaction constants for forward and backward reactions as shown above.

Considering the equilibrium constant of reaction *k*, the following can be written:

$$K_{C,k} = K_{P,k} \left(\frac{RT}{P_0}\right) = e^{\left(-\frac{\Delta G_{XR}}{RT}\right)} \left(\frac{RT}{P_0}\right)$$

where P_0 is the reference pressure at 1 bar. Alberty's model considers that either the forward or backwards reaction constants are the same for all reactions which allows for a simple computational model yet the results are in agreement with more sophisticated ones[151]. The generated reaction set is in a matrix form. For the first three reactions shown above, this matrix would be as follows:

$$Reaction Set = \begin{bmatrix} 2 & 2 & 4 \\ 2 & 3 & 5 \\ 3 & 3 & 6 \end{bmatrix}$$

with each row corresponding to one reaction, and each of the first two columns being the carbon numbers of reactants and the last column being the carbon numbers of the products. The thermodynamic properties of each isomer group are calculated based on Alberty's correlations [147,150]. These values are then used to determine the desired thermodynamic properties, Gibbs free energy and enthalpy of formation for the differential equations and the energy balance for the reactor, respectively. The kinetic parameters used in this model derived from heptane cracking [152].

In Figure 25 a parametric study on the effects of temperature, pressure and WHSV on the conversion of olefins and the produced gasoline fraction is shown. Temperature increment beyond 350°C has a negative effect on the oligomerization of olefins and cracking reactions prevail producing lighter olefins from oligomerized products. This can also be seen in the last plot of Figure 25, where the molar flow of gasoline and diesel fractions along catalyst bed in the reactor is shown. Lower temperatures favor the chain growth and production of heavier products (diesel) while at high temperatures the production of light fraction is favored. As expected, lower space velocities favor the overall conversion of the reaction mixture, while high temperatures and high space velocities are required if high gasoline product fraction is needed. Pressure increase is positively correlated to overall olefins conversion, however lower pressure favors the production of a gasoline rich liquid.



Figure 25. Effect of operating parameters on conversion and gasoline fraction feed C₂:C₃:C₄ 1:1:1. Top left: effect of pressure and temperature on olefins conversion (WHSV 0.5 h⁻¹). Top right: Effect of temperature and WHSV on olefins conversion (P 400kPa). Mid left: effect of temperature and WHSV on gasoline fraction (P 400 kPa). Mid right: effect of pressure and temperature on gasoline fraction. Bottom left effect of temperature on product profiles in the reactor (P 400 kPa, WHSV 0.5 h⁻¹).

3.6 SULFUR REMOVAL, WGS REACTOR AND GAS SEPARATIONS

 H_2S and COS removal on ZnO/Al₂O₃ were determined by 1D isothermal plug flow model based on kinetic parameters from [153–155]. For H_2S sorption on ZnO an average state of 50 % consumption was considered [154].

For WGS reactor, most of the modelling approaches focus on the kinetic reactor modelling [156–158] with Langmuir-Hinshelwood kinetics models adequately predicting the behavior of industrial WGS reactors [157,159,160]. In this study a heterogenous 1-D model was developed based on the work from Mobeb et al. [86] and Adams and Barton [161]. Detailed description of the models is outside the scope of the report and the reader should consult the references for details.

Wherever gas separation and/or purification is needed, PSA units based on activated carbon, zeolites or combinations thereof are employed. Separation efficiencies are determined based on (extended) multi component Langmuir adsorption models.

The multicomponent Langmuir adsorption model estimates the amount of i^{ih} compound, n_i , sorbed on the PSA sorbent.

$$n_{i} = \frac{q_{m,i}b_{i}(Py_{i})^{\eta_{i}}}{1 + \sum_{1}^{n} 1 + b_{i}(Py_{i})^{\eta_{i}}}$$

where $q_{m,i}$, $b_i \eta_i$ and correspond to the pure gas isotherm parameters of component *i*.

The extended multicomponent Langmuir model is of the following form[162]:

$$n_{i} = \frac{q_{m,i}\overline{b_{j}}Py_{i}}{2\bar{s}a}\ln\left(\frac{1+ae^{\bar{s}}}{1+ae^{-\bar{s}}}\right)$$

where

$$a = \sum \overline{b_i} P y_i$$
$$\overline{s} = \frac{1}{N} \sum s_j$$
$$s_j = \frac{3^{1/2}}{RT} \sigma_j$$
$$\overline{b_j} = b_{j0} e^{\varepsilon_j/RT}$$

The parameters ε and σ are the mean and square root of variance of energy, q_m and b are the Langmuir constants, and s is the heterogeneity parameter related to the spread of the energy distribution. The required coefficients for the models were retrieved from experimental data reported in the literature by regression [100,162–165]. For olefins' separation prior to MOGD process two PSA units in series followed by a VSA were considered.

4 PROCESS INTEGRATION AND TECHNO-ECONOMIC ANALYSIS

Based on the parametric studies for the individual process units described in section 3, the process was integrated based on the different scenarios to be analysed. The integration aimed at maximizing the carbon efficiency by satisfying the current and future fuel mix as described by gasoline to diesel ratios. Thermal integration and waste heat utilization for electricity generation was also carried out. Process parameters for individual unit operations are detailed in the Appendix.

Three different process schemes were considered: (i) O_2 blown biomass gasification; (ii) integrated pyrolysis of biomass with O_2 gasification of char and (iii) pyrolysis of biomass integrated with air gasification of biomass. The difference lies in the thermochemical treatment technique that biomass undergoes, and the oxidizer used in the gasification section. The different process schemes are shown below (Figure 26, Figure 27 and Figure 28).

In the 1^{st} process scheme, the O₂ blown direct gasification, biomass is gasified in an entrained flow gasifier and O₂ is used as oxidizer. The produced syngas is cleaned from impurities and is fed to a SE-WGS reactor where its composition is adjusted to a H₂/CO ratio of 2. The tailored syngas is cooled and passes through an activated carbon filter before entering a syngas to olefins reactor train (or FTO). The train consist of three reactors in series, after each reactor the gas is cooled down and enters a separation unit where olefins are removed from the gas stream before the next FTO reactor. The carbon utilization can be improved by recycling unreacted CO back to the first syngas to olefins reactor, however purging of the gas is needed to avoid build-up of inert gases that will result in reduced partial pressures of the reactants.

The separated olefins are then fed to a series of MOGD reactors where they are oligomerized to produce gasoline and diesel range hydrocarbons.

The 2^{nd} process scheme consists of an integrated pyrolysis-gasification unit, where the biomass is pyrolyzed and the char is gasified with O₂ to produce syngas. Here it must be mentioned that the most suitable reactors for this conversion are of cone type [166], downer with fluidised bed gasifier [123] or similar. With such arrangements the need for sweeping gas in the pyrolysis section is minimized. The pyrolysis vapours are converted to olefins, then the resulting gases are separated from the olefins and are fed together with syngas to the WGS reactor to adjust the H₂/CO. The syngas conversion to olefins is the same as for process scheme 1. The olefins from pyrolysis and gasification section both fed to olefins oligomerization reactors to produce longer chain molecules.

The last process scheme is similar to the second, but air is used as oxidizing medium in the gasifier instead of O_2 . This alteration requires the addition of a N_2 removal unit after the syngas tailoring step. The rest of the process scheme is identical to the second.

For all process schemes the adjustment in the composition of the liquid according to the fuel mix demand is done by manipulating process conditions (temperature, pressure) and the recycling rate of streams to the oligomerisation reactors.



Figure 26. Process Scheme 1- Biomass O₂ gasification for olefins production.



Figure 27. Process Scheme 2- Biomass pyrolysis with O₂ gasification of char for olefins production.





4.1 YIELDS AND COMPOSITIONS

4.1.1 Carbon efficiency

A very important part of the study is to evaluate the attainable carbon efficiency to the desired liquid products. The carbon flow for each process scheme and fuel mix demand are shown in Figure 29, Figure 30, Figure 31, Figure 32, Figure 33, and Figure 34.

The carbon losses refer to carbon containing products that cannot be utilized for production of olefins within the system, i.e., CO_2 , CH_4 and light paraffins (C_2 - C_4).

In process scheme 1 (standalone gasification), the carbon losses are equal to 27 % and are mainly due to formation of CO_2 and secondly of methane. In process schemes 2 and 3, combined losses are ~17 % because the operation at lower temperature allows the production of light olefins in the gas phase (in the pyrolysis reactor) and CO, which can be utilised in subsequent steps. The pyrolysis reactor is operated at 485°C for both process schemes (2 and 3) because in practice it is very difficult to maintain very short residence times at ~500°C (in order to maximize the liquid production); therefore slightly lower temperatures with longer residence times are usually employed [166]. Moreover, lower temperatures produce higher amounts of char, which provide the necessary heat for the pyrolysis in the gasifier. In all process schemes the conversion of gasified carbon to CO exceeds 70 %. Minimum amount of steam is used (S/B 0.3) in order to avoid soot formation and assist with the reduction of refractory tars. Detailed process conditions are listed in the Appendix.

The conversion of biomass carbon to bio-oil-contained carbon is 51.7% (Figure 31,Figure 32, Figure 33 and Figure 34) and its conversion to olefins approaches 60 % selectivity, resulting in 30 % conversion of biomass-containing carbon into olefins. CO that is produced in the biomass pyrolysis and the bio-oil to olefins processes accounts for ~9 % of the total carbon and can be

added to the producer gas from char gasification for additional olefins production, while it would have been unused in a standalone process.

Syngas tailoring is the processing step with the highest carbon penalty (27 % of carbon is lost in the composition adjustment in the process scheme 1 and 19-22 % of total carbon input in process schemes 2 and 3). The carbon lost for syngas tailoring accounts for 36 % and 58 % of the carbon at the inlet of the WGS reactor for process concepts 1 and 2, respectively. The individual process carbon loss is considerably lower for process scheme 1, because the H₂/CO ratio of the gas obtained gasification is higher than in process concept 2 (0.88 vs 0.24). This is due to the higher H/C ratio in the biomass compared to the char.

The selectivity of syngas conversion to olefins is 50-60 % for all the process schemes with differences in selectivity due to different CO_2 content in the feeds of the FTO reactors, which has a negative impact on the olefin selectivity as described in section 3.3.

A considerable amount of the rejected carbon is in CO_2 which has been captured in the sorption enhanced WGS reactor and could further be utilized in CCU applications. The amount of captured CO_2 for each of the process schemes is listed in Table 5.

As shown, there is a considerable potential for additional carbon utilization for transportation fuel production in power to liquids processes [167].



Figure 29. Carbon flow for process scheme 1- 2020 transportation fuel mix.



Figure 30. Carbon flow for the process scheme 1 - 2030 transportation fuel mix scenario.



Figure 31. Carbon flow for process scheme 2 -2020 transportation fuel mix scenario.



Figure 32. Carbon flow for process scheme 2 - 2030 transportation fuel mix scenario.



Figure 33. Carbon flow for process scheme 3 -2020 transportation fuel mix scenario.



Figure 34. Carbon flow for process scheme 3- 2030 transportation fuel mix scenario.

	(kg CO ₂ / ton biomass daf)	% of total C
Process scheme 1	914.3	48.7
Process scheme 2	500.2	26.7
Process scheme 3	474.4	25.3

Table 5. Captured CO₂ for the different process scenarios.

4.1.2 Liquid yield and composition

The yield and composition of the obtained liquid product is of particular interest. In Table 6 the achieved yield and composition of liquid products are listed. The product composition fits the required fuel mix for 2020 and 2030. The calculated liquid fractions densities are in agreement with densities obtained from industrial operation of MOGD plant (Table 2).

The changes in liquid composition without compromising the overall liquid yield is one of the advantages of the MOGD process.

The alteration of the composition was achieved by increasing the temperature or reducing the pressure in the first oligomerization reactor which produced more C_4 - C_{11} olefins, with considerable conversion of the C_2 fraction and prevention of oligomerization to long chains due to cracking reactions (see also Figure 25). For process schemes 2 and 3, running the 1st oligomerization reactor at higher pressures and lower temperatures allows the chain growth already in the 1st reactor but there is still a considerable fraction of C_2 and C_3 olefins still in the reactor effluent due to low temperature and slow kinetics of the reactions. Therefore, these molecules will oligomerize to shorter chains (gasoline range) in the second reactor. For process scheme 1, the tailoring of the liquid product composition was achieved by recycling more of the effluent from the second reactor to the first one. In this way the partial pressure of the reactant (C_2 - C_5) olefins in the first reactor is reduced due to the presence of CO, methane, and CO₂ in the gas, then the chain growth is reduced, so that more gasoline range hydrocarbons are produced.

The weight and volumetric composition of the different product blends is shown in Figure 35.

	Liquid Product Yield	Gasoline/Diesel Cuts	Liquid product density (kg/m ³)*		
(kg/ton _{biom daf})		(vol/vol)	Gasoline Cut (C ₇ -C ₁₁)	Diesel Cut (C ₁₂ -C ₂₀)	
Biomass O ₂ gasification - 2020	171.0	0.41	732	783	
Biomass O ₂ gasification - 2030	168.9	0.15	735	788	
Pyr O ₂ gasification -2020	231.5	0.43	732	784	
Pyr O_2 gasification -2030	230.9	0.17	734	788	
Pyr Air gasification -2020	236.3	0.41	732	784	
Pyr. – Air gasification -2030	236.1	0.18	735	787	

Table 6. Liquid product yields and properties for the different scenarios investigated.

* Estimated based on average densities of pure 1- and iso- olefinic compounds of corresponding carbon number.



Figure 35. Liquid product composition for different fuel demand. Top row: O₂ gasification of biomass 2020 (left) 2030 (right); Middle row: pyrolysis and O₂ gasification of char 2020 (left) 2030(right); Bottom row: pyrolysis and air gasification of char 2020 (left) 2030 (right).

The obtained liquid product from MOGD is still subject to hydrotreatment to be considered as finished gasoline and diesel product, and therefore additional hydrogen is needed. The estimated H_2 demand per m³ of product is listed in Table 7. The lower and upper boundaries are estimated based on the assumption of completely mono-olefinic or tri-olefinic composition of the produced liquid.

Table 7. Additional H2 requirement	ts (kg/m ³) for compl	lete hydrogenation o	f MOGD product.
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	Process scheme 1	Process Scheme 2	Process scheme 3
2020 – fuel mix demand	8.6-25.7	8.4-25.1	8.3-24.9
2030 – fuel mix demand	7.4 –22.1	7.5-22.4	7.5-22.6

As listed in Table 7 the H_2 demand is slightly smaller for the future mix due to the higher diesel demand.

Even though a direct comparison cannot be made, the bio-oil obtained from pyrolysis process would theoretically require² ~74.5 kg of hydrogen per m³ to be converted to paraffinic liquid. The big difference in H₂ requirements is reasonable, since the deoxygenation of the biooil has taken place in the biooil to olefins reactor.

Assuming that the hydro-conversion of MOGD liquid has minimal carbon losses, the CO₂ savings per ton of dry biomass can be estimated [168] based on liquid products.

	Process scheme 1	Process Scheme 2	Process scheme 3
2020 – fuel mix demand	427.3	774.0	790.5
2030 – fuel mix demand	573.0	774.6	792.2

Table 8. CO₂ savings (kg CO₂/ton biomass daf).

4.2 HEAT INTEGRATION

Heat integration was performed to verify that the processes did not require external utilities supplying heat in any temperature range, and to assess the excess of heat released from the processes could be recovered by a thermodynamic cycle generating electricity.

The HEATSEP methodology [169] was applied to the flowsheet of the processes, leaving the heat exchanger network undefined and having all the heat loads from the processes, i.e. those associated with reactors and streams, free to interact in a "black box" (the only exceptions are the streams of air and steam entering the gasifier, which are directly matched with part of the heat released by the gasifier itself). Heat integration follows the rules of Pinch Analysis: all reactors requiring/releasing heat and all streams requiring heating/cooling are listed together with their heat loads and the temperature ranges in which these loads are required/released. From this list, it is possible to calculate the heat surpluses and deficits due to the processes in all temperature ranges, and, since heat can only be transferred from higher to lower temperature ranges, surpluses and deficit can be cumulatively summed up from the highest temperature to the lowest, obtaining the net cumulated heat surplus. This can be shown in a diagram called "Grand Composite Curve" (GCC).

The GCC is a fundamental tool in Pinch Analysis, because it clearly visualizes the temperature ranges in which heat is required/released in a set of processes. It also shows qualitatively how the set of processes could be integrated with other sets of processes and, quantitatively, the amounts of heat potentially involved in this integration. A classic application is the coupling of heat engines to the given set of processes. The GCC resulting from the thermal streams of the thermodynamic cycle(s) defining the heat engines can be even plotted in the GCC diagram of the processes to show the level of integration between the two. This type of diagram is then called "Integrated Grand Composite Curve" (IGCC).

In this case, a simple steam Rankine cycle (one evaporation pressure level and one condensation pressure level) was chosen to generate electricity from the excess heat released by the processes. This choice is justified given the relatively small size of the cycle. The evaporation pressure is to be

² An average density of 1200kg/m³ was assumed.

optimized, but an upper limit was set to 100 bar for the same reason. Two different condensation pressure were considered: 1.1 bar for a condenser operating above the atmospheric pressure, but limiting the expansion of steam in the turbine, and 0.05 bar for a condenser operating at vacuum pressures, condensing steam at ambient temperatures so that a larger power output can be obtained from the turbine.

The main features of the IGCC diagrams for O_2 gasification, pyrolysis with air gasification of char and pyrolysis with O_2 gasification of char are shown in the following with 0.05 bar condensation pressure and 2020 fuel transportation mix. The differences in the GCC of the processes between 2020 and 2030 fuel transportation mixes are not significant, and the difference in the GCC of the steam Rankine cycle between 0.05 and 1.1 bar condensation pressure is limited to the bottom segment of the curve, the one related to the condensation process. In fact, the optimal coupling between the set of processes and the steam Rankine cycle is determined in all cases by the operating temperature of syngas-to-olefins reactors (R60x), which also sets the optimal evaporation pressure level of the cycle.

Figure 36 shows the IGCC diagram (red curve: GCC of the processes, blue curve: GCC of the steam Rankine cycle) in the O₂ gasification scenario. In this scenario the largest amount of excess heat is available for electricity generation because the gasifier and all reactors are exothermic, moreover the gases rejected from the gas separation units are combusted (for sake of simplicity, the red GCC shows this heat load just as sensible heat starting from the calculated adiabatic temperature of combustion, although at the highest temperatures heat transfer occurs as radiation from the flame). The only streams requiring heat are those entering reactors R60x and R70x, since they must be heated from 298 K to the operating temperature of the reactors, but their heat loads are not large enough to cause deficits in any temperature range. Given the operating temperature of reactors R60x (563 K), the optimal evaporation pressure for the steam Rankine cycle is 46 bar.



Figure 36. IGCC for the O₂ gasification scenario (condensation pressure 0.05 bar - 2020 transportation fuel mix). Red curve: GCC of the processes; blue curve: GCC of steam Rankine cycle.

Figure 37 shows the IGCC diagram in the pyrolysis with air gasification of char. In this diagram the excess heat released by the gasifier is lower because part of it is used for the pyrolyzer. Moreover, there is a large request of heat by the endothermal reactor R301 (bio-oil to olefins) in a relatively high temperature range (600°C), which causes a significant heat deficit in the same range. This is by far the scenario with the lowest amount of excess heat available for electricity generation. Given the operating temperature of reactors R60x (290°C), the optimal evaporation pressure for the steam Rankine cycle is 54 bar.



Figure 37. IGCC for process scheme 3 (condensation pressure 0.05 bar - 2020 transportation fuel mix). Red curve: GCC of the processes; blue curve: GCC of steam Rankine cycle.

Figure 38 shows the IGCC diagram in the pyrolysis with O₂ gasification of char. This diagram has similar features compared to the previous one, however the overall excess heat available for electricity generation is much higher. Given the operating temperature of reactors R60x (563 K), the optimal evaporation pressure for the steam Rankine cycle is still 54 bar.



Figure 38. IGCC for process scheme 2 (condensation pressure 0.05 bar - 2020 transportation fuel mix). Red curve: GCC of the processes; blue curve: GCC of steam Rankine cycle.

Finally, Table 9 summarizes the electricity output from the recovery of excess heat for all the considered scenarios and cases.

sidered scenarios and cases.						
Fuel transportation	Condensation	O ₂ gasification of	Biomass Pyrolysis with air	Biomass Pyrolysis with		
mix (year)	pressure (bar)	biomass	gasification of char	O ₂ gasification of char		
2020	0.05	848.1	470.7	655.0		
2020	1.1	617.5	321.5	457.9		
2030	0.05	840.8	470.1	665.1		
2030	1.1	612.8	321.1	465.4		

Table 9. Power (kW/ton/h of biomass_{daf} input) generated from the recovery of excess heat in the considered scenarios and cases.

The electricity requirements for compression and the net electricity demand for the different scenarios are listed in Table 10. The high energy demand for air separation before the gasifier results in lower energy efficiencies for the both the pyrolysis integrated and the gasification standalone plant. The electricity needed for air separation accounts for 47 and 33.2 % of the total electricity demand of process schemes 1 and 2, respectively. The electricity need for air separation is considerably lower for the integrated plant due to the smaller volumes of oxidizer needed in the gasifier.

Fuel transportation mix (year)	Electricity requirements kW _e /ton _{b daf}	Electricity production kW _e /ton _{b daf}	Net Electricity Demand kW _e //ton _{b daf}	Energy efficiency η _{ннv} (% of biomass HHV)	Overall Energy efficiency ηε
O ₂ gasification of biomass -2020	975.6	617.5	358.1	39.40	37.1
O ₂ gasification of biomass -2030	973.9	612.8	360.5	38.59	36.32
Biomass pyrolysis & O ₂ gasification of char-2020	502.0	457.9	44.1	52.37	51.97
Biomass pyrolysis & O ₂ gasification of char-2030	502.0	465.4	36.6	52.19	51.86
Biomass pyrolysis & air gasification of char-2020	450.6	321.5	129.1	54.64	53.42
Biomass pyrolysis & air gasification of char-2030	423.1	321.1	102.0	54.54	52.4

Table 10. Electricity requirements and energy efficiencies for the different scenarios investigated.

4.3 COST ESTIMATE AND ANALYSIS

The total plant investment is estimated by dividing the plant in different areas (as presented in section 2) and estimating the cost of the equipment in each of the area based on literature data. Adjustment of the equipment cost to required sizes and to construction time allow the estimation of cost in a common time basis. The final estimate is done by adding all the balance of plant and indirect costs that are required. The projection of cost estimate in construction year 2020 are based on of the CEPCI cost index, which is shown in Figure 39.





The total capital (TC) for each unit is calculated as the sum of the total direct capital (TDC) plus the indirect costs (IC). IC include engineering, start-up, spares, royalties, and contingencies and is estimated at 32% of the TDC [170].

$$TDC = (1 + BOP)C_0 \left(\frac{S}{S_0}\right)^{sf} \left(\frac{CEPCI_{2020}}{CEPCI_{year0}}\right)$$

where BOP is the balance of plant, C_0 and S_0 and CEPCI_{year0} are the base costs, capacity and CECPI index of the corresponding year, respectively, taken from the literature. *sf* is a scaling factor which depends on the individual process. If a number of trains (n) is required (due to equipment constraints), the nearest integer number greater than (Sr / S_{max}) is calculated and the size of each reactor train is:

$$S = \frac{S_r}{n}$$

For multiple unit-trains the cost is determined as:

$$C_t = C n^{0.9}$$

where C_t is the train cost and C is the cost of the individual unit, *n*, is the number of units in the train. For indirect costs the assumption from Kreutz et al. [171] is used (32 % for biomass processing related processes and 27 % for power plant components). For balance of plant costs (BOP) 20 % is assumed [170].

In the absence of information on the bio-oil to olefins unit, its cost was based on MTO plants. The syngas to olefins plant was considered as an FT reactor. The following exchange rates were assumed for the costs found in the literature: 1 =8.31 SEK and 1 €=10.12 SEK.

Compressors purchase cost was estimated (assuming a 78% isentropic efficiency) as:

$$C = 7.9(hp)^{0.62}$$

Installation cost was assumed to be 30% of purchased cost and BOP and indirect cost equalled the values of the general process equipment described above.

The cost of the PSA units was estimated according to the following [172]:

$$C_{PSA} = C_{column} + C_{adsorbent}$$

Stainless steel, SS304, was considered as material of construction with 0.5 in thickness and L/D of 3.

The cost for the vessel was estimated according to [173]:

$$C = F_M C_b + C_a$$

 $C_b = 1.672 e^{(9.1+0.2889lnW+00.0456(lnW)^2)}$

$$C_{a} = 480D^{0.7396}L^{0.7066}$$

Where F_M is a material factor equal to 1.7 for SS304. The steel density cis equal to 7850 kg/m³.

Two vessels per PSA unit were considered.

Installation cost of 70% has been considered for PSA, while BOP and indirect costs are similar to the compressors. The cost of zeolites and activated carbons used in PSA column are:

able 11 Adsorbent costs used in gas separation units.

	Cost	Ref.
Zeolite adsorbent	66.42 SEK/kg*	[172]
Activated carbon adsorbent	27.71 SEK/kg*	[174]

* Compensated to 2020 price by considering an average inflation from the year reported until 2020.

For compressors cost, the highest compression capacity was considered comparing the 2020 and 2030 needs, however the corresponding electricity requirements for the electricity costs. The total investment costs for the different processes are summarized in Table 13, Table 14 and Table 15.

Table	12.	Cost	estimate	references.

	Co	S ₀	Units	sf	ВОР	IC	ref
Entrained flow gasifier*	0.3M€ (2011)	220	kg/h	0.75	20%	32%	[175]
Pyrolyzer/Gasif.**	29.5MSEK(2014)	20	MW_{th}	0.7	included	0.6%	[176]
Dolomite cleaning (including ZnO)	190k\$ (2004)	5	ton/day	0.67	included	32%	[65]
Ash Cyclone	1.063M\$ (2009)	2473	kg/s	0.7	20%	32%	[177]
Ceramic filter	21.724M\$ (2009)	518	kg/s	0.65	20%	32%	[177]
HT-WGS	5.29MSEK (2014)	905,267	lb/h	0.7	20%	32%	[77]
AC filter	10.6MSEK (2014)	20	MWth biom	0.8	included	32%	[176]
FT	12.26 M\$ (2009)	23.79	Kg/s	0.72	20	32%	[177]
PSA	6.38M\$ (2009)	3.8	mol/s	0.74	20%	32%	[177]
Bio Oil to Olefins	90M€ (2014)	86	t/h	0.85	included	32%	[178]
MOGD	3.48M\$ (2011)	10.628	kg/s	0.65	20%	32%	[179]
HRSC	66.7M\$ (2007)	275	MWe	0.67	15.5%	included	[171]

* Installation factor 1.86.

** The GoBiGas reactor cost was chosen even though that a twin bed system in this arrangement is not the most desirable. The cost of the BTG cone reactor is equivalent based on literature data [173]. GoBiGas data were selected because they are more recent and adjusted to Swedish prices.

For the O_2 gasification plant, the PSA and compressor costs represent 56-69 % of the total cost depending on the plant size (more important at smaller scales i.e., 5 and 10 MW, see Table 13 and Figure 40). For the integrated pyrolysis- O_2 blown gasification plant these costs correspond to 48-67 % of the TDC, since the air separation needs are smaller compared to process scheme 1.

It worth mentioning that air separation and compression costs correspond to ~ 20 % of the TDC for process scheme 1 (Figure 40) while the gasifier cost, which implies that considerable cost reductions can be achieved if other means of air separation or oxygen supply are employed. The cost for gasifier becomes more important at bigger plant sizes (~9 % for 5 MWth plant ~13.5 % 50 MWth).

The cost associated with air separation for process scheme 2, accounts for 13 % in small scale plant i.e., 5 MW_{th}, while its effect on total direct cost is reduced at bigger plant sizes ~11 % (see Figure 41). The capital investment cost for bio-oil to olefins conversion unit represents 16 % of the total direct capital of a 50 MW_{th} plant and the cost associated with syngas conversion to olefins is approximately 4 % for a plant of the same size (i.e. 50 MW_{th}).

The cost of the final MOGD process represents less than 2 % of the total direct capital for all process schemes and plant sizes in investigated.

The cost associated with N_2 removal downstream the gasifier in process scheme 3 represents a significant capital cost ~17-23 % of the TDC (see Figure 42 – denoted as ASU); however as mentioned removal of other compounds from the gas after the WGS reactor offer improved performance to the FTO reactors. Nevertheless, the cost penalty for bigger HT-WGS should not be overlooked since the highly N_2 diluted gas flow results in increased costs for the WGS unit (the WGS unit represents less than 1 % of the TDC, though).

The high cost for air separation and gas compression is also reflected to the total capital investment per barrel-per-day (bpd) of liquid product which for the O_2 gasification plant varies from 2 400 000 SEK/bpd to 6 700 000 SEK/bpd as the plant size decreases from 50 MW_{th} to 5 MW_{th}.

For the integrated plants described by process schemes 2 and 3 the investment cost per barrel-perday varies from 1 700 000 to 4 800 000 and from 1 700 000 to 3 900 000 SEK/bpd respectively.

	Plant Size				
	(MWth _{biom daf})				
	5	10	50		
Gasification	12.82	21.57	72.11		
Ash Cyclones	0.03	0.05	0.14		
Dolomite cleaning (including ZnO)	5.50	8.74	25.70		
Ceramic filter	2.51	3.93	11.19		
SE-WGS	1.20	1.94	6.00		
AC filter	3.63	6.31	22.86		
FTO	7.07	11.65	37.12		
MOGD	1.99	3.12	8.88		
PSA	81.03	101.37	217.46		
Compressors	19.89	30.57	82.91		
HRSC	11.09	17.64	51.87		
TDC	147.33	206.89	536.25		
тс	190.93	367.45	691.247		

 Table 13. Total capital investment estimation (MSEK-2020) for process scheme 1.





	Plant Size					
	(MWth _{biom daf})					
	5	10	50			
Pyrolysis -Gasification	11.56	18.78	57.93			
Ash Cyclones	0.02	0.04	0.10			
Dolomite cleaning (including ZnO)	5.49	8.74	25.70			
Ceramic filter	1.90	2.98	8.47			
SE-WGS	0.74	1.20	3.71			
AC filter	3.62	6.31	22.86			
FTO	3.52	5.79	18.46			
Bio Oil to Olefins	10.83	19.52	76.67			
MOGD	2.18	3.43	9.76			
PSA	82.08	101.38	183.11			
Compressors	15.08	23.17	62.85			
HRSC	9.08	14.44	42.45			
TDC	143.24	228.82	508.23			
TC	188.81	265.22	657.28			

Table 14. Total capital investment estimation (MSEK-2020) for process scheme 2.





	Plant Size (MWth _{biom daf})				
	5	10	50		
Pyrolysis -Gasification	11.56	18.78	57.93		
Ash Cyclones	0.02	0.04	0.10		
Dolomite cleaning (including ZnO)	5.49	8.74	25.70		
Ceramic filter	1.90	2.98	8.47		
SE-WGS	1.07	1.74	5.38		
AC filter	3.62	6.31	22.86		
FTO	3.65	6.01	19.16		
Bio Oil to Olefins	10.83	19.52	76.67		
MOGD	2.35	3.63	10.34		
PSA	50.2	70.37	197.23		
Compressors	14.11	21.69	58.85		
HRSC	7.17	11.39	33.49		
TDC	111.95	171.2	516.20		
TC	145.48	222.36	670.66		

Table 15. Total capital investment estimation (MSEK-2020) for process scheme 3.





The annualized cost for each of the process scenarios can be determined by [180]:

$$AC = TC \frac{i(1+i)^n}{(1+i)^n - 1}$$

Considering a lifetime n of 20 years and an annual interest rate i of 10 % the annualized cost for the different process can be determined.

Table 16. Annualized costs (MSEK/y) for different plant sizes.

O2 gasification of biomass		Biomass pyrolysis & O ₂ gasification of char			Biomass pyrolysis & air gasification of char			
Plant Size (MW _{th})								
5	10	50	5	10	50	5	10	50
22.4	31.37	81.10	22.18	31.15	77.20	17.4	26.12	78.78

The operating costs include the costs for electricity, heat, and raw materials. The needs for raw material and electricity have been defined by the mass and energy balances as well as thermal integration of the plant. The electricity and biomass prices considered in the study are shown in Table 17.

Table 17. Electricity and Biomass costs.

	Cost	Ref.
Biomass	340 SEK/MWh	[181]
Electricity	0.6 SEK/kWh	[182–185]

The overall operating costs for each scenario are presented in Table 18.

Table 18. Operating costs (MSEK/y) for different plant sizes.

O ₂ gasification of biomass		Biomass pyrolysis & O ₂ gasification of char			Biomass pyrolysis & air gasification of char			
Plant Size (MW _{th})								
5	10	50	5	10	50	5	10	50
22.4	31.37	81.10	21.18	31.15	77.20	17.4	26.62	73.10

The annualized production cost of liquid product per litre can be determined by dividing all the costs (annualized capital cost and the operating costs) by the liquid volume that is produced annually (Table 19).

Table 19. Total production costs for MOGD liquids (SEK/I).

	Plant Size (MW _{th})				
	5	10	50		
O2 gasification of biomass	25.09	20.72	15.79		
Biomass pyrolysis & O_2 gasification of char	17.90	14.73	10.96		
Biomass pyrolysis & air gasification of char	14.67	12.78	10.34		

As illustrated, the integrated pyrolysis-gasification offers better economies compared to gasification-based plant. Sensitivity of productions costs to biomass and electricity prices for the $50MW_{th}$ plants is shown in Figure 43.



Figure 43. Sensitivity of production costs to biomass and electricity prices for 50MWth plant size.
As shown, the production costs are mainly sensitive to biomass prices while they are relatively insensitive to electricity costs. The latter is directly proportional to the net electricity requirements (Table 10) for the different process schemes and therefore process scheme 1 is the most sensitive to electricity price changes followed by process scheme 2. An electricity price change of 5 % corresponds to 0.5, 0.3 and 0.1 % change in production cost for process schemes 1, 2 and 3, respectively. Conversely, production costs for all process schemes process schemes are equally sensitive to changes in biomass prices. A 5 % change in biomass prices induces 2.8, 3 and 3.1 % change in production costs for process schemes 1, 2 and 3, respectively.

The liquids from the MOGD process are still subject to hydrotreatment and therefore a cap of hydrogenation costs should be added on top of the ones listed in Table 19³. Assuming a renewable H_2 production cost of 51.9 SEK/kg in 2020 [186] and a cost based on additional H_2 requirements estimated in section 4.1.2, a minimum cost of production can be estimated. Additional costs are expected to be lower for 2030 since it is estimated that H_2 cost will be equal to 21.6 SEK/kg. The projected production cost of final hydrotreated product for the years 2020 and 2030 for the process schemes studied are shown in Figure 44.



Figure 44. Projected production cost including H₂ generation cost for the different process schemes.

Due to the shifted fuel demand towards diesel and to the reduced H_2 production costs in 2030 a reduction of 2.3-3.5 %, 3-5 %, 3.5 % in production costs is expected in 2030 for process schemes 1, 2 and 3, respectively.

³ Additional costs associated with the hydro-processing should also be added.

5 CONCLUSIONS

The production of liquid fuel precursors via thermochemical treatment of biomass and light olefins synthesis was investigated. Given the logistics limitations of biomass, small to medium plant sizes were considered (5-50 MWth biomass HHV).

Unit operation and conversion models were set up to predict conversion and production rates based on reaction models or data from the open literature. Integration of the individual process models allowed the simulation of the conceptual process to obtain mass and energy flows, which were then used to estimate the cost of process equipment. Three main process scenarios were investigated, namely: (i) biomass gasification with O_2 ; (ii) biomass pyrolysis and char gasification with O_2 ; and (iii) biomass pyrolysis and char gasification with air.

Mass and energy balances indicate that the production of carbon-containing liquid feedstock is more efficient when the biomass is pyrolyzed and the produced char subsequently gasified. Of the process scenarios studied, the pyrolysis of biomass and char air-gasification shows 39.5 % carbon efficiency for the fuel mix (gasoline/diesel) scenarios investigated in the years 2020 and 2030. The least efficient process is the direct O_2 blown gasification of biomass which exhibits ~29 % carbon efficiency. All process scenarios investigated are self-sufficient in terms of thermal energy thanks to combustion of the off-gases. The HRSC system reduces the net electricity demand and thus the overall energy efficiency is not reduced considerably. The processes were flexible in adjusting the fuel mix by altering the operating conditions (temperature, pressure) or the gas recycling rates of the oligomerization reactors (MOGD).

The higher overall carbon conversions from the integrated pyrolysis-gasification plant can be attributed to the production of useful CO, during conversion of bio-oil, to olefins which can be utilized together with the syngas from the char gasification for further production of olefins. The carbon selectivity to olefins both from the biooil to olefins and the syngas to olefins processes are in the vicinity of 50-60 % and improvement in catalysis can further enhance the overall conversions.

A lack of published data on commercial bio-oil to olefins and syngas to olefins processes significantly increases the uncertainty of economic report because some potential performance and cost parameters had to be deduced from other similar systems such as Fischer-Tropsch and methanol to olefins processes. However, it is evident that the air separation and O_2 supply costs are one of the bottle necks for small scale implementation. The net electricity requirements for the O_2 blown gasification plants (both integrated pyrolysis-gasification and the stand-alone gasification plant) are higher due to increased needs for air separation. The capital costs associated to air separation and compression represent 10-15 % of the total capital investment and thus considerable cost reduction can be achieved if other means of O_2 supply/generation are employed. In connection to the latter and the high carbon penalty paid in the WGS reactor, synergies with renewable hydrogen production via electrolysis can boost the overall carbon efficiency (theoretical carbon efficiencies >50% can be achieved) and at the same time provide pure oxygen supply for the gasification of char.

The best-case scenario (biomass pyrolysis-air gasification of char) for a 50MWth plant indicated a capital investment of 1 700 000 SEK/bpd of liquid product and a total production cost of 10.34 SEK/l of non-hydrotreated liquid product.

Concluding, the integrated pyrolysis gasification with parallel upgrading of bio-oil and syngas to light olefins offer considerably higher carbon efficiencies when compared to stand alone gasification of biomass. Improvements in catalysis for syngas and bio-oil upgrading and direct CO_2 hydrogenation as well as synergies with renewable hydrogen technologies can benefit both the carbon conversion and the process economics.

REFERENCES

- [1] United Nations, Transforming our world: the 2030 Agenda for Sustainable Development | Department of Economic and Social Affairs, United Nations Gen. Assem. (2015). https://sdgs.un.org/2030agenda (accessed March 16, 2021).
- [2] T. Bennich, S. Belyazid, I. Stjernquist, A. Diemer, S. Seifollahi-Aghmiuni, Z. Kalantari, The bio-based economy, 2030 Agenda, and strong sustainability – A regional-scale assessment of sustainability goal interactions, J. Clean. Prod. 283 (2021) 125174. https://doi.org/10.1016/j.jclepro.2020.125174.
- [3] Statens Offentliga Utredningar, Agenda 2030 och Sverige: Världens utmaning världens möjlighet, 2019.
- [4] Regeringskansliet, (n.d.). https://www.regeringen.se/regeringens-politik/globala-malen-ochagenda-2030/globala-mal-for-hallbar-utveckling/ (accessed January 7, 2021).
- [5] S. Eriksson, AB AT LEAST 3 MM3 DROP IN FUELS FROM FOREST RESIDUES IN 2030, n.d.
- [6] Fuels Europe Statistical Report 2019, (2019). https://www.fuelseurope.eu/wpcontent/uploads/FuelsEurope-Statistical-Report-2019.pdf (accessed January 11, 2021).
- [7] E. Kantarelis, W. Yang, W. Blasiak, Biomass pyrolysis for energy and fuels production, in: Technol. Convert. Biomass to Useful Energy, CRC Press, 2013: pp. 245–277.
- [8] R.M. Swanson, A. Platon, J.A. Satrio, R.C. Brown, Techno-economic analysis of biomassto-liquids production based on gasification, Fuel. 89 (2010) S11–S19. https://doi.org/10.1016/j.fuel.2010.07.027.
- [9] E.F. Iliopoulou, K.S. Triantafyllidis, A.A. Lappas, Overview of catalytic upgrading of biomass pyrolysis vapors toward the production of fuels and high-value chemicals, Wiley Interdiscip. Rev. Energy Environ. (2018) e322. https://doi.org/10.1002/wene.322.
- [10] E. Rytter, E. Ochoa-Fernández, A. Fahmi, Biomass-to-Liquids by the Fischer-Tropsch Process, in: Catal. Process Dev. Renew. Mater., Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2013: pp. 265–308. https://doi.org/10.1002/9783527656639.ch10.
- [11] F. Jiao, J. Li, X. Pan, J. Xiao, H. Li, H. Ma, M. Wei, Y. Pan, Z. Zhou, M. Li, S. Miao, J. Li, Y. Zhu, D. Xiao, T. He, J. Yang, F. Qi, Q. Fu, X. Bao, Selective conversion of syngas to light olefins, Science (80-.). 351 (2016) 1065–1068. https://doi.org/10.1126/science.aaf1835.
- F. Gong, Z. Yang, C. Hong, W. Huang, S. Ning, Z. Zhang, Y. Xu, Q. Li, Selective conversion of bio-oil to light olefins: Controlling catalytic cracking for maximum olefins, Bioresour. Technol. 102 (2011) 9247–9254. https://doi.org/10.1016/J.BIORTECH.2011.07.009.
- [13] M. Fakhroleslam, S.M. Sadrameli, Thermal/catalytic cracking of hydrocarbons for the production of olefins; a state-of-the-art review III: Process modeling and simulation, Fuel. 252 (2019) 553–566. https://doi.org/10.1016/j.fuel.2019.04.127.
- [14] M. Stöcker, Methanol to Olefins (MTO) and Methanol to Gasoline(MTG), in: J. Cejka, A. Corma, S. Zones (Eds.), Zeolites Catal. Appl. Vol2., Weinheim, 2010: pp. 687–711.

- [15] A. Morschbacker, Bio-Ethanol Based Ethylene, Polym. Rev. 49 (2009) 79–84. https://doi.org/10.1080/15583720902834791.
- [16] S.N. Naqvi, M. Asaro, R.J. Chang, IHS CHEMICAL Direct Syngas to Light Olefins Direct Syngas to Light Olefins, 2017. https://cdn.ihs.com/www/pdf/RP299-toc.pdf (accessed February 18, 2019).
- [17] J. Sichinga, N. Jordaan, M. Govender, E. Van De Venter, Sasol Coal-to-Liquids Developments Presentation to the Gasification Technologies Council Conf, 10-12 October 2005, San Francisco, n.d.
- [18] D. Lestander, Competition for forest fuels in Sweden-Exploring the possibilities of modeling forest fuel markets in a regional partial equilibrium framework, (2011). http://stud.epsilon.slu.se (accessed February 21, 2019).
- [19] J. de Jong, C. Akselsson, G. Egnell, S. Löfgren, B.A. Olsson, Realizing the energy potential of forest biomass in Sweden – How much is environmentally sustainable?, For. Ecol. Manage. 383 (2017) 3–16. https://doi.org/10.1016/j.foreco.2016.06.028.
- [20] C.M. Nwachukwu, A. Toffolo, C. Wang, C.-E. Grip, E. Wetterlund, Systems analysis of sawmill by-products gasification towards a bio-based steel production, 2018. http://ltu.divaportal.org/smash/get/diva2:1228708/FULLTEXT02.pdf (accessed February 21, 2019).
- [21] A. Vidlund, L. Thesis, Sustainable production of bio-energy products in the sawmill industry, n.d. www.liu.se/energi (accessed January 23, 2021).
- [22] IRENA, Bioenergy from boreal forests: Swedish approach to sustainable wood use, 2019. www.irena.org (accessed March 16, 2021).
- [23] A. Kumar, S. Adamopoulos, D. Jones, S.O. Amiandamhen, Forest Biomass Availability and Utilization Potential in Sweden: A Review, Waste and Biomass Valorization. 1 (2020) 3. https://doi.org/10.1007/s12649-020-00947-0.
- [24] Drivkraft Sverige, Volymer, (n.d.). https://drivkraftsverige.se/statistik/volymer/ (accessed January 11, 2021).
- [25] A.V. Bridgwater, Principles and practice of biomass fast pyrolysis processes for liquids, J. Anal. Appl. Pyrolysis. 51 (1999) 3–22. https://doi.org/10.1016/S0165-2370(99)00005-4.
- [26] E. Kantarelis, R. Javed, S. Stefanidis, A. Psarras, E. Iliopoulou, A. Lappas, Engineering the Catalytic Properties of HZSM5 by Cobalt Modification and Post-synthetic Hierarchical Porosity Development, Top. Catal. 62 (2019). https://doi.org/10.1007/s11244-019-01179-w.
- [27] G. Kabir, B.H. Hameed, Recent progress on catalytic pyrolysis of lignocellulosic biomass to high-grade bio-oil and bio-chemicals, Renew. Sustain. Energy Rev. 70 (2017) 945–967. https://doi.org/10.1016/j.rser.2016.12.001.
- [28] R.H. Venderbosch, A Critical View on Catalytic Pyrolysis of Biomass, ChemSusChem. 8 (2015) 1306–1316. https://doi.org/10.1002/cssc.201500115.
- [29] R.C. Brown, ed., Thermochemical Processing of Biomass, John Wiley & Sons, Ltd, Chichester, UK, 2011. https://doi.org/10.1002/9781119990840.
- [30] H.H. Storch, The Fischer-Tropsch and Related Processes for Synthesis of Hydrocarbons by Hydrogenation of Carbon Monoxide, Adv. Catal. 1 (1948) 115–156. https://doi.org/10.1016/S0360-0564(08)60674-4.

- [31] G.P. Van Der Laan, A.A.C.M. Beenackers, Kinetics and Selectivity of the Fischer-Tropsch Synthesis: A Literature Review, Catal. Rev. Sci. Eng. 41 (1999) 255–318. https://doi.org/10.1081/CR-100101170.
- [32] H.A. Choudhury, S. Chakma, V.S. Moholkar, Biomass Gasification Integrated Fischer-Tropsch Synthesis: Perspectives, Opportunities and Challenges, in: Recent Adv. Thermochem. Convers. Biomass, Elsevier Inc., 2015: pp. 383–435. https://doi.org/10.1016/B978-0-444-63289-0.00014-4.
- [33] S. Abelló, D. Montané, Exploring Iron-based Multifunctional Catalysts for Fischer-Tropsch Synthesis: A Review, ChemSusChem. 4 (2011) 1538–1556. https://doi.org/10.1002/cssc.201100189.
- [34] D. Förtsch, K. Pabst, E. Groß-Hardt, The product distribution in Fischer-Tropsch synthesis: An extension of the ASF model to describe common deviations, Chem. Eng. Sci. 138 (2015) 333–346. https://doi.org/10.1016/j.ces.2015.07.005.
- [35] J.G. Speight, Coal gasification processes for synthetic liquid fuel production, in: Gasif. Synth. Fuel Prod. Fundam. Process. Appl., Elsevier Ltd, 2015: pp. 201–220. https://doi.org/10.1016/B978-0-85709-802-3.00009-6.
- [36] AMF, (n.d.). https://www.iea-amf.org/content/fuel_information/diesel_gasoline (accessed January 27, 2021).
- [37] S.D. Phillips, J.K. Tarud, M.J. Biddy, A. Dutta, Gasoline from Wood via Integrated Gasification, Synthesis, and Methanol-to-Gasoline Technologies, 2007. http://www.osti.gov/bridge (accessed January 22, 2021).
- [38] J. Cooper, FuelsEurope- Statistical report 2020, n.d. https://www.fuelseurope.eu/wp-content/uploads/SR_FuelsEurope-_2020.pdf (accessed March 16, 2021).
- [39] F. Yu, T. Lin, X. Wang, S. Li, Y. Lu, H. Wang, L. Zhong, Y. Sun, Highly selective production of olefins from syngas with modified ASF distribution model, Appl. Catal. A Gen. 563 (2018) 146–153. https://doi.org/10.1016/j.apcata.2018.07.006.
- [40] S. Wang, P. Wang, D. Shi, S. He, L. Zhang, W. Yan, Z. Qin, J. Li, M. Dong, J. Wang, U. Olsbye, W. Fan, Direct Conversion of Syngas into Light Olefins with Low CO2 Emission, ACS Catal. 10 (2020) 2046–2059. https://doi.org/10.1021/acscatal.9b04629.
- [41] A.A. Avidan, Gasoline and distillate fuels from methanol, in: Stud. Surf. Sci. Catal., 1988: pp. 307–323. https://doi.org/10.1016/S0167-2991(09)60524-3.
- [42] J. Wei, Q. Ge, R. Yao, Z. Wen, C. Fang, L. Guo, H. Xu, J. Sun, Directly converting CO2 into a gasoline fuel, Nat. Commun. 8 (2017) 15174. https://doi.org/10.1038/ncomms15174.
- [43] S.A. Tabak, A.A. Avidan, F.J. Krambeck, Production of synthetic gasoline and diesel fuel from non-petroleum resources., in: Am. Chem. Soc., Div. Gas Fuel Chem., Prepr. Am. Chem. Soc. Natl. Meet., New York, 1986.
- [44] A. V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading, Biomass and Bioenergy. 38 (2012) 68–94. https://doi.org/10.1016/j.biombioe.2011.01.048.
- [45] J. Piskorz, D.S. Scott, D. Radlein, Composition of oils obtained by fast pyrolysis of different woods, in: ACS Symp. Ser., 1988: pp. 167–178. https://doi.org/10.1021/bk-1988-0376.ch016.
- [46] P. Basu, Biomass Gasification and Pyrolysis Practical Design and Theory, 2010.

- [47] G. Wiltsee, A. Consultants, Lessons Learned from Existing Biomass Power Plants, n.d. http://www.doe.gov/bridge (accessed January 22, 2021).
- [48] R.G. Jenkins, Thermal Gasification of Biomass A Primer, in: Bioenergy, Elsevier, 2015: pp. 261–286. https://doi.org/10.1016/b978-0-12-407909-0.00016-x.
- [49] A. Larsson, M. Kuba, T. Berdugo Vilches, M. Seemann, H. Hofbauer, H. Thunman, Steam gasification of biomass – Typical gas quality and operational strategies derived from industrial-scale plants, Fuel Process. Technol. 212 (2021) 106609. https://doi.org/10.1016/j.fuproc.2020.106609.
- [50] E. Dahlquist, Technologies for converting biomass to useful energy, CRC Press, 2013.
- [51] T.A. Milne, R.J. Evans, Biomass Gasifier "Tars": Their Nature, Formation, and Conversion, Constraints. (1998) v. https://doi.org/10.2172/3726.
- [52] P. Basu, Gasification theory, in: Biomass Gasification, Pyrolysis Torrefaction Pract. Des. Theory, Elsevier, 2018: pp. 211–262. https://doi.org/10.1016/B978-0-12-812992-0.00007-8.
- [53] Kiel, van Paasen, Neft, Devi, Ptasinsky, Jansen, Meijer, Berets, Temmink, Bren, Padman, Bramer, Primary measures to reduce tar formation in fluidised bed gasifiers, 2004.
- [54] T.B. Vilches, THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING Strategies for controlling solid biomass conversion in dual fluidized bed gasifiers, 2016.
- [55] U. Birk, Status-2000 Hours of Operation with the Viking Gasifier STATUS-2000 HOURS OF OPERATION WITH THE VIKING GASIFIER, 2004.
- [56] M. Amovic, P. Donaj, B. Moner, R. Alzuheri, R. Ljunggren, Fuel testing procedure for pyrolysis and gasification of biomass using TGA and WoodRoll test plant, (2014) 1–47. www.sgc.se (accessed January 22, 2021).
- [57] S. Nilsson, A. Gómez-Barea, D. Fuentes-Cano, P. Ollero, Gasification of biomass and waste in a staged fluidized bed gasifier: Modeling and comparison with one-stage units, Fuel. 97 (2012) 730–740. https://doi.org/10.1016/j.fuel.2012.02.044.
- [58] EXCEPTIONAL GASIFICATION RESULTS FOR CORTUS | Cortus Energy AB, (n.d.). https://www.mynewsdesk.com/se/cortus/pressreleases/exceptional-gasification-results-forcortus-735626 (accessed January 23, 2021).
- [59] E.J. Leijenhorst, W. Wolters, B. Van De Beld, W. Prins, Staged Biomass Gasification by Autothermal Catalytic Reforming of Fast Pyrolysis Vapors, Energy and Fuels. 29 (2015) 7395–7407. https://doi.org/10.1021/acs.energyfuels.5b01912.
- [60] C. Guizani, M. Jeguirim, S. Valin, L. Limousy, S. Salvador, Biomass Chars: The Effects of Pyrolysis Conditions on Their Morphology, Structure, Chemical Properties and Reactivity, Energies. 10 (2017) 796. https://doi.org/10.3390/en10060796.
- [61] M. Morin, S. Pécate, M. Hémati, Y. Kara, Pyrolysis of biomass in a batch fluidized bed reactor: Effect of the pyrolysis conditions and the nature of the biomass on the physicochemical properties and the reactivity of char, J. Anal. Appl. Pyrolysis. 122 (2016) 511–523. https://doi.org/10.1016/j.jaap.2016.10.002.
- [62] S.D. Stefanidis, K.G. Kalogiannis, P.A. Pilavachi, C.M. Fougret, E. Jordan, A.A. Lappas, Catalyst hydrothermal deactivation and metal contamination during the in situ catalytic pyrolysis of biomass, Catal. Sci. Technol. 6 (2016) 2807–2819. https://doi.org/10.1039/C5CY02239H.

- [63] J. Zhou, M. Gao, J. Zhang, W. Liu, T. Zhang, H. Li, Z. Xu, M. Ye, Z. Liu, Directed transforming of coke to active intermediates in methanol-to-olefins catalyst to boost light olefins selectivity, Nat. Commun. 12 (2021) 1–11. https://doi.org/10.1038/s41467-020-20193-1.
- [64] J.H. Harrhy, A. Wang, J.S. Jarvis, P. He, S. Meng, M. Yung, L. Liu, H. Song, Understanding zeolite deactivation by sulfur poisoning during direct olefin upgrading, Commun. Chem. 2 (2019) 1–13. https://doi.org/10.1038/s42004-019-0141-4.
- [65] R.C. Brown, J. Smeenk, S. Sadaka, G. Norton, R. Zhang, A. Suby, K. Cummer, J. Ritzert, M. Xu, S. Lysenko, J. Nunez, N. Brown, BIOMASS-DERIVED HYDROGEN FROM A THERMALLY BALLASTED GASIFIER, n.d. https://www.osti.gov/servlets/purl/901792 (accessed January 24, 2021).
- [66] K. Engvall, H. Kusar, K. Sjöström, L.J. Pettersson, Upgrading of Raw Gas from Biomass and Waste Gasification: Challenges and Opportunities, Top. Catal. 54 (2011) 949–959. https://doi.org/10.1007/s11244-011-9714-x.
- [67] V. Nemanova, K. Engvall, Tar Variability in the Producer Gas in a Bubbling Fluidized Bed Gasification System, Energy & Fuels. 28 (2014) 7494–7500. https://doi.org/10.1021/ef5015617.
- [68] Nexant Inc., Survey and Down-Selection of Acid Gas Removal Systems for the Thermochemical Conversion of Biomass to Ethanol with a Detailed Analysis of an MDEA System Task 1 : Acid Gas Removal Technology Survey and Screening for Thermochemical Ethanol Synthesis, 2009. http://www.osti.gov/bridge (accessed January 29, 2020).
- [69] D. Chiche, C. Diverchy, A.C. Lucquin, F. Porcheron, F. Defoort, Purification des gaz de synthèse, Oil Gas Sci. Technol. 68 (2013) 707–723. https://doi.org/10.2516/ogst/2013175.
- [70] H. Hofbauer, R. Rauch, K. Ripfel-Nitsche, Report on Gas Cleaning for Synthesis Applications, (2007) 75. www.thermalnet.co.uk. (accessed January 29, 2020).
- [71] J.K. Stolaroff, Carbonate solutions for carbon capture : A summary, (2013) 1–19. https://digital.library.unt.edu/ark:/67531/metadc870716/ (accessed January 29, 2020).
- [72] H.F. Garces, H.M. Galindo, L.J. Garces, J. Hunt, A. Morey, S.L. Suib, Low temperature H2S dry-desulfurization with zinc oxide, Microporous Mesoporous Mater. 127 (2010) 190– 197. https://doi.org/10.1016/j.micromeso.2009.07.022.
- [73] A.J. Hernández-Maldonado, R.T. Yang, Desulfurization of liquid fuels by adsorption via π complexation with Cu(I)-Y and Ag-Y zeolites, Ind. Eng. Chem. Res. 42 (2003) 123–129. https://doi.org/10.1021/ie020728j.
- [74] P.R. Westmoreland, D.P. Harrison, Evaluation of Candidate Solids for High-Temperature Desulfurization of Low-Btu Gases, Environ. Sci. Technol. 10 (1976) 659–661. https://doi.org/10.1021/es60118a010.
- [75] E. Sasaoka, K. Taniguchi, M.A. Uddin, S. Hirano, S. Kasaoka, Y. Sakata, Characterization of reaction between ZnO and COS, Ind. Eng. Chem. Res. 35 (1996) 2389–2394. https://doi.org/10.1021/ie950370+.
- [76] C. Frilund, P. Simell, N. Kaisalo, E. Kurkela, M.L. Koskinen-Soivi, Desulfurization of Biomass Syngas Using ZnO-Based Adsorbents: Long-Term Hydrogen Sulfide Breakthrough Experiments, Energy and Fuels. 34 (2020) 3316. https://doi.org/10.1021/acs.energyfuels.9b04276.

- [77] R. Dagie, X.S. Li, K. Spies, J. Rainbolt, B. Braunberger, D. King, R. Xing, Y. Zhu, L. Li, Coal-Derived Warm Syngas Purification and CO 2 Capture- Assisted Methane Production Final Report, 2014.
- [78] K.A. Spies, J.E. Rainbolt, X.S. Li, B. Braunberger, L. Li, D.L. King, R.A. Dagle, Warm Cleanup of Coal-Derived Syngas: Multicontaminant Removal Process Demonstration, (2017). https://doi.org/10.1021/acs.energyfuels.6b02568.
- [79] J. Schlather, B. Turk, Comparison of a New Warm-Gas Desulfurization Process versus Traditional Scrubbers for a Commercial IGCC Power Plant, 2007.
- [80] K.R. Gunugunuri, P. Smirniotis, Water gas shift reaction : research developments and applications, n.d.
- [81] O. Maurstad, An Overview of Coal based Integrated Gasification Combined Cycle (IGCC) Technology, MIT LFEE 2005-002WP, 2005. http://lfee.mit.edu/publicationsPublicationNo.LFEE2005-002WP (accessed January 29, 2020).
- [82] R. Hakkarainen, T. Salmi, R.L. Keiski, Water-gas shift reaction on a cobalt-molybdenum oxide catalyst, Appl. Catal. A, Gen. 99 (1993) 195–215. https://doi.org/10.1016/0926-860X(93)80099-C.
- [83] R. Hakkarainen, T. Salmi, R.L. Keiski, Water-gas shift reaction on a cobalt-molybdenum oxide catalyst, Appl. Catal. A, Gen. 99 (1993) 195–215. https://doi.org/10.1016/0926-860X(93)80099-C.
- [84] R.J. Bartholomew, C. H. Farrauto, Fundamentals of Industrial Catalytic Processes, 2006.
- [85] P. Hou, D. Meeker, H. Wise, Kinetic studies with a sulfur-tolerant water gas shift catalyst, J. Catal. 80 (1983) 280–285. https://doi.org/10.1016/0021-9517(83)90253-1.
- [86] P. Mobed, J. Maddala, R. Rengaswamy, D. Bhattacharyya, R. Turton, Data reconciliation and dynamic modeling of a sour water gas shift reactor, in: Ind. Eng. Chem. Res., 2014: pp. 19855–19869. https://doi.org/10.1021/ie500739h.
- [87] G. Alptekin, Impact of Contaminants Present in Coal-Biomass Derived Synthesis Gas on Water-Gas Shift and Fischer-ropsch Synthesis Catalysts, 2013. https://www.osti.gov/servlets/purl/1070176 (accessed January 21, 2021).
- [88] S. Chianese, J. Loipersböck, M. Malits, R. Rauch, H. Hofbauer, A. Molino, D. Musmarra, Hydrogen from the high temperature water gas shift reaction with an industrial Fe/Cr catalyst using biomass gasification tar rich synthesis gas, Fuel Process. Technol. 132 (2015) 39–48. https://doi.org/10.1016/j.fuproc.2014.12.034.
- [89] E.M. Grieco, G. Baldi, Effects of tar model compounds on commercial water gas shift catalysts, Chem. Eng. Res. Des. 90 (2012) 1997–2001. https://doi.org/10.1016/j.cherd.2012.04.004.
- [90] P.H. Moud, E. Kantarelis, K.J. Andersson, K. Engvall, Biomass pyrolysis gas conditioning over an iron-based catalyst for mild deoxygenation and hydrogen production, Fuel. 211 (2018). https://doi.org/10.1016/j.fuel.2017.09.062.
- [91] E. Abbasi, A. Hassanzadeh, S. Zarghami, H. Arastoopour, J. Abbasian, Regenerable MgObased sorbent for high temperature CO2 removal from syngas: 3. CO2 capture and sorbent enhanced water gas shift reaction, Fuel. 137 (2014) 260–268. https://doi.org/10.1016/j.fuel.2014.07.088.

- [92] C.H. Lee, K.B. Lee, Sorption-enhanced water gas shift reaction for high-purity hydrogen production: Application of a Na-Mg double salt-based sorbent and the divided section packing concept, Appl. Energy. 205 (2017) 316–322. https://doi.org/10.1016/j.apenergy.2017.07.119.
- [93] D. Jansen, E. van Selow, P. Cobden, G. Manzolini, E. Macchi, M. Gazzani, R. Blom, P.P. Henriksen, R. Beavis, A. Wright, SEWGS Technology is Now Ready for Scale-up!, Energy Procedia. 37 (2013) 2265–2273. https://doi.org/10.1016/j.egypro.2013.06.107.
- [94] H.A.J. (Eric) van Dijk, P.D. Cobden, L. Lukashuk, L. van de Water, M. Lundqvist, G. Manzolini, C.-C. Cormos, C. van Dijk, L. Mancuso, J. Johns, D. Bellqvist, STEPWISE Project: Sorption-Enhanced Water-Gas Shift Technology to Reduce Carbon Footprint in the Iron and Steel Industry, Johnson Matthey Technol. Rev. 62 (2018) 395–402. https://doi.org/10.1595/205651318X15268923666410.
- [95] T.J. Stadler, P. Barbig, J. Kiehl, R. Schulz, T. Klövekorn, P. Pfeifer, Sorption-Enhanced Water-Gas Shift Reaction for Synthesis Gas Production from Pure CO: Investigation of Sorption Parameters and Reactor Configurations, Energies. 14 (2021) 355. https://doi.org/10.3390/en14020355.
- [96] C.A. Grande, Advances in Pressure Swing Adsorption for Gas Separation, ISRN Chem. Eng. 2012 (2012) 1–13. https://doi.org/10.5402/2012/982934.
- [97] S. Cavenati, C.A. Grande, A.E. Rodrigues, Separation of CH4/CO2/N2 mixtures by layered pressure swing adsorption for upgrade of natural gas, Chem. Eng. Sci. 61 (2006) 3893– 3906. https://doi.org/10.1016/j.ces.2006.01.023.
- [98] T.E. Rufford, S. Smart, G.C.Y. Watson, B.F. Graham, J. Boxall, J.C. Diniz da Costa, E.F. May, The removal of CO2 and N2 from natural gas: A review of conventional and emerging process technologies, J. Pet. Sci. Eng. 94–95 (2012) 123–154. https://doi.org/10.1016/j.petrol.2012.06.016.
- [99] C.A. Grande, F.V.S. Lopes, A.M. Ribeiro, J.M. Loureiro, A.E. Rodrigues, Adsorption of Off-Gases from Steam Methane Reforming (H 2, CO 2, CH 4, CO and N 2) on Activated Carbon, Sep. Sci. Technol. 43 (2008) 1338–1364. https://doi.org/10.1080/01496390801940952.
- [100] S. Il Yang, D.Y. Choi, S.C. Jang, S.H. Kim, D.K. Choi, Hydrogen separation by multi-bed pressure swing adsorption of synthesis gas, Adsorption. 14 (2008) 583–590. https://doi.org/10.1007/s10450-008-9133-x.
- [101] S. Cho, S. Han, J. Kim, J. Park, H. Rhee, Adsorptive Ethylene Recovery from LDPE Off-Gas, Korean J. Chem. Eng. 19 (2002) 821–826.
- [102] J.H. Park, S.S. Han, J.N. Kim, S.H. Cho, Vacuum Swing Adsorption Process for the Separation of Ethlene/Ethane with AgNo3/Clay Adsorbent, Korean J. Chem. Eng. 21 (2004) 236–245. https://doi.org/10.1007/BF02705404.
- [103] A.G. Gayubo, A.T. Aguayo, A. Atutxa, R. Aguado, M. Olazar, J. Bilbao, Transformation of oxygenate components of biomass pyrolysis oil on a HZSM-5 zeolite. II. Aldehydes, ketones, and acids, Ind. Eng. Chem. Res. 43 (2004) 2619–2626. https://doi.org/10.1021/ie030792g.
- [104] A.G. Gayubo, A.T. Aguayo, A. Atutxa, R. Aguado, J. Bilbao, Transformation of oxygenate components of biomass pyrolysis oil on a HZSM-5 zeolite. I. Alcohols and phenols, Ind. Eng. Chem. Res. 43 (2004) 2610–2618. https://doi.org/10.1021/ie0307910.

- [105] E.A. Uslamin, B. Luna-Murillo, N. Kosinov, P.C.A. Bruijnincx, E.A. Pidko, B.M. Weckhuysen, E.J.M. Hensen, Gallium-promoted HZSM-5 zeolites as efficient catalysts for the aromatization of biomass-derived furans, Chem. Eng. Sci. (2019) 305–316. https://doi.org/10.1016/j.ces.2018.09.023.
- [106] Y.T. Cheng, G.W. Huber, Chemistry of furan conversion into aromatics and olefins over HZSM-5: A model biomass conversion reaction, ACS Catal. 1 (2011) 611–628. https://doi.org/10.1021/cs200103j.
- [107] P.R. Patwardhan, R.C. Brown, B.H. Shanks, Product Distribution from the Fast Pyrolysis of Hemicellulose, ChemSusChem. 4 (2011) 636–643. https://doi.org/10.1002/cssc.201000425.
- [108] H.M. Torres Galvis, K.P. De Jong, Catalysts for production of lower olefins from synthesis gas: A review, ACS Catal. 3 (2013) 2130–2149. https://doi.org/10.1021/cs4003436.
- [109] C.T. O'Connor, M. Kojima, Alkene oligomerization, Catal. Today. 6 (1990) 329–349. https://doi.org/10.1016/0920-5861(90)85008-C.
- [110] H. Er-Rbib, C. Bouallou, F. Werkoff, Production of synthetic gasoline and diesel fuel from dry reforming of methane, in: Energy Procedia, 2012: pp. 156–165. https://doi.org/10.1016/j.egypro.2012.09.020.
- [111] H. Owen, S.A. Tabak, B.S. Wright, Process for converting olefins to gasoline, distillate and alkylate liquid hydrocarbons, US005485919A, 1982. https://doi.org/US005485919A.
- [112] H. Er-Rbib, C. Bouallou, F. Werkoff, Production of synthetic gasoline and diesel fuel from dry reforming of methane, in: Energy Procedia, 2012: pp. 156–165. https://doi.org/10.1016/j.egypro.2012.09.020.
- [113] Standard Motorbränslen Diesel Krav och provningsmetoder (Rättad version 2017-12) SS-EN 590:2013+A1:2017, (n.d.). https://www.sis.se/produkter/petroleum-ochmotsvarande-tekniker/bransle/flytande-branslen/ss-en-5902013a12017/ (accessed January 29, 2020).
- [114] S.A. Tabak, F.J. Krambeck, W.E. Garwood, Conversion of propylene and butylene over ZSM-5 catalyst, AIChE J. 32 (1986) 1526–1531. https://doi.org/10.1002/aic.690320913.
- [115] R.J. Quam, L.A. Green, S.A. Tabak, F.J. Krambeck, Chemistry of Olefin Oligomerization over ZSM-5 Catalyst, Ind. Eng. Chem. Res. J. J. Chem. Tech. Biotechnol. 2731 (1988). http://pubs.acs.org/doi/pdf/10.1021/ie00076a006 (accessed January 11, 2018).
- [116] J. Pechstein, M. Kaltschmitt, Liquid Hydrocarbon Fuels Derived from Alcohols, in: Energy from Org. Mater., Springer New York, 2019: pp. 1023–1046. https://doi.org/10.1007/978-1-4939-7813-7_1039.
- [117] S.A. Tabak, United States Patent TWO STAGESYSTEM FOR CATALYTIC CONVERSION OF OLEFINS WITH DISTILLATE AND GASOLINE MODES, US 4433185, 1984.
- [118] G. Haarlemmer, G. Boissonnet, E. Peduzzi, P.-A. Setier, Investment and production costs of synthetic fuels – A literature survey, Energy. 66 (2014) 667–676. https://doi.org/10.1016/j.energy.2014.01.093.
- [119] Trafik Analys, Fordon 2020, n.d. www.trafa.se/uppdrag/coronapandemin/transportlaget/ (accessed March 16, 2021).

- [120] Transport Analysis, Vehicle Statistics, (2020) 4–7. https://www.trafa.se/en/road-traffic/vehicle-statistics/ (accessed March 16, 2021).
- [121] H. Thunman, M. Seemann, The GoBiGas plant, in: Substit. Nat. Gas from Waste, Elsevier, 2019: pp. 455–474. https://doi.org/10.1016/B978-0-12-815554-7.00017-9.
- [122] Fast pyrolysis Biomass Technology Group BV, (n.d.). https://www.btgworld.com/en/rtd/technologies/fast-pyrolysis (accessed January 24, 2021).
- [123] J. -X Zhu, Z. -Q Yu, Y. Jin, J.R. Grace, A. Issangya, Cocurrent downflow circulating fluidized bed (downer) reactors — A state of the art review, Can. J. Chem. Eng. 73 (1995) 662–677. https://doi.org/10.1002/cjce.5450730510.
- [124] Prakash Rao, Michael Muller, Industrial Oxygen: Its Generation and Use, 2007 ACEEE Summer Study Energy Effic. Ind. (2007) 124–135. http://aceee.org/files/proceedings/2007/data/papers/78_6_080.pdf (accessed January 24, 2021).
- [125] D. Ferreira, M. Boaventura, P. Bárcia, R.D. Whitley, A. Mendes, Two-Stage Vacuum Pressure Swing Adsorption Using AgLiLSX Zeolite for Producing 99.5+% Oxygen from Air, Ind. Eng. Chem. Res. 55 (2016) 722–736. https://doi.org/10.1021/acs.iecr.5b03535.
- [126] D. Baruah, D.C. Baruah, Modeling of biomass gasification: A review, Renew. Sustain. Energy Rev. 39 (2014) 806–815. https://doi.org/10.1016/j.rser.2014.07.129.
- [127] A.V. Bridgwater, The technical and economic feasibility of biomass gasification for power generation, Fuel. 74 (1995) 631–653. https://doi.org/10.1016/0016-2361(95)00001-L.
- [128] A.L. Villanueva Perales, A. Gomez-Barea, E. Revuelta, M. Campoy, P. Ollero, Guidelines for selection of gasifiers modelling strategies, in: 16th Eur. Biomass Conf. Exhib., ETA Renewable Energies, [Florence?], 2008: pp. 980–986.
- [129] M. Puig-Arnavat, J.C. Bruno, A. Coronas, Review and analysis of biomass gasification models, Renew. Sustain. Energy Rev. 14 (2010) 2841–2851. https://doi.org/10.1016/j.rser.2010.07.030.
- [130] J. Andersson, Techno-Economic Analysis of Integrated Biomass Gasification for Green Chemical Production, 2013.
- [131] S. Ferreira, E. Monteiro, P. Brito, C. Vilarinho, A Holistic Review on Biomass Gasification Modified Equilibrium Models, Energies. 12 (2019) 160. https://doi.org/10.3390/en12010160.
- [132] C.R. Altafini, P.R. Wander, R.M. Barreto, Prediction of the working parameters of a wood waste gasifier through an equilibrium model, Energy Convers. Manag. 44 (2003) 2763– 2777. https://doi.org/10.1016/S0196-8904(03)00025-6.
- [133] S. Jarungthammachote, A. Dutta, Equilibrium modeling of gasification: Gibbs free energy minimization approach and its application to spouted bed and spout-fluid bed gasifiers, Energy Convers. Manag. 49 (2008) 1345–1356. https://doi.org/10.1016/j.enconman.2008.01.006.
- [134] M. Materazzi, P. Lettieri, L. Mazzei, R. Taylor, C. Chapman, Thermodynamic modelling and evaluation of a two-stage thermal process for waste gasification, Fuel. 108 (2013) 356– 369. https://doi.org/10.1016/j.fuel.2013.02.037.

- [135] A. Molino, S. Chianese, D. Musmarra, Biomass gasification technology: The state of the art overview, J. Energy Chem. 25 (2016) 10–25. https://doi.org/10.1016/j.jechem.2015.11.005.
- [136] C.C. Sreejith, P. Arun, C. Muraleedharan, Thermochemical Analysis of Biomass Gasification by Gibbs Free Energy Minimization Model—Part: I (Optimization of Pressure and Temperature), Int. J. Green Energy. 10 (2013) 231–256. https://doi.org/10.1080/15435075.2011.653846.
- [137] K. Qin, Entrained Flow Gasification of Biomass, DTU, 2012.
- [138] B. Peters, C. Bruch, Drying and pyrolysis of wood particles: Experiments and simulation, J. Anal. Appl. Pyrolysis. 70 (2003) 233–250. https://doi.org/10.1016/S0165-2370(02)00134-1.
- [139] X. Wang, S.R.A. Kersten, W. Prins, W.P.M. Van Swaaij, Biomass pyrolysis in a fluidized bed reactor. Part 2: Experimental validation of model results, Ind. Eng. Chem. Res. 44 (2005) 8786–8795. https://doi.org/10.1021/ie050486y.
- [140] M. Garcia-Perez, X.S. Wang, J. Shen, M.J. Rhodes, F. Tian, W.J. Lee, H. Wu, C.Z. Li, Fast pyrolysis of oil mallee woody biomass: Effect of temperature on the yield and quality of pyrolysis products, Ind. Eng. Chem. Res. 47 (2008) 1846–1854. https://doi.org/10.1021/ie071497p.
- [141] H. Yang, S. Kudo, H.P. Kuo, K. Norinaga, A. Mori, O. Mašek, J.I. Hayashi, Estimation of enthalpy of bio-oil vapor and heat required for pyrolysis of biomass, Energy and Fuels. 27 (2013) 2675–2686. https://doi.org/10.1021/ef400199z.
- [142] T. Olewski, B. Todic, L. Nowicki, N. Nikacevic, D.B. Bukur, Hydrocarbon selectivity models for iron-based Fischer-Tropsch catalyst, Chem. Eng. Res. Des. 95 (2015) 1–11. https://doi.org/10.1016/j.cherd.2014.12.015.
- [143] M. Hillestad, Modeling the Fischer-Tropsch Product Distribution and Model Implementation, Chem. Prod. Process Model. 10 (2015) 147–159. https://doi.org/10.1515/cppm-2014-0031.
- [144] T.N. Do, J. Kim, Green C2-C4 hydrocarbon production through direct CO2 hydrogenation with renewable hydrogen: Process development and techno-economic analysis, Energy Convers. Manag. 214 (2020) 112866. https://doi.org/10.1016/j.enconman.2020.112866.
- [145] S. Najari, G. Gróf, S. Saeidi, F. Gallucci, Modeling and optimization of hydrogenation of CO 2 : Estimation of kinetic parameters via Artificial Bee Colony (ABC) and Differential Evolution (DE) algorithms, Int. J. Hydrogen Energy. 44 (2019) 4630–4649. https://doi.org/10.1016/j.ijhydene.2019.01.020.
- [146] R.A. Alberty, K.C. Chou, Representation of standard chemical thermodynamic properties of isomer groups by equations, J. Phys. Chem. 94 (1990) 1669–1674. https://doi.org/10.1021/j100367a082.
- [147] R.A. Alberty, Extrapolation of standard chemical thermodynamic properties of alkene isomer groups to higher carbon numbers, J. Phys. Chem. 87 (1983) 4999–5002. https://doi.org/10.1021/j150642a045.
- [148] J.R. Shahrouzi, D. Guillaume, P. Rouchon, P. Da Costa, Stochastic Simulation and Single Events Kinetic Modeling: Application to Olefin Oligomerization, Ind. Eng. Chem. Res. 47 (2008) 4308–4316. https://doi.org/10.1021/ie0712151.

- [149] W.E. Garwood, CONVERSION OF C2-C10 OLEFINS TO HIGHER OLEFINS OVER SYNTHETIC ZEOLITE ZSM-5., in: Am. Chem. Soc. Div. Pet. Chem. Prepr., 1982: pp. 563–557. https://doi.org/10.1021/bk-1983-0218.ch023.
- [150] R.A. Alberty, Thermodynamics of the catalytic polymerization of alkenes in the gas phase, Chem. Eng. Sci. 42 (1987) 2325–2330. https://doi.org/10.1016/0009-2509(87)80105-7.
- [151] R.A. Alberty, Kinetics of the polymerization of alkenes on zeolites, J. Chem. Phys. 87 (1987) 3660–3667. https://doi.org/10.1063/1.452963.
- [152] L. Ying, J. Zhu, Y. Cheng, L. Wang, X. Li, Kinetic modeling of C2-C7 olefins interconversion over ZSM-5 catalyst, J. Ind. Eng. Chem. 33 (2016) 80–90. https://doi.org/10.1016/j.jiec.2015.09.021.
- [153] D. Chiche, J.M. Schweitzer, Investigation of competitive COS and HCN hydrolysis reactions upon an industrial catalyst: Langmuir-Hinshelwood kinetics modeling, Appl. Catal. B Environ. 205 (2017) 189–200. https://doi.org/10.1016/J.APCATB.2016.12.002.
- [154] R. Turton, D.A. Berry, T.H. Gardner, A. Miltz, Evaluation of Zinc Oxide Sorbents in a Pilot-Scale Transport Reactor: Sulfidation Kinetics and Reactor Modeling, Ind. Eng. Chem. Res. 43 (2004) 1235–1243. https://doi.org/10.1021/ie030364a.
- [155] S. Tong, I.G. Dalla Lana, K.T. Chuang, Kinetic modelling of the hydrolysis of carbonyl sulfide catalyzed by either titania or alumina, Can. J. Chem. Eng. 71 (1993) 392–400. https://doi.org/10.1002/cjce.5450710308.
- [156] B. Smith R J, M. Loganathan, M.S. Shantha, A review of the water gas shift reaction kinetics, Int. J. Chem. React. Eng. 8 (2010). https://doi.org/10.2202/1542-6580.2238.
- [157] P. Kumar, E. Akpan, H. Ibrahim, A. Aboudheir, R. Idem, Kinetics and Reactor Modeling of a High Temperature Water–Gas Shift Reaction (WGSR) for Hydrogen Production in a Packed Bed Tubular Reactor (PBTR), Ind. Eng. Chem. Res. 47 (2008) 4086–4097. https://doi.org/10.1021/ie071547q.
- [158] Y. Choi, H.G. Stenger, Water gas shift reaction kinetics and reactor modeling for fuel cell grade hydrogen, J. Power Sources. 124 (2003) 432–439. https://doi.org/10.1016/S0378-7753(03)00614-1.
- [159] J. Sun, J. Desjardins, J. Buglass, K. Liu, Noble metal water gas shift catalysis: Kinetics study and reactor design, Int. J. Hydrogen Energy. 30 (2005) 1259–1264. https://doi.org/10.1016/j.ijhydene.2005.02.013.
- [160] N.E. Amadeo, M.A. Laborde, Hydrogen production from the low-temperature water-gas shift reaction: Kinetics and simulation of the industrial reactor, Int. J. Hydrogen Energy. 20 (1995) 949–956. https://doi.org/10.1016/0360-3199(94)00130-R.
- [161] T.A. Adams II, P.I. Barton, A dynamic two-dimensional heterogeneous model for water gas shift reactors, Int. J. Hydrogen Energy. 34 (2009) 8877–8891. https://doi.org/10.1016/j.ijhydene.2009.08.045.
- [162] A. Kapoor, J.A. Ritter, R.T. Yang, An extended Langmuir model for adsorption of gas mixtures on heterogeneous surfaces, Langmuir. 6 (1990) 660–664. https://doi.org/10.1021/la00093a022.
- [163] N. Tzabar, H.J.M. ter Brake, Adsorption isotherms and Sips models of nitrogen, methane, ethane, and propane on commercial activated carbons and polyvinylidene chloride, Adsorption. 22 (2016) 901–914. https://doi.org/10.1007/s10450-016-9794-9.

- [164] M.-H. Lai, R.Q. Chu, H.-C. Huang, S.-H. Shu, T.-W. Chung, Equilibrium Isotherms of Volatile Alkanes, Alkenes, and Ketones on Activated Carbon, J. Chem. Eng. Data. 54 (2009) 2208–2215. https://doi.org/10.1021/je800826d.
- [165] D.D. Do, X. Hu, P.L.J. Mayfield, Multicomponent adsorption of ethane, n-butane and npentane in activated carbon, Gas Sep. Purif. 5 (1991) 35–48. https://doi.org/10.1016/0950-4214(91)80047-9.
- [166] A. V. Bridgwater, D. Meier, D. Radlein, An overview of fast pyrolysis of biomass, Org. Geochem. 30 (1999) 1479–1493. https://doi.org/10.1016/S0146-6380(99)00120-5.
- [167] C. Panzone, R. Philippe, A. Chappaz, P. Fongarland, A. Bengaouer, Power-to-Liquid catalytic CO2 valorization into fuels and chemicals: Focus on the Fischer-Tropsch route, J. CO2 Util. 38 (2020) 314–347. https://doi.org/10.1016/j.jcou.2020.02.009.
- [168] Energiinnehåll, densitet och koldioxidutsläpp Drivkraft Sverige, (n.d.). https://drivkraftsverige.se/uppslagsverk/fakta/berakningsfaktorer/energiinnehall-densitetoch-koldioxidemission/ (accessed January 27, 2021).
- [169] A. Toffolo, A. Lazzaretto, M. Morandin, The HEATSEP method for the synthesis of thermal systems: An application to the S-Graz cycle, Energy. 35 (2010) 976–981. https://doi.org/10.1016/j.energy.2009.06.030.
- [170] L.R. Matthews, A.M. Niziolek, O. Onel, N. Pinnaduwage, C.A. Floudas, Biomass to Liquid Transportation Fuels via Biological and Thermochemical Conversion: Process Synthesis and Global Optimization Strategies, Ind. Eng. Chem. Res. 55 (2016) 3205–3225. https://doi.org/10.1021/acs.iecr.5b03319.
- [171] T.G. Kreutz, E.D. Larson, G. Liu, R.H. Williams, Fischer-Tropsch Fuels from Coal and Biomass, n.d.
- [172] M.T. Ho, Techno-economic Modelling of CO2 Capture Systems for Australian Industrial Sources, 2007.
- [173] J.R. Couper, W.R. Penney, J.R. Fair, S.M. Walas, Costs of Individual Equipment, in: Chem. Process Equip., Elsevier, 2012: pp. 731–741. https://doi.org/10.1016/b978-0-12-396959-0.00021-5.
- [174] A. Carballo-Meilan, Regeneration of Activated Carbon by Photocatalysis using Titanium Dioxide, 2015. https://dspace.lboro.ac.uk/dspace-jspui/handle/2134/19065 (accessed January 25, 2021).
- [175] J. Andersson, J. Lundgren, M. Marklund, Methanol production via pressurized entrained flow biomass gasification - Techno-economic comparison of integrated vs. stand-alone production, Biomass and Bioenergy. 64 (2014) 256–268. https://doi.org/10.1016/j.biombioe.2014.03.063.
- [176] H. Thunman, C. Gustavsson, A. Larsson, I. Gunnarsson, F. Tengberg, Economic assessment of advanced biofuel production via gasification using cost data from the GoBiGas plant, Energy Sci. Eng. 7 (2019) 217–229. https://doi.org/10.1002/ese3.271.
- [177] R.C. Baliban, J.A. Elia, C.A. Floudas, Optimization framework for the simultaneous process synthesis, heat and power integration of a thermochemical hybrid biomass, coal, and natural gas facility, Comput. Chem. Eng. 35 (2011) 1647–1690. https://doi.org/10.1016/j.compchemeng.2011.01.041.

- [178] I. Hannula, V. Arpiainen, Light olefins and transport fuels from biomass residues via synthetic methanol: performance and cost analysis, Biomass Convers. Biorefinery. 5 (2015) 63–74. https://doi.org/10.1007/s13399-014-0123-9.
- [179] R.C. Baliban, J.A. Elia, C.A. Floudas, X. Xiao, Z. Zhang, J. Li, H. Cao, J. Ma, Y. Qiao, X. Hu, Thermochemical Conversion of Duckweed Biomass to Gasoline, Diesel, and Jet Fuel: Process Synthesis and Global Optimization, Ind. Eng. Chem. Res. 52 (2013) 11436–11450. https://doi.org/10.1021/ie3034703.
- [180] R. Smith, Chemical_Process Design and Integration 2nd Edition.pdf, (2016) 896.
- [181] D.C. Rosenfeld, H. Böhm, J. Lindorfer, M. Lehner, Scenario analysis of implementing a power-to-gas and biomass gasification system in an integrated steel plant: A technoeconomic and environmental study, Renew. Energy. 147 (2020) 1511–1524. https://doi.org/10.1016/j.renene.2019.09.053.
- [182] Industrins elkostnader ligger Sverige så lågt som många säger? | SKGS, (n.d.). https://www.skgs.org/industrins-elkostnader-ligger-sverige-sa-lagt-som-manga-sager/ (accessed January 26, 2021).
- [183] K. Lundell, Billig el i svensk industri minskar drivkraften att spara, (2019). https://www.sverigesnatur.org/aktuellt/billig-el-i-svensk-industri-minskar-drivkraften-attspara/ (accessed January 26, 2021).
- [184] Kontrollrummet | Svenska kraftnät, (n.d.). https://www.svk.se/drift-avtransmissionsnatet/kontrollrummet/ (accessed January 26, 2021).
- [185] Sweden: industrial prices for electricity 1996-2019 | Statista, (n.d.). https://www.statista.com/statistics/596262/electricity-industry-price-sweden/ (accessed January 26, 2021).
- [186] G. Kakoulaki, I. Kougias, N. Taylor, F. Dolci, J. Moya, A. Jäger-Waldau, Green hydrogen in Europe – A regional assessment: Substituting existing production with electrolysis powered by renewables, Energy Convers. Manag. 228 (2021) 113649. https://doi.org/10.1016/j.enconman.2020.113649.

APPENDIX



Figure 45. Process Scheme 1 -O2 blown biomass gasification.



Figure 46. Process Scheme 2 -Biomass pyrolysis O₂ blown gasification of char.



Figure 47. Process scheme 3 - Biomass pyrolysis air gasification of char.

PROCESS CONDITIONS

Process scheme 1- Biomass O₂ gasification

Table 20. 2020 fuel mix scenario for process scheme 1.

Unit	P (bar)	Т (°С)	Heat (kW/ton _{biomass daf}) *	WHSV (h ⁻¹)/ GHSV (l kg _{cat} ⁻¹ h ⁻¹)
Gasifier (R101)	2.5	1151	233.5	-
WGS Reactor(R501)	2.5	388**		28/ 49 660
Syngas to Olefins Reactor(R601)	2	280	448	-/ 60.3
Syngas to Olefins Reactor(R602)	2	280	209.2	-/ 32
Syngas to Olefins Reactor(R603)	2	280	59.4	-/ 5.8
MOGD Reactor (R701)	5	340	76	0.5 /-
MOGD Reactor (R702)	2.5	340	3.5	0.5 /-
Off-gases combustor	1	1759	1325	-

* Negative values indicate heat requirement.

** Average temperature between inlet and outlet in adiabatic operation.

Unit	P (bar)	Т (°С)	Heat (kW/MW _{th.biom daf}) *	WHSV (h ⁻¹)/ GHSV (l kg _{cat} -1h-1)
Gasifier (R101)	2.5	1151	233.5	-
WGS Reactor(R501)	2.5	388**		28/ 49 660
Syngas to Olefins Reactor(R601)	2	280	448	-/ 60.3
Syngas to Olefins Reactor(R602)	2	280	209.2	-/ 32
Syngas to Olefins Reactor(R603)	2	280	59.4/ton	-/ 5.8
MOGD Reactor (R701)	5	340	80.5	0.5 /-
MOGD Reactor (R702)	2.5	340	1.6	0.5 /-
Off-gases combustor	1	1759	1328	-

Table 21. 2030 fuel mix scenario for process scheme 1.

* Negative values indicate heat requirement.

** Average temperature between inlet and outlet in adiabatic operation.

Process scheme 2 - Biomass Pyrolysis -char O₂ gasification

Table 22. 2020	fuel mix	scenario for	process scheme 2.
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Unit	P (bar)	Т (°С)	Heat (kW/ton _{biomass daf}) *	WHSV (h [.] 1)/ GHSV (l kg _{cat} ^{.1} h ^{.1})
Pyrolizer (R101)	2.5	485	-146.2	-
Gasifier (R102)	2.5	950	263	-
Bio-oil to olefins Reactor(R301)	2	600	-613	0.4
Olefins oligomerization reactor - MOGD (R401)	5	300	42.51	0.5
WGS Reactor(R501)	2.5	307**		2.02/2520
Syngas to Olefins Reactor(R601)	2	290	124	174.7
Syngas to Olefins Reactor(R602)	2	290	78.42	90.2/.
Syngas to Olefins Reactor(R603)	2	290	36.7	17/-
MOGD Reactor (R701)	5	330	63.5	0.5/-
MOGD Reactor (R702)	2.5	300	3.96	0.5/-
Off-gases combustor	1	1708	1586.3	-
* Negative values indicate heat requirement.				

** Average temperature between inlet and outlet in adiabatic operation.

Unit	P (bar)	Т (°С)	Heat (kW/ton _{biomass daf})*	WHSV (h ⁻¹)/ GHSV (l kg _{cat} -1h-1)	
Pyrolizer (R101)	2.5	485	-146.2	-	
Gasifier (R102)	2.5	950	263	-	
Bio-oil to olefins Reactor(R301)	2	600	-613.1	0.4	
Olefins oligomerization reactor - MOGD (R401)	5	300	10.41	0.5	
WGS Reactor(R501)	2.5	307**		2.02/2520	
Syngas to Olefins Reactor(R601)	2	290	124	174.7/-	
Syngas to Olefins Reactor(R602)	2	290	78.42	90.24/-	
Syngas to Olefins Reactor(R603)	2	290	36.7	17/-	
MOGD Reactor (R701)	5	330	100.26	0.5/-	
MOGD Reactor (R702)	2.5	300	2.41	0.5/-	
Off-gases combustor	1	1708	1618.7	-	
* Negative values indicate heat requirement					

Table 23. 2030 fuel mix scenario for process scheme 2.

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** Average temperature between inlet and outlet in adiabatic operation.

Process scheme 3- Biomass Pyrolysis -char air gasification

Table 24. 2020 fuel mix scenario for process scheme 3.

Unit	P (bar)	Т (°С)	Heat (kW/ton _{biomass daf})*	WHSV (h ⁻¹)/ GHSV (l kg _{cat} ⁻¹ h ⁻¹)	
Pyrolizer (R101)	2.5	485	-146.2	-	
Gasifier (R102)	2.5	950	190	-	
Bio-oil to olefins Reactor(R301)	2	600	-613	0.4	
Olefins oligomerization reactor - MOGD (R401)	5	320	33.8	0.5	
WGS Reactor(R501)	2.5	318**		3.5/ 5 3411	
Syngas to Olefins Reactor(R601)	2	290	209.2	-/151	
Syngas to Olefins Reactor(R602)	2	290	117.6	-/171.5	
Syngas to Olefins Reactor(R603)	2	290	25.99	-/119	
MOGD Reactor (R701)	5	340	72.8	0.5 /-	
MOGD Reactor (R702)	2.5	340	5.6	0.5 /-	
Off-gases combustor	1	1585	954	-	
* Negative values indicate heat requirement.					

** Average temperature between inlet and outlet in adiabatic operation.

Unit	P (bar)	Т (°С)	Heat (kW/ton _{biomass daf}) *	WHSV (h ⁻¹)/ GHSV (l kg _{cat} ⁻¹ h ⁻¹)	
Pyrolizer (R101)	2.5	485	-146.2		
Gasifier (R102)	2.5	950	190	-	
Bio-oil to olefins Reactor(R301)	2	600	-613	0.4	
Olefins oligomerization reactor - MOGD (R401)	2	340	42.51	0.5	
WGS Reactor(R501)	2.5	318**		3.5/ 5 3411	
Syngas to Olefins Reactor(R601)	2	290	157	-/151	
Syngas to Olefins Reactor(R602)	2	290	70.5 /ton	-/171.5	
Syngas to Olefins Reactor(R603)	2	290	36/ton	-/119	
MOGD Reactor (R701)	5	310	106.7	0.5 /-	
MOGD Reactor (R702)	2.5	300	3.2	0.5 /-	
Off-gases combustor	1	1585	954	-	
* Negative values indicate heat requirement.					

Table 25. 2030 fuel mix scenario for process scheme 3.

** Average temperature between inlet and outlet in adiabatic operation.











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