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Flexible Production of Liquid Biofuels via Thermochemical Treatment of Biomass and Olefins Oligomerization: a Process Study

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The use of residual biomass streams for production of liquid fuels will help in achieving the goal of renewable transportation fuels and sustainable society. Hence, efficient, and reliable processes offering a flexible product distribution proven at commercial scale are required.

This study explores the technical feasibility of producing gasoline and diesel range hydrocarbons from thermochemical processing of biomass via the production of light olefins (C_2-C_4) and their subsequent oligomerization through mathematical modelling and simulation using MATLAB software.

Different biomass processing scenarios were considered, including a standalone biomass gasification plant and integrated biomass pyrolysis- char gasification (O_2- or air-blown) process.

Process analysis indicated that the integrated plant offers 10-11% higher carbon efficiency. The processing step with the highest carbon penalty for all the cases is the syngas composition tailoring via water-gas shift reaction.

1. Introduction

Transition to a bio-based economy entails the development of innovative and highly efficient processes based on renewable materials. In Sweden, this transformation urges the production of millions of cubic meters of bio-based transportation fuels (Eriksson 2017). At the same time, the fuel type (gasoline or diesel) demand is expected to fluctuate considerably, and thus different fuel mix (gasoline and diesel) will be required.

Thermochemical conversion of biomass to transportation fuels via catalytic deoxygenation of pyrolysis liquids results in low overall carbon efficiencies (Venderbosch 2015); in addition, Fischer-Tropsch synthesis (FT) exhibits low carbon efficiency to specific fuel cuts due to the unfavourable Anderson-Schulz-Flory (ASF) product distribution (Abelló et al.,2011). The production of highly valuable intermediates such as light olefins (C_2-C_4) would allow the selective production of diesel and/or gasoline at desired proportions by adjusting the operating conditions, as demonstrated by Mobil's Olefins to Gasoline and Distillate process (MOGD) (Keil, 1999).

MOGD shows great selectivity to gasoline and diesel (>95%) and is versatile (Tabak et al. 1986). The product composition varies from <1% to 83% diesel with the rest being gasoline (Tabak et al. 1990). It is mainly iso-paraffinic (after hydrotreatment) and has a very high cetane number, when compared to the typical FT process which produces low octane normal paraffins (Wei et al., 2017).

Recent developments indicate that direct synthesis of lower olefins from syngas is achieved with high selectivity without the limitations of the ASF product distribution (Jiao et al. 2016), offering higher carbon efficiencies. Separation of pyrolysis and gasification steps in an integrated plant can offer higher carbon efficiency (Rytter et al. 2013). Light olefins are of high demand in the chemical industry which adds extra product flexibility considering that in the future the transportation fleet will be electrified.

All the above suggest that the direct conversion of pyrolysis vapors and syngas to olefins is a more carbon efficient route and thus, is a promising alternative for conversion of biomass to liquids fuels.

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In this study, the technical feasibility of gasoline and diesel range hydrocarbons production via oligomerization of olefins synthesized from biomass-derived syngas, is investigated through mathematical modelling and simulation using MATLAB software. Different scenarios with biomass and/or bio-char feeding were regarded for meeting different proportions of product (gasoline or diesel) demand based on Swedish forecast for 2030.

2. Methods

Two different process layouts were considered, based on biomass gasification, or combined biomass pyrolysis- char gasification process, coupled to syngas and/or biooil-to-olefins conversion followed by the MOGD process. The two simplified layouts are shown in Figure 1.

Biomass/char gasification is followed by gas cleaning and conditioning (water-gas shift reaction -WGS), direct syngas-to-olefins synthesis, and subsequent olefins oligomerization (MOGD process).

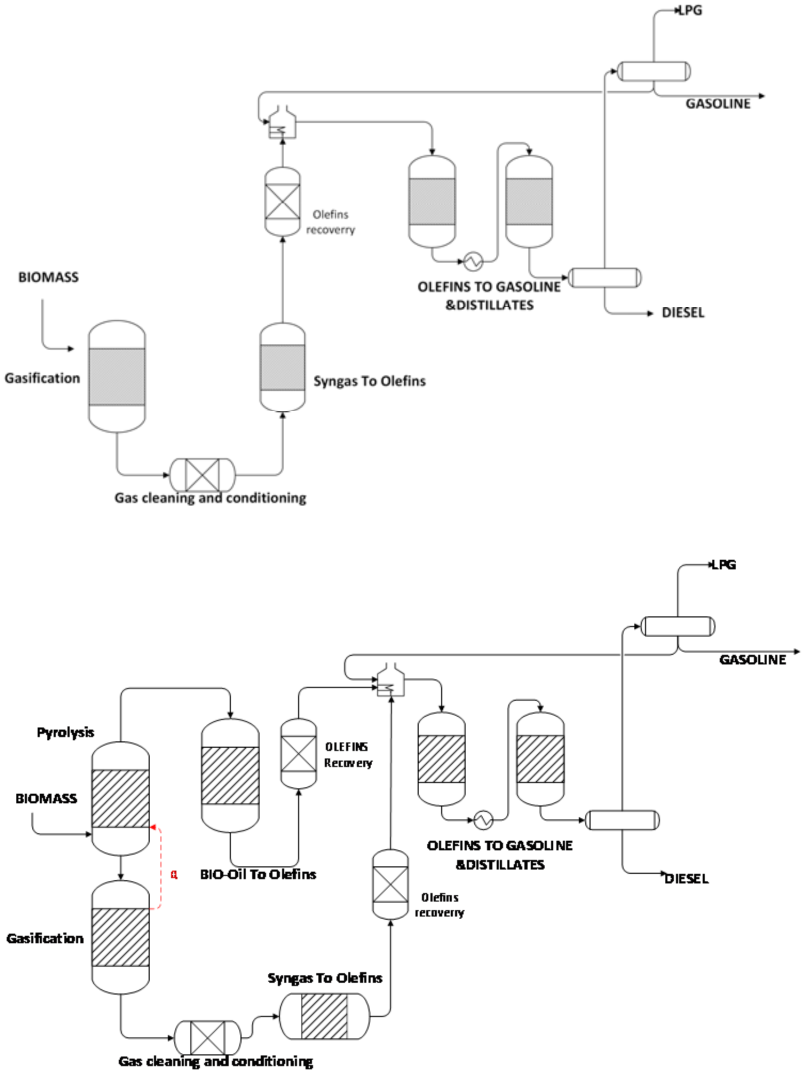

Figure 1: Simplified process flow diagram of biomass gasification and MOGD process (top) and combined pyrolysis-gasification and MOGD process (bottom).

The fuel type (fossil-based Gasoline and Diesel) demand ratio (G/D) for the years 2020 and 2030 was determined based on statistics for transportation fuel consumption, assuming a linear projection for the year 2030 without accounting for any other market parameters (e.g., electrification etc.) (Figure 2). Three process scenarios were investigated with the thermochemical treatment of the biomass being the differing point, namely, O_2-blown biomass gasification in entrained-flow gasifier; biomass pyrolysis-char air gasification in fluidized-bed reactor; biomass pyrolysis-char O_2 gasification in fluidized-bed reactor (*Table 1*).

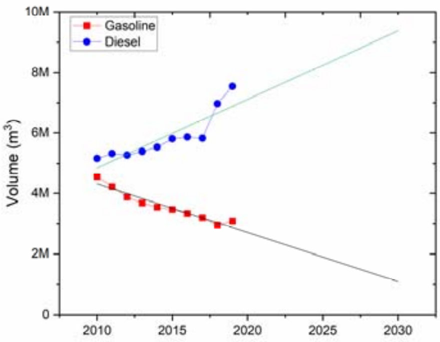

Figure 2: Fossil-based gasoline and diesel demand in Sweden with projection for the year 2030

Table 1: Different Scenarios investigated

Biomass Process	G/D	Notes
O_2-blown gasification of biomass	2020	Entrained-flow gasification (T>1000 °C)
O_2-blown gasification of biomass	2030	Entrained-flow gasification (T>1000 °C)
Biomass pyrolysis-air gasification of char	2020	Fluidized-bed gasification (T< 1000 °C)
Biomass pyrolysis-air gasification of char	2030	Fluidized-bed gasification (T< 1000 °C)
Biomass pyrolysis-O_2 gasification of char	2020	Fluidized-bed gasification (T< 1000 °C)
Biomass pyrolysis-O_2 gasification of char	2030	Fluidized-bed gasification (T< 1000 °C)

Gasification of biomass and/or char was modelled using a constrained non-stoichiometric Gibbs minimization model with temperature approach for methane reforming and tuned with the data from a pilot plant in Sweden (Cortus Energy). Contaminants such as H_2S, COS, NH_3 and HCN were included in the model while the tar was not considered. The latter holds as a valid assumption given the high operating temperature of the gasifier (>1000 °C) in the biomass gasification scenarios; in addition, the gasification of the volatile-stripped char in the integrated pyrolysis-gasification case should not produce any tars.

Producer gas cleaning section included high- and low- temperature sulfur removal units using ZnO for H_2S and COS removal and hydrolysis. H_2/CO tailoring for olefins synthesis was achieved by sorption enhanced sour water-gas shift (WGS) reactor (Mobed et al. 2014). The combination of WGS catalyst with CO_2 sorbents has shown itself to be an efficient method to improve conversion with simultaneous CO_2 capture (Abbasi et al. 2014). A heterogeneous plug flow packed bed model was employed for the WGS reactor.

Gas separation units (for plant capacities 5-50 $MW_{th\ biomass}$) were based on pressure- and vacuum swing adsorption processes and were modelled using multi-component Langmuir adsorption models. The limitation of $50MW_{th\ biomass}$ was considered due to biomass logistics constraints (Haarlemmer et al. 2014).

Syngas-to-olefins process used a pseudo homogeneous plug flow model based on kinetic expressions from Do et al. (2020), while biomass pyrolysis model used experimental data from Garcia-Perez et al. (2008) for fast pyrolysis conditions (fast heating rates and short (<2s) residence time). The bio-oil to olefins process was based on data by Gong et al., (2011).

Oligomerization of olefins considered compounds from C_2 to C_{20}.The oligomerization model was based on (Alberty, 1987) while isomer group properties were estimated based on Alberty's model (Alberty,1987). C_7-C_{11} fraction was considered as gasoline cut and C_{12} to C_{20} as diesel cut.

The different scenarios and process layouts were evaluated with regards to carbon efficiency (η_C) and well as to energy efficiency based on biomass HHV (η_{EHHV}), defined as:

$$\eta_{EHHV}=\frac{m_{gasoline\ and\ diesel}HHV_{gasoline\ and\ diesel}}{m_{biomass}HHV_{biomass}} \tag{1}$$

The overall energy efficiency includes the electricity requirements for gas compression and any additional heat for the process.

$$\eta_{Eoveral}=\frac{m_{gasoline\ and\ diesel}HHV_{gasoline\ and\ diesel}}{m_{biomass}HHV_{biomass}+Electricity+Heat} \tag{2}$$

3. Results and Discussion

It was found that gasification operation at 2.5 bar was enough to overcome pressure drop of the system until the syngas-to-olefins section which operated at 1.5 bar. It is assumed that the slightly increased pressure does not affect the pyrolysis reactor yields. The obtained carbon efficiencies for the different scenarios are shown in Figure 3.

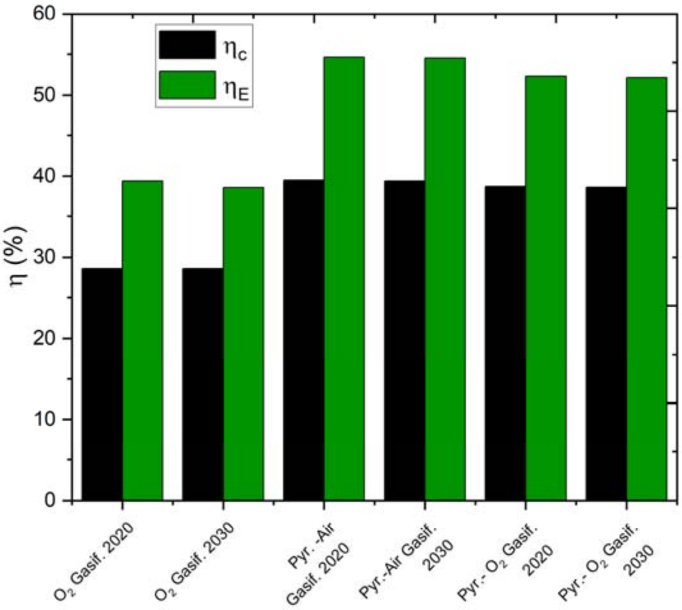

Figure 3: Carbon and energy efficiencies (based on biomass HHV) to gasoline and diesel for the different scenarios studied.

As seen, the combined pyrolysis-gasification route offers a carbon effciency of ~40%, while for the biomass gasfication route this is approximately 29%. The efficiency achieved for the biomass gasfication route is typical for reported Fischer-Tropsch processes using entrained-flow gasfication for syngas generation with the exception that the olefins generation from the syngas here is performed at considerably lower pressure while the product compositon can be readiliy alterred.

The combined pyrolysis-gasification route offers higher efficieny. The difference of the two routes lies in the utilization of gases from conversion of bio-oil to olefins and also to the high carbon penalty one has to pay tailoring the H_2/CO for olefins synthesis from the syngas (Figure 4). Indeed, more than 25% of biomass contained carbon is lost to CO_2 during CO shifting(WGS Losses). Therefore, external renewable H_2 supply can further improve overall carbon effciencies.

It has to be noted that the final MOGD product is still subject to hydrotreatment and thus additional H_2 will be required. The H_2 needed for MOGD product for full hydrogenation and hydrotreatment of bio-oil are shown in Table 2.

Table 2: H_2 requirements for complete hydrogenation of products

Biomass Process	G/D	H_2 Requirements (kgH_2/m^3 product)
O_2-blown gasification of biomass	2020	8.6 – 25.7
O_2-blown gasification of biomass	2030	7.4 – 22.1
Biomass pyrolysis-air gasification of char	2020	8.3 – 24.9
Biomass pyrolysis-air gasification of char	2030	7.5 – 22.6
Biomass pyrolysis-O_2 gasification of char	2020	8.4 – 25.1
Biomass pyrolysis-O_2 gasification of char	2030	7.5– 22.4
Bio-oil hydrotreatment		62 – 80

The amount of H_2 is determined assuming purely mono-olefinic or purely tri-olefinc composition of the product (Tabak et al. 1990). Carbon efficiencies of ~35% have been reported for pyrolysis-hydrotreatment processing route (Venderbosch 2015), however the H_2 requirements for complete hydrogenation are high.

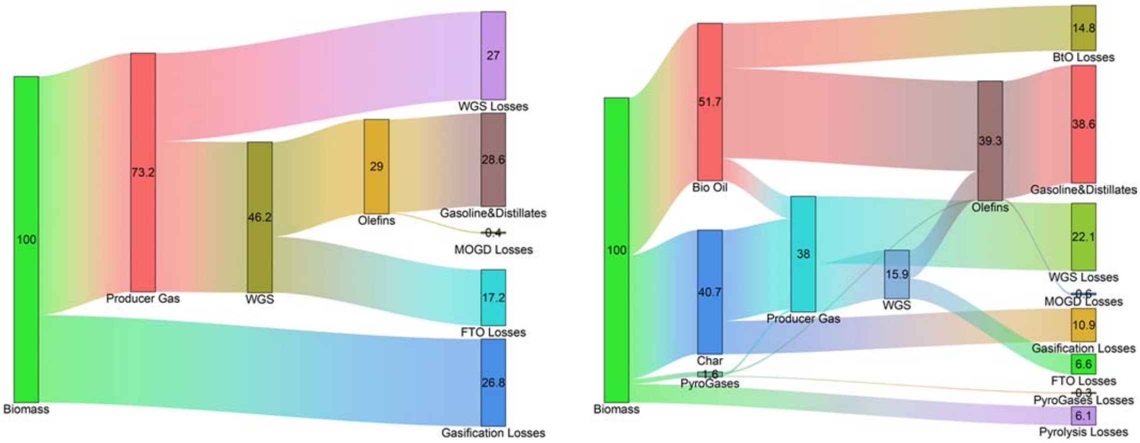

Figure 4: Carbon flow for the O_2-blown biomass gasification (left) and the combined biomass pyrolysis- O_2 gasification (right) for the 2030 scenario.

The energy efficiency based on biomass energy content, as expected, follows the carbon effieciency trends exceeding the 50% mark (for the MOGD product) for the integrated plant. In all cases process integration resulted in heat self-suffiecnt process by combustiing the off-gases. A simple steam Rankine cycle (one evaporation pressure level and one condensation pressure level) was chosen to generate electricity from the excess heat (Table 3).

The electricity requirements for compression and separation are higher for the O_2-blown gasification due to the air separation unit.

Table 3: Electricity production and requirements and energy efficiency of the scenarios investigated.

Process	G/D	El. Requirements for compression (kW_e/ton biom. daf)	El. production (kW_e/ton biom daf)	Overall energy efficiency (%)
O_2-blown gasification of biomass	2020	975.6	617.5	37.1
O_2-blown gasification of biomass	2030	973.9	612.8	36.3
Biomass pyrolysis-air gasification of char	2020	423.1	321.5	53.4
Biomass pyrolysis-air gasification of char	2030	450.6	321.1	52.4
Biomass pyrolysis-O_2 gasification of char	2020	502.0	457.9	52.0
Biomass pyrolysis-O_2 gasification of char	2030	502.0	465.4	51.9

4. Conclusions

In this study, the conversion of biomass-derived syngas and pyrolysis vapours to liquid fuels with an integrated stepwise process targeting for the production of gasoline and diesel via the selective MOGD has been studied. Separation of pyrolysis and gasification steps result in similar carbon losses to direct gasification, but the reduced need for syngas tailoring improves the overall carbon conversion. WGS as syngas tailoring step is the stage with the highest carbon penalty both for the standalone gasification as well as the integrated process with carbon losses greater than 25% of the total carbon. Thus, external renewable hydrogen supply would improve the overall efficiency considerably. The targeted production of light olefins in the standalone gasification route results in carbon efficiencies comparable (but lower) to direct FT synthesis without the use of high pressure. An increase of ~10-11% in carbon efficiency is achieved when biomass pyrolysis and char gasification are combined due to the utilisation of gases from bio-oil to olefins process.

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