

LIQUID FUELS FROM LOW Btu GAS: DILUTE PHASE FISCHER-TROPSCH SYNTHESIS

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Methods of producing liquid hydrocarbons from coal and other solid carbonaceous substrates may be roughly characterized as direct or indirect. Direct methods include various pyrolysis and catalytic hydro-genolysis techniques which are described in the literature (1,2). Indirect liquefaction methods first gasify the carbonaceous substrate to produce a synthesis gas which can then be converted into liquid hydrocarbons. The composition of the synthesis gas can be tailored to fit the needs of the subsequent hydrocarbon synthesis by proper choice of gasifying conditions, gasifying agents, CO-shift conversion and removal of undesirable constituents. Extensive investigations have been made on the use of synthesis gas composed of H₂ and CO for producing liquid hydrocarbons suitable as fuel and specialized chemicals. These reactions are categorically referred to as the Fischer-Tropsch synthesis although significant contributions have been made by a number of different investigators. The Fischer-Tropsch synthesis has been almost exclusively used with synthesis gas consisting of pure H₂ and CO of various stoichiometric ratios. In the following discussion a new application of this old technology for indirect coal liquefaction will be presented. This application consists of using synthesis gas diluted with inerts such as N₂, CH₄ and CO₂ and is referred to as the Dilute Phase Fischer-Tropsch Synthesis.

CONVENTIONAL FISCHER-TROPSCH SYNTHESIS

The synthesis of hydrocarbons from H₂ and CO has been of considerable academic and practical interest since the discovery of methane synthesis by Sabatier in 1902. These simple reactants constitute the necessary building blocks for producing a large spectrum of essential organic chemicals and fuels. The synthesis has been reviewed several times over the past 50 years by Vannice, (3) Pichler, (4) Anderson, (5,6) Hofer, (7) and Storch et al. (8)

The diversity of the conventional Fischer-Tropsch synthesis is demonstrated in Figure 1. It is evident that a considerable spectrum of hydrocarbons can be obtained from pure H₂ and CO synthesis gas by proper choice of reaction conditions. The choice of catalyst is perhaps the most critical variable in the synthesis although pressure, temperature, H₂/CO ratio and space velocity or residence time are clearly important in determining product composition. Methane is the predominant product with nickel catalysts over a considerable pressure range at 200-300°C. Paraffins and olefins are produced over iron and cobalt catalysts in both the low (1 atm) and medium (5-20 atm) pressure synthesis at 185-300°C. At higher pressures (~100 atm) and temperatures (~400°C) the product over iron catalysts consists mostly of oxygenated hydrocarbons (Synthol). High molecular weight (100,000-200,000) paraffins are produced with ruthenium catalysts at 100-1000 atm pressure and 200-250°C. Methanol and higher alcohols are obtained from zinc oxide and alkali promoted zinc oxide catalysts, respectively, at high pressures (100-300 atm) and temperatures of 250-350°C. Using difficult to reduce metal oxide (ThO₂, Al₂O₃ + ZnO) catalysts at high pressures and temperatures of 400-500°C aromatics, naphthenes and iso-paraffins are produced.

DULITE PHASE FISCHER-TROPSCH SYNTHESIS

In spite of the extensive work on the Fischer-Tropsch synthesis, little attention has been directed at employing diluted synthesis gas in the synthesis. Dilute synthesis gas is similar in composition to low Btu gas. It is obtained by gasifying carbonaceous material with air-steam or oxygen enriched air-steam mixtures. Contrary to gasification with O_2 -steam, the gas will contain moderate to high concentrations of nitrogen. The work that has been done with dilute synthesis gas, although sketchy, indicates that significant yields of liquid hydrocarbons can be obtained with conventional Fischer-Tropsch catalysts. Hall and Smith (9) examined the effect of nitrogen dilution on the F-T synthesis; the results are summarized in Table 1. As with non-diluted synthesis gas at constant temperature, the yield of product per volume of synthesis gas decreased with increasing space velocity. Furthermore, at constant space velocity replacement of synthesis gas with nitrogen results in an increase yield of liquids plus solids per cubic meter of $2H_2 + 1CO$. This is readily seen by comparing yields of the first with the second row at 1 atm and the fourth with the fifth row for the 10 atm synthesis. Gibson and Hall (10) studied the F-T synthesis with diluted synthesis gas over a Co-ThO₂-MgO-kieselguhr catalyst concluding that the dilution affected the rate of synthesis by reducing the partial pressure of reactants ($2H_2 + 1CO$). Dilution of the synthesis gas was also observed to increase the proportion of the low-boiling product. The observed variation in liquid product and CO conversion with dilution by these investigators is shown in Figure 2. Although the yield per unit volume of gas will be less in the dilute phase F-T synthesis, the product composition is likely to be similar to conventional F-T synthesis under similar operating conditions. A typical product composition over a cobalt catalyst in the conventional F-T synthesis is shown in Figure 3.

UTILITY OF DILUTE PHASE F-T SYNTHESIS

In the preceding section we have shown that dilute phase F-T synthesis can be used to obtain liquid hydrocarbons from synthesis gas ($H_2 + CO$) that is highly diluted with N_2 , CH_4 and CO_2 . With this capability, the dilute phase Fischer-Tropsch synthesis is viewed as an add-on facility where liquid hydrocarbons are obtained as a byproduct from low Btu gas. Although any low Btu gas could be used in the synthesis, in situ generated low Btu coal gas has been used to carry out preliminary engineering and economic feasibility studies. The conceptualized process is shown in Figure 4. Stepwise, coal is first gasified in situ with air. The in situ generated gas is then subjected to a gas clean-up where H_2S , H_2O , CO_2 and dust are removed. This is followed by dilute phase F-T synthesis and product fractionation to obtain the liquid hydrocarbon byproduct from the low Btu gas. Material balance calculations based on situ coal gasification data by Brandenburg et al. (13) and the dilute phase F-T synthesis data of Gibson and Hall (10) for a 50,000 bbl/da plant are shown in Table 2. Hence, 86×10^8 SCF/da of air is used for the in situ gasification of 2.16×10^5 ton/da of coal. The removal of impurities provides 147.7×10^8 SCF/da of dry, dilute, low Btu (152 Btu/SCF) synthesis gas. Dilute phase F-T synthesis yields 50,000 bbl/da of liquid byproduct with the primary product being 121.0×10^8 SCF/da of low Btu (148 Btu/SCF) fuel gas. The liquid yield amounts to 1/4 bbl/ton of in situ coal gasified. The liquid would be sulfur and nitrogen free and estimated to contain up to 25% olefins with 57% boiling below 150°C and 34% boiling between 150-270°C.

TABLE 1. Effect of Diluted Synthesis Gas on F-T Synthesis (9)
(Co-ThO₂-MgO-kieselguhr catalyst)

Temperature °C	Pressure atm	Feed Gas Composition					Space Velocity hr ⁻¹	Yield of Liquids and Solids	
		volume %						g/m ³	
		H ₂	CO	N ₂	CO ₂	CH ₄		Feed Gas	2H ₂ +1CO
193	1	68.7	30.0	1.0	--	0.3	184	109.2	110
193	1	58.2	24.2	16.3	--	1.3	91	106	127
193	1	44.4	26.7	28.8	--	0.1	133	87.8	123
192	10	62.0	31.5	4.0	2.5	--	131	106	113
193	10	41.8	20.0	35.1	3.1	--	138	112	120

TABLE 2. Process Stream Compositions

Process Stream #	Description	Composition, Vol. or Wt. %	Flow
1	Air	80 N ₂ , 20 O ₂	86 x 10 ⁸ SCF/da
2	Coal	6.3 H ₂ O, 18.4 ash, 0.5 S, 4.6 H, 55.3 C, 0.7 N, 14.2 O	2.16 x 10 ⁵ tn/da
3	Low Btu gas (102 Btu/SCF)	26.9 H ₂ O, 12.2 H ₂ , 6.1 CO, 0.6 O ₂ , 36.5 H ₂ , 3.3 CH ₄ , 0.4 C ₂ , 14.0 CO ₂ , 0.05 H ₂ S	253 x 10 ⁸ SCF/da
4	Scrubbed gas impurities	? dust, 0.12 H ₂ S, 64.8 H ₂ O, 35.0 CO ₂	105 x 10 ⁸ SCF/da
5	Dry dilute phase synthesis gas (152 Btu/SCF)	20.7 H ₂ , 10.3 CO, 1.0 O ₂ , 61.8 N ₂ , 5.6 CH ₄ , 0.7 C ₂	147.7 x 10 ⁸ SCF/da
6	Synthesis product and unconverted gas	0.35 C ₁ H _{2.4} (estm.), 8.1 H ₂ , 4.6 CO, 69.6 N ₂ , 6.5 CH ₄ , 1.7 C ₂ , 8.8 H ₂ O, 0.2 C ₃ , 0.2 C ₄	133.6 x 10 ⁸ SCF/da
7	Liquid hydrocarbon	C ₁ H _{2.4} (estm.), density = 0.85 g/cm ³ (estm.)	5 x 10 ⁴ bb1/da
8	Low Btu gas (148 Btu/SCF)	8.9 H ₂ , 5.1 CO, 76.5 H ₂ , 7.1 CH ₄ , 1.9 C ₂ 0.2 C ₃ , 0.2 C ₄	121.0 x 10 ⁸ SCF/da
9	Water	100 H ₂ O	11.9 x 10 ⁸ SCF/da

PROCESS ECONOMICS

Preliminary economics have been calculated for the conceptualized dilute phase F-T synthesis coupled with in situ coal gasification. These calculations, based on the material balance shown in Table 2 and certain necessary assumptions, indicate that high quality sulfur-free liquid fuels can be produced for as little as \$13/bbl. This assumes use of an iron catalyst costing \$0.10/lb, low Btu gas from in-situ gasification at \$0.43/MM Btu as described by A. D. Little, (11) and a 10% return on capital investment.

The cost of the liquid fuel produced is highly dependent on capital investment and raw materials costs so any increase in space velocity or increase in yield would significantly reduce the cost of the liquid product. Likewise an increase in the cost of raw materials (low Btu gas, catalyst, etc.) would increase the liquid fuel cost. The influence of these variables on liquid fuel cost is shown in Table 3. These liquid fuel costs are based on a 10% return on investment and a six month catalyst life. Two different space velocities, 1000 hr⁻¹ and 2000 hr⁻¹ have been used in the calculations. The parenthesized cost figures are for the 2000 hr⁻¹ space velocity operations. The economic incentive for operating at higher space velocities or larger through-puts is clearly evident from the data in Table 3. It is also evident from the tabulated data that as the catalyst cost increases so does the benefit from operating at higher space velocities.

TABLE 3. Liquid Fuel Cost

<u>Catalyst Cost</u>	<u>Product Cost \$/bbl</u>		
	<u>Cost of Low Btu Gas \$/MM Btu</u>		
	<u>\$0.43</u>	<u>\$0.75</u>	<u>\$1.00</u>
\$0.10/lb	13 (12)	18 (16)	21 (20)
\$1.00/lb	23 (16)	28 (21)	32 (25)

Total capital investment for a dilute phase F-T facility producing 50,000 bbl/da of liquid fuels would be \$300-400 million in 1976 dollars. The major processing unit required is the synthesis reactor. Cost of the reactors is about one third of the total capital investment because of the large heat transfer area required to maintain proper control of reaction temperature. The heat of reaction will be recovered by generating steam to be used as process feed, in steam driven pumps and compressors, and for electrical power drives. Types of reactors that could be used range from a simple vertical boiler with catalyst packed in the tubes to a design where the catalyst is sprayed on the heat transfer surface. (12)

CONCLUSIONS

The dilute phase F-T synthesis is a new application of old technology. It provides a means of obtaining significant yields of liquid hydrocarbon byproduct from low Btu gas. Since the low Btu gas is obtained by gasifying with air in place of oxygen the need for separating O₂ and N₂ is eliminated. Engineering and economic evaluations were made of dilute phase F-T synthesis coupled with in situ coal gasification. The complex was scaled to produce 50,000 bbl/da of liquid byproduct and 121×10^6 SCF/da low Btu (148 Btu/SCF) fuel gas primary product. Considering such economic factors as return on capital investment, catalyst cost and life, space velocity and low Btu gas cost, the liquid product cost was estimated to be between \$13-35 bbl. The most significant contributions to the product cost were identified as return on investment, capital cost and catalyst cost. Technical indications are good that significant reductions can be made in the latter two areas which will improve the overall economics.

ACKNOWLEDGEMENT

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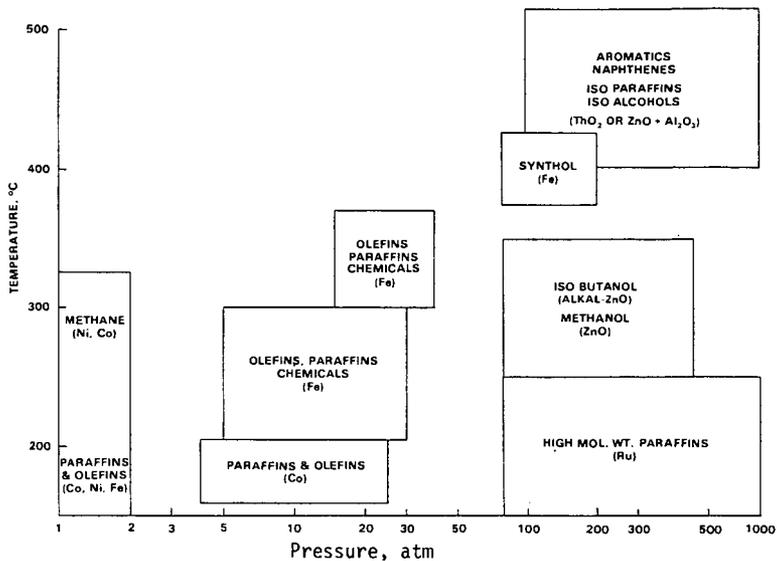


FIGURE 1. Pressure-Temperature Regions for Synthesis with CO and H₂

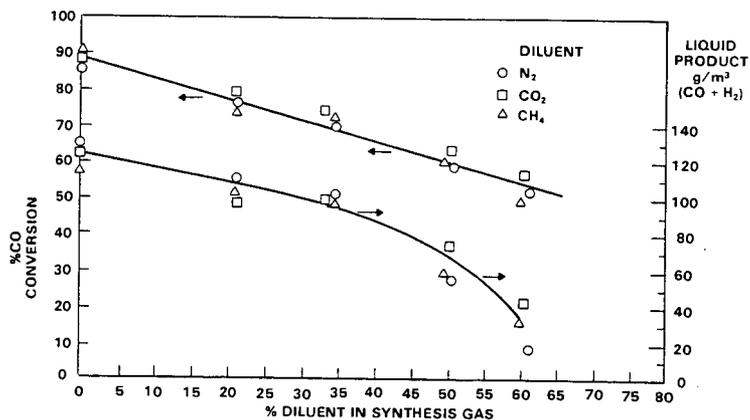


FIGURE 2. Dilute Phase Fischer-Tropsch Synthesis (Co-Catalyst, 1 atm, 185°C, 2H₂/lCO, 900 hr⁻¹ Space Velocity)

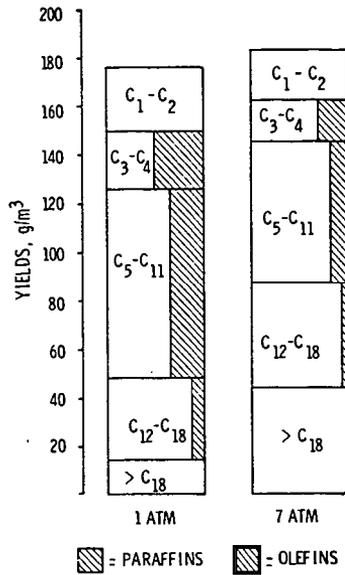


FIGURE 3. Typical yields with Co-ThO₂- MgO-kieselguhr catalyst at 1 atm. and 7 atm.

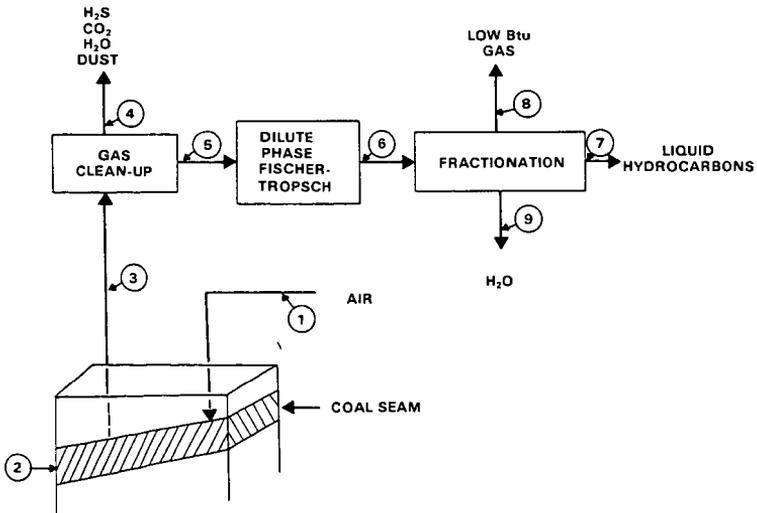


FIGURE 4. Dilute Phase Fischer-Tropsch Synthesis for In Situ Coal Gasification