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Integration of Biomass Gasification-Based Olefins Production in a Steam Cracker Plant—Global GHG Emission Balances

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This paper investigates two options for integration of biomass-based olefin production with a fossil-based steam cracker plant at the heart of a chemical cluster. The work was conducted in the form of a case study considering the possible future partial replacement of a fraction of the cracker olefins with approx. 220 kt/y of biomass-based olefins (ethylene, propylene, and butylene) (approx. 25 % of total capacity) produced via gasification, methanol synthesis, and the methanol-to-olefins (MTO) process. Two options were compared with base case operation with fossil-only feedstock: (i) purchase of methanol produced off-site, and (ii) on-site methanol production. In both cases, the MTO section was assumed to be located at the cracker site, making use of existing olefin separation equipment. Consequences of such partial feedstock substitution for the steam, fuel gas, and electric power balances of the cracker plant were investigated. Potentials for generation of steam and electric power were estimated by assuming integration with a heat recovery steam cycle. Greenhouse gas (GHG) emission balances of the proposed options were estimated by applying a system boundary expansion approach. The GHG emission reduction potentials are shown to be between 50 % and 70 %, compared with the base case. The reduction potential depends on the choice of reference grid electricity generation technology but the major contribution comes from the introduction of renewable feedstock.

1. Introduction

To reduce fossil feedstock dependence and greenhouse gas (GHG) emissions in the chemical industry sector, the primary long-term option is to shift to renewable feedstock. Efficient integration into existing process infrastructure is a key factor for a successful transition, where direct substitution of petrochemicals with drop-in biomass-based equivalents is expected to achieve the easiest market penetration (IEA, 2012). One important aspect is the integration point in the process value chain and the associated effects on the overall material and energy balances. Thermochemical gasification is one promising technology to convert lignocellulosic biomass into value-added products via syngas. Biomass gasification-based routes are generally associated with high-temperature excess heat, which makes these processes particularly interesting from an energy integration point of view. Haro et al. (2013) reviewed potential routes for thermochemical conversion of biomass for the multi-production of chemicals and fuels via selected platform chemicals, e.g. methanol. Hannula and Arpiainen (2015) performed a techno-economic assessment of the production of light olefins and transportation fuels via biomass gasification and methanol synthesis in which possibilities for material and heat integration with a steam cracker plant were discussed. However, no systematic analysis of detailed integration consequences was performed and the environmental performance was not investigated either. Integration of biomass gasification-based methanol production has also been investigated in connection with ethanol production in the sugarcane industry (Albarelli et al., 2014).

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This work was conducted as a case study investigating opportunities to partially replace fossil feedstock in a steam cracker plant that supplies light olefins to neighbouring plants in a chemical cluster. The paper quantifies the global GHG emission consequences of such a partial switch. The biomass value chain considered was gasification followed by methanol synthesis and downstream conversion to olefins via the methanol-to-olefins (MTO) process. Partial feedstock substitution enables the use of existing olefin separation equipment for upgrading of the crude MTO product stream, thereby enabling substantial capital cost reductions. A previous study (Arvidsson et al., 2015) showed that such a feedstock switch could substantially modify the site's steam balances. Moreover, the fuel gas and electric power balances could be affected. Theses consequences could in turn substantially affect the plant's global GHG emissions. In this study, two biomass-based process concepts were investigated and compared with the fossil-based *base case* process: (i) partial substitution of cracker units with MTO units fed with purchased biomass-based methanol produced off-site (MTObioOFF), and (ii) partial substitution of cracker units with MTO units fed with methanol produced on-site (MTObioON).

2. System overview

Figure 1 provides a general overview of the investigated systems, including both the fossil-only base case and the cases with a MTO process fed with biomass-based methanol produced off-site or on-site. Three subsystems are considered: the cracker, the MTO process, and the methanol process. More detail is provided below. A steam boiler and steam network are connected to the cracker plant.

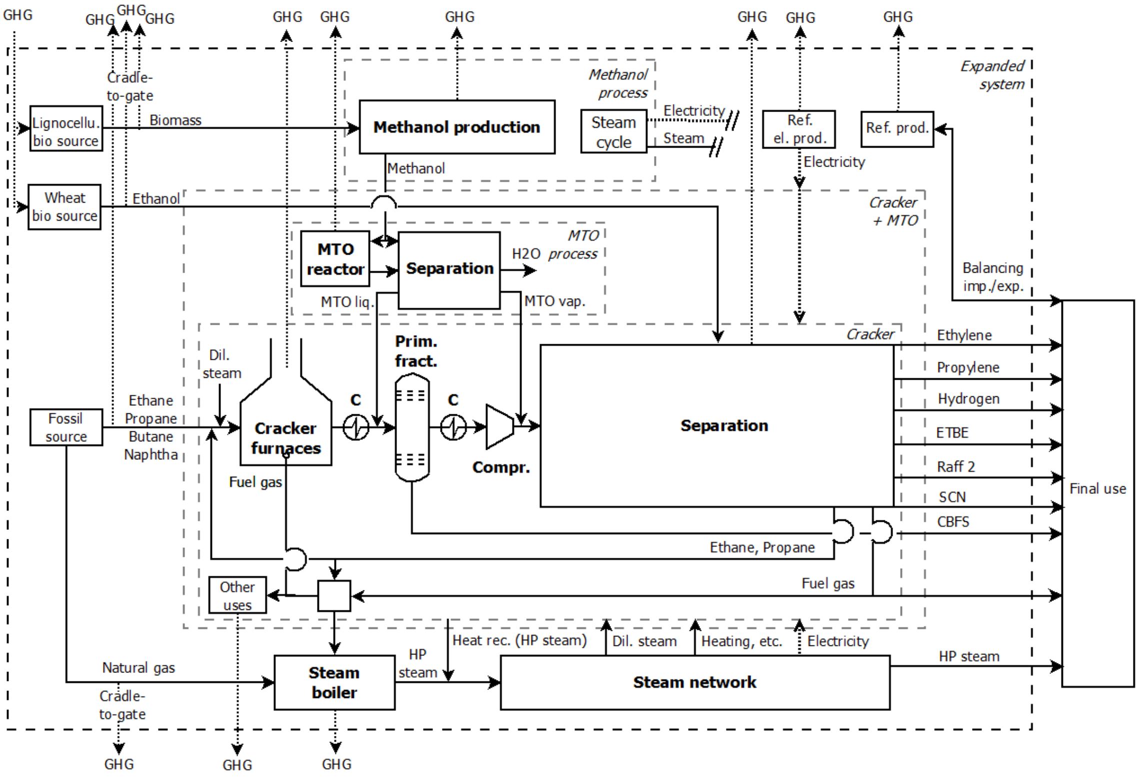

Figure 1: General system overview.

2.1 The cracker plant

The cracker plant includes several units that are fed with a mix of fossil-based ethane, propane, butane, and naphtha, as well as medium pressure (MP) steam (at 10 bar). Heat for the cracking reactions is provided by firing a hydrogen and methane-rich fuel gas, which is a by-product of the cracking itself. The cracked gas exits the pyrolysis section at about 850 °C and is thereafter cooled in a waste heat recovery unit producing high pressure (HP) steam (at 86 bar), and further quenched with oil before entering the primary fractionator. In the bottom of the primary fractionator, the heavier hydrocarbons are liquefied and collected to be sold as carbon black feedstock (CBFS). The lighter hydrocarbons in the top fraction are cooled, partially condensed, and the gas fraction is compressed before entering the separation section which includes a caustic wash, a stripper, dryers, compressors, reactors, and distillation columns. The separation section generates a wide range of products, such as ethylene, propylene, hydrogen, and an aromatics-rich stream referred to as steam cracked naphtha (SCN), see Figure 1. The crude C4-containing stream can be further processed to form the gasoline additive ethylene-tert-butyl-ether (ETBE) and a purified C4 stream mainly consisting of butylene and some butane (referred to as Raff 2). As mentioned above, fuel gas is obtained as an additional by-product which is primarily used in the cracker furnaces, steam boilers and exported to neighbouring sites. Unreacted ethane and propane are recycled to the cracker or used as fuel gas. The cracker plant steam network consists of several pressure levels. HP steam is produced by heat recovery in the cracker process and by firing of fuel gas and purchased natural gas fuel (when required) in steam boilers. Several of the cracker plant compressors and pumps are steam turbine-driven, requiring HP or MP steam. Other steam requirements include HP steam export to other site users, dilution MP steam, and various process heaters. Steam can also be expanded in a turbo-generator.

2.2 The MTO process

In the MTO process, methanol is catalytically converted into dimethyl ether (DME) and thereafter mainly into ethylene, propylene, and butylene. The overall carbon selectivity towards ethylene and propylene is approx. 75 % to 80 % and the ethylene/propylene ratio is between 0.7 to 1.4, depending on process conditions (Vora et al., 2001). In this study, operation targeted towards high propylene production was assumed. During the MTO reactions, the catalyst is progressively deactivated due to the formation of coke. The catalyst is continuously regenerated by burning coke with air in a separate unit. The reactor setup is similar to conventional fluid catalytic cracking (FCC) arrangements in oil refineries. To reach the MTO gas quality specifications, several separation steps are required, such as quenching, absorption to recover DME and oxygenates, as well as a separation sequence very similar to that in conventional cracker plants including caustic washing, drying, and distillation. In this work, it was assumed that the MTO plant is located at the cracker site, enabling use of the existing separation processes. Two crude process streams are generated by the MTO process, a heavier liquid stream and a lighter vapour stream, which are assumed to be fed to the primary fractionator and the caustic wash, respectively.

2.3 The biomass-based methanol process

Methanol was assumed to be produced via thermochemical gasification of wood chips in an oxygen steam blown pressurised circulating fluidised bed (CFB) gasifier, similar to the concept proposed by VTT (Technical Research Centre of Finland) (Hannula and Kurkela, 2012) in which the raw syngas is cleaned from tar and methane in an advanced CFB catalytic reformer and an autothermal reformer. The desired synthesis ratio, $(H_2 - CO_2)/(CO + CO_2)$, and CO_2 concentration are adjusted by water gas shift and CO_2 removed by the Rectisol process, prior to methanol synthesis. Methanol synthesis in conventional medium pressure fixed bed reactors was assumed. Water-free methanol is obtained with a two column distillation train. Generally, processes involving gasification and chemical synthesis result in high temperature excess heat, which can potentially be recovered in a steam cycle to produce useful heat and electricity. The different investigated concepts, or locations, allow for different integration opportunities, thereof the undefined use of electricity and steam from the heat recovery steam cycle in Figure 1.

3. Methods

3.1 Process integration

Mass and energy balances were obtained for the different cases using an in-house production planning simulation program provided by the cracker site, as discussed in Johansson and Pettersson (2014). Mass balance and heat demand data for the MTO process were based on information provided by a licensor. Table 1 provides an overview of the main inputs and outputs for base case fossil-only operation. The biomass feedstock cases were sized to match the ethylene production in the base case, i.e. 590 kt/y.

Table 1: Overview of the base case flows (Johansson and Pettersson, 2014). Note: NG=Natural Gas.

Ethane (kt/y)	Butane (kt/y)	Naphtha (kt/y)	Ethanol (kt/y)	NG (MW)	Electricity (MW)	Ethylene (kt/y)	Propylene (kt/y)	Raff 2 (kt/y)	ETBE (kt/y)	SCN (kt/y)	CBFS (kt/y)
525	523	169	13	53	42	590	149	86	29	115	18

In addition to feedstock consumption and resulting product flows, the in-house program was used to estimate steam flows through turbines and compressors, dilution steam consumption and HP steam production from the cracker furnaces. Detailed steam balance characteristics are presented in Arvidsson et al. (2015). A fuel gas balance was then developed based on the overall steam balance as well as the overall mass and energy balances obtained from the company in-house program and accounting for requirements of fuel gas to export (92 MW) and uses other than cracking furnace and steam boiler fuel (7.2 MW), as well as the assumed HP steam export requirement (200 kt/y). Based on these balances, the boiler fuel demand was estimated by assuming natural gas fuel and a boiler efficiency of 85 %.

Changes in the electricity balance were also accounted for, such as a reduced (by 2.0 MW) power demand for the raw cracked gas compressor (Johansson and Pettersson, 2014) and an estimated electricity demand for the MTO process (Joosten, 1998). Furthermore, the analysis was conducted considering a fixed amount of products. In order to achieve this, the product mixes obtained for the MTObioON and MTObioOFF cases were balanced to match the base case product mix by assuming import/export from/to a fossil-based reference production site, see Figure 1.

Mass and energy balances for the biomass-based methanol process were obtained using Aspen Plus process simulation models developed by Isaksson et al. (2012) and updated by Morandin and Harvey (2015). Pinch Analysis tools were used to estimate targets for maximum heat recovery between process heat sources and sinks, assuming a global minimum allowable temperature difference of 20 K for heat exchanging. The cogeneration potential of steam and electric power for the investigated concepts were estimated by investigating integration with a heat recovery steam cycle. For the MTObioOFF case, excess heat from methanol production was assumed to be recovered and used in a steam cycle for maximum electricity production. For the MTObioON case, export of superheated HP steam to the cracker’s steam network was prioritised to minimise import of natural gas fuel for steam production, and the remaining excess heat was used for electricity production. The assumed steam turbine inlet data were 86 bar and 485 °C. The turbine isentropic efficiencies were estimated from performance curves as functions of mass flow rates and pressure differences, based on the work of Savola and Keppo (2005). The steam extraction and turbine outlet pressures were chosen to match the corresponding process steam pressure levels.

3.2 GHG emission reduction potential

The GHG emission sources considered are highlighted in Figure 1. Emissions were accounted for as CO_2 equivalents (CO_{2eq}), i.e., CO_2, methane, and N_2O were considered in accordance with their global warming potential for a 100 y period (GWP_{100}). A system boundary expansion approach was applied in order to account for off-site emissions, as shown in the “expanded system” in Figure 1. This approach considers emissions associated with extraction and transportation to the plant battery limit in addition to on-site process-related emissions. Data were collected from databases and literature, see e.g., Plastics Europe (2013). The complete biomass value chain was included within the system boundary for the two investigated concepts. Carbon uptake during biomass growth was included in the GHG emission balance. Changes in the electricity balance were assumed to affect power generation in high-efficiency coal-fired power plants (coal PP) with and without carbon capture and storage (CCS). The end-use of the cracker products was assumed to be identical for all investigated concepts. In this way, emissions associated with end-use do not play any role when comparing changes in GHG emissions and they are therefore not included in the expanded system boundary.

4. Results and discussion

4.1 Process integration

Table 2 presents the relative change for the partial feedstock switch cases compared with the base case, where an increase or a decrease are indicated with a + or a -, respectively. Note that the ethylene production was considered fixed in the analysis, thus resulting in a relative change of zero. 622 MW (lower heating value (LHV) basis) of biomass (50 % moisture) is required to produce approx. 220 kt/y olefins (ethylene, propylene, and butylene) via biomass gasification, methanol synthesis, and the MTO process. This corresponds to a conversion efficiency just below 60 % (LHV basis) and a mass yield of approx. 0.2 kg/kg dry biomass. HP steam production in the steam boilers increases by approx. 70 % compared with the base case, corresponding to approx. 50 MW fuel gas. Other main fuel gas balance consequences of the feedstock switch include reduction of fuel gas production (approx. 20 %) and reduced fuel gas demand (approx. 15 %) in the cracker furnaces. The overall fuel gas demand in fact decreases to some extent (approx. 1 %) compared with the base case. However, if no integration with a nearby heat source is considered (as in the MTObioOFF case), the import of natural gas is significantly increased (by approx. 170 %) compared with the base case, due to the reduced fuel gas production. The on-site MTObioON configuration could potentially produce enough HP steam to completely off-load the cracker steam boiler, corresponding to a natural gas import reduction of approx. 50 % compared with the base case. Recovery of excess heat could either be targeted towards export of HP steam (MTObioON), thus decreasing natural gas import, or towards maximised electricity production (MTObioOFF), minimising overall system electricity import. The electric power generation potentials are estimated at 65 MW and 27 MW for the off-site and on-site cases. Compared with the base case, the overall system electricity import is decreased by approx. 10 % for the off-site case, or increased by approx. 80 % for the on-site case.

Table 2: Overview of the relative change in flows for the partial feedstock switch cases compared with the base case. The case dependent results are reported as MTObioOFF/MTObioON. Note: NG= Natural Gas.

Biomass (MW)	Ethane (kt/y)	Butane (kt/y)	Naphtha (kt/y)	Ethanol (kt/y)	NG (MW)	Electricity (MW)	Propylene (kt/y)	Raff 2 (kt/y)	ETBE (kt/y)	SCN (kt/y)	CBFS (kt/y)
+622	-5.2	-248	-1.7	-4.6	+90/-25	-4.6/+33	+61	+11	-10	-2.1	-3.5

4.2 GHG emission reduction potential

The calculated GHG emission reduction potentials for partially switching to biomass feedstock range between approx. 960 to 1,100 kt CO_{2eq}/y, corresponding to a reduction of the base case total emissions of approx. 50 % to 70 %. Further break-down details are shown in Figure 2.

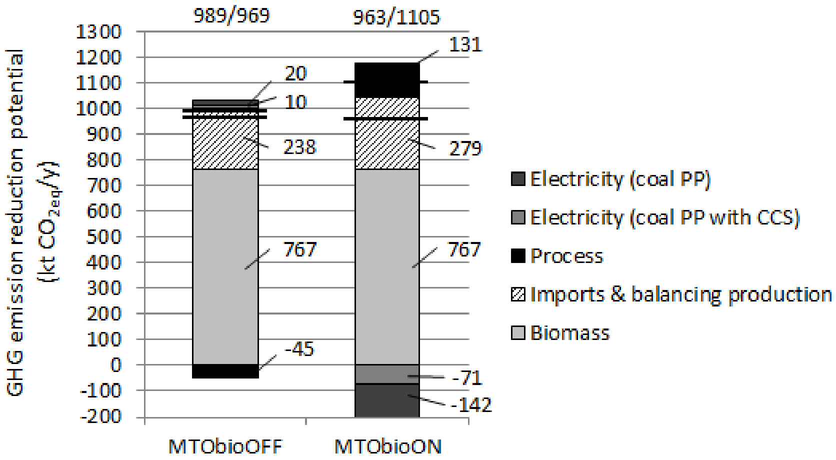

Figure 2: Break-down of the GHG emission reduction potentials (kg CO_{2eq}/y). The total GHG emission reduction potentials are reported as coal PP/coal PP with CCS.

The largest contributing factor to the GHG emission reduction potential is the switch to biomass feedstock, corresponding to 767 kt CO_{2eq}/y for both cases. The process-related emissions show a negative (-45 kt CO_{2eq}/y) and a positive (131 kt CO_{2eq}/y) contribution to the GHG emission reduction potential for the MTObioOFF and MTObioON casesy. The difference between the two cases is due to the steam export opportunity in the on-site case (MTObioON), which can completely eliminate natural gas firing in the steam boiler, whereas natural gas fuel import must be significantly increased in the off-site case (MTObioOFF) in order to satisfy the overall steam balance. The cradle-to-gate-related emissions for the change in imports and balancing product mix correspond to 238 and 279 kt CO_{2eq}/y for the MTObioOFF and MTObioON cases, respectively. The main contributing factor is the change in butane feed and the difference between the two concepts is due to the difference in natural gas import for the reasons mentioned above. The contribution of the electric power balance to the GHG emission reduction potential show opposite trends compared with the process-related emissions. This is due to the trade-off between the cogenerated products from the heat recovery opportunities. The results show that the overall system electricity imports are decreased or increased compared with the base case for the off-site and on-site cases, respectively. This translates to a greater contribution to the GHG emission reduction for a high emitting reference electric power generation technology (coal PP) for the off-site case (MTObioOFF). Conversely, the on-site methanol production case (MTObioON) achieves the highest GHG emission reduction potential when a low emitting electric power generation technology is assumed (coal PP with CCS). Accordingly, the electricity-related emissions show a positive (30/10 kt CO_{2eq}/y) and a negative (-213/-71 kt CO_{2eq}/y) contribution to the GHG emission reduction potential for the MTObioOFF and MTObioON cases (coal PP/coal PP with CCS), respectively. Note that the total emission contribution of coal PP should be considered as the combined coal PP with CCS and coal PP contributions in Figure 2.

5. Conclusions

This study investigated the GHG emission consequences of a fossil-based steam cracker plant partially switching to biomass feedstock for production of olefins (approx. 220 kt/y, corresponding to approx. 25 % of total production) via gasification, methanol synthesis, and the MTO process. The switch affects the site steam, fuel gas, and electricity balances, compared with base case operation with fossil feedstock. Even though the overall fuel gas demand decreases compared with the base case, the demand for HP steam production in the steam boilers increases considerably. The opportunities for heat recovery from the methanol process differ significantly for off-site and on-site biomass-based methanol production, where a trade-off between the possible cogenerated products can be observed. In the off-site case, heat recovery was assumed to be targeted towards maximised electric power production without HP steam export to the cracker site, thereby significantly increasing the natural gas requirements of the steam boilers (by approx. 170 %) and decreasing the overall electricity import (by approx. 10 %). Conversely, on-site production of bio-methanol allows enough HP steam to be produced from heat recovery to completely off-load the steam boiler, thus reducing natural gas import by approx. 50 % compared with the base case while the overall electricity import is increased (by approx. 80 %). By applying a system boundary expansion approach, the GHG emission reduction potentials for the two investigated cases were shown to range between approx. 960 and 1,100 kt CO_{2eq}/y compared with the base case, corresponding to a reduction potential of approx. 50 % to 70 %. The choice of reference grid electricity generation technology significantly impacts the ranking of the cases, where a high and low emitting technology favours the off-site (989/969 kt CO_{2eq}/y) and on-site (963/1,105 kt CO_{2eq}/y) cases (coal PP/coal PP with CCS). The main contributing factor to the GHG emission reduction potential is the introduction of biomass feedstock, corresponding to 767 kt CO_{2eq}/y.

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