The American Effort

The Pittsburgh Coke and Chemical Co., and the U.S. Bureau of Mines at Bruceton (now known as Pittsburgh Energy Technology Center) cooperated to develop the slurry bubble column for the synthesis of liquid hydrocarbons from coal. A detailed pilot-plant study was conducted to develop effective catalysts, to establish the effect of operating variables, and to perform product characterization. Results were reported in several publications but two research papers [18,19] included many of the essential details and these are described here in brief.

The catalyst plays a very important role in F-T synthesis in a slurry column and these workers used both fused and precipitated iron catalysts. In their earlier effort [18] the copper - and alkali- promoted iron catalyst was prepared by precipitating the metal nitrates with sodium carbonate. After washing and calcination, the oxides were impregnated with alkali and ground to less than 60 μm. In the final catalyst (iron, copper and potassium monoxide) were found to be in the proportion of 100, 10 and 1 respectively by weight. The later publication [19] reported the composition of the fused and precipitated catalysts as given in Table V. The catalysts were reduced with commercial grade hydrogen until x-ray analysis revealed at least 90 percent conversion to the metallic state. These were then nitrided with anhydrous ammonia until the nitrogen-iron atomic ratio was about 0.45 and x-ray analysis showed that hexagonal iron nitride was predominant. The details of the iron nitride catalysts preparation are given by Anderson and coworkers [20-22]. Reduction and nitriding operations could be accomplished either in fixed beds or in slurry reactors under oil. The catalyst was inducted by operation at mild conditions which were changed gradually to the synthesis conditions.

This procedure required a lower synthesis temperature and yielded a more active catalyst which produced more oxygenates and less C_1 and C_2 hydrocarbons, [19]. During synthesis iron nitrides were found to be converted to carbon nitride and iron oxide, [20] An electron micrograph of used nitrided catalyst showed fine particles of catalyst embedded in the oil gel. The original fused iron oxide particles were reduced from mostly <60μm size to about 1μm. A possible mechanism of the probable degradation of these catalyst particles was proposed as involving the deposition of elemental carbon in the catalyst pores and subsequent bursting of the granules during phase changes when the crystal structure changed. It was believed that attrition was not responsible for this size reduction even though the nitrided granules were brittle on the basis that the particles were not in violent motion and were further surrounded in an oil gel.

The synthesis gas comprising hydrogen and carbon monoxide in the ratio of 1:1 at 400 psig was used in this work. The gas was passed through a chamber, 2, containing activated carbon to remove any traces of sulfur after its pressure was reduced to about 350 psig by a pressure controller valve, 1, as shown in Figure 5. The gas flow was controlled by a calibrated capillary, 3, fitted with appropriate indicating, 4, and recording, 5, devices. The gas flow was measured directly by a high pressure wet-test meter, 6, before entering into the surge tank, 7, and the preheater, 8. The gas then entered at the bottom of the converter, 9, through a 0.12-in. internal diameter nipple which expanded gradually to the reactor diameter, 3 in. Originally porous plate gas distributors were used but they were discarded in subsequent work because of high pressure drop and no observable improvement in performance. The converter pipe was 10 ft high and was attached to a parallel 1.5 in. slurry recycle line, 10. The latter also had valved cross-
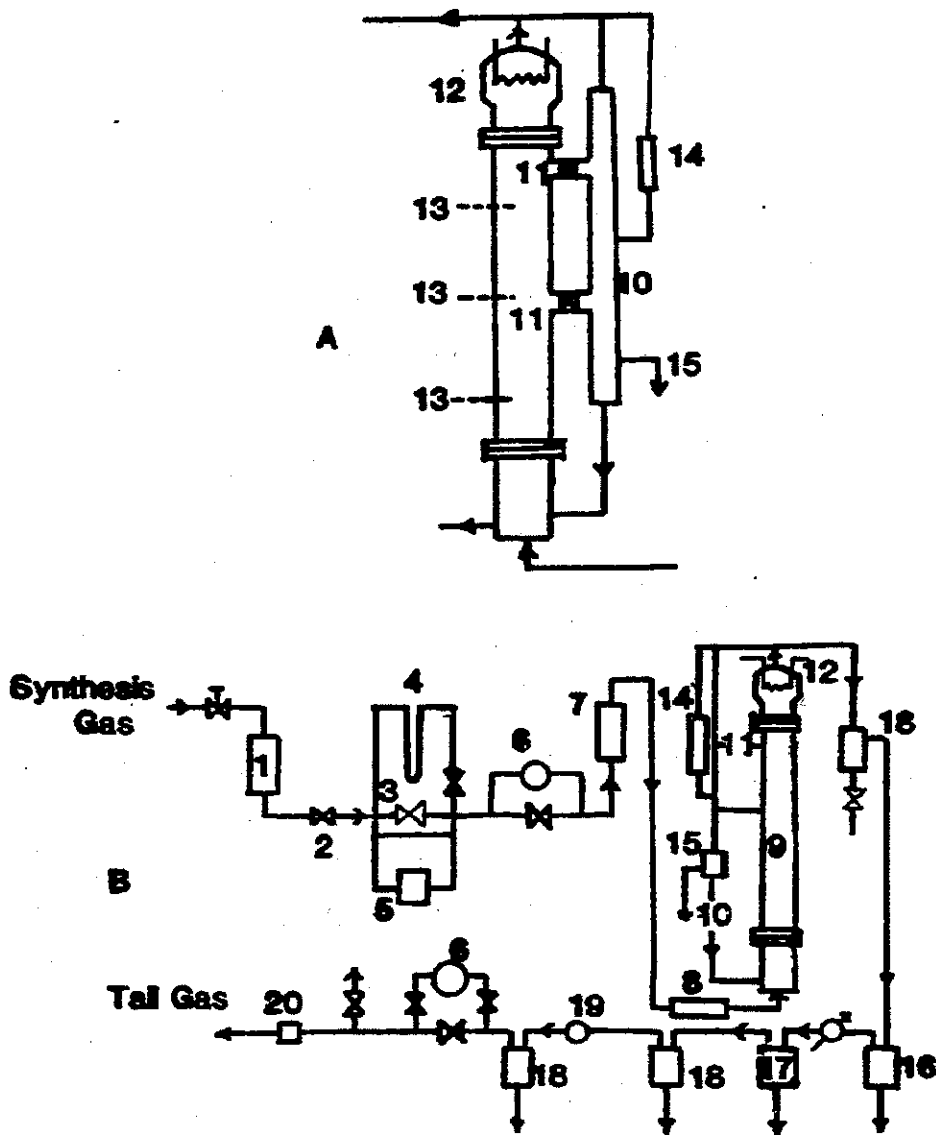
Figure 5. Slurry Bubble Column Reactor (A) and Flow Diagram (B) of the Fischer-Tropsch Synthesis Process of Schlesinger et al. [18, 19]. 1: Pressure Controller Valve, 2: Charcoal Scrubber, 3: Calibrated Capillary, 4: Differential Manometer, 5: Recorder, 6: Wet Flow Meter, 7: Surge Tank, 8: Preheater, 9: Slurry Reactor, 10: Recycle Line, 11: Cross-Over Lines, 12: Expanded Dome Section, 13: Thermocouples, 14: Level Gauge, 15: Filter, 16: Wax Trap, 17: Light Oil Receiver, 18: Entrainment Trap, 19: Back Pressure Regulator, and 20: CO_2 Analyser.

over lines at 5 ft and 10 ft levels, 11. A total capacity of 17ℓ was available in the system including 13·5 ℓ in the reactor. The expanded dome section, 12, at the top prevented entrainment of slurry into the product lines by reducing the linear velocity and at the same time it provided space for foam to break up and excess reactor oil to accumulate. Three thermocouples, 13, projecting into the convertor were used to measure temperature. A coil in the expanded section provided evaporative cooling of the reflux stream and thus removed a portion of the reaction heat. The amount of reflux was controlled by using cold water or steam in the coil. The level of the oil in the converter was maintained above the 10 ft crossover line as indicated by the steam heated level gauge, 14. The excess oil was withdrawn through the porous metal filter, 15, installed in the recycle leg. Product gases passed through a series of traps to remove entrained slurry and to recover condensable oils (middle and light) and water as shown in the figure. The resulting off-gas passed through a back pressure regulator, a low pressure gas meter, and a continuous carbon dioxide analyzer and finally the tail gas was vented from the system. The unreduced catalyst was suspended in a synthetic diesel-oil fraction, boiling above 573K, to facilitate charging to the converter. The catalyst concentration was 25 percent by weight, approximately 300 g per liter. The induction pressure and temperature chosen were 100 psig and 473K respectively. Several experimental runs were carried out for durations varying from 900 to 3200 hours. During a 1241 hour operation, the pressure was varied from 100 to 250 psig, the space velocity from 130 to 300 ft^3/h. ft^3 of slurry volume, and temperature from 515 to 549K. A general remark regarding the catalyst settling and deactivation is in order before discussing the explicit parametric dependence. At most conditions, a steady decline in activity was observed and sometimes it could be balanced by increasing

temperature or pressure. Sometimes the cause of deactivation was catalyst settling. It was concluded that the catalyst exhibited a tendency to deactivate and reactivation was resorted to by lowering the pressure to one atmosphere while maintaining the temperature at 548K and passing hydrogen through the system for 30 hours. The activity levels were found to fall into several groups. Mild treatment of the slurry phase with hydrogen activated the catalyst. It was also noticed that the highest activation energy was required by the least active catalyst.

Several distinct features of synthesis with increasing reactor temperature were worth noting and are as follows. Carbon monoxide conversion to form methane, ethane and ethylene were all found to increase with increasing temperature possibly due to mild cracking. The increased conversion rates were about the same for methane and ethylene and were larger than for ethane. The ratio of water to carbon dioxide produced was not found to vary much in the temperature range 523 to 548K due to very little change in equilibrium constant. Water was formed as the primary product of synthesis and carbon dioxide was formed via the water-gas shift reaction. In a run with nitrided fused iron catalyst the effect of temperature on the yield of oxygenates at the maximum equipment pressure of 300 psig was investigated. A decrease in the yield of oil-soluble oxygenated compounds above 513K was observed and was attributed to the instability of the oxygenates of high molecular weight at higher temperatures. Experiments conducted at two space velocities to compare the effectiveness of fused and precipitated iron nitrides revealed that the percentage of total oxygenates was greater for the latter at 532K although the amount of oil soluble oxygenates had decreased. Experimental results suggested that precipitated catalysts were to be preferred for the production of oxygenates of higher molecular weight. In a few tests, the fused catalyst

appeared to be more active than precipitated catalyst and it was proposed
that better induction methods be employed to keep the activity of precipi-
tated catalyst up.

At a constant space velocity of $240h^{-1}$, an increase in pressure from 100
to 200 psig increased the carbon monoxide conversion from 56 to 78%. This
could be understood in terms of the increased gas residence time resulting
from an increase in system pressure at a constant throughput which decreased
the volumetric flow through the converter. The reduced degree of agitation
was found still adequate to keep the catalyst in suspension. At an increased
space velocity of $300h^{-1}$ at 250 psig, a 10% lower conversion was obtained. These
experiments also revealed that the effect of pressure on light hydrocarbons
was almost insignificant. The pressure did influence the distribution of
heavier hydrocarbons, but the evidence was not regarded as conclusive.

Variations in the catalyst composition were noted during synthesis over
a period of 1300 hours which suggested several very systematic trends. Carbon
build-up occurred at a constant rate for the entire period except it appeared
that the rate of carbon and/or carbide formation was very high during the
initial stage of synthesis. The content of iron in the catalyst steadily de-
creased with use; however, correction for the carbon produced indicated that
the total iron content was constant. The analysis also indicated that no change
in the concentration of copper and potassium oxide occurred due to leaching by
the reactor oil.

Condensed liquid products and the off-gas were measured and analyzed to
infer the trends of yields, selectivity, and gas conversion. The yields were
found to be relatively constant and an overall synthesis gas conversion of
about 55% was obtained. The distribution of reacted carbon monoxide in various

products was determined with the representative selectivity as : 5% in $C_1 + C_2$, 43% in C_3 and heavier, 42% in CO_2, and 10% remained unaccounted for. Changes in the wax content of the slurry as the run progressed are of great interest for efficient operation and therefore some comments are in order. Wax was defined as the fraction boiling above 723K at atmospheric pressure. The concentration of wax increased during the early period of synthesis, and the maximum value reached was 81% as determined by the viscosity of oil in the reactor. With cooling water in the reflux coil an average wax content of 55% was obtained. No deleterious effects on operability or catalyst activity were found at high wax concentrations above 50%.

Analysis of the liquid products and of gas streams was done to determine the distribution of hydrocarbons. The distribution was relatively constant at the initial pressure of 200-250 psig viz., about 41 to 44% of the C_3 and heavier products boiling in the gasoline range (478K end point). However, when the temperature was raised slightly to maintain adequate conversion level for carbon monoxide, a significant shift to lighter products occurred. To increase the yield of heavy products, relatively low synthesis temperatures should be used. The use of iron catalysts produced an appreciable fraction of oxygenated compounds. The predominant oxygenated compounds were ethyl, propyl and butyl alcohols. The equivalent amount of acetic acid was computed as 4.4%. Oxygenated materials in the light product oil were found to be about 43.6% by weight. Ultimate analysis of the reactor oil yielded an oxygen content of 1.51% by weight, which is equivalent to a large proportion of oxygenated compounds of high molecular weight.

The effect of space velocity in the range 200 to 500 h^{-1} was investigated at 523K and 300 psig on the yield of oxygenated products for nitrided

fused iron catalyst. It was found that the yield of oxygenates was about constant in the range 300 to $500h^{-1}$. For similar conditions at an hourly space velocity of 300, the effect of recycle ratio on product distribution was investigated. For a recycle ratio of 0.5, the yield of C_1 and C_2 hydrocarbons was lowered by 25% and that of oxygenates increased by 15%. The yield of oxygenates would probably be still greater at higher recycle ratios.

The oxygenated products were recovered from an aqueous layer, containing the compounds of lower molecular weight, and an oil layer containing the compounds of higher molecular weight. Ethyl alcohol was found to be about 40% of all the alcohols and the quantities of higher alcohols decreased with increasing molecular weight. It appeared that some alcohols above C_6 were also present. Small quantities of acetone, and methyl ethyl and methyl propyl ketones in descending order of abundance were found in water. Titration with alkali indicated an acid equivalent of about 0.5% acetic acid from fused catalyst and about 2% from precipitated catalyst in aqueous product. The oil was found to contain mostly oxygenates of higher molecular weight and only some of light oxygenates. The oil was distilled into six fractions viz., initial boiling point to 373K, 373 to 423, 423 to 473, 473 to 523, 523 to 573, and over 573K. Results were analysed with products from the fused catalyst operated at 503, 513 and 531K. It was found that the concentrations of alcohols and other oxygenates decreased sharply at higher temperatures especially in the higher boiling fractions.

In the oil layer of the products with nitrided catalysts, about 60 to 70% was oxygenates and of this about 80% was alcohols, the remainder being predominantly aldehydes or ketones, esters, and a small amount of acids. Based on earlier tests it was concluded that aromatics were not formed. For an experimental run at 503K and 200 hourly space velocity with nitrided fused

catalyst, the water and oil layers in the products were used to calculate the distrubution of alcohols by carbon number, The ethyl alcohol peak was only half of that obtained with reduced iron. It was inferred that the separation and recovery of oxygenated compounds from both the oil and aqueous layers should be possible on a large-scale plant since they were present in high concentrations and predominantly alcoholic.

TABLE $\underline{V}$ [19]

Catalyst Composition Before Reduction, Weight Percent

	Fused Catalyst	Precipitated Catalyst
Total Iron	66.8	56.5
Magnesia	4.6	-
Copper	-	5.7
Chromia	0.75	-
Silica	0.62	-
Potassium Monoxide	0.61	0.4

In recent years major experimental efforts have been initiated in the United States under the sponsorship of the United States Department of Energy at Air Products and Chemicals, Inc.; and at Mobil Research and Development Corporation to examine and develop the F-T slurry bubble column method with the ultimate goal of converting the synthesis gas into transportation fuels. To the extent these works are relevant to the scope of our present review, we will discuss them in the following.

The objective of the effort at Air Products and Chemicals [23] is to evaluate catalysts and slurry reactor systems for the selective conversion of synthesis gas into transportation fuels via a single stage liquid phase process. These workers' activities fall in two different categories. The first major area covers the development of a slurry catalyst using stirred test reactors to optimize selectivity and activity. Though the establishment of a catalyst which could maximize the space time yield of hydrocarbons in the transportation fuels range is basic to the successful operation of a slurry bubble column, no research work has been conducted in this latter mode dealing with a chemically reactive system. The second major area of this effort is dealing with the cold flow models of two different dimensions. These are : a 5'x5" plexiglas column and a 15'x12" glass column. A variety of investigations dealing with gas holdup, solids dispersion, measurement of gas bubble diameter, heat transfer coefficients for plain and finned vertical tubes immersed in the slurry bubble columns, mass transfer, liquid dispersion etc. have been undertaken. Experimental data are generated for water and paraffin, gas and liquid superficial velocities in the range 0.05 - 0.5 ft/s and 0 - 0.015 ft/s, solid particles of silica and iron oxide with sizes in the range 1.5, 45-53, 90 - 106 μm with solids concentration in the range 0 - 30 wt percent. Distributor hole size chosen are 0.035, 0.125 and 0.5 inches. The total results

obtained with this coherent effort will provide a sound basis and data for an effective reactive F-T slurry bubble column for optimum operation. The major thrust of their current work dies not lie within the main aim of this report and hence these details [24] are not being discussed here.

At Mobil, a thoroughly modernized version of the F-T process is developed which converts syngas to high octane gasoline and diesel fuel. This two-stage process is referred to as MFT system in which the syngas is fed into a slurry bubble column F-T reactor, and the total F-T product is passed into a second-stage ZSM-5 reactor which contains Mobil's proprietary zeolite catalyst. This results in a high yield of high octane gasoline and only smaller amounts of LPG and light olefins [25]. The problem with F-T synthesis is that it produces a wide variety of products. By using better catalysts, many attemps have been made to shrink the F-T product distribution but these have met with very little success. This is understood in terms of the so-called Anderson-Schulz-Flory rule according to which a wide product distribution is an inherent feature of all F-T processes. The catalyst composition and operating conditions can influence and control the product distribution [25] but it seems that the Anderson-Schulz-Flory rule always holds. If a light product such as gasoline is made, it is accompanied by a lot of less desirable gases with one to four carbon atoms. If this gas formation is suppressed, compounds with large carbon numbers, such as undesirable heavy waxes, are produced. The zeolite catalyst of Mobil cracks the high boiling distillate and wax fractions to naphtha and produces aromatic compounds of high octane number. It also converts the multitude of oxygen-containing compounds to water and hydrocarbons, all in a single step. As a result in this two-stage MFT process all heavier F-T products are eliminated without making additional light gases. The development, evaluation, and estab-lishment of this combined reactor system has been sucessfully accomplished by

Mobil with the support of the U.S. Department of Energy during the last few years on a bench-scale pilot plant unit. These results are described in the two papers [26, 27] presented at the DOE contractor's conference, and in a final report of the contract [28] to the U.S. Department of Energy. In what follows a brief resume of this effort is given.

The simplified flow diagram of the bench-scale pilot plant consisting of a slurry Fischer-Tropsch column, 3, 5.1 cm internal diameter and 762 cm high, and a fixed-bed ZSM-5 reactor, 8, in series is shown in Figure 6. The gas feed to the column comprised hydrogen and carbon monoxide from high pressure tanks at about 13.9 MPa, 1. After filtration and purification over activated charcoal to remove any carbonyls, and the gas feed wasn heated by passing through a preheater, 2. A desired quantity of high pressure nitrogen, 9, or any other gas such as methane was also mixed with the hydrogen and carbon monoxide stream to give a simulated synthesis gas with a known H_2/CO ratio. The gas flow was regulated and metered before entering the slurry reactor, 3. The latter consisted of one 150 cm and two 305 cm sections of schedule 40 stainless steel pipe connected together with flange joints to provide flexibility of design modifications. The hot synthesis gas was fed at the bottom below a distributor plate, held between flanges, and a drain was provided to remove any excess oil seeping through the distributor, 10. At the top, a disengaging section, 11, 12.7 cm internal diameter and 183 cm high, was provided to separate gases leaving the column from the gas-liquid suspension. Two inclined baffles were provided to break up any froth that might be formed and to minimize liquid entrained in the gas. The vapors left the reactor through a fine filter which prevented catalyst carryover. Surrounding the column was a jacket through which was circulated a coolant such as Mobiltherm-600, either to remove the heat of reaction or to add the heat as was required. Four sample taps were provided at 30, 152, 305 and 610 cm above the
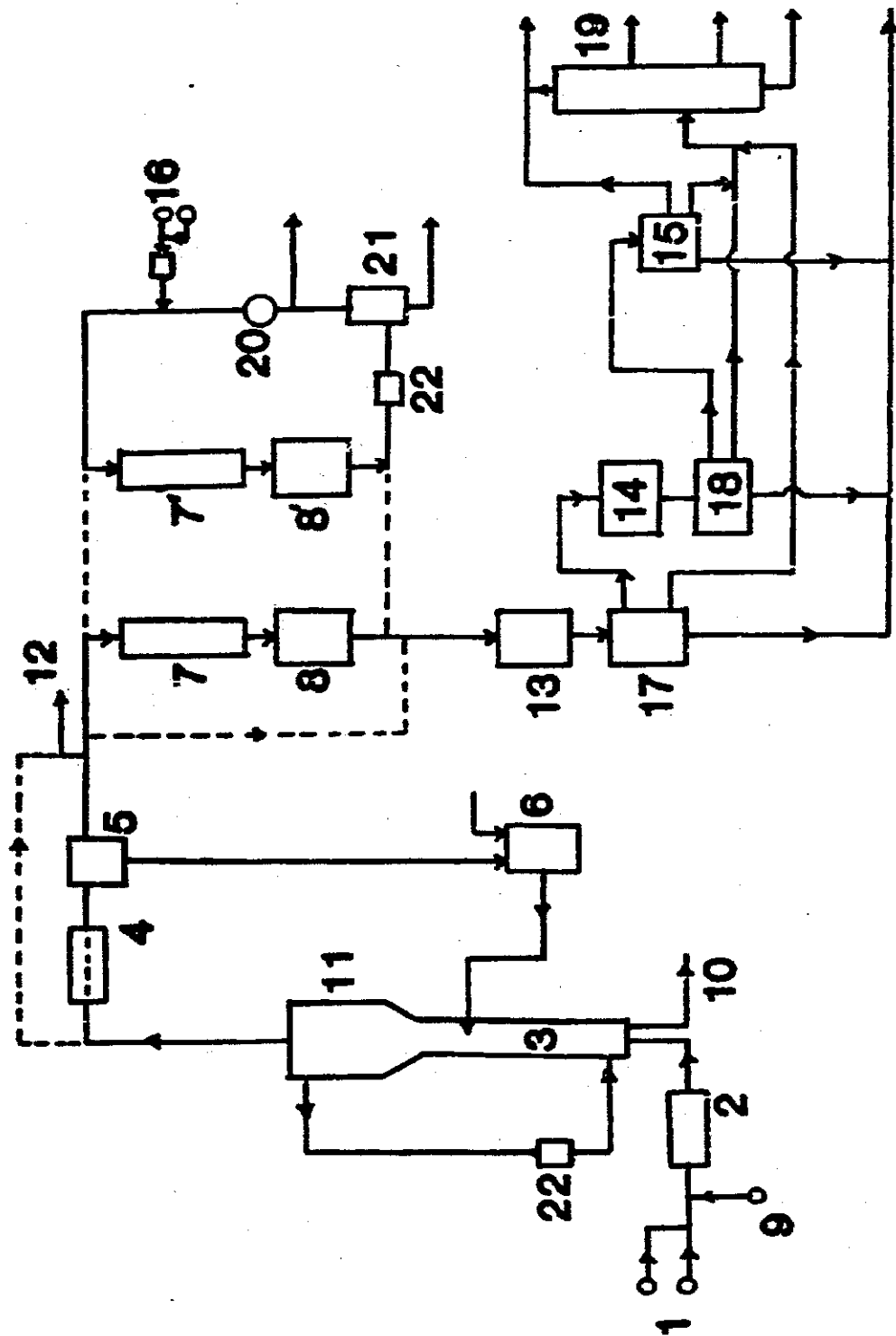
Figure 6. Flow Diagram of the Pilot-Plant Facility of Mobil [28]. 1: Syngas Feed, 2: Preheater
3: Slurry Column, 4: Partial Condenser, 5: Separator, 6: Slurry Charging Vessel, 7 and 7': Preheaters,
8: ZSM-5 Reactor, 9: Nitrogen Feed, 10: Excess Oil Removal Line, 11: Disengaging Section, 12: Inter-
Reactor Sampling Port, 13: Hot Condenser, 14: Cold Condenser, 15: Chilled Condenser, 16: Air Compresser,
17: Separator, 18: Separation Vessel, 19: Distillation Column, 20: Compressor, and 21: Cold Condenser
and Separator.

feed gas distributor to withdraw slurry into sample bombs.

The catalyst slurry was prepared in a 26,000 cm^3 slurry tank and it was transferred to the bubble column by pressurizing the tank with nitrogen. A small slurry transfer vessel, 6, was used as a make-up source for small quantities of slurry when needed during the operation of the reactor. If the liquid hydrocarbon product accumulated in the reactor, it was withdrawn through a fine filter located at a height of 213 cm.. A fresh wax reservoir stored the fresh liquid without catalyst. In the case of a loss of slurry in the column, the wax from these two tanks was pumped. In the product line a partial condenser, 4, was used and in case of a drop of slurry level in the column, this condenser was used to recover some of the heavier hydrocarbons. A small side stream was diverted from the effluent stream to analyze first-stage F-T reactor products, 12. The hot, 13, and cold, 14, condensers separate this sample stream into heavy and liquid hydrocarbons, aqueous phase, and light gases. These four streams were analyzed separately.

The second stage consisted of two fixed-bed reactors, 5.08 cm internal diameter and 10-46 cm in height, arranged in parallel for swing operation, 8 and 8'. While one was used in normal operational mode, the other was in regeneration mode. These reactors could be operated in both adiabatic and isothermal modes. The air supply needed for regeneration was provided by a compressor, 16, to which was fed filtered, regulated and metered air as well as nitrogen. This compressed mixture was then combined with the regeneration recycle gas, and the reactor containing the coked catalyst, 7 or 7', was regenerated under pressure with a controlled supply of oxygen (0.7 -21 mol %).

The effluent stream from this second stage reactor was passed through a series of three hot (373K), 13, cold (311K), 14, and ch..led (273K), 15, condensers. Each condenser was provided with a separator, 17 and 18, where liquid hydrocarbons and aqueous phases were separated and subsequently collected. The uncondensed light gas

17: Separator, 18: Separation Vessel, 19: Distillation Column, 20: Compressor, and 21: Cold Condenser and Separator

consisting mostly of carbon dioxide was metered, analyzed and finally vented
off. The liquid hydrocarbon products from the three separators were further
separated in a distillation column, 19, into a light gas, a gasoline range
product, and heavier fraction liquid products, if there were any. The light
gas from the distillation column was combined with the light gas from the chilled
condenser to be metered and analyzed. The bottoms of the second section of the
distillation column were collected as a light distillate. The design was such
that if found necessary this section could be completely bypassed. In this case,
light and heavy hydrocarbon liquid streams with largely overlapping hydrocarbon
distributions were obtained.

Five runs comprising a total of two hundred twenty days of operation
time were conducted to draw several general conclusions and to establish several
aspects of the pilot-plant operation. Three $Fe/Cu/K_2CO_3$ F-T catalysts were eval-
uated as were also two ZSM-5 catalysts. Process variables such as pressure,
temperature, feed-gas superficial velocity, feed gas H_2/CO ratio, and addition of
a potassium salt were examined in conjuction with the operation of the F-T slurry
reactor. Successful operation of the ZSM-5 reactor was demonstrated for its
capability to convert F-T hydrocarbon and oxygenate products in the effluent
stream of the slurry F-T reactor into high octane gasoline. The maximum gasoline
yield ranged between 80-90 weight percent excluding light paraffins in the feed
and reactor-wax for the severity index ratio between 0.8 and 1.0. The octane
numbers of the raw gasoline ranged from 90 to 94. It was demonstrated that F-T
catalyst/reactor wax could be successfully separated in external batch catalyst
settling vessels. It was shown that exposure of F-T catalyst slurry to air reduced
its catalytic activity and increased the methane + ethane yield. It was also
found that the addition of a potassium-salt to the F-T slurry reactor resulted in
rapid reduction of methane + ethane yield. However, its effect on the long-term

operation of the reactor could not be established. With the use of a F-T

catalyst I-B at 2.52 mPa and 530K, a methane + ethane yield of less than 5 weight

percent was found but the yield of reactor-wax increased to 46-51 weight percent.

It was found that a F-T catalyst designated as : I-C could be activated without

using a specific pre-treatment step.

In a typical experimental run, the slurry reactor was heated to 533K

with the nitrogen preheated to the same temperature at a superficial gas vel-

ocity of 1 cm/s. The top of the reactor was maintained at 477K to minimize wax

carryover in the effluent vapor phase. The second-stage fixed-bed reactor was

bypassed and the effuent gas was fed directly to the hot condenser and then was

diverted to a wax-stripper containing a mineral spirit to help avoid any plug-

ging downstream from the hot condenser. The distillation section was also by-

passed. The hot, cold, and chilled separators were initially filled with the

mineral spirit, again to dissolve any heavy hydrocarbons coming over during the

early part of the run. This procedure ensured a smooth start-up operation of

the unit. The reactor was maintained at 0.17-0.20 mPa with nitrogen flowing at

0.085 Nm^3/h. 600 g of FT-200 Vestowax was first loaded into the reactor through

a slurry-loading tank followed by slurry containing 319 g of catalyst, 750 g of

Mobil F-509 and 1400 g of FT-200 wax. The loading tank and the lines were then

rinsed twice and the unit was pressurized to 1.14 mPa with nitrogen bubbling

at a 2.2 cm/s superficial gas velocity in the reactor. To achieve high H_2+CO

conversion at a high synthesis gas throughout, it was essential to obtain high

catalyst loading in the slurry reactor.

The effect of reactor temperature on slurry reactor performance was

found as expected viz., the H_2+CO conversion went up strongly with temperature

in the range 541-555K. The yields of methane, ethane, and propane changed very

little over this temperature range. This is contrary to what was reported by Kolbel and Ralek [4]. An activation energy of 135 kJ/g mole was estimated for the H_2+CO conversion assuming first-order kinetics. The effect of the mass-transfer resistance on the H_2+CO conversion was neglected and accounting of this resistance would raise the value of the activation energy. However, this value is substantially larger than the values 81-94 kJ/g mole on Fe/Cu catalysts reported by Schlesinger et al. [19] and Deckwer et al.[10]. The exit H_2/CO ratio increased greatly with the higher H_2+CO conversion. This was expected as the feed H_2/CO ratio of 0.7 was higher than the H_2/CO usage ratio.

The effect of the reactor pressure was investigated in the range 1.14 to 1.83 mPa for runs with the same superficial feed-gas velocity. No appreciable change on the H_2+CO conversion was observed. At the lowest pressure, a moderate increase in the methane and ethane yield was observed. No definitive trend of the exit H_2/CO ratio was observed.

The variations in the feed-gas velocity reflected directly on the space velocity and it was found that the H_2+CO conversion went up with decreasing space velocity. No other significant variation on the reactor performance was observed.

The last process variable examined was the feed H_2/CO ratio. The effect on the H_2+CO conversion showed no definitive trend. High H_2/CO feed significantly increased the methane and ethane yield. Furthermore, when the feed H_2/CO ratios were substantially higher than the H_2/CO usage ratio (about 0.6), the exit H_2/CO ratios became very large because of the large excess of hydrogen.

Analyses of the F-T products which were altogether in five phases i.e., gaseous, light hydrocarbon liquid, heavy hydrocarbon liquid, reactor wax and aqueous, were very complicated and costly. Specific results of this nature on

Figure 6. For safety reasons, the reactor was physically isolated from rest of the system before regeneration. The regeneration circuit was pressurized by nitrogen to 1.14 mPa and the reactor was heated to 616K and the make-up air (0.079 Nm^3/h) was introduced. The maximum catalyst bed temperature was maintained at or below 758K, and oxygen concentration at the reactor exit was maintained at less than 1 mol percent. At the end of regeneration, the reactor exit-oxygen concentration was allowed to increase to 7 mole-percent. The axial catalyst bed temperature was practically uniform at about 756K and the total regeneration took about fourteen hours. After regeneration, the activity of ZSM-5 was restored.

The British Effort

The work on the Fischer-Tropsch synthesis of carbon monoxide and hydro-
gen to produce gaseous, liquid and solid hydrocarbons was initiated on pilot-
plant scale in 1949 at the Fuel Research Station, Greenwich, England, [29].
After a brief interruption, in 1958 this effort was continued at Warren Spring
Laboratory, Stevenage, and was finally stopped in June 1961 when it was real-
ized that the economic feasibility of the precess was unfavorable. It was
attributed to the higher cost of the feed gas in relation to that of the products.
The cost of the feed gas was estimated to be more than seventy percent of the
process. This plant was designed for a throughput of $70 m^3$/hr to produce 310-
450 ℓ of products for pressures up to 2.13 MPa at 573K. It has been described by
Farley and Ray [30] and is discussed briefly in the following. A flow sheet of
the pilot-plant is shown in Figure 7.

The synthesis feed gas was obtained from coal in a water-gas generator
which was so arranged that by feeding carbon dioxide along with steam its
composition in relation to hydrogen/carbon monoxide ratio could be varied be-
tween 0.6 and 1.2. The hydrogen sulfide was removed from the gas by passing it
through towers containing iron oxide, and carbon dioxide content was controlled
by washing it with caustic soda. The gas was then compressed to 1.52 MPa
and was scrubbed of organic sulfur compounds by passing over active-carbon. The
gas was finally stored in two cylinders each holding $566 m^3$ at a pressure of
12.2 MPa. The gas composition was continuously analyzed and residual sulfur
appeared as H_2S. The gas flow rate was measured on a specially designed pres-
sure mass flowmeter. The gas was passed through a heat exchanger, 1, where
it was preheated by the exit gases from the reactor, and then through the upper
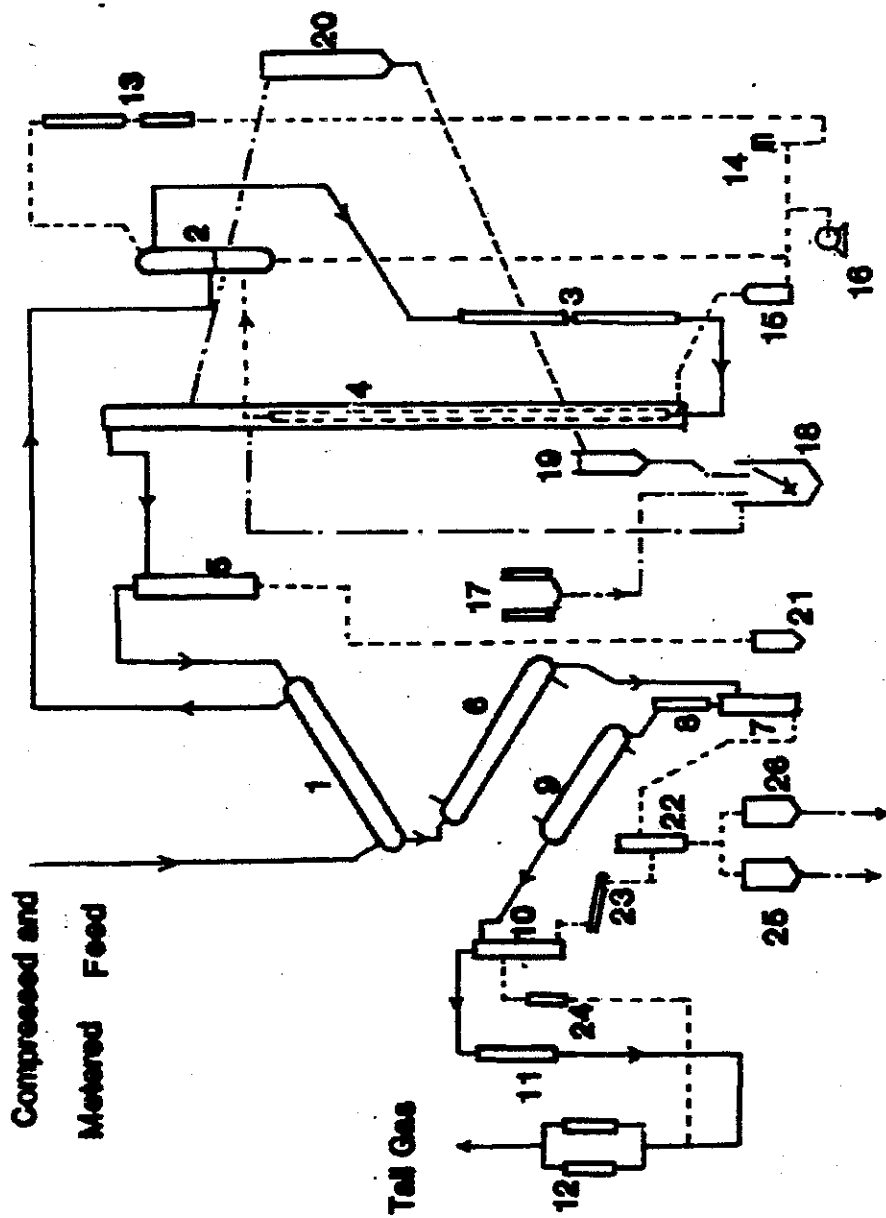section of steam chest, 2, and two gas preheaters 3, in series. The gas

Figure 7. Flow Diagram of the Hydrocarbon Synthesis Plant of Farley and Ray [30]. 1: Heat Exchanger,
2: Steam Chest, 3: Gas Heaters, 4: Slurry Reactor, 5: Partial Condenser, 6: Water Cooled Condenser,
7: High Pressure Separation Vessel, 8: Packed Column Scrubber, 9: Freon Cooled Refrigerated Condenser,
10: Dissolved Gas Condenser, 11: Residual Gas Heater, 12: Gas Rotameters, 13: Steam Condenser, 14: Dead
Weight Valve, 15: Water Heater, 16: Pump, 17: Jacketed Slurry Preparation Vessel, 18: Slurry Mixer, 19:
Filtration Vessel, 20: Sedimentation Vessel, 21: Wax Receiver, 22: Oil Separator, 23: Dissolved Gas
Cooler, 24: Dissolved Gas Heater, 25: Water Receiver, and 26: Oil Receiver.

was thus raised to the desired inlet temperature and fed into the reactor through a gas distributor comprising of a single nozzle of 1.91 cm bore having a simple non-return ball valve in the line.

The reactor, 4, consisted of a 1.27 cm thick mild-steel tube 8.53 m long having an internal diameter of 24.8 cm. The reaction space in the reactor was cooled up to a height of 6.1 m by a bundle of four tubes of 2.54 cm nominal diameter. The free reaction volume was 272.6 ℓ. The heat of reaction was removed by thermo-syphon circulation of water under pressure through these tubes having an external surface area of $2.61 m^2$ within the reactor. The steam thus produced was condensed in the lower section of the steam chest, 2, located at a high level, and the water so formed was returned to the cooling tube bundle through a water heater, 15. The heater was provided with an electric heating system and was installed at a low level. The upper part of the steam-chest served as a second stage for preheating the feed synthesis gas. The cooling tubes, steam-chest and the water heater constituted the primary cool-ing circuit. In a secondary circuit, the steam-chest was connected to the water heater through two steam condensers, 13, via a dead weight valve, 14. The flow in the circuit and steam pressure were controlled by applying external weights to this valve. The reactor temperature was thus brought to the desired level by choosing the steam pressure. The cooling system was a closed one but water could be pumped into it by a pump, 16. The water level in the steam chest could be monitored by a high pressure sight glass. The steam pressures up to as high as 7.45 MPa were used corresponding to a temperature of 563K. This cooling system worked quite efficiently and could maintain the reactor temperature constant within ± 1 K over the entire 6.1 m length of the cooling tubes.

A frothbreaker, comprising of a sheet metal spiral was installed in the disengaging section above the header of the cooling tubes at a height of 7.0-7.5 m. A demister consisting of a pack of cones of 200 mesh stainless steel gauze was fitted at 8.2 m just below the location of the product outlet from the reactor. However, after a number of runs it was removed as during operation if the bed of slurry expanded into it, the remaining dry catalyst caused uncontrolled reaction and thereby forced even the shut down of the plant. All temperatures were measured by chromel/constantan thermocouples using an automatic cold junction maintained at 273K. Twelve mounted thermocouples measured the reactor temperature. In all, temperatures at 45 places were recorded at intervals of four hours.

In early runs, the slurry was charged into the reactor from a 50-gallon steam heated vessel, 18, by gas pressure. It was prepared in the slurry mixer by mixing the catalyst with molten wax by an electric stirrer. In later work, the slurry was prepared in a steam-jacketed open-topped vessel, 17, located directly above the slurry mixer, 18. The hot wax could be charged from the former and catalyst was added incrementally into the upper vessel, 17, and stirred before transfering slurry to the mixer under gravity for charging to the reactor. The level of the slurry in the reactor, 4, was maintained constant by an outlet drain pipe. The slurry then passed into a sedimentation vessel, 20, where it remained static for the required time of sedimentation and the settled catalyst rich slurry flowed to the filter vessel, 19. Here the liquid was separated from the catalyst and the former was returned to the reactor to maintain a constant level in it. Great care was taken in designing and operating the sedimentation vessel and the gravity separation was found to be most efficient for catalyst particles (1-3μm) over other techniques such as centrifuges, magnetic, sintered-metal, and woven-wire cloth filters. The

separated catalyst particles were transferred to the slurry mixer, 18, and thence to the reactor, 4.

The relatively lower boiling product vapors from the reactor entered into the partial condenser, 5, a cylindrical vessel 170 cm tall and 25.7 cm internal diameter. It was provided with a side heating jacket and bottom flange heater to maintain a temperature of about 453 K. The hydrocarbons approximately in the range C_{17}-C_{30} retained inside the partial condenser were collected in a wax receiver, 21. The exit gases from the partial condenser next passed through the heat exchanger, 1, which provided the first stage preheating of the inlet gas. The outer shell of this cylindrical heat exchanger was 3.35 m long and 22.2 cm in diameter and contained twelve helically finned tubes 1.91 cm internal diameter. The product was then passed through a water-cooled condenser, 6, of identical dimensions as the heat exchanger, 1, but containing thirty tubes of 1.91 cm internal diameter and 3.35 m long. Both the condensed liquid as well as the gaseous product were then passed through a high-pressure cylindrical separator, 7, 1.14 m long and 20 cm internal diameter. The liquid fraction was withdrawn into a low pressure oil/water separator, 22, made of a cylindrical stainless steel tube 91.4 cm long and 15.2 cm internal diameter with a 7.0 cm square central tube. The separation into oil (C_{5+} hydrocarbons) and water was effected by a weir system and they collected into the reservoirs 25 and 26 respectively.

The gaseous products from the high pressure separator, 7, were scrubbed of water in a column, 8, packed with 1.27 cm ceramic Raschig-rings and then passed through Freon Cooled refrigerated condenser, 9, consisting of thirty tubes, 1.83 m long and 1.91 cm internal diameter. The condensed product from 9 and 8 was returned to the high pressure separator, 7. The outlet gases from the refrigerated condenser, 9, served to cool the gases from the low-

pressure separator, 22, in a dissolved gas condenser, 10. The condensed products were recycled into the low-pressure separator, 22, through the dissolved gas cooler, 23. The residual and dissolved gases were heated to the ambient temperature in the residual gas heater, 11, and in the dissolved gas heater, 24, respectively and were metered in two rotameters, 12, as total exit gases before being released. The plant was designed to produce 70-100 gallons of product per day at a throughput of 2500scf/h of feed gas.

A radioactive density-guage system using 20 millicurie Caesium 137 was developed to measure bed height and provide data for the calculation of bed density and hence the weight of the liquid medium, catalyst and gas holdup. The catalyst used in all the runs was a precipitated iron oxide incorporating small amounts of potassium and copper oxides as promoters. A typical analysis of the catalyst is given in Table VI. The catalyst activity at 533K was found to be high initially but it fell rapidly and this was explained due to the malfunction of the sedimentation system which caused a drop in the catalyst concentration in the reactor. The pronounced fall in performance when the reactor temperature was raised to 553K was attributed to the formation of free carbon and its effect on the physical rate processes of the system. It was noticed that whenever the catalyst composition changed due to the oxidation of components during synthesis there was a fall in the catalyst activity. The results suggested that at the same reaction temperature, a better performance was obtained for a higher amount of iron carbide.

Initial runs were carried out at superficial linear velocities of about 3.5 cm/s. However, this velocity was found too low to expand the bed fully and uniformly. Hence in later operations, a greater velocity of about 6.95 cm/s corresponding to a volumetric flow rate of 2500 scft/h was used. The gas holdup was found to steadily decrease during a run and it was attributed to the

increase in the amount of free carbon in the reactor. During the experiments free carbon was generated and as much as 30 weight percent of the slurry accumulated in 450 h of operation. In fact the gas holdup was found to be inversely proportional to the weight percent of carbon in the slurry due to the substantial increase in the slurry viscosity. Their experiments suggested that the slurry behaved as a Newtonian fluid as long as the concentration of free carbon is less than approximately one weight percent and it behaved as non-Newtonian for greater percentages of carbon in the slurry. The interfacial area, A , was calculated using the relation: 6 (holdup)/ bubble diameter. Values of holdup and bubble diameter varied from 40% and 0.24 cm respectively at the start of the run to 12% and 0.78 cm respectively at the end of the run. This clearly indicated a decrease in the value of the interfacial area per unit volume of the slurry with the passage of the run. The mean diameter of the bubble in cm was estimated from the correlation: $d_b = 0.093\mu^{0.781}$, where μ is the viscosity in centipoise of the liquid medium. This correlation is independent of the inlet velocity of the gas and was established from experimental measurements on water and glycerine mixtures.

A decline in the catalyst activity was associated with the fall in the total yield. The average molecular weight of the hydrocarbon increased with the increase in the reaction temperature, and also with the age of the catalyst at the same temperature. The amount of oxygenated compounds decreased with the increase in the reaction temperature as long as the oxidation of Fe_2C to Fe_3O_4 occurred at higher temperatures, the production of oxygen compounds increased. During the activation of the catalyst a minimum hourly gas space velocity of thirty was required to ensure that water and carbon dioxide were effectively removed from the reactor in order to prevent re-oxidation of the talyst.

Detailed accounts of the total heat balance and calculation of the specific
exothermic heat of reaction for six periods from experimental data are reported
during which the product distribution was known. This yielded a mean value
of 76.0 Btu/cu. ft. of $(CO + H_2)$ at N.T.P. A theoretical calculation based on
the heats of formation of the inlet gas, residual gas and condensed products
was also made and that gave a value of 74.1 Btu/cu. ft. of $(CO + H_2)$ at N.T.P.
In this calculation the contributions arising because of the changes in catalyst
composition and carbon formation were regarded as negligibly small. The agree-
ment between the calculated and experimental values was therefore regarded as
quite good. The overall material balance agreed within $\pm 3\%$ indicating adequate
and satisfactory measurements and estimation procedures.

The overall heat transfer coefficient for slurry.water system was found to
be 70 Btu/hr sq. ft. °F for the best conditions. This coefficient as well as the
slurry/tube metal coefficient fell off with the duration of a run and was
correlated with the increase in the bed viscosity and decrease in gas hold-
up during the same time. The radiation loss from the reactor and the cooling
system was found to be 31,911 Btu/hr and was in good agreement with the electrical
power input needed to maintain the system at a constant temperature.

The experimental data were interpreted on the basis of an overall rate
for Fischer-Tropsch synthesis controlled by a physical diffusion and a chemical
reaction resistance. The experimental data accorded with the modelled linear
dependence of the overall resistance to reaction on solids concentration per
unit interfacial area. They also found that for an efficient operation of the
slurry reactor with iron catalyst, the gas holdup should be around 50% so as to
eliminate the physical resistance.

TABLE VI
Analysis of a Typical Catalyst

Component	Composition (%)
Total Iron (Fe_2O_3)	91.86
Fe^{++}	0.36
SO_3	0.10
K_2O	1.27
Copper (Cu_2O)	1.15
CO_3	0.77
Water (1073K)	1.87
Carbon (1073K)	0.35
Manganese (MnO)	0.39
Titanium (TiO_2)	0.42
Calcium (CaO)	0.28
Magnesium (MgO)	0.17
Difference	1.01
	100.0

Another parallel effort to understand the F-T synthesis of the gas from a water gas plant to produce hydrocarbons and oxygenated compound was made by Calderbank and coworkers [31] and also at Warren Spring Laboratory. Special efforts were made to understand the rate controlling processes and the formation of carbon and its influence on the bubble dynamics and gas-liquid interfacial area through the changes in the slurry viscosity. To accomplish this experiments were conducted in two cylindrical column reactors one small (5.08 cm internal diameter and 4.6 m tall) and another relatively large (25.4 cm internal diameter and 9.1 m tall) and the results were interpreted in conjunction with the supporting information generated from separate experiments dealing with density and viscosity of the molten F-T wax; diffusion coefficient, solubility and Henry constant of hydrogen in the wax; gas hold-up and interfacial area variations with superficial gas velocity etc. In the following we describe these efforts.

The synthesis gas used in this work was generated in a water gas plant equipped with gas cleaning devices and comprised of sulfur-free carbon monoxide and hydrogen. A typical proportion for the two gases was 60% CO and 40% H_2. It was stored in gas tanks at 20.26MPa and was fed into the slurry reactor through pressure reducing valves at pressures of about 1.11 MPa and 2.23 MPa. Two cylindrical reactors were employed in this work, one 5.08 cm in diameter and 4.6 m in height and another 25.4 cm in diameter and 9.1 m in height. The schematic of the flow diagram of 5.08 cm diameter reactor is shown in Figure 8. External electrically heated jackets were employed in the smaller column to maintain its temperature at the desired level. An internal cooling tube bundle was installed in the larger reactor through which water was circulated to remove the heat of reaction. It was connected to a steam drum whose pressure was controlled to regulate the reactor temperature.
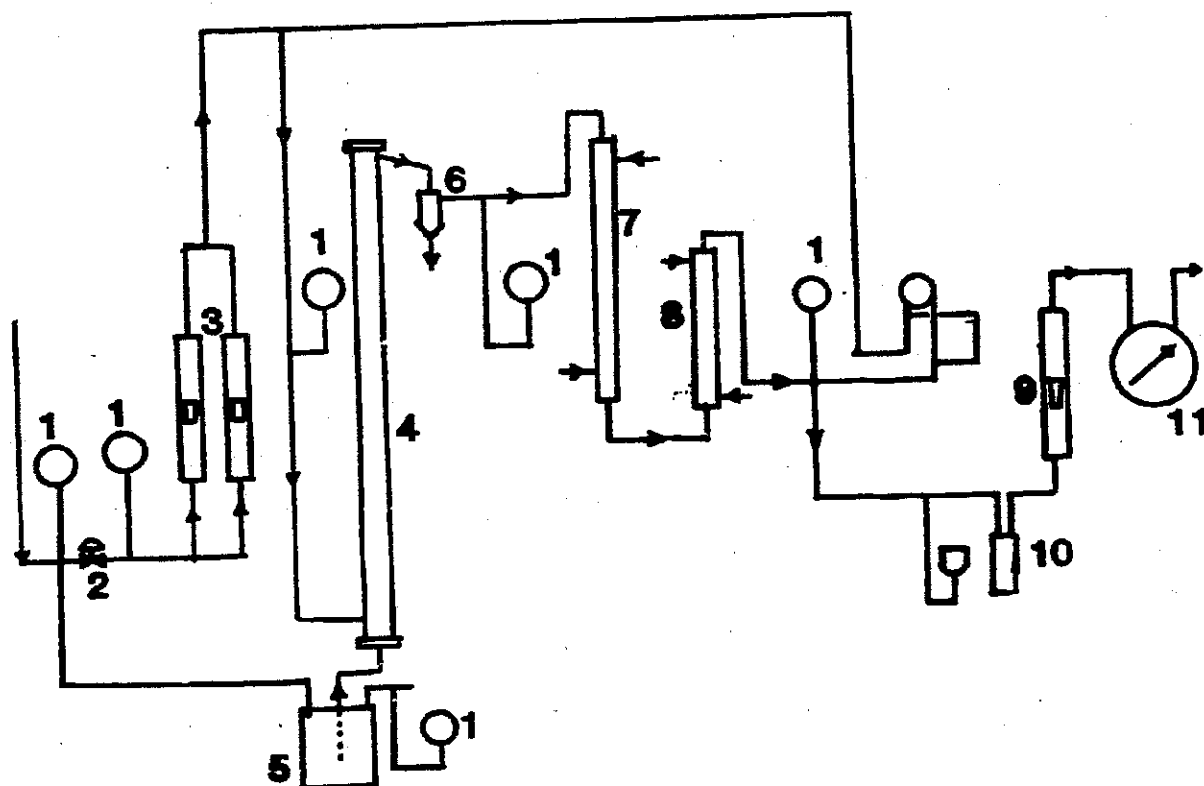
Figure 8. The Experimental Arrangement of the Slurry Bubble Column of
Calderbank et al. [31]. 1: Pressure Gauge, 2: Pressure Control Valve, 3:
Gas Rotameters, 4: Slurry Reactor, 5: Slurry Preparation Vessel. 6: Catch
Pot, 7: Water Cooled Condenser, 8: Refrigerated Condenser, 9: Residual Gas
Flow Meter, 10: Spirit Trap, and 11: Wet Gas Flow Meter.

The synthesis gas was fed to the reactor through an open-ended conical pipe containing a steel ball. This acted both as a non-return valve and as a variable orifice. The catalyst used was iron oxide formed by precipitation from ferric chloride solution. The precipitate was dried, dispersed in the wax, charged into the reactor, and was activated with the synthesis gas at 558K. In the case of small reactor, the level was maintained constant by removing the wax through a streamline filter. To the larger reactor was connected a sedimentation vessel, from which the liquid reaction products were withdrawn as an overflow without appreciable entrainment of catalyst.

The slurry level as well as the gas hold-up in the reactor was determined by means of a gamma-ray transmission device, whose details are given by Calderbank and Rennie [32]. For a constant gas flow-rate, the gas hold-up was found to vary with time. This was attributed to the formation of colloidal carbon which increased the viscosity of the liquid-solid suspension i.e. slurry. This caused the formation of appreciably large bubbles by coalescence of the small ones initially produced at the reactor base. Larger bubbles have relatively smaller surface area per unit volume as compared to smaller bubbles and therefore a reduction in the gas-liquid contacting occurred which lowered the gas conversion by reducing the mass transfer.

The volatile products exited from the reactor and were cooled in condensers at temperatures down to 261K. The uncondensed residual gases were sampled, metered and then released in the atmosphere. The gas flow rate was adjusted to a value which gave satisfactory initial production rate at a reaction temperature of 538K. Over a period of continuous operation of a run which was typically 400-500h, a slow-decline in the catalyst activity was observed. The conversion level could be maintained constant by progressive

reduction of the flow rate or increase in reaction temperature. At the end of the run, the contents of the reactor were discharged and a fresh charge of the slurry was replaced in the reactor.

A special effort was made to understand the kinetics of the catalyst slurry system and to interpret the observed overall rate constant in terms of the various rate controlling processes. It was argued that the overall reaction rate in the presence of an active catalyst would be primarily determined by the transfer rate of hydrogen in the liquid. This was experimentally demonstrated by choosing the chemical reaction involving the hydrogenation of ethylene in an inert liquid containing finely divided Rancy nickel catalyst. This was a reaction similar to F-T reaction system and it was know to be controlled by the rate of solution of hydrogen. Calderbank and coworkers showed that the experimental results were in accord with the mechanism based on the assumption of hydrogen diffusion was the rate-controlling step. Having established that it was necessary to evaluate certain physical properties to interpret the physical resistance in the F-T catalyst-slurry system. These properties were: solubility and diffusivity of hydrogen in molten wax, viscosity, and density of the slurry, all at the reaction temperature. The values of gas hold-up, and gas-liquid interfacial area must also be known for the gas sparger arrangement and gas flow-rates. These properties were determined for the ranges of experimental conditions and F-T materials. The measured overall rate constant at 538K over a range of conversions from 0.3 to 0.8 were used to interpret the model developed theoretically and slurry bubble column operation.

Their theoretical model was based on the relationship between the overall resistance, mass transfer resistance, and kinetic resistance by modeling

the gas-liquid mass transfer and reaction at the catalyst surface as first order rate processes which occur in series. It was implied that an excess of active catalyst existed in the reactor so that the ratio of catalyst surface to surface area of the gas bubbles was quite high. Under this condition mass transfer of hydrogen from the liquid phase to the catalyst surface was regarded as relatively rapid. It was found that the theoretical model could not represent the entire range of conversion data. A modification of the model result involving the conversion factor, gas holdup, mass transfer resistance, and kinetic resistance measured at the beginning of an experimental run, was therefore developed and proposed.

These authors suggested that the physical significance of the conversion factor was based on the formation of free carbon. This increased the slurry viscosity and hence increased the bubble diameter and decreased the gas-liquid interfacial area. Free carbon also reduced the catalyst activity by fouling the catalyst surface. They suggested that the conversion factor was directly proportional to the free carbon concentration on the consideration that its formation occurred according to the Boudouard reaction and is inhibited in the presence of steam which is formed by the water-gas shift reaction. This modified theory revealed that the overall rate constant decreased with reactor height and attributed it to a reduction in the mass transfer efficiency due to increased bubble coalescence. This investigation specially brought to light the importance of bubble coalescence, a phenomenon which has not been considered in any design effort of slurry bubble column operation in an explicit fashion.