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# Integrating a Fischer-Tropsch Fuel Production Process into Pulp Mills

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For the production of liquid transportation fuels based on hydrogen and carbon dioxide multiple process routes are known. The Fischer-Tropsch process producing a synthetic crude oil is one promising option to produce a renewable fuel. The work investigates the production of Fischer-Tropsch fuels in a pulp mill with four different process configurations. Based on the educts hydrogen and carbon dioxide the required synthesis gas for the synthesis is generated via either the water gas shift reaction or $CO_2$ electrolysis. After the reactor, the product is split into two liquid streams and one gaseous stream.
The major aspect of the work is the integration into a pulp mill. Surplus heat from the process can be used in the pulp mill and can in return increase the electricity output of the pulp mill. Another option for integration is the utilization of purge streams of the process for the combustion in the lime kiln replacing natural gas.
The process was simulated with a chemical engineering software to generate the mass and energy balance of the processes. The four process configurations are evaluated based on performance indicators like carbon efficiency, Power-to-Fuel efficiency and $CO_2$ emissions. The process with the reverse water gas shift and closed-loop design showed the highest carbon (79.8 %) and Power-to-Fuel efficiency (37.7 %). The open-loop gas loop designs show the highest emission reduction potential.

## 1. Introduction

Anthropogenic greenhouse gas emissions (GHG) causing climate change need to be reduced in future in order to mitigate the impact of climate change. The transport sector is a substantial emitter of greenhouse gas emissions due to the combustion of mostly fossil fuels. Besides electric vehicle, the utilization of green fuels is an option to reduce GHG emissions. Biobased fuels like biodiesel or ethanol from fermentation are available. Another option is the utilization of a carbon source like carbon dioxide ($CO_2$) in combination with renewably produced hydrogen. Multiple products like for example methanol, dimethylether (DME) and Fischer-Tropsch (FT) fuels are known.
The FT process produces a mixture of alkanes, alkenes and alcohols with a variety of chain lengths. The reaction equation of the production of an alkane is depicted in Equation 1. The output of the process is a syncrude that can be further processed with hydrocracking and refined in a crude oil refinery (De Klerk and Maitlis, 2013).

$$n\,CO + (2n+1)\,H_2 \rightarrow C_nH_{2n+2} + n\,H_2O \tag{1}$$

For the process, $CO_2$ needs to be converted to carbon monoxide. This can be done for example via the reverse water gas shift (RWGS) reaction (König at al., 2015), co-electrolysis (Herz et al., 2021) or $CO_2$ electrolysis (van Bavel et al., 2020). So far, only one study for the utilization of the $CO_2$ electrolysis is available for the syngas preparation of the FT process. Additionally, the integration of the FT process in pulp mills and other industrial processes has not been discussed yet widely. A limited number of studies on integrating a FT process with an industrial process like biogas plant (Marchese et al., 2020) or ethanol industry (Borugadda et al., 2020) are available. The integration into the biogas plant can make use of the $CO_2$ from the biogas stream. Integrating the FT process with a pulp mill has several advantages like the availability of green electricity, combustion of purge streams in the lime kiln and the availability of biogenic $CO_2$. In the pulp mill tree trunks are converted into pulp.

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Pulp is mostly used for papermaking. In a first step, the trunks are debarked and chipped. The wood chips are cooked with a cooking liquor yielding pulp and a residual stream called black liquor. Black liquor and bark is burned onsite to generate heat and electricity. Usually pulp mills are net electricity exporters. When burning black liquor, the inorganic pulping chemicals are recovered. In order to also close the calcium cycle in the mill, a lime kiln is needed that converts calcium carbonate into calcium oxide. Pulp production in Europe (Cepi members) was around 36.3 Mt with Sweden and Finland having a market share of approximately 61 % in 2020 (Cepi, 2021). The pulp industry is with the production of green electricity and mostly biogenic $CO_2$ emissions an important industry to consider for the energy transition and sector coupling.

This paper investigates the integration of a FT production process in a pulp mill considering the $CO_2$ electrolysis as a new option for the activation of $CO_2$. The paper aims at showing the benefits of integrating a FT process with a pulp mill in terms of efficiency and $CO_2$ emission reduction. An economic assessment is not performed. As syngas preparation steps, the reverse water gas shift process based on $CO_2$ and $H_2$ or the $CO_2$ electrolysis are investigated for different process configurations. Additionally, different gas loop designs are investigated. The FT production process based on $CO_2$ and $H_2$ is a well-known process which relies mostly on established process steps. However, the integration of the FT process in a pulp mill has not been published in literature yet and the utilization of the $CO_2$ electrolysis is new for the FT process. Therefore, the paper presents a novel approach for integrating the FT process in a pulp mill in order to make the production process more efficient and sustainable.

## 2. Modelling

The material and energy balances of the process configurations were calculated using the chemical process simulation software Aspen Plus V12. As property method, the Peng-Robinson equation of state was used. Four process configurations (Table 1) were defined based on different syngas preparation processes (reverse water gas shift process or $CO_2$ electrolysis) and gas loop designs (open or closed-loop). The scale of the models was set to 50 $MW_{el}$ for the power consumption of the electrolyzers. For all scenarios, the process was integrated into the pulp. Integration means the combustion of purge streams in the lime kiln and the heat integration into the pulp mill's energy system.

*Table 1: Definition of evaluated cases with integration in a pulp mill (CL: closed-loop, OL: open-loop, RWGS: reverse water gas shift process, CO2E: $CO_2$ electrolysis)*

| Case | Syngas preparation | Gas Loop Design |
|---|---|---|
| A: RWGS-CL | RWGS | CL |
| B: RWGS-OL | RWGS | OL |
| C: CO2E-CL | CO2E | CL |
| D: CO2E-OL | CO2E | OL |

Figure 1 depicts the flowsheet of the process. The process model consists of the syngas preparation process either via RWGS or $CO_2$ electrolysis, the FT reactor section and the product separation. A pressure drop of 1 bar in the RWGS reactor and 2 bar in the FT reactor is used to account for pressure losses in the whole system. The pressure loss influences the compression power required for educt compression and in case of recycle stream for the compression of recycled gases. The power required for compression is between 0.6 MW and 0.9 MW. Hydrogen is supplied at 80 °C and 30 bar. The efficiency of the electrolysis is 70 % (based in the lower heating value of hydrogen). The energy consumption of the $CO_2$ electrolysis is 7 kWh/m$^3$ (Haldor Topsoe, 2022). The CO is supplied with a purity of 99.5 mol-% at 1 bar and 40 °C. $CO_2$ is supplied at 25 °C and 1 bar.

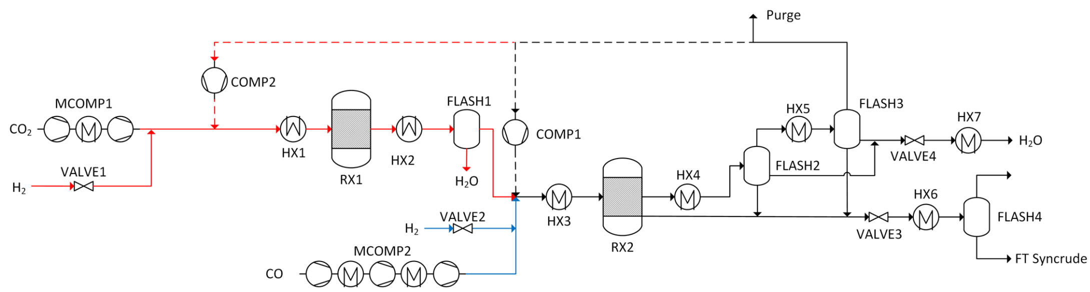


*Figure 1: Flowsheet of the simulation. The dashed lines show the internal and external recycle streams for the closed-loop configurations. Red lines indicate the syngas preparation via RWGS (for case A and B) and blue lines indicate the case for $CO_2$ electrolysis (for case C and D)*

In the RWGS model, the feed gas stream is preheated to 300 °C in HX1. The RGWS shift reactor is operated at 900 °C and 26 bar. The reactor is modelled with a Gibbs minimization principle. The main reaction happening in the reactor is shown in Eq.2. After the reactor, the gas stream is cooled to 30 °C and flashed to remove the water produced during the reaction. Purge streams and additional natural gas (only in case A) are fired in the RWGS reactor for heat supply to the endothermic reaction. The heat supply efficiency is assumed to be 90 % based on the lower heating value of the fuel.

$$H_2 + CO_2 \rightleftharpoons H_2O + CO \quad \Delta H = 41.2\ kJ/mol \tag{2}$$

After preheating the gas to 180 °C in HX3, it enters the FT reactor (RX2) with 25 bar. The low temperature FT reactor is modelled as a stoichiometric reactor with a per pass conversion of 60 % for carbon monoxide. The product distribution is derived based on the Anderson Flory Schulz distribution with a chain growth probability calculated based on the approach from (Vervloet et al., 2012). Only alkanes are modelled. The chain length from C1 to C30 are modelled. Molecules with the chain length C33 and C38 are modeled to present C31-C35 and C36-C40 alkanes. The temperature of the reactor is set to 220 °C. The $H_2$/CO ratio of the reactor feed is kept at 2 for all cases. Liquid products are already separated from the reactor as a separate stream. The gaseous product is cooled to 155 °C and separated in two liquid streams and one gas stream. The gas stream is further cooled to 15 °C. In FLASH 3, water, liquid alkanes and a gas stream is separated.
Depending on the gas loop design, the gas stream is split into an internal (via COMP1), an external (via COMP2) recycle stream and a purge stream for the closed-loop design. The internal recycle stream is mixed to the FT reactor feed and the external recycle stream is sent to the RWGS reactor. In case of the closed-loop design with $CO_2$ electrolysis, the recycle stream only consists of the internal recycle. The purge stream is defined as 5 % of the recycle stream. The internal and external recycle streams are 60 % and 35 % of the total recycle stream (case A). In the open-loop design, all gas is purged and utilized for combustion.

## 3. Process evaluation

### 3.1 Carbon efficiency

The carbon efficiency (Eq.3) is defined as the ratio of carbon contained in the product (syncrude) compared to the carbon of the raw material ($CO_2$). Since $CO_2$ is energy intensively separated from a gas stream, the efficient utilization is key for an efficient and economic process.

$$\eta_{CE} = \frac{\dot{n}_{C,out}}{\dot{n}_{C,in}} \tag{3}$$

### 3.2 Power-to-Fuel efficiency

The efficiency is defined by the ratio of energy content of the syncrude to the electrical power used for the electrolysis $P_{Electrolysis}$ and compressors $P_{Comp}$. The lower heating value was determined with Aspen Plus (at 0 °C).

$$\eta_{PtF} = \frac{\dot{m}_{Syncrude} \cdot LHV_{Syncrude}}{P_{Electrolysis} + P_{Comp}} \tag{4}$$

### 3.3 Heat utilization

A simplified analysis for the utilization of waste heat streams was performed. Heat from the FT reactor was identified as the major surplus heat source that can be used for the production of steam. The remaining heat streams are sufficient to supply the process with heat when required. Since the reactor operates at 220 °C the steam can be used for electricity generation. The total efficiency for power generation was assumed to be 60 %. A detailed heat integration via Pinch Analysis was not in the scope of this paper.

### 3.4 $CO_2$ balance

The $CO_2$ balance differentiates the origin of carbon. $CO_2$ used as raw material for the process is separated from flue gases from the bark boiler or recovery boiler and are thus of biogenic origin. The system boundary of the $CO_2$ balance includes the pulp mill and the FT process.
A fired heating is used for heating the reverse water gas shift reactor. The purge stream of the FT process is used for supplying heat to the reactor. If the heat from purge stream combustion is not sufficient, natural gas is combusted. The emissions of natural gas combustion are calculated using an emission factor of 0.201 t $CO_{2\,eq}$/MWh (Juhrich, 2016). Excess purge stream that is not used for heating the reverse water gas

shift reactor is used to fire the lime kiln in the pulp mill. There it replaces natural gas leading to an emission reduction.
Due to the heat surplus of the process, generated steam can substitute steam extracted from the steam turbine. This leads to a lower amount of steam extracted from the turbine and consequently to a higher electricity generation capacity. The additionally generated electricity is assumed to substitute grid electricity with the current German emission factor of 0.380 t $CO_{2\ eq}$/MWh (Icha et al., 2021).

## 4. Results

It should be noted that process simulations have a certain degree of uncertainty. The modeling was done under ideal assumptions like pure educt streams and no heat losses of reactors and piping. Additionally, the models are simplifications of the reality. A validation of the simulation with experimental data was not performed. Nevertheless, the paper's focus is a comparison between the different cases with similar modelling assumption. Consequently, the comparability is valid.

### 4.1 Mass and energy balance

Table 2 and 3 show the mass and energy balance for the four process configurations. The oxygen production is similar for cases A and B, and Case C and D since the electrolysis capacities are similar. For the open gas-loop designs (B and D) the purge streams are higher than for the closed-loop design. The cases with RWGS produce a higher amount of waste water compared to the cases with $CO_2$ electrolysis since every mole of $CO_2$ converted to carbon monoxide produces one mole of water according to Eq.2. For the closed-loop cases (A and C) the syncrude output is higher since unconverted gas is recycled and consequently more efficiently used.

*Table 2: Mass balance comparison in t/h*

| | Case A: RWGS-CL | Case B: RWGS-OL | Case C: CO2E-CL | Case D: CO2E-CL |
|---|---|---|---|---|
| Input | | | | |
| $H_2O$ | 9.4 | 9.4 | 5.2 | 5.2 |
| $CO_2$ | 7.6 | 10.6 | 6.3 | 6.3 |
| $H_2$ | 1.1 | 1.1 | 0.6 | 0.6 |
| Output | | | | |
| $O_2$ | 8.3 | 8.3 | 6.9 | 6.9 |
| Purge | 0.9 | 5.8 | 0.5 | 2.2 |
| $H_2O$ | 5.8 | 4.9 | 2.4 | 1.5 |
| Syncrude | 2.0 | 0.9 | 1.5 | 0.9 |

The power of the electrolysis was set to 50 $MW_{el}$. In case C and D, the power input is split between the water and $CO_2$ electrolysis. Since the $H_2$/CO ratio of the feed to the FT reactor was fixed, the split in cases C and D vary due to the recycle stream in case C (closed-loop design). For all cases, the required electricity for gas compression is below 1 $MW_{el}$. Case A requires natural gas for the RWGS reactor heating. For case B, the heat requirement can be covered by the purge stream. The heat input and output for cases A and B are higher than for cases C and D. This is explained by the heating and cooling demand in the reverse water gas shift section. The heating required in the $CO_2$ electrolysis was not included in the heat calculations.
The purge streams for cases with open-loop design (B and D) are considerably higher than in the case with closed gas loop design. Case A shows the highest syncrude output in terms of energy flow. The heat from the FT reactor used for electricity production is also shown in Table 3. For a closed-loop design (A and C), the heat from the FT reactor is greater than for the closed-loop design since the conversion in the reactor is higher because of the recycle stream.

### 4.2 Efficiency indicators

Figure 2 shows the Power-to-Fuel and carbon efficiency. The Power-to-Fuel and carbon efficiency drastically increase for case A and C with a closed-loop design. The carbon efficiency of case B is the lowest. In this case, a lot of carbon is lost as $CO_2$ which was not converted to carbon monoxide in the RWGS reactor. Since $CO_2$ is not reacting in the FT reactor, it leaves the process with the purge stream. The $CO_2$ electrolysis converts $CO_2$ very efficiently to carbon monoxide, case D shows a better carbon efficiency compared to case B since no unreacted $CO_2$ leaves the process.
Case A shows the highest Power-to-Fuel efficiency with 37.7 %. Comparable studies report efficiencies of 43.3 % for the same process configuration (König et al. 2015). The efficiencies for closed-loop design are higher

than for the open-loop design. In cases B and D, the Power-to-Fuel efficiency are in the same range. For the calculation of the efficiency, the need for natural gas heating of the RWGS reactor was not included. When included, the efficiency for case A drops to 34.8 %.

*Table 3: Energy balance comparison in MW*

| | Case A: RWGS-CL | Case B: RWGS-OL | Case C: CO2E-CL | Case D: CO2E-CL |
|---|---|---|---|---|
| Input | | | | |
| Electricity water electrolysis | 50 | 50 | 28.4 | 27.5 |
| Electricity $CO_2$ electrolysis | - | - | 21.6 | 22.5 |
| Electricity compressors | 0.7 | 0.9 | 0.6 | 0.6 |
| Heat (including fired heater) | 12.4 | 7.2 | 0.9 | 0.2 |
| Natural gas | 4.2 | - | - | - |
| $H_2$ | 35 | 35 | 19.9 | 19.3 |
| Output | | | | |
| Purge | 4.7 | 20.3 | 3.6 | 15.2 |
| Heat | 22.7 | 14.9 | 9.2 | 5.8 |
| Syncrude | 19.1 | 8.8 | 15.2 | 8.9 |
| Electricity (generated from FT reactor heat) | 4.7 | 2.4 | 3.5 | 2.3 |

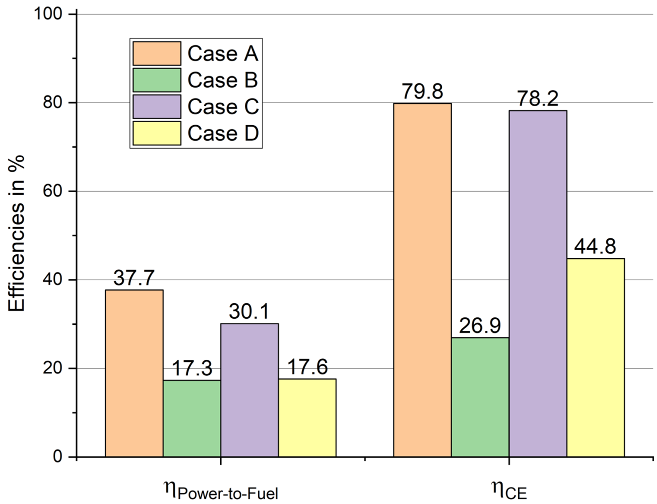


*Figure 2: Power-to-Fuel efficiency and carbon efficiency for the scenarios*

### 4.3 $CO_2$ balance

Table 4 shows the $CO_2$ balance for the four cases. The emissions are differentiated in fossil and biogenic emissions. A negative value represents a reduction of $CO_2$ in the system compared to a pulp mill without FT synthesis. The total reduction is in all cases between 6.7 and 7.1 t/h. It is important to notice that the output of syncrude is different for all cases. Therefore, the emission related to the output of syncrude is reported in the last row. For all cases, this emission factor is negative. In terms of emission factor, cases B and D are the configurations with the highest emission reduction for the produced fuel. For comparison, the emission factor of gasoline is 0.069 kg $CO_2$/MJ (IPCC 2006).

The total reduction of fossil emissions is substantially the smallest in case A. Reasons are that no natural gas can be replaced in the lime kiln and that additional fossil emissions are generated through the combustion of natural gas in the RWGS reactor. However, the reduction by substitution of grid electricity is the greatest in case A. Cases B and C show the biggest reduction in fossil emissions due to the utilization of the purge stream in the lime kiln.

*Table 4: $CO_2$ balance differentiated into fossil and biogenic emissions (units are in t/h if not stated otherwise)*

| | Case A: RWGS-CL | | Case B: RWGS-OL | | Case C: CO2E-CL | | Case D: CO2E-OL | |
|---|---|---|---|---|---|---|---|---|
| | fossil | biogenic | fossil | biogenic | fossil | biogenic | fossil | biogenic |
| $CO_2$ (raw material) | - | - 7.6 | - | - 10.6 | - | - 6.3 | - | - 6.3 |
| Purge combustion | - | 1.5 | - | 7.7 | - | 1.3 | - | 3.5 |
| Natural gas fired heating of RWGS | 0.8 | - | - | - | - | - | - | - |
| Natural gas substituted in lime kiln | - | - | - 3.0 | - | - 0.7 | - | - 3.1 | - |
| Electricity generation | - 1.8 | - | - 0.9 | - | - 1.3 | - | - 0.9 | - |
| Total | - 1.0 | - 6.1 | - 3.9 | - 2.9 | - 2.1 | - 5.0 | - 3.9 | - 2.8 |
| Total (in kg $CO_2/MJ_{syncrude}$) | - 0.10 | | - 0.21 | | - 0.13 | | - 0.21 | |

## 5. Conclusion

The paper presents a study of the integration of FT process into a pulp mill. Four process configurations are investigated. The configurations differ in the gas loop design and the syngas preparation technology. The configurations with $CO_2$ electrolysis show a lower water consumption and water production as side product compared to the configurations with the RWGS process. For all process configurations a high heat surplus is calculated. Carbon efficiencies for the closed loop design are almost 80 %. For the open-loop design, the efficiencies drop to 26.9 % or 44.8 %. The highest Power-to-Fuel efficiency could be reached for case A. The efficiency for open-loop configurations only reach approximately 17 %. The open-loop configurations show a substantially higher $CO_2$ reduction potential compared to the closed loop design mainly due to saving through the substation of natural gas.

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