partial oxidation reaction promotes the formation of CO relative to H_2.

e. CO Water Shift and Gas Purification

From this point onwards, both processes are similar. The CO water shifts is designed to convert enough CO to H_2 and CO_2 to a final synthesis gas H_2/CO molar ratio of 2.54. The shifted gas is scrubbed to remove ammonia by the U.S. Steel Phos-Am process. The scrubbed gas is then passed through an acid gas removal system such as Lurgi Rectisol or the Selexol process to remove CO_2 and H_2S. The CO_2 removal is selectively controlled such that there is a proper content of CO_2 in the purified gas going to the Synthol reactor. The Rectisol or Selexol process also·acts as an extremely efficient drying agent such that the moisture content is reduced to nil. The CO_2 removed is vented to the atmosphere and the H_2S is sent to a sulfur recovery plant.

The purified synthesis gas composition is indicated in Table V-8.

5.3.6 All-Liquid Products

The all-liquid products output is shown in Table V-9.

It will be noted that the Shell-Koppers combined with Synthol produces about 10% more liquids. This is due to the Shell-Koppers gasifier's greater efficiency. Even though Shell-Koppers requires a greater CO shift, i.e., from 0.48 to 2.54 H_2/CO molar ratio as compared to Texaco having to go from 0.68 to the same 2.54,

109

TABLE V-8

PURIFIED SYNTHESIS GAS

	TEXACO		SHELL–KOPPERS	
Component	Mol %	Lb. Mols Hr	Mol %	Mols/Hr
H_2	68.56	88,760	69.04	97,280
CO	27.00	34,950	27.18	38,380
CO_2	4.20	5,425	3.63	5,120
CH_4	0.11	150	---	---
H_2S	---	---	---	---
COS	---	---	---	---
NH_3	---	---	---	---
N_2	0.03	40	0.09	120
A	0.10	160	0.06	80
H_2O	---	---	---	---
TOTAL	100.00	129,485	100.00	140,900
H_2/CO Molar Ratio	2.54			

TABLE V-9

ALL-LIQUID PRODUCTS - B/D

	TEXACO	SHELL-KOPPERS
C_3 LPG	2,876	3,157
C_4 LPG	382	417
Gasoline	31,445	34,455
Diesel Fuel	6,004	6,579
Fuel Oil	1,617	1,774
Alcohols	4,737	5,204
TOTAL	47,061	51,586
Net Thermal Efficiency (HHV)	48.6	53.3%
Total Liquids/Ton M.F. Coal	2.35	2.58
C_4 Plus Liquids/Ton M.F. Coal	2.21	2.42
By-Products:		
Ammonia	167 TPD	–
Sulfur	84 TPD	–

the increased CO shift does not affect the capability to make more barrels of liquids per day. It is clear that this higher output is the result of the greater amount of syngas (H_2/CO) produced by the Shell-Koppers gasifier. The lower syngas production from the Texaco gasifier resulted from the necessity of burning a greater percentage of carbon to CO_2 in order to produce the heat necessary to raise the water in the Texaco feed slurry to reaction temperature. An analysis of the sensitivity of entrained flow gasifiers to excess moisture may be found in Section 8.0.

5.3.7 Cost Impact of Texaco and Shell-Koppers Gasification

Table V-10 compares the estimated construction cost of an all-liquid plant employing Texaco and Shell-Koppers gasification with plants previously considered.

Where possible, component costs have been determined by scaling from corresponding units in the SASOL-U.S. Base Case. Prices for units downstream of the gasifier are generally higher for the entrained-flow gasifiers because of the greater quantity of syngas and products which are processed. Coal and ash handling costs are higher because of addition at grinding requirements and costs associated with handling the extra coal consumed in the coal dryers. In the case of Texaco, coal slurry preparation facilities are also required.

The construction costs for Texaco gasifiers have been derived from other studies. Details and references are given in Appendix C. In lieu of published sources, the cost of Shell-Koppers gasifiers has been assumed to be the same as Texaco.

112

TABLE V-10

CONSTRUCTION COST COMPARISONS
Base Case SASOL-U.S. and BGC
$M (1977)

	ALL-LIQUID OUTPUT PLANTS			
	Base Case	BGC Synthol	Texaco	Shell-Koppers
Coal & Ash Handling	71.4	71.4	95.2	89.0
Steam Plant	212.9	172.8	48.7	48.7
Oxygen Plant	148.5	155.5	245.7	245.7
Gasification	200.7	100.4	53.0	53.0
Raw Gas Cooling	13.3	--	67.0	67.0
Shift	12.8	30.0	30.0	30.0
Gas Cooling & Cleaning	104.8	127.9	149.8	157.7
Sulfur Recovery	59.0	64.8	69.3	83.0
Gas/Liquor Separation & Product Recovery	51.4	15.5	6.3	7.1
Waste Water Treatment	26.3	18.4	9.7	19.3
F-T Synthesis	109.1	147.7	149.2	159.1
F-T Product Upgrading	172.1	186.9	179.8	191.8
F-T Catalyst Preparation	48.0	53.6	54.1	57.7
Auto Thermal Reformer	40.7	36.5	23.2	30.1
Miscellaneous	108.0	108.0	108.0	108.0
TOTAL	1,382.7	1,289.4	1,289.0	1,347.2

113

Plants employing Texaco and Shell-Koppers gasifiers obviates the need for coal fired boilers and stack scrubbers. The cost saving in the steam plant is partially offset by the cost of the raw gas coolers (e.g., waste heat boilers) from which the heat for steam production is recovered.

Studies of gasification plants employing Texaco gasification for SNG production and combined cycle applications [7, 24] have concluded that all waste water could be consumed in slurry preparation resulting in the virtual elimination of waste water treatment facilities. In the case of indirect liquefaction by Synthol synthesis, the waste water produced exceeds slurry requirements.

The net result of all changes is a price for the plant using Texaco gasification which is virtually identical to the BGC plant and 8% lower than the SASOL-U.S. Base Case. The cost of the Shell-Koppers plant is higher than Texaco or BGC by about 5%, primarily because more synthesis gas is produced and all downstream units are scaled accordingly.

architecture, which would have enhanced plant performance with the advanced gasifier, were beyond the scope of this study.

Table V-11 shows the gasoline costs which result from the use of Texaco and Shell-Koppers gasifiers in plants producing all-liquid products. The SASOL-U.S. and the BGC all-liquids plants discussed previously are shown for reference. The results show that costs for gasoline from the Texaco plant are similar to the BGC, with costs from the Shell-Koppers plant slightly lower.

114

TABLE V-11

GASOLINE COST COMPARISONS FOR ALL-LIQUID
PLANTS EMPLOYING VARIOUS GASIFIERS

	GASIFIER/SYNTHESIS SYSTEM			
	SASOL-U.S.	BGC/Synthol	Texaco/Synthol	Shell-Koppers/Synthol
Thermal Product Basis				
$/MM Btu	11.95	9.99	9.91	9.41
$/Gallon	1.43	1.19	1.19	1.13
Market Basis[1]				
$/Gallon	1.51	1.24	1.23	1.16

[1] Assumes products other than gasoline are sold for prices given in Table IV-7.

115

5.3.8 Environmental Considerations

The entrained flow gasifiers offer the same environmental advantages relative to the base case as did the BGC (Section 5.2.2.4). Specifically:

- benign, non-leachable ash

- reduced water requirements

- less waste water requiring treatment

- lower levels of CO_2 generation, and

- less mining required per unit of output as a result of higher overall efficiency

5.3.9 Conclusions

The advantages offered by Texaco gasifiers are comparable to those previously shown for BGC gasification. Shell-Koppers offers still better results if the efficiency advantages stemming from dry coal feed can be realized in a safe and reliable operational system.

All advanced gasifiers considered show distinct advantages in gasoline cost relative to the SASOL-U.S. Base Case. The best savings are believed to be conservatively stated, since changes in system architecture, which would have enhanced plant performance with the advanced gasifier, were beyond the scope of this study.

However, conclusions regarding the relative merits of the three advanced gasifiers should cautiously be considered. In the case of Texaco vs. Shell-Koppers, the advantage of the Shell-Koppers is directly traceable to, and therefore depend on the success of the dry feed systems. We have concluded that both systems produce sufficient waste heat to eliminate the need for a coal-burning steam

116

plant. This capability is marginal, and requires a more sophisticated use of waste heat than was assumed with BGC or in the Base Case. The heat balance is more critical with Shell-Koppers than in Texaco since the more efficient Shell-Koppers gasifier has less sensible heat in the exiting gases. If a more detailed analysis proves that the Shell-Koppers system requires an additional steam plant, then its advantage over Texaco would be compromised.

Construction cost estimates for plants employing entrained flow gasification have a greater margin of error than the BGC plant since they represent a larger departure from the SASOL-U.S. plant or which costs are based. It is possible that alternative sources (primarily vendors) were less conservative than MRDC. If so, then the cost of plants employing Texaco and Shell-Koppers gasification may be optimistic compared to plants employing BGC gasification.

On balance, we would conclude that all three systems are worthy of careful consideration for U.S.-built indirect liquefaction plants. The ultimate decision would be influenced by detailed consideration of coal type, the plant gate value of an SNG co-product, and licensing arrangements.

6.0 ADVANCED SYNTHESIS PROCESSES

6.1 Background and Fundamentals

New second generation gasifiers like TEXACO, SHELL-KOPPERS and BCG LURGI produce raw synthesis gases of low H_2/CO ratio.

      TEXACO ~ 0.70

      SHELL-KOPPERS ~ 0.52

      BCG LURGI ~ 0.50

The commercial dry bottom LURGI produces an off gas having a high H_2/CO ratio of ~ 2.1.

The required H_2/CO feed ratios for conventional Fischer-Tropsch reactors are also high.

      ARGE (Fixed Bed) 0.7 - 1.7

      SYNTHOL (Fast Fluid Bed) 2.4 - 3.0

However there is a F-T reactor developed by Herbert Kolbel [25] that is capable of accepting a synthesis gas with a low H_2/CO ratio of between 0.5 and 0.7.
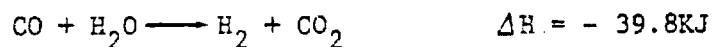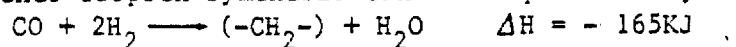
Thus, if this reactor were used in conjunction with a gasifier producing a low H_2/CO ratio off-gas, no separate external water-gas shift reactor would be necessary to increase the H_2/CO ratio. In the case of the Kolbel reactor the shift occurs internally in the same reactor as the F-T synthesis.

It would therefore be instructive to analyse if the elimination of external water-gas shift has a significant economic or technical impact on the conventional indirect liquefaction process in conjunction with second generation gasifiers.

The analysis should also determine whether the Kolbel reactor promises other advantages over using SYNTHOL or ARGE in the F-T synthesis, i.e., what potential does this reactor have and what are the process implications?

The Fischer-Tropsch synthesis can be simplistically represented:

$$CO + 2H_2 \longrightarrow (-CH_2-) + H_2O \qquad \Delta H = - 165KJ$$

$$CO + H_2O \longrightarrow H_2 + CO_2 \qquad \Delta H = - 39.8KJ$$

$$2\ CO + H_2 \longrightarrow (-CH_2-) + CO_2 \qquad \Delta H = - 204.8KJ$$

The Kolbel reactor accomplishes this two-step synthesis in one reactor, thus the overall thermal efficiency is potentially higher since high value steam is not required to produce externally the high H_2/CO ratio synthesis gas needed. Of course either way the overall stoichiometry is the same and in the Kolbel case carbon is rejected as CO_2 whereas for the Synthol reactor the by-product of the synthesis is water.

The stoichiometric yield of hydrocarbons is 207.5 g. per Nm^3 (0.013 lb/SCF) of synthesis gas, if the usage ratio is the same as the feed ratio.

The main technical problems associated with the F-T synthesis have been:

- rapid removal of heat of reaction

- avoiding local overheating of the catalyst that would favor methane formation and carbon deposition

- good solid (catalyst) gas contacting

120

Three designs of F-T reactors have been used to address these problems. The first two are used commercially at SASOL, the third is presently not commercial.

- Fixed bed reactors (ARGE)

- Entrained or fast fluid bed reactors (SYNTHOL)

- Three-phase slurry reactors (Bubble Column Kolbel)

6.2 Conventional F-T Synthesis Reactors

At SASOL commercial use is made of two F-T reactors. The fixed bed Arge reactor is used on a limited basis and only at the small SASOL I plant. The SYNTHOL, fast fluid bed reactor, is used exclusively at the SASOL II complex.

The operating details of these conventional F-T synthesis reactors have already been given in Section 2.0 of this report.

The product distributions from these two reactors are quite different, and these are shown later. Both reactors require recycle for high conversions. (2.2:1 recycle to fresh feed ratio).

Both these reactors require a H_2/CO ratio greater than 1.7 and neither can accept a synthesis gas of low H_2/CO ratio (0.5). A severe limitation of the SYNTHOL is adequate removal of heat of reaction. Thus if too high a conversion is achieved per cycle the excess heat produced would rapidly deactivate the catalyst.

## 6.3 General Principles of the Liquid Phase Fischer-Tropsch Synthesis

The exothermicity of the CO/H_2 F-T reaction over iron catalysts

can, because of inadequate heat transfer, cause catalyst particles to produce local hot-spots and high overall temperature increase in the reactor. If this is allowed to occur excess methane formation results and when using low H_2/CO synthesis gas feeds the Boudouard reaction is increasingly favored causing excessive carbonization of the catalyst and the possible formation of free carbon particles. A reactor was developed by Kolbel to counteract this problem. The reactor is a bubble column liquid slurry reaction where the synthesis gas is converted to hydrocarbons on finely divided catalyst particles in constant fluidized motion in suspension in a molten slack wax liquid medium. The advantages claimed for this system are:

- Uniform temperature throughout the reactor and excellent heat exchange characteristics because of the liquid medium

- High reactor efficiency because of good catalyst reactant contact

- Allows feed gases with low H_2/CO ratio to be used without the risk of clogging by carbon deposition or the rapid deactivation of the catalyst

- Simple construction and hence potentially low investment costs.

Figure 6-1 shows the operating principle of the reactor.[25]

The synthesis gas is introduced in the form of small bubbles at the bottom of the reactor through a distribution device. These small gas bubbles form a dispersed gas-liquid system with the slack wax liquid medium. The finely divided catalyst particles

Gas Exit

Slurry

Gas Distribution

Gas Inlet
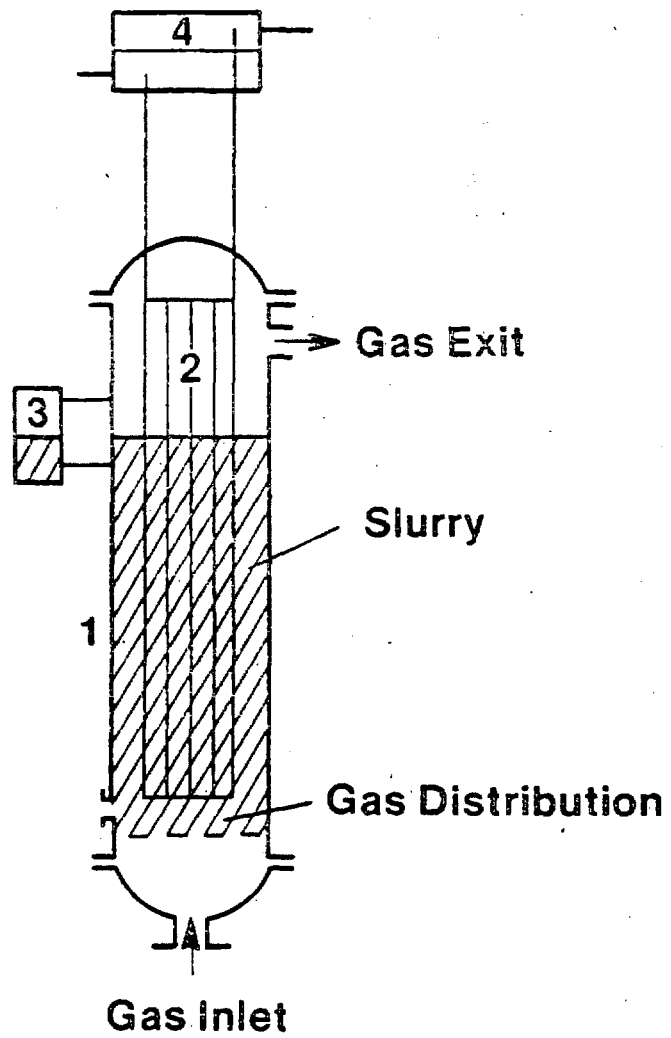
FIGURE 6-1
THE SLURRY REACTOR

123

are thoroughly mixed in this gas-liquid dispersion. The unconverted gas leaves the reactor at the top and carries with it the products of the synthesis boiling below the bulk temperature of the liquid medium. Higher boiling liquids may remain with the slack-wax but when conditions are optimized for the production of gasoline boiling range hydrocarbons, most of the products from the synthesis are sufficiently volatile to leave the reactor.

6.3.1 Fluid Dynamic Behavior in 3-Phase F-T Reactors

The fluid dynamics effect the catalyst/reactant gas contact efficiency. The parameter of prime importance in this respect is the specific interfacial surface area (a) between the gaseous and liquid phases. This is determined by:

1) Gas hold up (relative gas content) (H) defined as the volume fraction of the gas in a unit volume of the gas-liquid dispersion. .

2) Average bubble diameter (D_p)

The relationship connecting these parameters is:

$$a = 6H/D_p$$

Kolbel has estimated the interfacial surface area to be in the order of 1500 M^2/M^3 for an average bubble diameter of 4mm. However, this in fact means that the gas holdup would have to be 100 percent, an unreal situation.

The fluid dynamics are critical in determining the operability of the reactor and in this respect it is claimed that:[25,26,27]

- Since the catalyst particles are finely divided, the particle dispersion becomes almost identical to the liquid dispersion

- For homogeneous bubble flow (low superficial gas velocities, bubbles rising uniformly and approximately monosize) the gas hold up and the specific interfacial areas increase linearly with gas throughput

- The high axial dispersion coefficients of liquids and solids result in uniform contact loading of the catalyst and hence increased catalyst life

- The mixing in the gas phase is in the same order of magnitude as the mixing in the liquid phase.

If the above conditions are met then the slurry reactor should provide:

- Effective dispersion of catalyst particles

- High accessibility of catalyst surface to reacting gases

- Even loading of catalyst surface with reacting gases.

However, the catalyst concentration in the slurry does have an upper limit. Apparent density and viscosity of the suspension increase with the solids content of the slurry. This facilitates formation of large bubbles at much lower superficial gas velocities, resulting in a decrease in the interfacial surface areas. This situation is illustrated graphically in Figure 6-2. Kolbel recommends the suspension should contain a solids loading of approximately 10% by weight.[25] At 9.5 cm/sec superficial gas velocity, point A on Figure 6-2, represents the operating regime used by Kolbel in his pilot plant experiments.

The high values of convective heat transfer coefficients are explained by the good mixing in the liquid phase. Increase in the concentration of solid material causes further increase in the

FIGURE 6-2

**OPERATIONAL RANGE FOR A BUBBLE COLUMN
REACTOR WITH SUSPENDED SOLID MATTER**
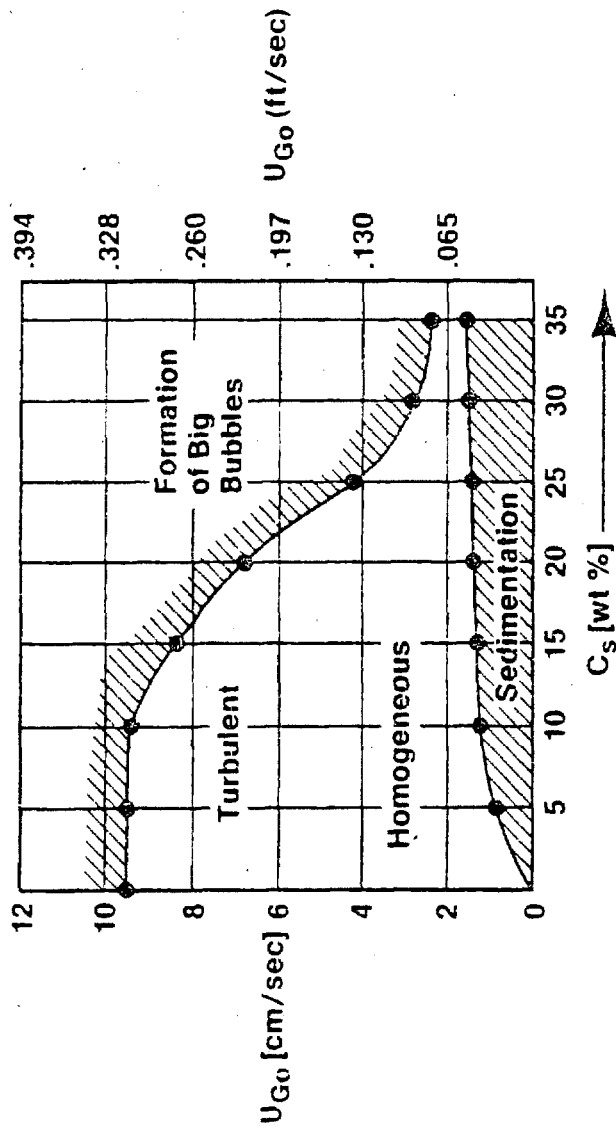
U_{Go} = Superficial gas velocity

C_s = Solids concentration

heat transfer rate as the solids interfere with the formation of liquid boundary films. In the homogeneous flow region at superficial gas velocities of 2.5 cm/sec^{-1}, values of heat transfer coefficients range between 600 and 800 KJ/M^{2}S^{o}K. [25] A limiting value of 1100 KJ/M^{2}S^{o}K is reached in heterogeneous flow when it becomes independent of gas throughout.

The conditions under which the synthesis reaction is chemically rate controlled or diffusion controlled in the slurry reactor have not been positively identified. Kolbel has concluded that in his studies the reaction was chemically controlled by reaction at the catalyst surface and not limited by diffusion of reactants to the surface. This result is in agreement with studies on CO conversion by Zaidi et al [28] who also conclude that F-T synthesis in a slurry reactor is not controlled by mass transfer resistances at the gas/liquid interface. Currently work is being conducted at MIT on the effects of mass transfer on F-T synthesis in slurry reactors. [29]

6.4 Description of the F-T Slurry Reactor Units

In order to make a comparative assessment of the use of the slurry reactor in F-T synthesis, four studies have been evaluated. These are:

- work supervised by Kolbel at the Rheinpreussen-Koppers demonstration plant (1938-53) [25]

- British experiments at the DSIR on a small pilot plant (1953-61) [30]

127

- Work at the USBM using a bench-scale unit (~1951)[31]

- Bench-scale work carried out at the Indian Institute of Technology (1963)[32]

    In addition the recent assessment of slurry reactors by Poutsma was reviewed[33]

Table VI-1 gives reactor dimensions of these four experimental reactor units and some design specifications.

The reactor used by IIT is just at the lower limit advisable for bubble column use, as for diameters in the range 2-3 inches the gas hold up is effected by the reactor walls. Also larger diameters insure that during operation some backmixing will occur which more closely approximates to industrial practice.

The work conducted at the Rheinpreussen-Koppers demonstration plant is of most interest to this report since this study was of large enough scale and long enough duration to generate fairly detailed information. The other studies were on a smaller scale and were frequently plagued by operational difficulties and unsatisfactory performance. More detailed experimental and operational procedures can be obtained by consulting the appropriate literature references.[25,30,31,32]

In addition to the work on F-T slurry phase synthesis mentioned above, work was conducted at the Department of Synthetic Chemistry at Tokyo University.[34] Successful operation was apparently achieved using a reactor of 2 inches diameter and 18 feet high. CO conversions were in excess of 80%.

TABLE VI-1

REACTOR DIMENSIONS OF F-T SLURRY REACTORS

	KOLBEL	DSIR	USBM	IIT
Reactor Dimensions	5' 1" x 28' 2" (155cm x 8.6m)	9.7" x 30' (24.8cm x 8.53m)	3" x 10' (7.6cm x 3.05m)	2" x 10' (5.1cm x 3.05m)
Height/Diameter Ratio	5.6	34	40	60
Slurry Volume (Liters)	10,000	320	14	~ 6
Catalyst Used (kgFe)	800	11.5	4.2	–
Design Specs	11.5 tonnes/day (≃80 bbls)	2500 SCFH 70-100 gals/d	–	
Gas Distribution	Many jets 2-3mm diam.	Single nozzle 3/4" bore	Single nipple injector 0.12" i.d.	Single injector nozzle

129

Heat exchange was accomplished by using internal cooling pipe registers in the German and British reactors. The USBM reactor used a reflux cooling condenser system above the slurry bed but did not incorporate a cooling register within the slurry. The IIT reactor was jacketed with a Downtherm boiler. All experimeters reported excellent heat control and operability under isothermal conditions with temperature fluctuations of about $\pm 1^{o}C$.

During operation of the reactor, liquid hydrocarbon product not volatile at reaction temperature remained in the reactor, hence the slurry volume increased during a synthesis run. Facilities must therefore be available to remove excess liquid. No difficulties were experienced with the German reactor in liquids removal through a pressure filter system at various intervals during the run. Their product distribution was geared towards the production of light liquids so heavy liquid accumulation was slow and therefore manageable. However, the DSIR produced substantial quantities of heavy liquids and constantly had to remove this product and separate out the finely divided catalyst particles. This necessitated the design and construction of a gravity separation unit to handle the volume of heavy liquid produced. The USBM removed excess liquid by withdrawing it through a porous metal filter installed in the recycle leg.

6.4.1 Catalysts

All the catalysts used by the various experimental groups in this study were precipitated iron catalysts with varying amounts of copper and potassium as promoters.

130

The large variations in the promoter level used by the groups could account for the observed differences both in initial catalyst activity and product selectivity. Generally higher K_2O promotion leads to higher olefin contents and higher molecular weight products.[35]

K_2O levels varied from 0.05 - 1.4. Potassium is essential as it promotes the water gas shift reaction which is required in this case, however, excess K_2O can also cause carbon formation and this effect of overpromotion is illustrated by the experience of the British group.

The levels of copper promotion also varied markedly among the catalysts used. The USBM used a catalyst with the highest copper content. Copper is used to promote selectivity to oxygenates and the light oil product from the USBM work had an oxygenate content of over 40%.[36]

Kolbel stresses the importance of correct catalyst pretreatment before synthesis and the fact that formation temperature depends on the activity of the catalyst and the intended product spectrum. If catalyst activation temperature is too high, over carbonization results and if too low the catalyst is not properly activated. The other workers surprisingly did not experiment with optimising catalyst activation procedures. It is also surprising that the USBM and the DSIR made no attempt to duplicate the Kolbel catalyst composition or try to enlist Dr. Kolbel's assistance in catalyst preparation. If another group had been successful using a Kolbel catalyst, this would have been an independent verification of the