1.0 INTRODUCTION

1.1 Objectives

The U.S. Department of Energy (DOE) has been supporting a research and development program designed to improve both the technology and economics of indirect liquefaction. These new developments have included investigations of the potential advantages of slurry-phase Fischer-Tropsch (SFT) reactors, novel catalyst developments for F-T liquids production, and utilization of shape-selective catalysts for upgrading of raw F-T liquids to premium transportation fuels. The overall objectives of this DOE program are to significantly improve the efficiency and selectivity to liquids of the synthesis process compared to the conventional SASOL process and thus to reduce the cost of gasoline and diesel fuels produced from clean synthesis gas.

Mobil Central Research has been operating a slurry-phase F-T bench-scale unit (BSU) in combination with a second-stage, fixed-bed ZSM-5 reactor for raw product upgrading to high-octane gasoline. This is known as the Mobil two-stage SFT/ZSM-5 process. The objective of this Mobil program is to attempt to improve the conventional Fischer-Tropsch product selectivity in the first-stage slurry F-T unit and then to upgrade this liquid product to high-octane gasoline in a closely coupled, single-step, fixed-bed zeolite reactor.

The specific objective of this MITRE study is to perform a techno/economic assessment of the results of the ongoing Mobil program. This has been achieved by critically evaluating the results from the bench-scale unit on both the performance and operability of the F-T and zeolite stages. In addition, BSU raw data has been used as the basis for the preparation of conceptual, commercial-scale, indirect liquefaction plant designs producing specification gasoline and diesel fuel employing Mobil two-stage technology, in combination with a British Gas Corporation slagging Lurgi for synthesis gas production. This gasifier was selected because of its higher efficiency and lower C_1-C_2 make than the dry-ash Lurgi used by SASOL. Economic analyses have been conducted on these prepared designs and the resulting economics and gasoline costs have been compared to those obtained by both conventional SASOL technology and by the advanced Koelbel technology. The results of these economic analyses can then be used as a yardstick to measure progress obtained in the ongoing Mobil program towards obtaining the performance claimed by the Koelbel slurry-phase F-T technology.

1.2 Methodology

The U.S. SASOL base case described in the 1980 DOE-sponsored report (DOE/ET/10280T1), Impact of Developing Technology on Indirect Liquefaction, will be used to provide the basis against which the Mobil two-stage SFT/ZSM-5 process performance and economics are compared. In this report, MITRE(1) presented an analysis for the combination of a Koelbel SFT reactor, an advanced gasifier (BGC-Lurgi), and sophisticated state-of-the-art refining and product upgrading system to maximize the yield of premium motor fuels from the SFT products. The experimental data from the Mobil two-stage SFT/ZSM-5 bench-scale unit test runs will be used as the basis for developing conceptual designs for a commercial-size process with a total coal input of 27,800 tons of as-received Wyoming coal per day. Projected production costs and efficiencies of these plants will be compared to the base case production cost and efficiencies provided in the aforementioned DOE-sponsored report. Economic implications and impacts on product costs due to possible changes in operating conditions, catalyst activity, stability and selectivity, as well as variations in product slate of the commercial unit will also be examined.

1.3 Background

All approaches to indirect liquefaction of coal involve three main processes: gasification of coal to produce a raw synthesis gas (syngas) which is mainly a mixture of carbon monoxide (CO) and hydrogen (H_2); gas cleanup and water-gas-shift reaction to adjust the H_2:CO ratio if necessary to that required for the Fischer-Tropsch (FT) synthesis step and catalytic conversion of the clean synthesis gas over an FT catalyst into various hydrocarbon products. A major challenge in any indirect coal liquefaction process conception and design is to integrate these steps in the most economic, thermally efficient way that would overcome such major operating and yield limitations as needed for external shift, intensive heat generation and broad unselective product slate.

1.3.1 External Shift Problem

As shown by Shinnar(2) and MITRE(1) the lowest cost synthesis gas can be produced from certain second generation gasifiers such as the Slagging Lurgi or Texaco which use the minimum amounts of oxygen and steam feed. In contrast with the more established gasifiers, however, the syngas so produced is carbon monoxide rich with a low H_2:CO ratio of 0.4 to 0.7. Since the gasification step represents more than 70 percent of the total cost of indirect liquefaction, it would be an added advantage if the FT synthesis step would accept a carbon monoxide rich syngas feed directly to eliminate the need for external water-gas-shift. The conventional FT synthesis process, using either fixed bed or transport bed reactors, cannot accept such a low H_2:CO ratio syngas feed. On the other hand, however, Koelbel et al(3,4) reported an apparently satisfactory operation of a new approach to FT synthesis featuring large slurry reactor using a precipitated iron catalyst with a carbon monoxide rich syngas feed having a H_2:CO ratio of 0.67. This capability of the slurry reactor to process low H_2:CO ratio syngas feed may be due to the mixing pattern characteristic of such a reactor, together with the use of Fe-based catalysts that can cause the water-gas-shift reaction to occur simultaneously with the synthesis reaction.(5)

1.3.2 Heat Generation Problem

The hydrocarbon formation by FT synthesis is accompanied by intense heat generation which amounts to about 20 percent of the heat of combustion of the syngas feed.(6) Effective heat removal, therefore, represents a major element of industrial FT processes. Another advantage of the Koelbel reactor over conventional fixed or transport bed reactors is that the superior heat transfer properties of such well mixed, liquid filled reactors allow the highly exothermic FT reaction to be carried out at very high single-pass conversion (up to 90 percent) without significant catalyst deactivation or the need for gas recycling.

1.3.3 Broad Product Slate Problem

Although the mechanism of the synthesis of hydrocarbons from syngas on a FT catalyst (i.e., FT synthesis) is still subject to many interpretations, it can be viewed as starting from an initial C_1 unit which gradually build up in molecular size in single-carbon increments to produce higher hydrocarbons.(7) The FT synthesis is thus similar to a nonselective type of polymerization. Such polymerization has been shown to follow a Schultz-Flory, SF, chain growth probability distribution and results in a broad product slate.(7) As shown in Figure 1-1,(8) the SF distribution results in a significant limitation on the maximum yield of transportation fuel product fraction. This selectivity limitation appears to be an intrinsic feature of the FT process if carried on conventional catalysts such as cobalt or iron-based catalyst at high conversion levels. For indirect liquefaction plants producing liquid transportation fuels, such a selectivity limitation results in a significant economic penalty due to the need

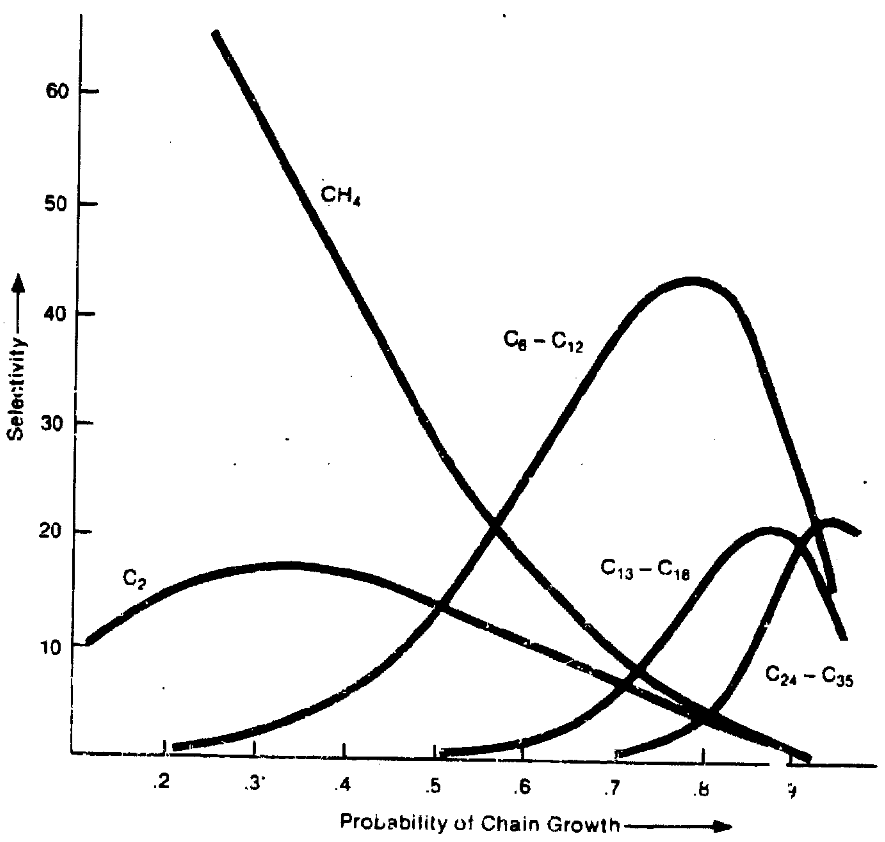

FIGURE 1-1
CALCULATED PRODUCT SELECTIVITIES FROM SCHULTZ-FLORY ANALYSIS

to reform C_1-C_2 gases, product separation, and further upgrading of lower grade fractions. It is, therefore, desirable and, in many cases, essential for an economically viable F-T process to obtain high selectivity to a single product or a narrow distribution of hydrocarbon products.

Several approaches are currently being pursued in an effort to develop highly selective systems for conversion of syngas to transportation fuels (e.g., gasoline). These approaches include use of slurry-phase F-T reactors, modification of conventional F-T catalyst to permit the formation of liquids in higher yields than predicted by a SF mechanism, the use of shape selective catalyst such as Mobil ZSM-5 zeolite-base catalyst to limit the chain-growth mechanism which characterizes F-T polymerization process, and the development of new F-T catalysts which function by mechanisms that are not selectivity limited by a F-T polymerization mechanism (e.g., organometallic clusters).

1.4 A Comparative Overview of Available F-T Processes

At present, it is only SASOL in South Africa which produces hydrocarbons from F-T plants using improved fixed bed (ARGE, Lurgi-Ruhrchemie) (Figure 1-2) and entrained fluidized bed (Synthol, Kellog-SASOL) reactors (Figure 1-3). A viable alternative reactor is the slurry or bubble column reactor in which the catalyst particles are suspended in a molten wax and the synthesis gas is bubbled through the suspension. This alternative (Figure 1-4) was

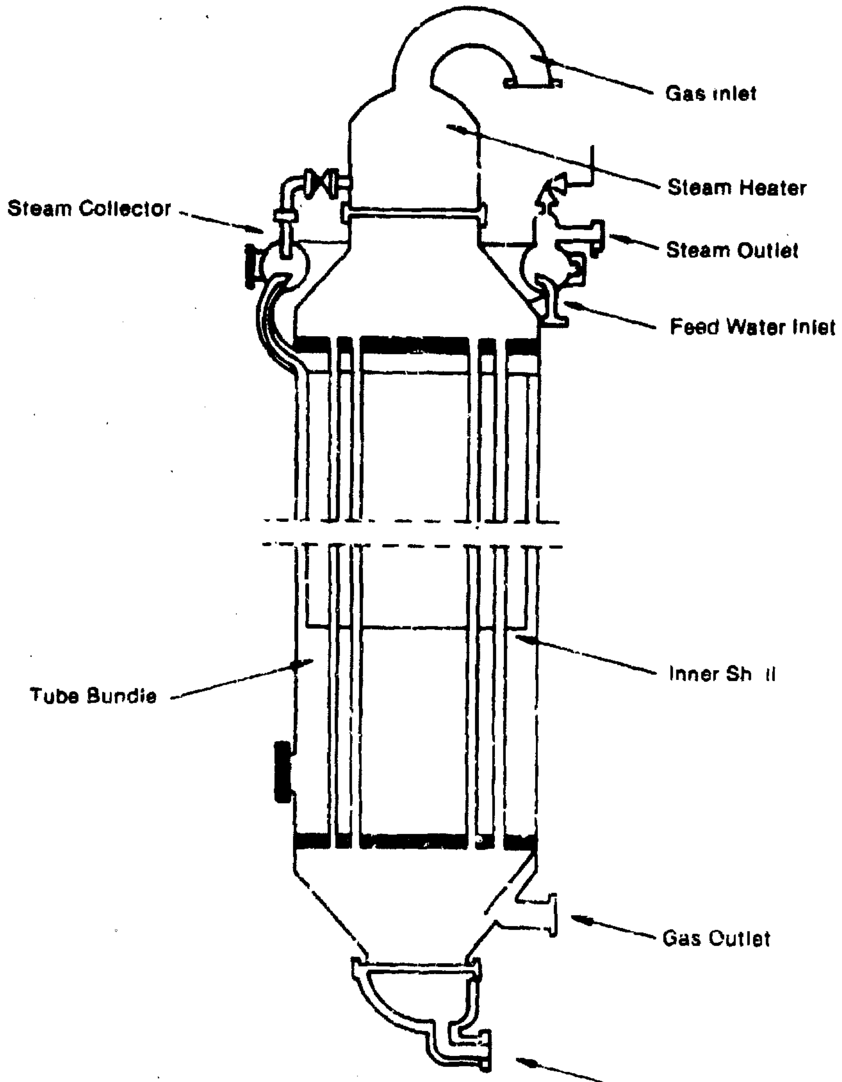

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FIGURE 1-2
SASOL ARGE REACTOR SYSTEM

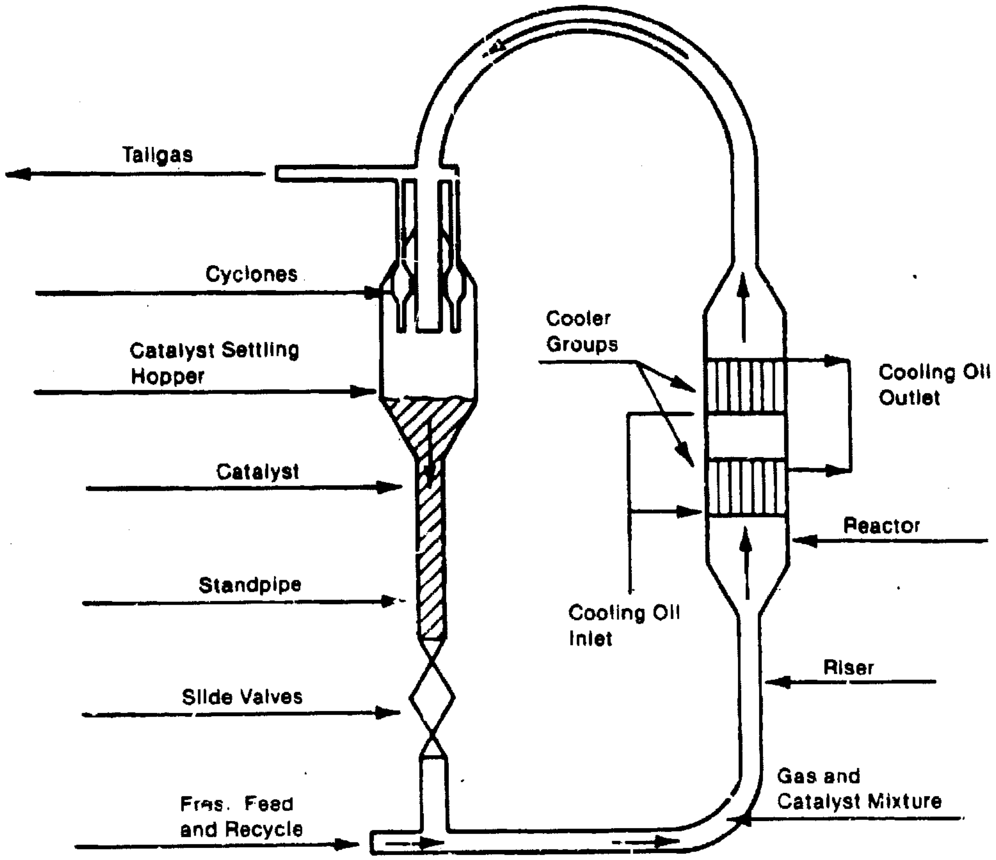

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FIGURE 1-3
SASOL SYNTHOL REACTOR SYSTEM

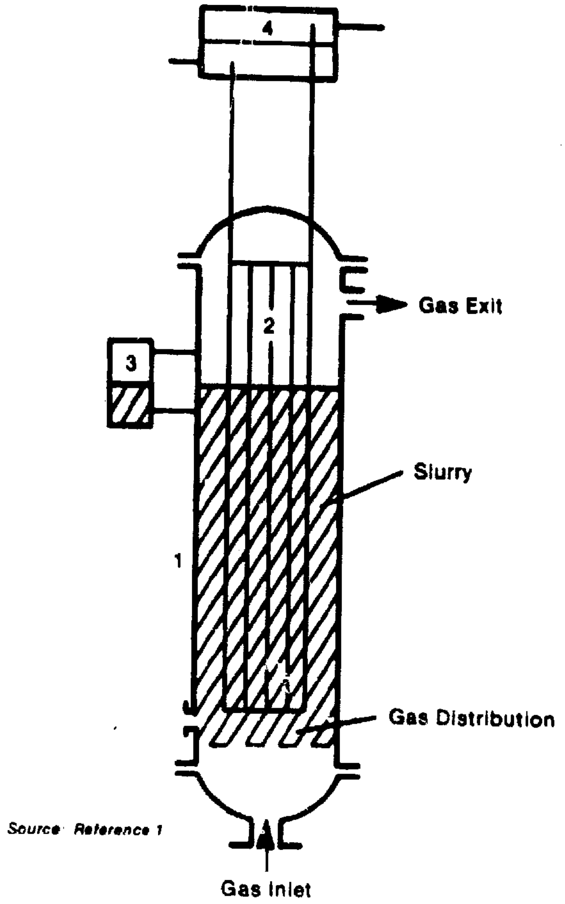

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FIGURE 1-4
THE KOELBEL SLURRY-PHASE REACTOR

demonstrated by Koelbel in the Rheinpreussen-Koppers slurry phase pilot plant reactor.

According to Koelbel and Ralek,(4) the Rheinpreussen-Koppers slurry phase reactor was able to operate with CO rich syngas (H_2:CO = 0.67), at a high conversion of 89 percent with no recycle. The contrast is evident in Table 1-2(6) between this reactor and the Arge and Synthol reactors at SASOL, which operates with H_2 rich syngas, at recycle ratios of 2.0-2.5. Though each of these reactors has some favorable features, the slurrry phase reactor seems to be most advantageous. The particular advantages of the Koelbel slurry-phase F-T process are: its high single pass conversion, low methane formation, high yield of C_3+ products, large content of transportation fuel in C_3+ products, high catalyst and reactor performance and the possibility of using synthesis gas of high CO content, as produced by second generation gasifiers, such as the BGC/Lurgi or Texaco gasifiers without the need for an external shift. In addition, the slurry phase reactor is also attractive from the engineering point of view as heat removal and reactor design is simple and there is no serious catalyst attrition problem.

It should be noted, however, that the effluent from a "successful" second generation gasifier-slurry Fischer-Tropsch reactor combination would still require upgrading for gasoline use as does the effluents of a conventional F-T process. Since there are now indications that the Mobil-ZSM-5 catalyst may accept a much

TABLE 1-2

COMPARISON OF VARIOUS F-T PROCESSES

	Fixed Bed (ARGE) SASOL I	Entrained Fluidized Bed SASOL I	Three-Phase Slurry Reactor Rheinpreussen-Koppers
Operational Condition			
Temperature, °C	220–250	300–350	260–300
Pressure, bar	23–25	20–23	12 (24)
Ratio CO/H_2 (feed)	0.5–0.8	0.36–0.42	1.5
Recycle/feed gas ratio	2.5	2–2.4	0
Catalyst loading, Nm^3 $(CO+H_2)/m^3$ cat h	500–700	700	5,000 (10,000)
Performance Data			
$(CO+H_2)$ conversion, %	50/70	77–85	90
Yield of C_{3+}, $g/Nm^3(CO+H_2)$	104	110	166
Catalyst performance, tC_{3+}/t cat day	1.35	1.85	5.3 (10.6)
Reactor performance, tC_{3+}/m^3 reactor vol. day	1.25	2.1	0.93 (1.86)
Content in primary C_{1+} products			
Gasoline, % wt.	18	40	54
Diesel, % wt.	14	7	10

wider range of feed that possibly includes F-T products, the potential for hybrid processes coupling both the slurry F-T and Mobil ZSM-5 upgrading process is encouraging. Such coupling might conceivably occur either in a two step sequential mode, with each process operating at its optimum conditions or in a more integrated one step mode in which the F-T catalytic function and the upgrading (zeolite) catalytic function are conducted in a single slurry reactor either by use of physical mixtures of catalysts or truly "hybrid" catalysts.

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