

Influence of Different Pretreatment Methods on Biomass Gasification and Production of Fischer-Tropsch Crude Integrated with a Pulp and Paper Mill

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In this paper, the influence on the system performance of different biomass pretreatment methods before gasification and subsequent production of Fischer-Tropsch crude is considered. Entrained flow gasification at high pressure is a well proven technology for coal as feedstock with the benefit of producing a practically tar free raw gas with a close to complete carbon conversion. The short residence time in this type of gasifier requires a fuel, which is relatively dry and has a small particle size, to be pressurized from ambient conditions up to 20-50 bar. The small particle size can be acquired by grinding but this is highly energy intensive and feeding is challenging. Torrefaction is a thermal pretreatment method carried out at around 300 °C which makes the biomass easier to grind, thus requiring less electricity, and makes the material less fibrous, while on the other hand requiring heat for the process. Pyrolysis is a process carried out at around 500 °C which lets the biomass decompose into a gaseous, a liquid and a solid part. The solid part can be grinded and fed into the gasifier together with the liquid and gaseous phases. This will further facilitate the feeding but with a further increased heat demand compared to torrefaction. The different pretreatment methods and their impact on the overall biorefinery energy system have been studied and evaluated using process integration methodology. The results show that the excess heat from an FT process with a biomass input of 300 MW_{HHV} can replace the solid fuel boiler in a large chemical pulp and paper mill. With the preconditions given for this study, thermal pretreatment of the biomass can be beneficial in terms of system thermal efficiency.

1. Introduction

In this paper, integration of Fischer-Tropsch (FT) crude production, from gasified biomass, with an existing pulp and paper mill was studied. Three different pretreatment methods before entrained flow (EF) gasification are evaluated regarding mass and energy balances; grinding only, torrefaction followed by grinding, and pyrolysis (grinding of solid fraction). Integration of different biorefinery concepts with a pulp and paper mill has been discussed as a way of increasing profitability and to reduce global CO₂ emissions. Different pathways for sustainable and profitable biorefineries are discussed by for example Berntsson and Jönsson (2012), who also present an approach to analyse the potential of these concepts in terms of economy and CO₂ emissions. One potential route is gasification of biomass and upgrading into a gas consisting mainly of hydrogen and carbon monoxide, thus enabling downstream production of virtually any hydrocarbon, e.g. transportation fuels or chemicals. In many cases, commercial processes, developed for fossil feedstock, are available for the final synthesis step. Different biomass gasification technologies have been suggested for these types of processes, for example indirect dual bed gasification and direct gasification in a fluidized bed or in an entrained flow reactor, each having their specific benefits and drawbacks. The currently most used type is entrained flow gasification, using coal, which produces a raw gas practically free from hydrocarbons and tars, thus making subsequent crackers and reformers unnecessary. This type, however, puts rigorous demands on the feeding, particularly challenging if the raw material is biomass. The short residence time in the reactor requires a fuel, which is relatively dry and has

a small particle size, to be pressurized from ambient conditions up to typically 20-50 bar. Grinding of biomass is, however, energy intensive, meaning that there are reasons to keep the particle size as large as possible. When using coal as a fuel in entrained flow reactors, the size requirement is in the range 50-100 μm in order to reach high carbon conversion (99 %). However, since biomass is more reactive than coal, the size requirement can possibly be less stringent. Van der Drift et al. (2004) conclude that a size of 1 mm can be enough to reach sufficient conversion. Ways of tackling the sizing issue include a torrefaction or pyrolysis step prior to gasification, further described below.

2. Methodology

In order to solve mass and energy balances for the processes, the different process units, shown in Figure 1, have been simulated in Aspen Plus (Aspen Tech, 2010). Simulation conditions and assumptions are described below for each unit. The potential for heat integration between the existing mill and the FT process, as well as possibilities for integration of a steam cycle, have been performed by using Pinch technology and so called background/foreground analysis, described by for example Smith (2005). Global ΔT_{min} for the processes was set to 8 $^{\circ}\text{C}$ and the biomass input scale was set to 300 MW_{HHV} .

Two different performance indicators were used to evaluate the different cases, FT energy yield (1) and FT system thermal efficiency (2). For the second indicator, net electricity demand/surplus, compared to the mill, was valued on the same basis as the wood needed to produce the electricity in a power plant. The electrical efficiency was varied from 25 % to 55 % to represent different production alternatives.

$$FT \text{ energy yield} = (\dot{m}_{FT} / \dot{m}_{biomass}) \cdot (HHV_{FT} / HHV_{biomass}) \quad (1)$$

$$Wood \text{ to FT efficiency} = \frac{\dot{m}_{FT} HHV_{FT}}{\Delta(\dot{m}_{wood} HHV_{wood}) + \frac{\Delta \dot{P}_{el}}{\eta_{el}}} \quad (2)$$

3. Process description

The FT process is assumed to be integrated with the existing mill through its steam and hot water networks. If an excess of steam is generated, this is assumed to be expanded in a condensing turbine to generate electricity.

3.1 Existing pulp and paper mill

The existing plant, with which the FT process is to be integrated, is a chemical pulp and paper mill, producing approximately 350,000 t of bleached paperboard every year. The current steam production system consists of a recovery boiler and a biomass boiler, both connected to the same back-pressure steam turbine for electricity generation.

3.2 The Fischer-Tropsch process

Figure 1 shows a simplified scheme of the studied FT process with drying of incoming wet biomass, pretreatment, pressurization, gasification, gas cleaning and upgrade, and FT synthesis.

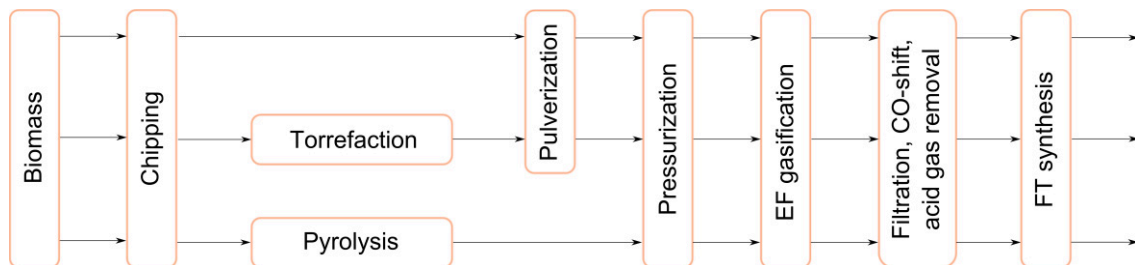


Figure 1: Process layout of the different proposed Fischer-Tropsch crude production paths using three different pretreatment methods

3.2.1. Drying

Drying of incoming biomass is essential in order to secure steady operation of the gasifier and a high quality syngas. A moisture content of 10 % is set as target and drying is assumed to take place in a low temperature air dryer, heated with excess hot water from the mill. After drying, the wood is either sent to

grinding, torrefaction or pyrolysis. Grinded, untreated wood is pressurized in lock-hoppers, using CO₂, and is fed to the gasifier with a screw feeder. Consumption of electricity for feeding devices has been estimated by Van der Drift et al. (2004).

3.2.2. Torrefaction

Torrefaction is a thermal pretreatment method which significantly improves several characteristics of biomass. The torrefied material has a higher energy density, is hydrophobic, brittle and has a more homogeneous composition. The benefit from torrefaction, when being performed as pre-treatment before gasification, is that the material is easier to grind, since the fibrous structure of the biomass has been destroyed. The biomass becomes more like coal and this method could therefore be appropriate connected to entrained flow gasification. Another benefit from torrefaction is increased homogeneity of the feedstock and a more even size distribution, which is important for steady downstream operation. Torrefaction is carried out without presence of oxygen at atmospheric pressure and at temperatures between 220 °C and 300 °C. For this study, information about the fraction of condensable species as well as the composition of permanent gases has been gathered from an article by Tapasvi et al. (2012). The composition of the condensable phase was estimated for larch by Prins (2005) and is here assumed to represent an approximate composition for a coniferous wood species. The torrefied wood is pressurized in lock-hoppers and fed to the gasifier pneumatically.

3.2.3. Pyrolysis

Biomass pyrolysis is a process carried out in an inert atmosphere around 500 °C where biomass decomposes into a gaseous, a liquid and a solid part. The composition of the pyrolysis products has been predicted by applying equations suggested by Neves et al. (2011). They have performed a literature review on pyrolysis characteristics which have been structured and analysed. From these data empirical relationships have been developed, which have been used in this paper to calculate mass and energy balances for the pyrolysis step. The model calculates the heat requirement for pyrolysis, the amount of ash, and the amount and composition of char and gases (condensable and permanent). Part of the char content is used to provide heat for the pyrolysis process while part is being grinded and mixed with the liquid fraction into pumpable slurry.

3.2.4. Entrained flow gasification

Entrained flow gasification is well proven for coal but is still undergoing development for biomass use. The fuel particles are entrained along with the flow of oxidant in a flame, which means that the fuel usually has relatively short residence time and that the process is carried out at high temperature. Thanks to the high temperature, the raw gas is near tar-free and contains very little hydrocarbons. The gasifier was modelled to operate at 30 bar with the assumption that the reactions reach equilibrium, justified by experimental results produced by for example Qin et al. (2012). Oxygen is added to reach a temperature of 1,350 °C. The hot raw gas can potentially contain molten particles which can foul downstream heat exchanger surfaces. To avoid this, the gas is cooled in a gas quench, i.e. by recycled cooler gas, down to 900 °C. The gas is then further cooled through steam generation down to 400 °C.

3.2.5. Gas cleaning and upgrade

The raw gas from the gasifier is prepared for FT synthesis in three steps, including filtration, adjustment of the H₂:CO ratio and separation of acid gases. Hot gas filtration typically operates at temperatures up to 900 °C, at pressures up to 8 MPa and can operate in both reducing and oxidizing atmosphere. At these high temperatures only ceramic or metal filters are applied, due to the high mechanical stress. Hot gas filters are often constructed as candle filters where the filter cake is building up on the outside of the tube, while the gas flows out through the open end. The tubes are cleaned in groups by back-pulsing gas (preferably clean syngas) from a storage tank. (Heidenreich, 2012)

The H₂:CO ratio is adjusted to around 2 in a partial shift reactor in order meet specifications for the FT synthesis. In the reactor an excess of steam is mixed with part of the gas flow to form hydrogen and carbon dioxide through complete conversion of carbon monoxide. The desired H₂:CO ratio is achieved by by-passing a certain part of the gas flow.

In order to prepare the gas for downstream processing, a Rectisol-like unit is used to remove acid gas, which can poison the FT catalyst. Cooled gas is entering the absorber where CO₂ and H₂S are absorbed in chilled methanol. The purified gas exits at the top of the column, while the absorbent is regenerated in three subsequent columns before it is recycled. (Linde, 2013)

3.2.6. FT synthesis

The Fischer-Tropsch process is a way to derive synthetic hydrocarbons from a mixture of hydrogen and carbon monoxide. The process has, both historically and recently, been used to produce liquid

transportation fuels from gasified coal, but there is a growing interest for renewable feedstock. In the FT process, hydrogen and carbon monoxide form carbon chains of various lengths approximated by the Anderson-Schultz-Flory distribution, assuming constant probability of chain growth independent of length, and is expressed as

$$\frac{W_n}{n} = (1 - \alpha)^2 \alpha^{(n-1)} \quad (3)$$

where W_n is the weight fraction of molecules containing n carbons and α is the growth probability factor. FT reactors are classified as either low temperature (200-240 °C) or high temperature (300 - 350 °C). For production of straight chained hydrocarbons in the diesel range the low temperature gives the higher yield (Ekbohm et al., 2009). To avoid an increase in temperature because of the exothermic polymerization reactions, and thereby deactivation of the catalyst and possible breakdown of the product into shorter molecules, sufficient cooling is necessary. Temperature control is one of the major practical concerns in FT synthesis. The process has been modelled as slurry phase reactor with Co-catalyst operating at 210 °C. Only the production of straight paraffins and short olefins have been considered here, in accordance with results reported by Fox and Tam (1995). For modern catalysts, a CO conversion of 90 % per pass can be assumed. The FT reactor can be operated with recycling (RC) to increase the overall conversion or, as a simpler solution, as a once through (OT) process. Off-gases are assumed to be combusted in a boiler with 87 % efficiency.

4. Results

The different process setups have been evaluated concerning absolute production of FT crude and electricity as well as through indicators presented in Section 2. As described earlier, the analysis was carried out graphically with background/foreground curves. Figure 2 shows the grinding case with 300 MW_{HHV} biomass input and once through FT synthesis as an example of this approach. The left figure shows the potential of integrating the FT process (foreground, black line) with the pulp and paper mill (background, grey line). The large temperature difference between the cooling demand of the FT process and the heat demand of the pulp and paper mill can be utilized in a steam cycle for electricity production. This approach is demonstrated in the right figure, showing a joint grand composite curve (GCC) for the two processes (FT process and pulp and paper mill) with an integrated steam cycle (dashed line). Remaining hot utility demand is covered with steam from the existing recovery boiler. Combustion of off-gases is visualized as a horizontal line at 900 °C.

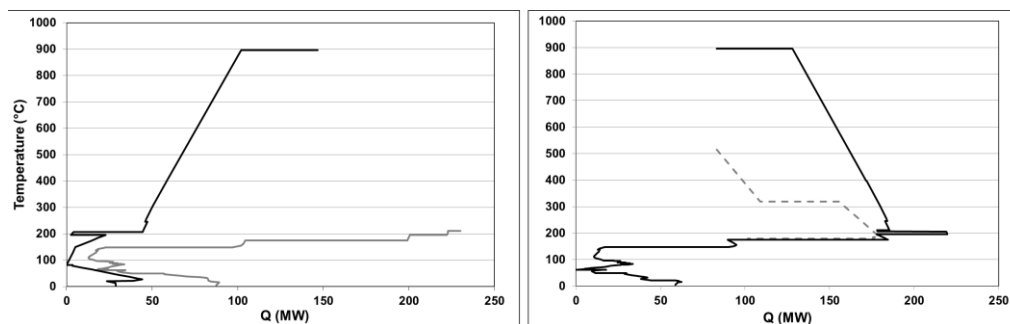


Figure 2: Example of background foreground analysis (left) and steam cycle integration (right). The figure shows the grinding case with once-through Fischer-Tropsch synthesis.

Table 1 shows some main comparative results, such as product output and the electricity balance. The main contributors to electricity generation (except back pressure generation from the recovery boiler, which is constant for all cases) and consumption are displayed separately, as well as net demand/surplus, in Figure 3. Since the thermal pretreatment methods require heat, in this case supplied by char for pyrolysis and off-gases for torrefaction, the FT yield for these cases will always be lower than for simple grinding. Not all the released volatiles from the torrefaction process are required to run the process, which are instead combusted for steam generation, whilst the extraction of char is set to exactly match the demand. The FT yield from the pyrolysis route is therefore higher, given those preconditions. Recycling increases the yield of FT with roughly eight to ten percentage points, but with substantially less off-gases for electricity generation. The difference in FT crude production between the case with the largest yield (grinding + FT with recycle) and the lowest (torrefaction + once-through FT) is more than 20 %. A biomass

input of 300 MW_{HHV} is enough for the FT process to fully replace the heat demand of the mill which is currently covered by the solid fuel boiler on site, and to leave an excess for a condensing turbine.

Table 1: The table shows comparative numbers for the evaluated cases, including purely grinding, torrefaction or pyrolysis as pretreatment method in combination with either recycle (RC) or once through (OT) FT synthesis. Back-pressure generation from the recovery boiler (44.7 MW) is the same for all cases and therefore excluded. The business as usual (BAU) case is given for comparison.

	BAU	Grind. OT	Grind. RC	Torr. OT	Torr. RC	Pyro. OT	Pyro. RC
Biomass usage [MW _{HHV}]	85	300	300	300	300	300	300
FT crude [MW _{HHV}]	-	129.2	159	125	154	128	156
FT yield [%]	-	43.1	52.9	41.7	51.3	42.6	52.0
Off gas [MW _{HHV}]	-	51.5	2.8	50	2.7	51.1	2.8
Electricity [MW]							
<u>Production</u>							
Back-pressure	13.8	18.9	11.7	18.9	12.4	20.0	12.4
Condensing	-	6.8	1.8	6.2	1.7	8.8	1.9
<u>Usage</u>							
Mill ^a	6.3	6.3	6.3	6.3	6.3	6.3	6.3
FT process	-	29.1	32.0	25.2	28.3	16.9	19.8
<u>Excess/deficit</u>	7.5	-9.7	-24.8	-6.4	-20.5	5.6	-11.8

^a Excluding generation from recovery boiler

Electricity is mainly consumed in processes which are not dependent on whether the FT process is run once-through or with recycle, except for additional acid gas removal for the latter case. Consumption is therefore rather similar for these two options. The production side, however, differs depending on if the off-gases are combusted for steam generation or recycled, seen from Figure 3. Preparation of the wood, as well as pressurization and feeding, constitutes quite large shares of the total consumption and has a significant impact on the overall performance.

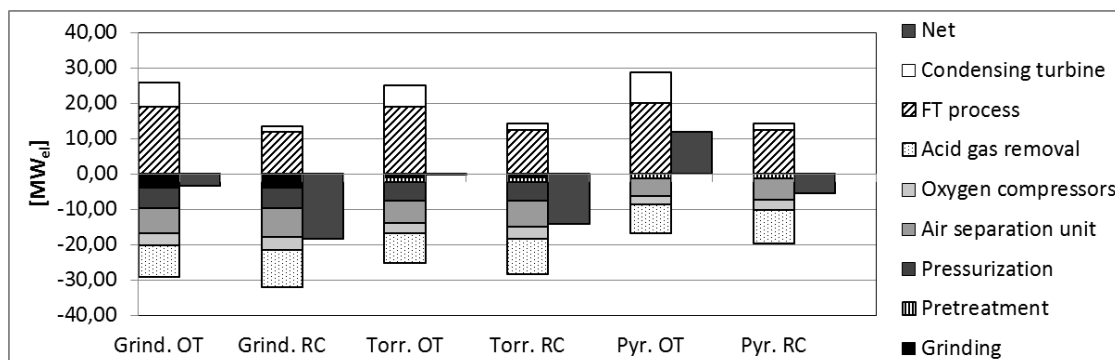


Figure 3. Distribution of electricity generation (back-pressure and extra condensing power) and consumption for the Fischer-Tropsch process

Looking at system thermal efficiencies (Equation 2) in Figure 4 one can see that all cases benefits from higher electrical efficiencies since they all have a deficit of electricity compared to the stand alone mill. Only the pyrolysis once-through case has a close to similar excess and is therefore shown as a close to straight line in the diagram. At lower wood to electricity efficiency the once-through cases perform well because of the higher electricity production, but as electrical efficiencies goes up, the system efficiencies for recycle cases have a steeper increase. Grinding and torrefaction show rather similar behaviour, where the lower yield of the torrefaction route is compensated by lower electricity consumption. Clearly, the way the off-site electricity is produced, highly influences the results.

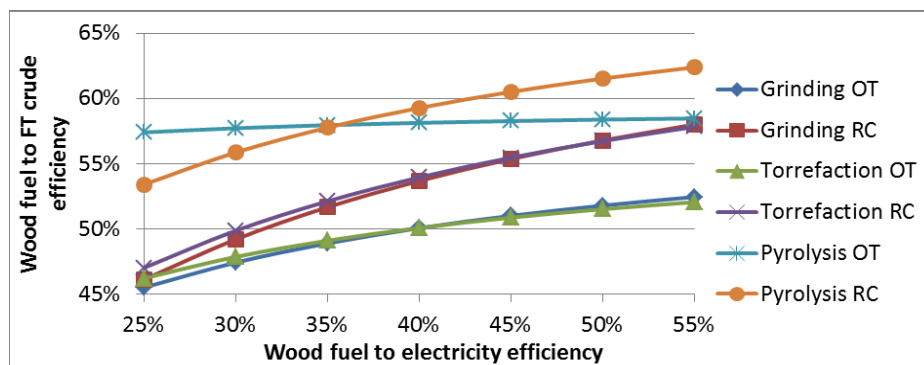


Figure 4: Wood to Fischer-Tropsch efficiency when electricity is valued as wood fuel, using varying wood to electricity efficiencies. Wood fuel energy flows are on HHV basis

5. Conclusions

Because of the large electricity deficit, the system thermal efficiency is highly dependent on the wood to electricity efficiency. The route with pyrolysis and an FT process with recycle was shown to have the highest system thermal efficiency, for a high wood fuel to electricity efficiency. The yield was slightly lower than when the wood is simply grinded but, on the other hand, needs less electricity for the production. Recycling was beneficial for the system performance for the grinding and torrefaction cases, even though the differences are very small at low off-site electrical efficiencies. One should bear in mind though that the recycle alternative comes with a significantly higher investment cost, and might therefore not be economically viable, even though more energy efficient. The routes with torrefaction performed similarly to the grinding cases, however, grinded raw biomass has proven to be very difficult to feed into an entrained flow gasifier, and may therefore be disqualified for technical reasons. For some of the cases it could be argued that the contribution from a condensing turbine is too small to justify an investment. In such cases it might be better to adjust the size of the FT process to enable a larger turbine, or to avoid it. Integration with a district heating system has not been evaluated in this study but is not expected to change the results since access to excess heat is similar for all cases.

Acknowledgements

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