Fischer-Tropsch synthesis using bio-syngas and CO₂

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While Fischer-Tropsch synthesis (FTS) using coal and natural gas in conventional reactors is an almost well-established technology, the production of liquid hydrocarbons from syngas obtained from biomass is in its preliminary stages of commercialization in countries like Germany. With concerns about global warming and ways of disposing of CO₂ being searched for, CO₂ hydrogenation using FTS to liquid hydrocarbons can act as a CO₂ sink. A brief review of FTS using CO₂-rich syngas is given in this paper, looking at FTS as a technology that can help reduce global warming and as a process integration alternative. The reverse water gas shift (r-WGS) reaction is vital for CO₂ hydrogenation. We have studied the effect of this using an FT kinetic model and have proposed a new flow sheet alternative for FTS using CO₂-rich syngas. Simulations suggested that this new process gives better conversion of CO₂. The product selectivity and yields from an FT plant are vital to make the process viable economically.

1. Introduction

Fischer-Tropsch synthesis (FTS) is one of the technology alternatives being used by SASOL, South Africa, for the past five decades to obtain liquid fuels from synthesis gas or syngas [Dry, 2002]. The synthesis gas feed can come from coal or residual oil gasification, methane reforming, or from biological wastes. Syngas obtained from biomass is termed “bio-syngas” and FTS using this is under development. With concerns about global warming and ways of disposing of CO₂ being searched for, CO₂ hydrogenation using FTS to liquid hydrocarbons can act as a CO₂ sink. This is more useful if H₂ can be produced without considerable CO₂ emissions, using hydel, solar or nuclear power [Riedel et al., 1999]. The conventional methods of syngas production (steam reforming of natural gas or coal gasification) also release good amounts of CO₂, which is separated before the syngas is fed to FT reactors. In the following sections, a review of the CO₂ hydrogenation studies reported in the literature is presented. Since the WGS and r-WGS reactions play an important role in maintaining the H₂ balance and CO₂ conversion, a study of r-WGS was carried out and the results are discussed.

In a novel approach, Gouse et al. [1993] present integrations of photovoltaic (PV) cells and integrated coal gasification combined cycle (IGCC) technologies to reduce carbon dioxide emissions. In one of these alternatives (Figure 1), liquid transportation fuels are produced by using the carbon dioxide emissions from the IGCC plant with hydrogen produced from PV electrolysis of water in an FT process. Thus, FTS for CO₂ hydrogenation can be viewed as a technology that can help reduce global warming and as a process integration alternative. FTS can

be seen as a process helping to maintain a closed carbon cycle – carbon from emissions of CO₂ from transportation fuels is fixed back in them utilizing H₂, which may be obtained from solar power, etc. The same principle may be applied for bio-syngas. Apart from CO₂ emission mitigation, CO₂ hydrogenation would help in bringing down the cost of the FT process. The FT process, be it from coal or biomass, involves a clean-up process where NH₃, H₂S and CO₂ are removed from the syngas before it is sent to the FT reactors. On the other hand, if CO₂ is hydrogenated in the FT reactor by means of a suitable catalyst, CO₂ removal from raw syngas is not needed. This would reduce to some extent the cost involved in the CO₂ separation step alone, while NH₃ and H₂S still need to be removed from the raw syngas.

2. CO₂ hydrogenation

2.1. Syngas from coal gasification

Rao et al. [1992] report that some gasifiers for coal gasification like the conventional Lurgi process give a CO₂-rich syngas (17 % CO, 38 % H₂, 32 % CO₂, rest others). Iron catalysts used in the conventional FT reactors exhibit WGS activity as well. WGS activity helps the reactors to handle CO-rich gas deficient in H₂ by generating hydrogen. On the other hand, for a CO₂-rich syngas, sufficient H₂ is necessary to first enable the reverse-WGS reaction to form CO, which then takes part in the FT polymerisation reactions. This is the mechanism for CO₂ hydrogenation perceived by many authors including [Riedel et al., 1999] and [Jun et al., 2004]. The important reactions for FTS using CO- or CO₂-rich syngas are as follows:

the time when the catalyst is still undergoing changes (in terms of getting carburized and the subsequent phase changes) and the product slate is also varying. Once the catalyst reaches steady state, the product distribution remains constant. They also report no deactivation with the CO₂-rich syngas. This was attributed to the low carbon formation tendency, as CO partial pressure is low owing to the WGS equilibrium constraints.

2.4. Selectivity and yield

The product selectivity and yields from an FT plant are vital to make the process viable economically. This depends on the catalyst used, reactor type, pressure, temperature and syngas conditions. Kim et al. [2006] compared the performance of the 3 main types of reactors, fixed bed, fluidized bed and slurry, for CO₂ hydrogenation using Fe catalyst. Similar to CO hydrogenation, they report that light olefins and heavy hydrocarbons were respectively formed in the fluidized bed (HTFT) and slurry reactors (LTFT). A common feature found in the literature for FTS using CO₂ is that the experiments used to report data were performed at 573 K and 10 bar using a H₂/CO₂ ratio of 3. Jun et al. [2004], who have used a model bio-syngas, however, report data for both a H₂-deficient and balanced feed at 573 K and 10 bar. Selectivity can also be predicted using kinetic models for product distribution, which are few in the literature. This was not observed in any of the literature studied for CO₂ hydrogenation. We have simulated one of the existing kinetic models in the literature to study the effects of CO₂ present along with the feed on the FT product selectivity, with emphasis on the WGS reaction considering an iron catalyst.

3. Simulation studies and results

3.1. Reaction conditions

In the case of CO₂ hydrogenation, the equilibrium of the CO shift reaction is vital as it limits the maximum extent to which CO or CO₂ can be converted in a mixture of CO, CO₂, H₂ and H₂O. It is reported in the literature that the WGS reaction is in equilibrium under FT conditions, while FT reactions are all kinetically controlled. As mentioned earlier, for FTS using CO₂, it has to be first converted to CO and H₂O through the r-WGS reaction. The CO thus formed is consumed in the monomer formation for FT polymerisation. While r-WGS is endothermic, FT monomer formation and WGS are exothermic reactions. Overall, this gives CO₂ hydrogenation an exothermic nature. But the lower exothermicity compared to CO hydrogenation makes the temperature control of the reactor easier [Riedel et al., 1999]. The main and deciding point is the additional demand for H₂, which has to be met when using CO₂-rich syngas. In the FT process, an increase in temperature thermodynamically favours methane formation and the selectivity moves towards CH₄. On the other hand, r-WGS, being endothermic in nature, is favoured at high temperatures. Besides, the water formed from the r-WGS is strongly inhibiting on iron catalysts [Schulz et al., 1994] and limits the syngas conversion per pass. Riedel et al. [1999] suggested the use of different reactor volumes with optimized conditions for the two reactions.

Considering the r-WGS reaction alone gives the following options to increase conversion of CO₂ to CO: removal of water formed, removal of CO or addition of H₂. CO removal is dictated by FT reactions, and increasing the temperature, which gives undesired methane, can increase this rate. Meeting additional H₂ demand is difficult and may again lead to more CH₄ in the product. The remaining choice of water removal seems possible and was investigated in this work through simulations, while proposing a flow sheet for it. A fixed-bed reactor model was considered for performing the simulation studies. The kinetic model predicting the product distribution is taken from [Wang et al., 2003], for an industrial Fe-Cu-K catalyst. It also includes the WGS kinetics in it. The results of the simulations for a H₂/CO syngas at different pressure, temperature, feed ratio and flow rate conditions were verified to be concurrent with the conclusions reached in the literature, like increase of CH₄ selectivity with increase in temperature and H₂/CO ratio and drop in conversion with increase in flow rate. The kinetic parameters reported in Wang's model were obtained for temperatures of 493-543 K, pressures of 11-31 bar and feed ratio of H₂/CO from 0.98 to 2.99. Since CO₂ formation is present in FT using CO-rich syngas, the model should predict the presence of CO₂ in feed gas as well.

Simulations were performed with a single reactor for two cases of hydrogen concentration, one with a fixed concentration and the other a balanced concentration, while varying the ratio of $R = \text{CO}_2/(\text{CO} + \text{CO}_2)$ between ~0 and 1. For the balanced H₂ case, the ratio $A = \text{H}_2/(2\text{CO} + 3\text{CO}_2)$ equals 1. The conditions used were 25-55 bar, 493-573 K, feed flow rate of 500 ml/min and 82 g of catalyst with a maximum carbon number of 50 in the product. The pressure (25 bar) and temperature (493 K and 573 K) used in these simulations are representative of the LTFT and HTFT process respectively. As R approached 1, FT, syngas and hydrogen conversions monotonically decreased, methane selectivity and water content in the exit stream monotonically increased, and CO and CO₂ conversions showed a change in sign (Figure 2). The reactors in the proposed process (Figure 3) should be operated in the range of R where CO₂ conversion is positive, e.g., $R > 0.72$ at 493 K and 25 bar (Figure 2). Also, as R further increases to 1, CO formation is observed, i.e., negative conversion of CO ($R > 0.90$ at 493 K and 25 bar). In this region, water removal would help not only the r-WGS to increase CO₂ conversion, but also help CO conversion by reducing the possible inhibition effects of water. At a constant pressure, as the temperature increases, the feasible region for R values with positive conversion of CO₂ expands (from 0.72 to 0.55 in Figure 2a). This would be expected, as at higher temperatures, r-WGS equilibrium conversion would increase. For a fixed temperature, as the pressure increases, there is not much change in the feasible range of R (Figure 2b), possibly because WGS, being an equimolar reaction, is not much influenced by change in pressure. The figures illustrated are for the case when A varied from 1.49 to 1, as R varied from ~0 to 1. Even when A equals 1 for varying R, not

Figure 2a. CO and CO₂ conversion at 25 bar

Figure 2b. CO and CO₂ conversion at 493 K

much change was observed in Figure 2. The arrows indicate the direction of increasing pressure or temperature in Figure 2.

In the region of R where CO₂ is formed, i.e., for negative conversions of CO₂, (e.g., $R < 0.55$ at 25 bar and 573 K), it is proposed that a shift reactor (with r-WGS) alone would be first used to convert the CO₂ in feed to

CO at relatively high temperatures (~673 K). The product then obtained would be subjected to the HTFT process. This is because of the conflicting requirements of pressure and temperature by the r-WGS and FT reactions, and hence both cannot be conducted in a single step. Joo et al. [1999] evaluated a similar process for methanol production. For the example considered in the next section (Section 3.2), we have performed simulations at $R = 0.91$, which satisfies the condition of $R > 0.72$ at 55 bar and 493 K. For any temperature between the two extremes (of 493 K and 573 K) at the same pressure (25 bar), the results lie within the region depicted in Figure 2.

At the chosen value of ratios for A and R in the paper, Figure 2 was generated with the help of simulations. Similar study can be done for different values of A . It is difficult to have a unique conclusion from the results shown owing to the variation in conversion if A is changed, and the example presented is an illustrative one. We have chosen a region that can be a potential candidate and carried out the simulation study.

3.2. Performance of the proposed flow sheet

To further improve CO₂ conversion in the feasible region of R where CO₂ conversion is positive, (e.g., $R > 0.55$ at 25 bar and 573 K), the flow sheet in Figure 3 is proposed with an intermediate water removal step between the two FT reactors. The flow sheet consists of FT reactors (FT), separators (S) to separate the condensed water (and hydrocarbon, if any) and heat exchangers (H). Feed having CO₂ is preheated in H1 and enters the reactor FT-1. The exit streams from the reactors are cooled down in heat exchangers, so that water gets condensed. The water is removed in separators (S) and the exit gas from here is heated back to the reaction temperature and sent back to another FT reactor. The sequence continues till the required conversion for CO₂ is achieved for a given volume of syngas feed and molar content of CO₂ present in it.

Simulations for this flow sheet were performed using MATLAB for the reactor model and DESIGN-II for the heat exchanger and separator (flash) calculations. The inputs to the reactor model were: $P = 55$ bar, $T = 493$ K, feed flow rate = 100 ml/min, $H_2/CO = 30$, $CO_2/CO = 10$ and a catalyst weight of 200 g in each of the reactors. The maximum carbon number considered was 20 for simulations, to keep the calculations easier. Care was taken to ensure that the heat exchangers in the process did not have a temperature crossover, and had enough approach when the simulations converged.

The simulation exercise was performed for a set of 3 reactors, and compared with the simulated performance of a stand-alone reactor with 600 g of catalyst using the same conditions. The simulation results are given in Tables 1 and 2, and the following conclusions/comments were arrived at from the simulations performed.

1. The conversion of CO₂ and syngas and the methane selectivity at exit of each reactor are nearly the same.
2. When compared with a single reactor, reactors in series showed better utilization of H₂ and CO₂ as seen from the conversion values. CO conversion and methane selectivity are similar in the two cases.

Figure 3. Proposed flow sheet for improved CO₂ conversion in FTS

Table 1. Performance comparison of proposed flow sheet with a single FT reactor^[1]

	Molar flow at exit (mol/sec)			Exit conversion (%)	
	Feed	Reactor 3	Single reactor	Reactor 3	Single reactor
CO	5.45E-05	6.80E-06	5.89E-06	87.54	89.20
H ₂	1.64E-03	5.93E-04	9.03E-04	63.74	44.80
CO ₂	5.45E-04	2.92E-04	3.78E-04	46.47	30.76
H ₂ O	0	1.68E-04	3.84E-04	-	-
CH ₄	0	1.49E-04	1.16E-04	-	-
CH ₄ sel.	-	79.93	83.43	79.93	83.43

Note

1. CH₄ selectivity is mole % hydrocarbon in exit stream.

Table 2. Performance of each FT reactor in the proposed flow sheet^[1]

	Reactor 1	Reactor 1	Reactor 2	Reactor 2	Reactor 3	Reactor 3
	In	Exit	In	Exit	In	Exit
CO	2.41	0.67	0.78	0.60	0.69	0.55
H ₂	73.20	59.65	68.40	53.91	61.89	47.59
CO ₂	24.39	22.54	25.85	22.85	26.23	23.43
H ₂ O	0.00	13.12	0.74	13.89	1.14	13.48
CH ₄	0.00	3.03	3.47	7.05	8.10	11.95
C ₂	0.00	0.34	0.39	0.72	0.83	1.22
C ₃	0.00	0.17	0.19	0.40	0.46	0.71
C ₄	0.00	0.08	0.09	0.28	0.32	0.50
C ₅	0.00	0.04	0.05	0.16	0.18	0.30
C ₆	0.00	0.02	0.02	0.08	0.09	0.17
C ₇	0.00	0.02	0.02	0.06	0.07	0.10
X _{co2} (%)	-	19.60	-	21.82	-	20.35
X _{ft} (%)	-	24.72	-	22.18	-	20.59
X _{syngas} (%)	-	30.58	-	30.33	-	31.39
CH ₄ sel. (mole %)	-	81.90	-	80.57	-	79.93
Vol. in ml/min	100	87.02	76.58	67.73	62.5	55.74

Note

1. Compositions of components are in mole %

3. The FT reactor operating temperature limited the temperature rise that can be achieved in the heat exchangers, and set an upper limit on them.
4. While doing the simulations, water and steam were used as utilities in the heat exchangers to ease calculations (and the primary aim was to see the effect of removal of water on CO₂ conversion). The heat integration proposed in the flow sheet can be studied by setting up a better model in ASPEN, etc.
5. In contrast to values published for CH₄ selectivity in the CO₂ hydrogenation [Jun et al., 2004] experiments, the simulation results show 80 % methane selectivity. This could be because of the kinetics considered, which was on a Fe-Cu-K catalyst, while most of the reported data is from experiments on a Fe-Al₂O₃-Cu-K catalyst. (The error probably lies in the activation energy for CH₄ used, and its value over a Fe-Al catalyst should be used to verify the simulations. Changing the chain-growth parameter value for methane did not have considerable effects on the CH₄ selectivity.) The higher methane selectivity may also be due to the high ratio of H₂/CO used in the simulations. The catalyst promoter effects on conversion of CO₂ and product selectivity for a Fe-Cu catalyst are reported by Yan et al. [2000]. A comparison of the reaction in slurry and fixed bed reactors is also included in their study.

4. Conclusions

Biomass offers the choice of producing liquid, carbon-neutral transportation fuels using FTS. Since bio-syngas contains good amounts of CO₂, technologies for CO₂ hydrogenation using FTS are needed. For a CO₂-rich syngas, the proposed flow sheet having multiple FT reactors in series with intermediate water removal gave a better CO₂ conversion compared to a single reactor. More detailed simulations of this with a more reliable kinetic model and a preliminary economic analysis are necessary to evaluate its commercial potential. A "conventional" FT conversion system works with a recycle of unconverted syngas to enhance the conversion and is not considered in this work.

Nevertheless, under a once-through conversion process, the proposed flow sheet performs better than a single reactor system. Whether a higher or lower CO₂ concentration in feed gas is good for FT liquid production would depend on both the H₂ balance and CO present in the feed. The analysis method illustrated in this paper can help to decide if one should have a single reactor or a reactors-in-series system. The conventional FT processes remove any CO₂ in the feed gas and take a feed of CO and H₂ only. So, one cannot really compare the option of using higher CO₂ concentration syngas with the conventional FT system. ■

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