Conceptual Design of an Autonomous Once-through Gas-to-Liquid Process with Microchannel Fischer-Tropsch Reactors

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Converting remote natural gas to liquid fuel is one possible solution to the problem of transporting remote gas to the energy market. However, the high investment cost of gas-to-liquid (GTL) plants prevents large scale exploitation of remote gas reserves. A lean GTL is suggested based on an autothermal reformer with enriched air as oxidant and a once-through Fischer-Tropsch synthesis. In order to maximize the syngas conversion and the production of heavy hydrocarbons, a staged microchannel reactor path with distributed hydrogen feed and product withdraw is proposed. The hydrogen is produced by steam methane reforming in a heat exchange reformer (gas heated reformer). A verified kinetic model for the Fischer-Tropsch reactor is used. This kinetic model was fitted to kinetic data of a 40 %CO/Al$_2$O$_3$ catalyst which was used in a microchannel reactor. A new chain propagation model was also fitted to the data. The new kinetic and rate propagation models are believed to be specifically suitable for microchannel reactors. The chain propagation model yields high C$_{5+}$ selectivities. The process is autonomous in the sense that it is self-sufficient with power and water.

1. Introduction

Increase in energy demand and depleting easily accessible oil have turned industries' focus on untapped resources that are unused for technical or economic reasons, such as associated gas or stranded gas reserves. Transportation of the gas is one of the biggest obstacles in exploiting these reserves. Converting natural gas to liquid fuels, gas-to-liquid (GTL), is one option in bringing remote natural gas to the market.

By placing a GTL unit on a floating production vessel, many offshore remote gas reserves can be monetized and also reduce flaring. However, placing a GTL plant on a vessel faces its' own challenges that an onshore plant does not. To mention a few are the need for operations autonomy in the sense that all production utilities, such as water and power, need to be available on board the ship. Pure oxygen streams may be problematic because of high explosion risk due to proximity with hydrocarbons. Also high columns with liquid inventory on board the ship may create problems. There have been some investigations looking at the feasibility of installing a gas-to-liquid (GTL) process on floating production storage and offloading (FPSO) vessel that are described by Ostadi et al. (2015).

2. The proposed process concept

The process configuration is the same as our previous study (Ostadi et al., 2015). The process flow diagram is shown in Figure 1. Here, the product upgrading process and the steam utility system are not shown. The specifications of natural gas feed are shown in Table 1. After sulfur removal, the natural gas is mixed with steam before entering the pre-reformer. Stream 100 is split into two streams, 101 and 102, the former to the ATR and the latter to the HER. The split ratio is 85 % to ATR and 15 % to HER. The energy required for the steam reforming reactions in the HER is provided by the hot outlet stream from the ATR. The outlet of the HER is cooled down before entering the high temperature water gas shift (WGS) reactor, shifting CO to CO$_2$ and H$_2$. After the WGS reactor, the stream is cooled and water is knocked out before entering the membrane unit for separation of H$_2$. The hydrogen rich stream with 99 % purity is then compressed and distributed

between the Fischer–Tropsch stages. The CO_2 rich stream, which also contains some H_2, CO and CH_4, is compressed and recycled to the ATR. By adding this stream, the H_2/CO ratio out of the ATR will be reduced, which is beneficial for the FT synthesis. Because of the under-stoichiometric H_2/CO ratio at the inlet of the first FT stage, this ratio continues to decrease along the reactor. In order to increase this ratio before the next stage, hydrogen is injected between the stages. The effluent stream from ATR after heat exchange with the HER, is further cooled to knock out water from the syngas. Without further compression the syngas stream is heated before entering the first Fischer–Tropsch stage. In order to increase the rate of the FT reactions, and also suppress catalyst deactivation, the gas outlet from FT reactors is cooled down and partly condensed where water and hydrocarbon products are separated from the gas. The tail gas, consisting of unconverted syngas, nitrogen and light gas components produced in the Fischer–Tropsch reactors, is used as fuel in the gas turbine to supply power to consumers.
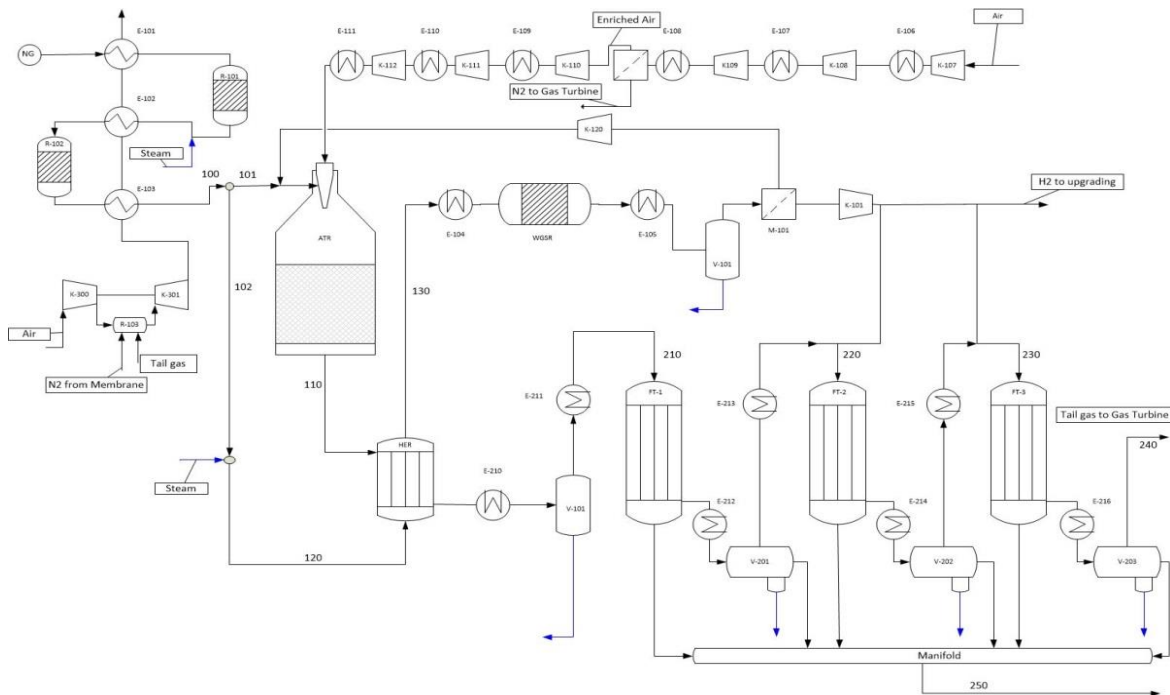

Figure 1: Process flow diagram of the GTL plant. Heat integration and the steam system are not shown here

2.1 Syngas production

An autothermal reformer is selected for syngas production. The main reasons are that the H_2/CO ratio can be adjusted to be close to the optimal ratio and the ease of scalability. A pre-reformer is used in front of the ATR to prevent coke formation on the ATR catalyst. With an air-blown ATR, it is practically impossible to recycle the unconverted syngas because of very high nitrogen concentrations. This is also the case with enriched air, and a once-through synthesis scheme is the only option to avoid high accumulation of nitrogen. PRISM membrane separators from Air Products are considered (Air Products, 2015). Considering the large air flow through the membrane and therefore avoiding very large membrane modules, a PRISM membrane is chosen to have 34 % oxygen purity. An alternative to air or enriched air is to use pure oxygen. Pure oxygen from cryogenic air separation poses significant safety challenges offshore, in addition to large investment costs. Although having enriched air increases the volume of equipment after ATR, but considering the cost of having an air separation unit, it will be beneficial to have larger volumes than having an air separation unit.

2.2 Hydrogen production

When H_2/CO ratio is slightly under-stoichiometric, more C_{5+} products can be obtained and in order to compensate for the consumption of hydrogen, it is added between the stages. Part of the produced hydrogen is also sent to the product upgrading unit. Steam reforming with the use of a heat exchange reformer is applied to produce hydrogen with H_2/CO ratios of more than three. Apart from being a hydrogen generator, the HER provides efficient heat integration and avoids the use of a waste heat boiler. The heat exchange reformer is counter current and consists of 1,000 steam reformer tubes of 10 cm diameter and 10 m long. Modeling of the heat exchange reformer is described in detail by Falkenberg (2015). The remaining CO is converted to

Table 1: Specifications of the natural gas feeds; NG1 is used for all the results produced here, while NG2 is used to see the effect of heavier natural gas

	NG1	NG2
Temperature [˚C]	50	50
Pressure [bar]	30	30
Flow [MMscmd]	3.4	3.4
Molar flow [kmol/h]	6,000	6,000
Mole fraction		
CH_4	0.95	0.85
C_2H_6	0.02	0.067
C_3H_8	0.015	0.033
$n\text{-}C_4H_{10}$	0.01	0.022
$n\text{-}C_5H_{12}$	0.005	0.011
CO_2	0.0	0.017

CO_2 by the use of a water gas shift reactor. The WGS effluent is cooled down to 30 °C to remove most of the water before entering the membrane to produce a hydrogen rich and a CO_2 rich stream. The CO_2 rich stream is recycled back to the ATR to decrease the H_2/CO ratio at the outlet of the ATR. The membrane used here is a carbon membrane with no sweep gas on the permeate side. This will produce very pure hydrogen on the permeate side.

2.3 Fischer-Tropsch synthesis
The Fischer–Tropsch synthesis is staged with product withdrawal and hydrogen addition between the stages. This enables high conversion of syngas and high selectivity to higher hydrocarbons. Studies on the kinetics of FT synthesis show that nitrogen only dilutes syngas and therefore has no influence on the kinetics if the partial pressures of carbon monoxide and hydrogen are kept constant (Jess et al., 1999). Moreover, nitrogen plays an important role in the operation of multi-tubular reactors by facilitating removal of generated heat.

2.4 Microchannel reactor
Reactors with microchannels are suited for reactions that are highly exothermic or highly endothermic. Channels filled with FT catalyst powder and channels with coolant water are arranged in a cross flow configuration. We assumed a two-dimensional homogeneous model with no axial dispersion. Boiling water is used as coolant and its temperature is assumed to be constant along the axial direction. Table 2 shows the design parameters of the microchannel reactor model. Isothermal behaviour of microchannel FT reactors has been demonstrated by Deshmukh et al. (2010). The hot-oil-cooled microchannel reactors were isothermal to within ± 1 °C. This is also verified with our reactor model. With very high heat removal capability, single pass conversions near 80 % can be realized.

Table 2: Design parameters of microchannel reactors

Catalyst bulk density [kg/m^3]	1,200
Catalyst particle diameter [mm]	0.2
Catalyst void fraction	0.4
Cooling water temperature [˚C]	220
Channel sides [mm]	2 × 2

2.5 Kinetic rate and chain propagation models
Here, an alternative kinetic rate model and a model describing the product distribution of the Fischer-Tropsch synthesis are applied (Ostadi and Hillestad, 2016). The kinetic rate model, suggested by Ma et al. (2014), is verified against data from a microchannel laboratory reactor (Yang et al., 2016). In addition, a model describing the product distribution and methane selectivity is developed (Ostadi and Hillestad, 2016) and fitted to data generated by Yang et al. (2016). It is well known that the selectivity of methane is higher than predicted by the ASF distribution. To account for this fact, a separate methanation reaction rate is introduced. The methanation reaction rate, Eq(2), is found to be proportional to the rate of methane production by ASF model. ν_1 is the stoichiometric coefficient of methane according to ASF distribution. The data used for the fitting of the reaction rate is from 40 % CO/Al$_2$O$_3$ catalyst. To account for gradual deactivation of catalyst, 80 %

of the activity of fresh catalyst is used to calculate the rate. The implemented kinetic rate model, Eq(1) and Eq(2), and the product distribution model, Eq(3), are as follows:

$$r_{FT} = K_1 \frac{P_{CO}^{-0.31} P_{H2}^{0.88}}{1 - 0.24 \cdot \frac{P_{H2O}}{P_{H2}}} \tag{1}$$

$$r_{CH4} = K_2 \cdot r_{FT} \cdot v_1 \tag{2}$$

$$\alpha = \frac{1}{1 + K_3 \frac{P_{H2}^{1.45}}{P_{CO} P_{H2O}^{0.253}}} \tag{3}$$

The production of alkanes and alkenes is described by two chain growth probabilities. The rate of production of alkenes is 70 % of that of alkanes. Since Fischer-Tropsch reaction can in theory produce infinite number of paraffins and olefins, the method suggested by Hillestad (2015) is used to handle infinite number of reactions and components. We have chosen to model alkane components individually up to C_{10} and a lump C_{11+}^{P} describing the tail distribution. While for alkenes, with less heavier components, we have chosen to model individual components up to C_4 and a lump C_{5+}^{O}. For the sake of brevity the lumps C_{5+}^{P} and C_{5+}^{O} are reported here, but they are made by adding individual components and the modeled lumps. This way of lumping is described in detail by Hillestad (Hillestad, 2015). The kinetic model is implemented in a model of the microchannel reactor with the use of Aspen Custom Modeler (ACM) language. The model is further exported to Aspen HYSYS process simulator for simulation and optimization of the entire GTL plant.

3. Results

In our previous investigation two reactor stages with 2 meter reactor length was used (Ostadi et al., 2015). This distribution of volumes is not optimal. Here three stages are used to increase C_{5+} production in less volume. Following the method of systematic staging of reactors (Hillestad, 2010), we did an optimization of reactor path and came up with different lengths of reactors. Table 3 shows different design parameters for different FT stages. The first, second and third FT stages have 54, 27 and 19 % of the total volume. The proposed chain propagation model yields low methane selectivity and high C_{5+} selectivity. Methane selectivities are less than 6 % in all stages. The important streams information is shown in Table 4. The important results of the plant are shown in Table 5.

3.1 Water and power
The tail gas from the last Fischer–Tropsch stage is used as fuel to the gas turbine for power production. Water balance and power balance are shown in Tables 6 and 7, respectively. The plant produces excess power of 4.97 MW and also excess water.

3.2 Carbon and energy efficiencies
The carbon efficiency is defined as the fraction of the feed carbon components ending up as carbon of product components. The carbon efficiency is about 61 %. For the calculation of the energy efficiency, we look at the fraction of the natural gas feed heating value (LHV) that is converted to LHV of the product and hydrogen streams, in addition to power export, energy of steam and finally lost energy. The excess power from the gas turbine, adjusted with the Carnot efficiency to be comparable to thermal energies, is reported as "Excess power". We should also keep this in mind that part of hydrogen will be transferred to products after the product upgrading. About 49 % of the natural gas LHV ends up in the product stream and about 12 % ends up as LHV of excess hydrogen. The amount of steam from the FT reactors is estimated to be 291.5 t/h. The amount of steam generated is calculated by heating and evaporating water from 20 ˚C and 23.19 bar. By using NG2 in Table 1, we can see the effect of heavier natural gas. By use of NG2, total CO conversion drops to 81.5 %, however, CH_4 selectivity and C_{5+} production remains the same. The carbon efficiency will also decrease to 54 %, which is because of lower conversion in the FT stages.

Table 3: Design parameters of different FT stages

	Stage 1	Stage 2	Stage 3
Channel Length [m]	0.8	0.6	0.5
Volume [m^3]	48	24	17
Inlet H_2/CO	2.0	2.0	2.0
H_2 addition between stage [kmol/h]	0	365.1	127.7
CH_4 selectivity [%]	5.95	5.39	4.26
CO conversion [%]	57.9	51.6	53.5
C_{5+} production [t/h]	35.65	13.99	7.26

Table 4: Important stream information

Stream	110	120	130	210	220	230	240	250
Temperature [˚C]	1060	441.2	1052	210	210	210	30	191
Pressure [bar]	28.5	28.5	28.1	26.93	24.84	22.95	21.69	21.69
Mass flow [t/h]	476.9	63.89	63.89	399.10	307.80	273.10	255.2	57.44
Mass fractions [1]								
CO	0.314	0.000	0.343	0.375	0.205	0.112	0.055	0.001
H_2	0.045	0.003	0.095	0.054	0.030	0.016	0.008	0.000
H_2O	0.165	0.727	0.428	0.002	0.001	0.001	0.001	0.002
CH_4	0.002	0.236	0.005	0.003	0.013	0.018	0.021	0.000
C_2-C_4	0.000	0.000	0.000	0.000	0.009	0.014	0.017	0.001
C_{5+}^P	0.000	0.000	0.000	0.000	0.009	0.012	0.013	0.945
C_{5+}^O	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.046
CO_2	0.107	0.033	0.129	0.128	0.166	0.188	0.201	0.003
N_2	0.366	0.000	0.000	0.438	0.567	0.640	0.684	0.002

Table 5: Overall plant results

Methane selectivity [%]	5.61
CO conversion [%]	90.55
C_{5+} production [t/h]	56.90
Carbon efficiency [%]	61
Catalyst volume [m^3]	89
Reactor productivity [t/m^3-h]	0.64
Surplus hydrogen [t/h]	5.96

Table 6: Water balance

Water stream [t/h]	
Steam demand	119.10
Retrieved water from syngas	96.4
Retrieved water from product	87.57
Excess water	64.86

Table 7: Power balance

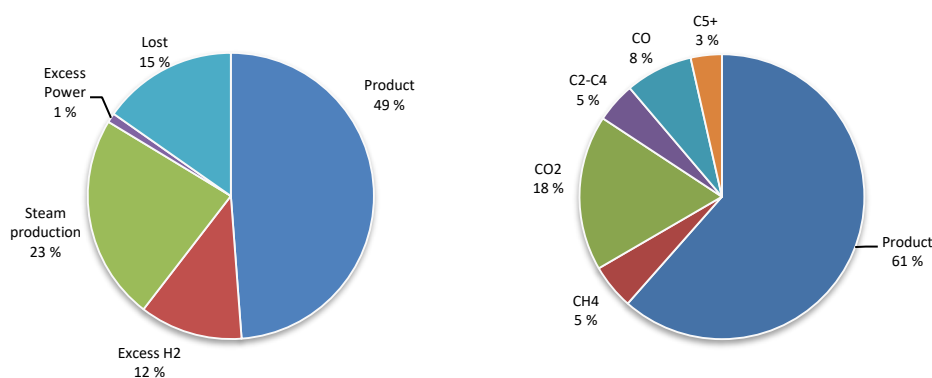| Category	Power source/sink	[MW]
Power sinks	Air compression	129.9
	H_2 Compression	4.5
	CO_2 recycle	0.2
Power sources	Gas turbine	139.6
Excess power production		4.97

Figure 3: (Left) The relative distribution of energy content of the natural gas in different product streams of the GTL plant, (Right) the relative distribution of carbon between the product stream and the tail gas

4. Conclusions

A novel process concept is proposed for converting natural gas to liquid hydrocarbon products. For the Fischer-Tropsch reactors, a verified kinetic rate and product distribution models of the Fischer-Tropsch synthesis are applied (Ostadi and Hillestad, 2016). The new and verified kinetic model yields higher reaction rates than what was used in our previous investigation (Ostadi et al., 2015). The new kinetic model along with the product distribution model is specifically suited for microchannel reactor and it gives us a more realistic view of the process in the large scale. With the proposed configuration, high once-through CO conversion, in the order of 90 % and more, is achieved. The carbon efficiencies for a once-through synthesis are calculated to be 61 % and the energy efficiency is about 49 %. Compared to our previous investigation, this study produces the same amount of C5+ but in 45 % less volume which means lower cost of the overall GTL plant.

Acknowledgments

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