Indirect Liquefaction of Coal:
Fischer-Tropsch Synthesis In Slurry Bubble Column Reactors

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ABSTRACT

Indirect liquefaction of coal via Fischer-Tropsch synthesis in a slurry bubble column is a viable and promising coal conversion technology for the production of liquid fuels and chemicals from coal. However all process details are not well understood at the present time and it is most often considered as economically unfavorable against the unstable and fluctuating oil prices from the middle east. One view that encourages the development of this technology is that in the optimum mode this process may turn out to be the most attractive way of producing petrochemicals from coal. This has provided the incentive to synthesize all the available information to enable a proper appraisal of our understanding of this process of indirect liquefaction of coal via Fischer-Tropsch Synthesis in a slurry bubble column. This report includes a description and discussion of all such efforts that have been made from time to time in different parts of the world. In particular, the German, American, British, Indian and Japanese efforts are considered. The details of these different initiatives are compared and various agreements and disagreements in their results are pointed out. The areas of particular concern where our understanding is deficient and further research and development work is in order are identified and emphasized.

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A slurry bubble column comprises either a stationary or a slowly moving liquid in continuous phase in which solid catalyst particles are kept suspended, and gases bubbling through in a discontinuous phase. Such three-phase reactors have been successfully used in a variety of applications but this report deals with a particular application in relation to the indirect liquefacation of coal with the motivation to produce gasoline range hydrocarbons. Here, the synthesis gas from one of the second generation gasifiers having a relatively low hydrogen to carbon monoxide ratio in the range of 0.6-0.7 is bubbled through a slurry of finely divided catalyst suspended in a heavy oil medium. Depending upon the process details a wide range of hydrocarbons, saturated and unsaturated compounds such as light hydrocarbons, gasoline, diesel fuel and heavy paraffins are produced. By-products such as alcohols, aldehydes, ketones, acids, esters and aromatic compounds are formed in smaller amounts. A number of such efforts either on the bench scale or on the pilot-plant scale have been made from time to time in different parts of the world to produce mainly gasoline by the hydrogenation of carbon monoxide with vary-ing degrees of sucess. It is the purpose of this report to review these works describing process details involving plant design, operating conditions, results and significant observations.

It is interesting and relevant to point out that slurry bubble columns

offer notable advantages over other reactor configurations such as offered by fixed or moving beds of catalyst in the absence of liquid medium for hydrocarbon synthesis starting from hydrogen and carbon monoxide. The principal advantages lie in ease of maintaining a uniform temperature in the reactor, efficient heat transfer between the bed and immersed tubes for the removal of heat of reaction, high catalyst conversion efficiency, ease in regenerating the catalyst, flexibility in controlling the product selectivity by the proper choice of catalyst, and simplicity of reactor design which keeps the capital cost down. To achieve these advantages, a plant must be appropriately designed and operated. One of the major disadvantages of the slurry bubble column resulting from the back-mixed nature of the phases is the poor selectivity of the reaction products. While discussing the various efforts particular attention will be given to those features which bring about these advantages to the fullest extent.

The Early German Effort

The hydrogenation of carbon monoxide by the liquid-phase Fischer-Tropsch (F-T) process is pioneered by Kolbel and coworkers in Germany and their efforts [1,2] are well described [3,4]. These efforts spanned a period of fifteen years during 1938 to 1953 when the results obtained on a laboratory-scale model were scaled-up by a factor of 1667 in reactor volume to produce 11.5 tons of hydrocarbons per day in a semi-industrial plant at Rheinpreussen-Koppers. The laboratory-scale model employed a cylindrical reactor, having the dimensions of 4.7cm internal diameter and 350cm height and an overall volume of 6 ℓ. The semi-industrial demonstration plant also had a cylindrical reactor, 155cm internal diameter and 8.6m high, with a volume of 10,000 ℓ.

The development of a suitable catalyst for the liquid-phase synthesis was pursued in great detail with iron catalysts which were successfully used in

the fixed-bed reactors. However, certain advantages in the use of catalysts in the slurry column are evident because of the operating conditions viz., maintenance of certain temperature ranges, high gas velocities, or a high hydrogen content in the synthesis gas is not necessary. In principle, all the catalysts which are appropriate for the Fischer-Tropsch synthesis can be successfully used in the liquid phase. Further, the mechanical strength of the catalyst is not essential. In fact it is preferable for the catalyst particles to decrepitate during the synthesis process because it leads to a slurry having more favorable thermophysical properties. Fine particles lead to more stable and uniform suspensions having smaller bubbles and hence higher values of the gas-liquid interfacial area per unit bubble volume, a condition very much preferable to mass transfer from the gas bubble phase to the liquid phase. The latter condition results in a higher percentage for gas conversion. It is for this reason that Kolbel and Ackermann [5,6] considered mainly support-free iron precipitation catalysts. It was thus possible to use highest concentration of iron in suspension. The optimum concentration was found to be 10 weight percent in terms of the iron present in the catalyst, higher concentration up to 20% may be used. Lower concentrations reduced the reactor efficiency while higher concentrations increased the slurry viscosity and thereby the bubble size was increased and hence the interfacial area per unit bubble volume decreased and that caused the conversion to decrease. Catalysts with a high content of supports were found to be less attractive since they resulted in a higher value for slurry viscosity as compared to support-free catalysts.

The details of catalyst preparation are given by Kolbel and coworkers in a series of papers and German patents [4-6]. The iron precipitation catalysts were prepared from iron (III) nitrate solutions or mixtures of nitrate solutions containing 80% iron (III) and 20% iron (II). Solutions of iron (II) were

found to be inappropriate for active catalysts because the iron in the oxide has to be present either as α-or γ - Fe_2O_3. For the preparation of greater quantities of catalysts, nitrate solutions were prepared by dissolving wrought iron scrap or steel turnings in nitric acid. It was established that the impurities like manganese, silica, carbon, sulfur and phosphorous present in these materials did not influence the activity. Presence of such metals as copper, silver, gold and nickel even in minute concentrations reduced the activity. Specific details of catalyst preparation and activation are not relevant to our present scope of this report. These catalysts were easily regenerated by simple oxidation when the full activity and efficiency was found to be regained. In addition to the conventional precipitated iron catalyst, Kolbel and coworkers also tested the coprecipitated Mn and Fe oxides in the proportion 8-10: 1, Poutsma [7].

Besides these two efforts involving the use of hydrogen and carbon monoxide to produce hydrocarbons, Kolbel and coworkers [3,8] have also employed feed mixtures of water-vapor or steam and carbon monoxide, usually referred to as Kolbel-Engelhardt synthesis. Experiments were carried out using blast furnance gas on a laboratory-scale model comprising a cylindrical reactor having an internal diameter of 5.0cm and height of 500 cm containing 6-7 ℓ of catalysts in oil suspension and 300-500 g of iron. The laboratory-scale reactors were provided with external cooling jackets while the semi-industrial reactor was cooled by an internal tube heat exchanger through which water was circulated to produce steam under pressure. Details of the operating conditions and results of all these three efforts are given in Table I. The primary goal of these investigations was to produce gasoline and hence the operating conditions were geared towards this ultimate aim. The details of the demonstration plant are given briefly in the following and its flow chart in Figure 1.

The synthesis gas was produced in a Koppers water gas generator having a composition of 54 to 56% CO, 36 to 38% H_2, 3 to 5% CO_2, 0.1% O_2, and 2.6 to 4% N_2. The ratio of H_2 to CO was about 0.67. It was purified to remove H_2S by passing over iron oxide, and over a hot purifying mass to remove organic sulfur compounds. The residual sulfur content was brought to a level of 1 to 2 mg of S/m^3 in the synthesis gas. It was then compressed in the compressors, 1, and its pressure and flow rate were measured in gas meter, 2, and orifice plate, 3. A sample was withdrawn at 4 to establish the initial composition of the synthesis gas. It was then passed through the heat exchanger, 5, where it was heated by the

tail gas stream coming from the reactor, 6. It was next introduced at the bottom of the reactor through a distributor plate provided with jets, 2 to 3mm in diameter. The reactor was a pressure-resistant steel cylinder having a steam collector, 7, at its top. The water from the steam collector drained into the cooling pipes of the heat exchanger, 8, provided in the reactor. This internal heat exchanger, 8, terminated at about 1.3m above the gas distributor plate. By controlling the pressure in the steam collector, 7, the reaction temperature was fixed.

An elevation in the reactor temperature will lead to methane formation and carbon deposition on the catalyst particles and these will lower the gas conversion to gasoline fraction in the product. An effective heat removal system was devised for this purpose, 8, as mentioned above. The temperatures were measured at different heights by twelve resistance thermometers. The temperature gradient in the reactor was always less than ±1K. No overheated regions in the reactor were found even when the reactor gas load was increased by five fold. A cooling pipe surface area of less than $50m^2$ was required for $1000m^3$ of synthesis gas per hour. Turbulent mixing of the suspension provided uniform distribution of um size catalyst particles. The difference in the catalyst concentrations at the top and bottom of the reactor was less than 0.2 to 0.6 wt% iron. Nine sampling ports at different levels permitted the removal of suspension samples from the reactor. No catalyst deposits were found on the walls of the cooling pipes.

The tube exchanger, 8, was also used to heat the suspension initially to the catalyst activation temperature by the addition of steam at the appropriate pressure. The fluid level in the reactor was maintained constant by a level-sensing float,9. The slurry was introduced or withdrawn as necessary by means of pumps, 10, through nozzels at the reactor bottom from or to the stirred tank, 11. The level regulator,9, could permit the overflow of the high-boiling fractions in the pressure filter 12, or the addition of high-boiling synthesis products from containers 13. The cooled tail gas condensed according to the boiling range of the liquid medium and were stored in containers 13 and 14. The medium boiling range products and bulk of water vapor formed during synthesis were condensed by indirect cooling with water in the condenser 15 at about 303K. The residual gas after passing through an orifice meter 3, and a gas meter 2, was scrubbed of carbon dioxide

in 16, and then fed into a recovery plant for light boiling and gaseous products. The carbon dioxide was cycled to the gas generator for the production of CO-enriched synthesis gases.

The reactor was filled with the fresh catalyst from the agitator tank, 11, where the fresh catalyst was mixed with the high-boiling synthesis products. The spent catalyst was withdrawn from the reactor by means of pump 10 and fed to the centrifuge 17 where it was separated from the liquid medium. The latter was stored in 18. The deactivated catalyst was regenerated and the recovered liquid medium was used to suspend the fresh or regenerated catalyst in the agitator tank, 11.

By properly adjusting the operating conditions, the production can be geared towards either a low or a higher molecular weight product. These studies were made in laboratory-scale models and yielded the following results. A low-molecular, olefin rich product containing more than 80% of hydrocarbons boiling below 473K with an olefinic content of 80% was obtained by operating at high temperatures (547-551K) and a regenerated catalyst. Another technique successfully employed was to recycle the synthesis fraction of the 563-593K boiling range into the reactor during synthesis over suitable iron catalysts to produce products rich in olefins. The production was also found to be favored when the liquid-phase reactor temperature from the gas inlet at the bottom to the gas outlet at the top was allowed to rise by 30 to 60K by employing decreasing cooling surface area from bottom to the top of the reactor. The formation of higher-molecular weight products was favored by low operating temperatures (489-503K) and a high alkali content of high-activity iron precipitation catalysts such as K_2CO_3 one weight percent. and also by the chain-extending molecular buildup of the hydrocarbons present in the catalyst suspension or recycled into it. By adding potassium carbonate into the catalytic suspension, the proportion of oxygen-containing compounds in the product was found to increase. The use of coprecipitated Mn and Fe oxides as catalyst yielded a high molecular weight product rich in olefins [4].

When the synthesis was adjusted for the production of low molecular weight compounds, the removal of the liquid medium was often greater than the addition due to

synthesis. In such cases, the higher molecular weight products collecting in the heat exchanger, 5, were fed into the reactor by pump 10, the flow being regulated by the liquid level controller, 9. On the other hand if the process was geared to produce products of higher molecular weights, these products were separated from the catalyst by continuous separation in filter 12 and removed. The catalyst was fed back into the reactor. The primary products in the liquid form were removed under pressure, and were separated from the water of reaction in separators, 13. The separator yielded oxygen-containing products, especially alcohols.

The listings of Table I suggested clearly that the results of laboratory-scale reactor and that of the semi-industrial demonstration plant were quite comparable when both were operated under similar conditions and using the same catalyst and feed gas. It was thus claimed on the basis of these results involving a reactor volume scale-up of 1667 times that successful design of industrial plants is possible on the basis of bench-scale laboratory results. The key factor responsible for this successful scale-up has been attributed to the maintenance of constant gas bubble residence time, Poutsma [7]. From Table I, it is clear that the reactor efficiency of the laboratory model was smaller than that of the demonstration plant. The lower space-time yield of the laboratory model was explained on the basis of the relatively narrow reaction cross-section which resulted in smaller gas load. The F-T synthesis was found to be relatively independent of pressure unlike the Kolbel-Engelhardt synthesis, Kolbel et al. [3].

Various experimental and theoretical investigations available in the literature have revealed that besides the catalyst and the reacting conditions (temperature and pressure), the catalyst concentration and dispersion, hydro-dynamic factors such as bubble size, interfacial area (solid-liquid and gas-solid), mixing in the gas, solid and liquid phases, solubility of the reactants, concentration of the reactants at the catalyst surface, intra- and intra-particle diffusional resistances etc., significantly affected the mass transfer and chemical resistances. The magnitudes and their relative values in turn influenced the product distribution. In general, for the conditions employed by Kolbel and coworkers in conjunction with classical iron catalysts, the products distribution found was that predicted by the Schulz-Flory polmerization kinetics. This predicted a maximum yield of C_5-C_{11} to be approximately fifty percent by weight.

Kolbel and coworkers have emphasized the importance of the thermophysical properties of the F-T slurry reactor. A summary of the relations used by them [4] and based on the works of a number of investigators [9-12] are compiled in Table II. In addition, the studies of solubilities of reactants and paraffins at constant temperatures and pressures were carried out by them [4]. Results indicated that the solubility of CO and H_2 increased with temperature at a given pressure but decreased for CO_2 and H_2O in molten paraffin. The Henry's constants for CO and H_2 at 543K in paraffin Gatsch were found to be approximately 340 and 413 (atm/mole fraction) respectively, indicating that CO is more soluble than H_2 in the hydrocarbon slurry.

From their studies on the laboratory scale model [4], Kolbel and coworkers established that a linear gas velocity of greater than 1.5 cm/s accomplished a uniform catalyst distribution and they recommended a velocity greater than 3.6 cm/s. Gas velocities upto 5 cm/s resulted in homogeneous bubbling, and uniform small bubbles of 0.7mm diameter were formed in solid free suspension. The bubble rise velocity was in the range 10 to 20 cm/s for gas velocities between 1.5 to 10 cm/s. In the semi-industrial demonstration unit, the bubble size was larger, 3-6mm in diameter. The difference in the bubble size in the two units is due to the use of different types of distributors. Higher gas velocities, greater than 10 cm/s, led to coalescence and resulted in a decrease in specific gas-liquid interfacial area, a. Estimates were made for a and gas to liquid mass transfer coefficient, k_L, for the homogeneous bubbling regime. Typical k_L values were of the order of 0.1 to 0.2 cm/s and a varied from 600 m^2/m^3 at the inlet gas superficial velocity, U_G, of 1.6 cm/s to 1700 m^2/m^3 at U_G of about 3.6 cm/s. These values agreed well with their initial estimates of 1500 m^2/m^3 in slack wax in industrial columns with suspended catalysts.

To reduce the reaction resistance, a higher catalyst concentration is desirable. However, too large values are not practical and the limitation is imposed by the fact that higher solids concentration lead to an increase in the apparent viscosity and density of the liquid giving rise to large bubbles. This causes a decrease in the value of a and an increase in the mass transfer resistance. In view of these findings, Kolbel and Ralek [4] employed unsupported fine catalyst (30 μm diameter) in their work. An operational range diagram of gas velocity versus catalyst concentration as reported by them [4] is shown in Figure 2. Low liquid viscosity and

surface tension were claimed by these workers as critical factors to be considered for controlling the appropriate size of the bubbles. From their experimental investigations, they [4] concluded that the liquid phase F-T synthesis cannot be inhibited by mass transfer of the gaseous reactants into the liquid phase when using catalyst concentrations of 10 weight percent or less.

Table I

Operating Conditions and Results of Liquid-Phase Fischer-Tropsch Synthesis [4,3]

Fischer-Tropsch Synthesis Process	A[1]	B[2]	C[3]
Effective Reactor Volume (ℓ)	6	10,000	9
Iron Precipitation Catalyst (kg Fe)	0.4	800	0.384
Synthesis Gas Pressure (10^{-5} Pa)	11	12	16
Synthesis Gas Composition [Volume Ratio, CO: H_2 (or H_2O)]	1.5	1.5	0.3833
Quantity of Synthesis Gas (m^3 at STP/hr)	1.3	2700	20
Linear Gas Velocity (cm/S)	3.5	9.5	3.5
Average Synthesis Temperature (K)	539	541	513-553
CO Conversion, %	90	91	92
CO + H_2 Conversion, %	88	89	—
Synthesis Products Based on CO + H_2 (g/m^3 at STP)			
C_1^+	176	178	182
$C_1 + C_3$	11	12	22
C_3^+	165	166	160
Space-Time Yield of C_3^+ Products (kg/m^3 of reaction chamber)	740	930	272

1. Hydrogenation of carbon monoxide, laboratory-scale model.

2. Hydrogenation of carbon monoxide, semi-industrial demonstration plant.

3. Steam and carbon monoxide synthesis, laboratory-scale model.

4. Feed gas composition: 7% CO_2, 34% CO, 2% H_2, and 57% N_2.

Table II

Correlations for Predicting Hydrodynamic Properties [4]

Liquid Phase	Molten Paraffin
Temperature	523–563 K
Pressure	400–1100 kPa
Gas Velocity	<4 cm/s
Solids Concentration	>5 weight percent

Gas Hold Up
$$\varepsilon_G = 0.053\ U_G^{1.1}$$
$$\varepsilon_G\ (1-\varepsilon_G)^{2.22} = U_G/U_t$$

Bubble Diameter, cm
$$d_b = 0.07$$

Gas-Liquid Interfacial area, cm^{-1}
$$a = 4.5\ U_G^{1.1}$$

Gas-Liquid Mass Transfer Coefficient, k_L
$$Sh = 0.0187(\beta Re^{\ 0.484} Sc^{0.339})^{1.61}$$
$$\beta = (d_b g^{1/3}/D_L^{2/3})^{0.072}$$
$$k_L Sc^{2/3} = 0.31\ (U_L \Delta\rho g / \rho_L^2)^{1/3}$$

Liquid-Solid Mass Transfer Coefficient k_s
$$Sh_s = 2$$

Liquid-Solid Interfacial area, cm^{-1}
$$a_s = \frac{6(1-\varepsilon_G)\rho_L}{d_s\ \rho_s}\ \bar{C}_s$$

Heat Transfer Coefficient, h
$$St = 0.1(Re\ Fr\ Pr^2)^{-1/4}$$

Axial Dispersion Coefficient for Liquid, cm^2/s
$$D_L = 2.7 U_G^{0.3}\ d_R^{1.4}$$

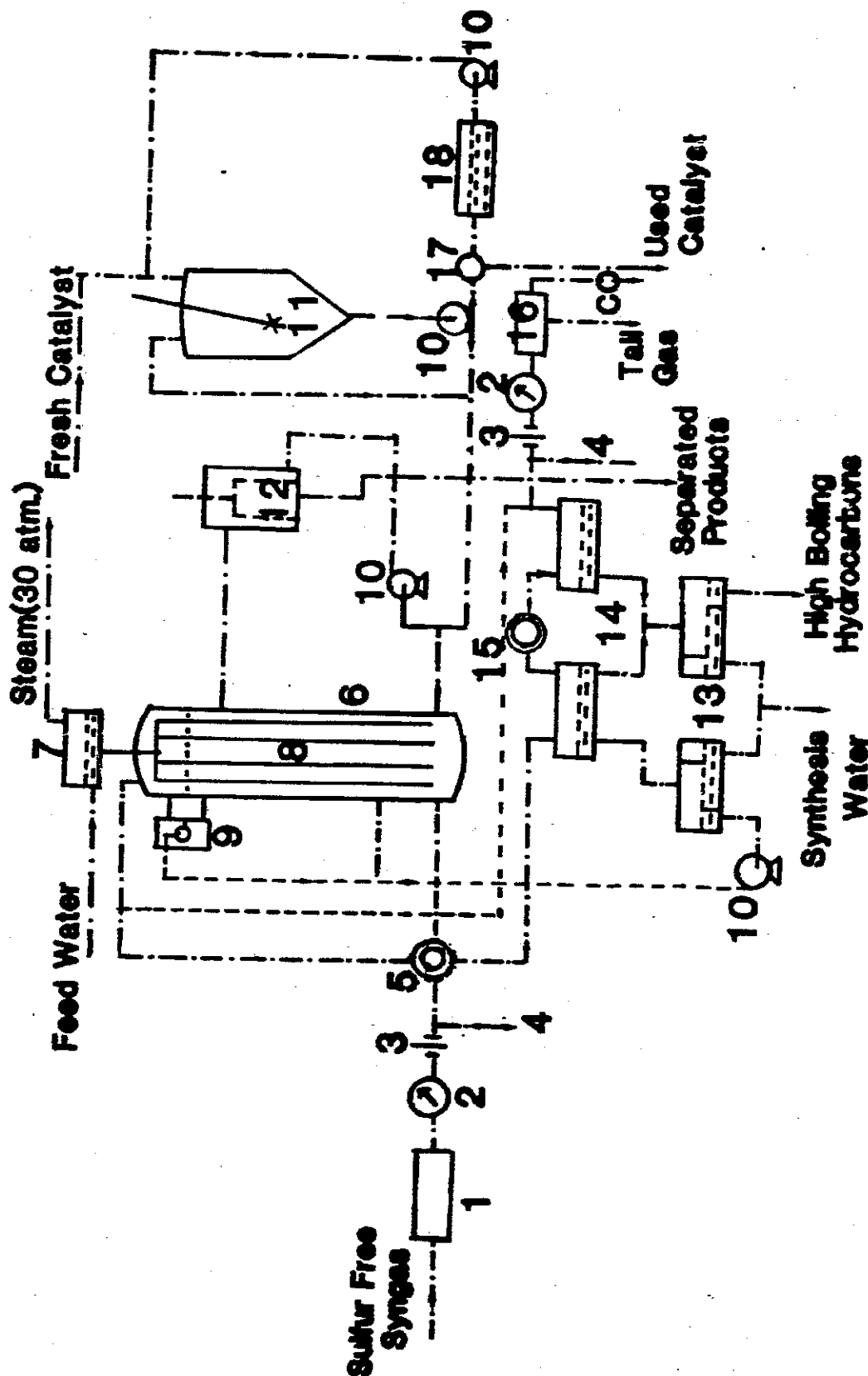Axial Dispersion Coefficient for Solids, cm^2/s/
$$D_s = D_L$$

Figure 1. Flow Diagram of the Liquid Phase Synthesis Semi-Industrial Demonstration Plant.

1: Compressor, 2: Gas Meter, 3: Orifice Meter, 4: Sampling Port, 5: Heat Exchanger, 6: Reactor, 7: Steam Collector,
8: Internal Heat Exchanger, 9: Level Controller, 10: Pumps, 11: Slurry Preparation Vessel, 12: Pressure Filter,
13: Separation Tanks, 14: Separators, 15: Water Cooled Condenser, 16: Scrubber for CO Removal, 17: Centrifuge,
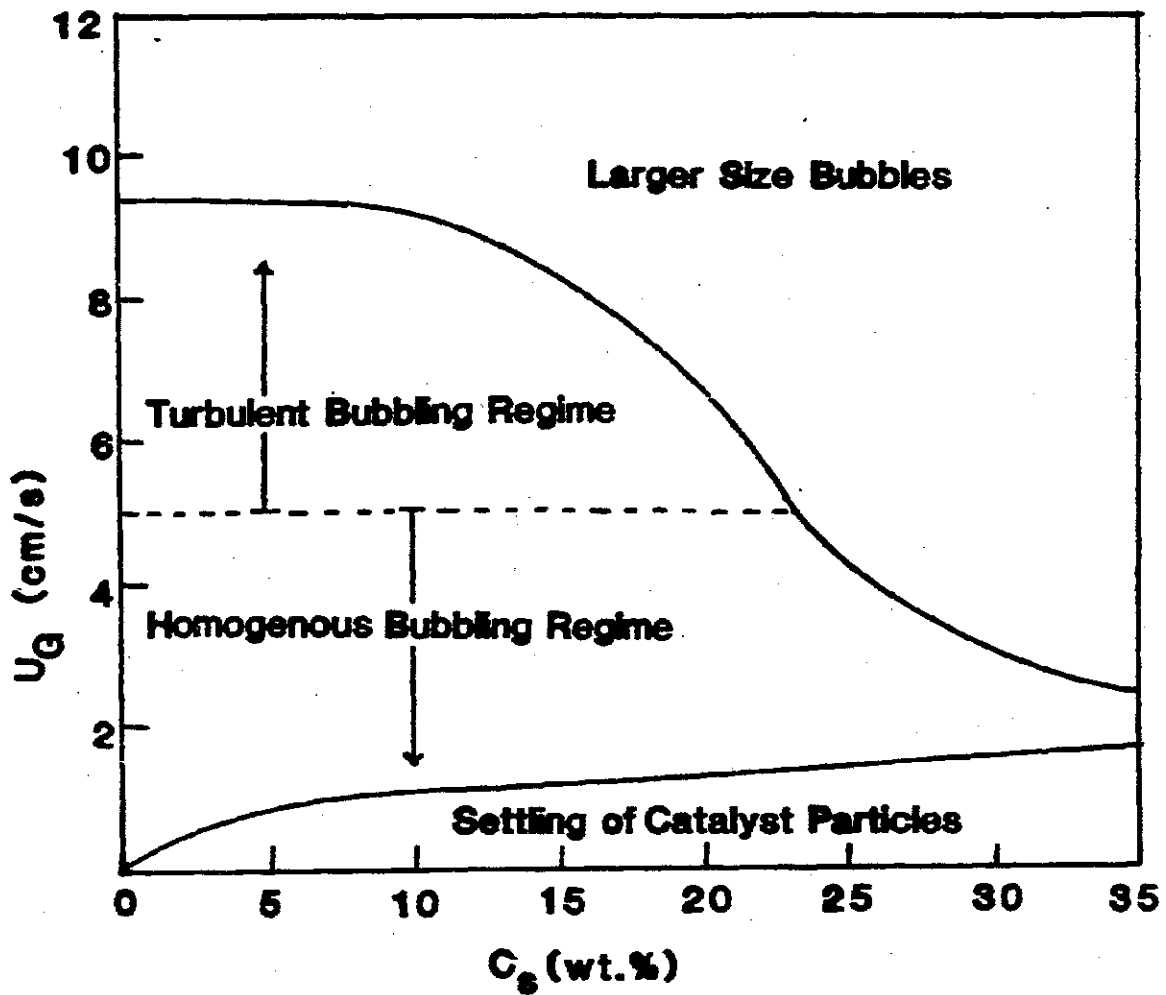and 18: Storage Tank.

Figure 2. Various Operational Regimes in a Three-Phase Slurry Column,
Kolbel and Ralek [4].

The Recent German Effort

The above discussed German technology was quite successful as judged by the fact that in Germany in 1944, nine F-T plants produced an estimated products of 560,000 ton/year [13]. The direct liquefaction technology, however, was more in use than the indirect liquefaction F-T technology with a production capacity which was about six times larger. The world wide production based on F-T technology was 1·1 million ton/year only. In fact after World War II, the economics of F-T process was found to be more unfavorable as abundant sources of cheap oil became available and the operating plants were closed. However, Deckwer and his coworkers have in recent years worked on bench-scale units to understand the process details and in the following a brief description of these efforts is summarized which got their boost from the energy crisis of the early seventies.

Zaidi et al. [14] operated a small bench-scale unit to investigate the mass transfer resistance in a slurry bubble column and its dependence on reaction rate which was varied by employing different amounts of catalyst in the liquid phase. For this purpose a column 2.09 m high and 4.14 cm in diameter with a metal sintered distributor plate having mean pore size 60 to 90 μm was used, Figure 3. As synthesis gas, mixtures of N_2, H_2 and CO from gas cylinders were adequately purified, metered and mixed with excess of water vapor, heated to the reactor temperature and then fed into the column. Excess of water vapor was used to ensure that the reaction was of a pseudo-first order with respect to CO and to suppress the Boudouard reaction. The latter was accomplished as the outlet gases were found to contain equal mole fractions of CO_2 and H_2. Infra-red gas analyzers and gas chromatographs were
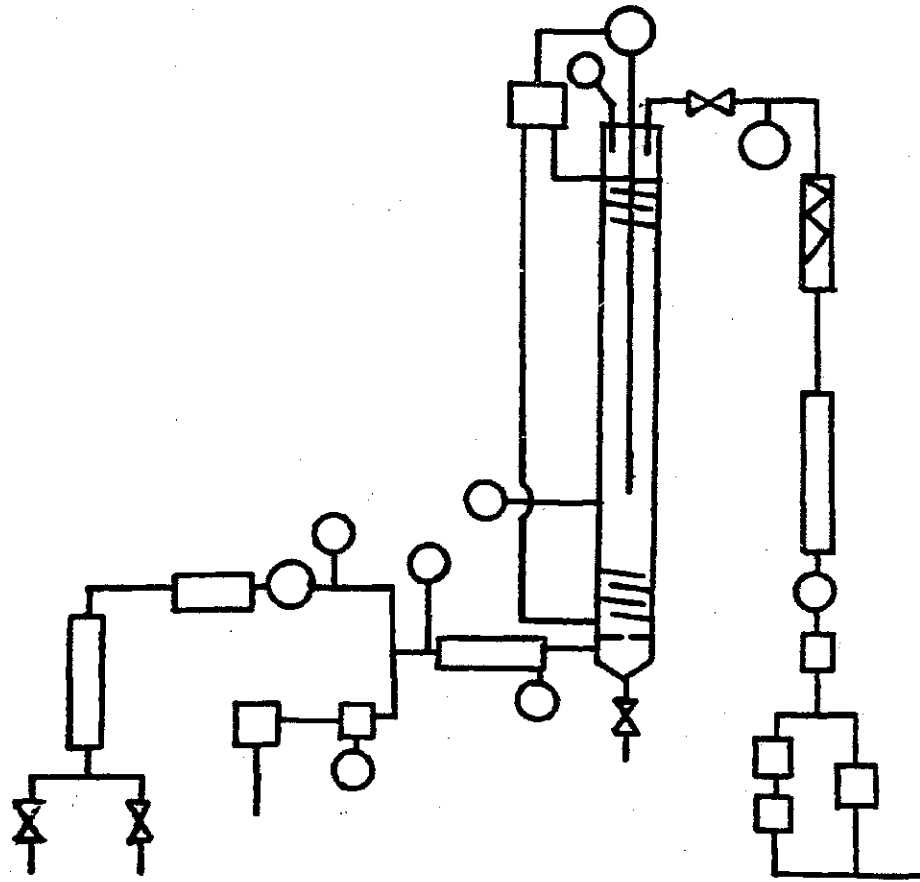
Figure 3.   Bubble Column Arrangement of Zaidi et al. [14].

used for establishing the gas analysis.

As slurry a mixture of wax with a melting point in the range 353-383K and a low temperature conversion catalyst (Girdler 66B) were used. Solid content in most of the work was about 70 g but in a few runs its amount was increased to about 100 g. The amount of wax used in all the experiments was fixed and was about 600 g of molten paraffin. The constant hydrodynamic conditions were ensured by keeping the solids concentration at a constant value. When the catalyst amount was changed, inert Al_2O_3 was added. The activated catalyst was ground in kogasin under nitrogen, and kogasin was removed by evaporation after the slurry was introduced in the column. The diameter of the catalyst particles was estimated as about 1 μm by microscopic analysis.

The gas hold-up of the slurry was established in a series of independent runs by means of a heat conductivity probe which was introduced in the column from the top and its position could be varied during the course of measurements. The experiments were conducted for a range of operating conditions and these are listed in Table III. The reaction rate in the liquid phase was varied by changing the amount of catalyst. The measurements involved determining the fractional conversion for a given catalyst concentration over the entire gas flow rate and at the lowest temperature of 523 K. The temperature was then raised and the entire series of measurements were repeated. For the computation of mass transfer coefficients only about 100 experiments were employed in which the inert gas (nitrogen) balance agreed on the average to within 2% and the overall balance to within 0.6%. Within a series of runs at the same temperature no fall in catalyst activity was found. On the other hand, a measureable loss of activity was found if the slurry used at a higher

temperature was re-used at a lower temperature. A discussion of their results and general conclusions drawn are reported below.

At a given temperature and pressure, the fractional conversion of carbon monoxide increased with catalyst concentration in the slurry and decreased with increasing gas velocity. From measurements as a function of temperature, it was found that the apparent activation energy decreased with concentration first rapidly and then slowly, the absolute values being dependent on the superficial gas velocity. At low catalyst concentration the activation energy was between 50 and 150 kJ/mol, and it decreased to lower values of < 20 kJ/mol at high catalyst concentration. It was inferred that at high catalyst loading the conversion rate in the slurry column became very fast and mass transfer was the rate determining step.

Based on the experimental measurements of the rate of fractional conversion for different concentrations of carbon monoxide in the feed gas it was inferred that the conversion rate was linearly dependent on the partial pressure of carbon monoxide in the feed gas. It was thus inferred that the conversion reaction rate is of first order with respect to carbon monoxide concentration. The reciprocal of the calculated $k_o a$ values at a fixed value of temperature, pressure and gas velocity were found to vary linearly with the reciprocal of catalyst concentration. Here $k_o a$ was the overall mass transfer coefficient and a was the gas/liquid interfacial area per unit volume of slurry. The rate constants computed from the slopes of these linear plots did not exhibit the expected temperature dependence and it was explained that catalyst deactivation and particle agglomeration may be responsible for this. From the intercepts of these linear plots on the ordinates, $k_L a$ values were computed, k_L being the liquid-phase mass transfer coefficient. The $k_L a$ values

computed as a function of gas velocity exhibited considerable scatter
and the values ranged between 0.08 to 0.2 s^{-1} for gas velocities between 1
to 4 cm/s .

The $\underline{a}$ values were computed from the independent measurements of gas
hold-up and estimated Sauter mean diameter of bubbles. The latter
were determined from photographs of sim lated dispersions of carbon monoxide
in molten paraffin at atmospheric pressure in a glass bubble column of
similar size as used in the reactive system. The Sauter mean diameter of the
bubbles was not found to be significantly affected by gas velocity as long as
it was less than 4 cm/s and was about 0.7 mm . Assuming that the bubble diameter
was independent of pressure and solids concentration in the bubble column, the
$\underline{a}$ values were computed from the following relation:

$$\underline{a} = 6 \, \varepsilon_G / d_s \ . \tag{1}$$

Here ε_G and d_s are the gas hold-up and Sauter mean diameter respectively. It
was pointed out that this procedure yielded only the geometric interfacial
area which corresponded to its maximum limiting value and did not necessarily
gave the area effective for mass transfer. Consequently it was inferred that
these k_L values represent only the minimum possible values for the liquid-
phase mass transfer coefficient. The temperature average k_L values were
found to vary within a rather narrow range of 0.01 to 0.02 cm/s for the CO/para-
ffin system valid for a wide range of physical and chemical systems and
different operating conditions.

Deckwer et al. [15] undertook a somewhat similar investigation with the
major aim to improve the selectivity with regard to C_2 to C_4 olefins. These
lower olefins were intended for use as chemical feed stock. The measure-
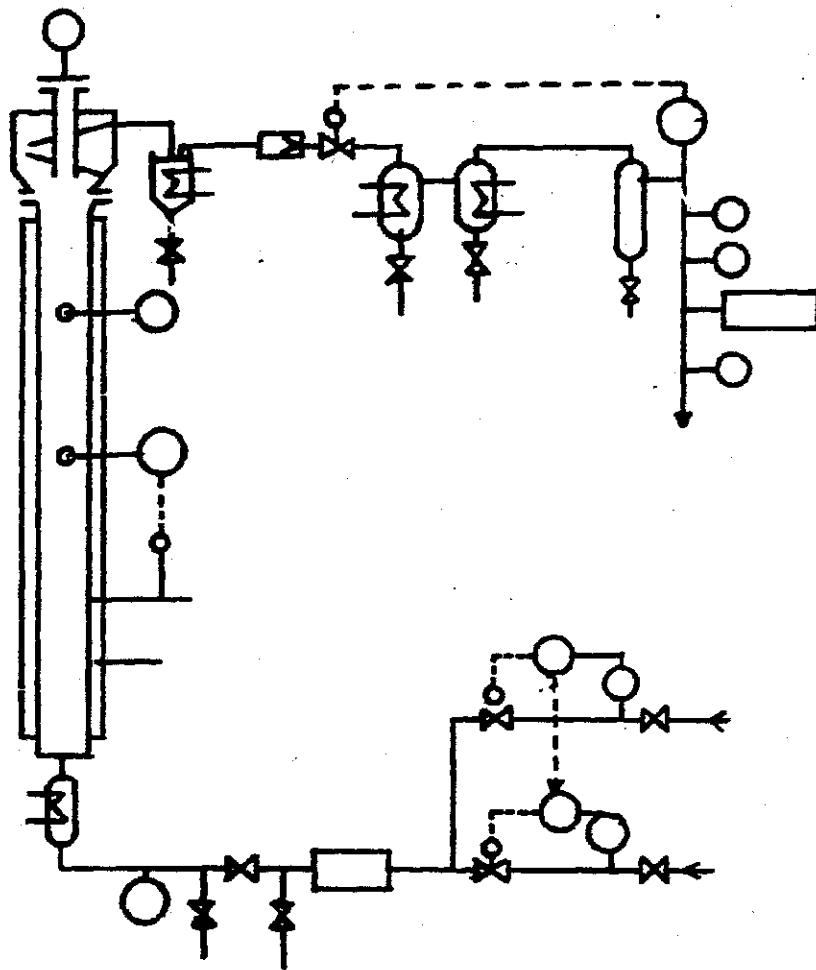ments were carried out in a stainless steel bubble column 3.8 cm internal

Figure 4. Schematic Arrangement of the Experimental Setup of Deckwer et al. [15].

diameter and a height of 2 m, the suspension height being 60 to 100 cm. Figure 4. The feed gas consisting of a mixture of hydrogen, nitrogen and carbon monoxide after proper control, metering, purification and heating was sparged by a metallic porous plate with 75 to 100 μm mean pore diameter into the liquid phase of a molten wax of melting point 363K and containing specially prepared Fe/Mn catalyst. The tail gas was passed through a baffled disengagement volume to prevent entrainment of the liquid phase. The liquid hydrocarbons were separated by cooling after pressure reduction.

Catalyst preparation procedure was developed so that reproducible catalysts could be obtained and further, the composition of the catalyst and the conditions of its precipitation and activation were optimized with regard to high selectivities of C_2 to C_4 olefins. The precipitator consisted of a glass tube 24 mm internal diameter and 500 mm high containing a stirrer shaft to which 12 mm square blades were fixed 12 mm apart. The residence time distribution corresponded to a cascade of about ten vessels. The preheated solutions of the metal nitrates and the preheated ammonia solution were introduced at the bottom and precipitation was carried out at a temperature of about 368K, and a stirrer speed of 800 rpm. The concentration of the solution was so chosen that the viscosity of the precipitate slurry was not too high. An optimum pH of 7 was found at which the precipitation of the metal hydroxides easily took place and the formation of manganese-ammonia complexes was avoided. The precipitate, Fe_2O_3/Mn_2O_3 was dried at 403K under vacuum for twenty four hours. It was next ground in a mortar to particles smaller than 50 μm. The majority of the particles had a diameter in the range of 10 μm. The activation of the catalyst was accomplished in the slurry bubble column, where 64G of the catalyst was suspended in the wax

at 403 K. The suspension was introduced into the preheated reactor at 423 K with nitrogen flowing at a rate of 50 N ℓ/h at 250 kPa. This was followed by CO treatment and reduction with hydrogen at the same temperature, pressure and flow rate for twenty-four hours in both cases. This treatment brought the catalyst in active form and the synthesis runs were started. The catalyst, denoted as Mn/Fe, catalyst did not contain Fe and Mn in the metallic state The catalytic phase was a mixture of Fe compounds (magnetite, carbides) and MnO.

The conversion measurements were conducted at 1.2 MPa, and such variables as temperature, CO/H_2 inlet ratio, and temperature were varied from run to run as shown in Table IV. When the space velocity or the feed ratio was changed, it took two hours to attain steady state, while an increase in temperature by 5 K took about 5 h. The space velocity was defined as the volume of gas per catalyst volume and hour. Experimental results revealed that in conformity with general expectations, the conversion decreased with increasing space velocity at a specified temperature and CO/H_2 ratio. The variation of gas conversion with space velocity at a specific temperature yielded somewhat unexpected results when CO/H_2 ratio was changed from 0.73 to 2.29. When the synthesis gas is rich in hydrogen, CO/H_2 = 0.73, the attainable conversion was remarkably small and the authors [15] found it hard to explain and have suggested additional experimental work. No systematic trend could be inferred from the measurements as regards the dependence of conversion on space velocity was concerned for varying values of CO/H_2 ratio.

The selectivities or yields were studied in greater detail as various parameters were varied in this work. The yields were expressed as grams of

hydrocarbons obtained per Nm^3 synthesis gas converted. The yields of $C_2 - C_4$ for a CO to H_2 inlet ratio, I, of 1.65 and at three different temperatures in the range 555-571 K have been reported as a function of space velocity, SV, in the range 200 to 1200 h^{-1}. In this temperature range and for these experimental conditions the effect of temperature was found to be negligible. The overall amount of $C_2 - C_4$ comprising all hydrocarbons was found to be independent of space velocity. However, the yield of olefins $C_2 - C_4$ only increased with SV till 600 h^{-1} and thereafter it also remained constant for further increases in SV up to SV = 1200 h^{-1}. For the same measurements the yields of CH_4 and C_5+ hydrocarbons were not affected by the temperature and space velocity at all. At a temperature of 576 K, the experiments were performed for four different values of I in the range 0.73 to 2.27. For I $\geq$ 1.35, similar results as for I = 1.65 were obtained, but for hydrogen rich synthesis gas (I = 0.73), the product slate was found to be very different. The yield of C_2 to C_4 all hydrocarbons was about the same and in the same range but its olefin content was drastically reduced, by about a factor of two. The CH_4 and C_{5+} yields were found to depend only slightly on space velocity in the range 300 - 1600 h^{-1} and for 1.35 $\leq$ I $\leq$ 2.27. When the inlet ratio (I) was reduced to 0.73, the CH_4 fraction increased by a factor of three and C_{5+} fraction decreased to very low values.

The important variable CO to H_2 usage ratio, U, defined as moles of CO converted per mole of H_2 consumed was also investigated as a function of inlet ratio, I. It was found that for this particular catalyst, the usage ratio was about equal to the inlet ratio when CO to H_2 ratio was close to 1.5. In CO rich gases (I > 2), the hydrogen conversion was considerably larger than the CO conversion while

ratios such as I = 0.73. For I close to 1.5, it was inferred that water gas

shift reaction yielded the required amount of H_2 to make $I = U$. The usage ratio was found to depend only slightly on temperature and the observed variation was attributed to changes in space velocities.

These authors also attempted to analyse the product distribution and found it in somewhat accord with the most probable distribution of Schulz and Flory further substantiated by Anderson et al. [16] based on a polymerization type reaction mechanism. This distribution is given by

$$x_i = i \ P^{i-1} \ (1-P)^2 \ , \tag{2}$$

where x_i is the weight fraction of hydrocarbons with carbon number i, i is the number of carbon atoms present, and P is the chain growth probability. According to this relation a plot of $\ln(x_i/i)$ versus $(i-1)$ will be linear with a slope equal to $\ln P$ and intercept on the Y-axis as $2 \ln (1-P)$. They analysed their data obtained up to C_{13} and found the data to lie along a straight line except for C_2 and C_3 fractions which deviated in opposite directions from the values based on linear plot. Further, from the regression analysis of the data, they found the chain growth probability P as 0.675. This value agreed well with the P values reported by Satterfield and Huff [17] in the range of 0.67 to 0.71 for data obtained on F-T synthesis in the slurry phase on a fused iron catalyst. These authors review the reasons for the departure of C_2 and C_3 fractions from those given by Schulz-Flory distribution and their most probable reasons. We do not present these and similar other details which lie beyond the scope of our present report. In passing we may mention a comprehensive effort of Deckwer et al. [18] which concentrates heavily on the hydrodynamic and thermal behavior of slurry columns relevant to understanding the transport processes occurring in such units.

TABLE III [14]

Experimental Operating Variables and Their Ranges

Feed Gas Composition	$0.2 \leq X_{CO} \leq 0.23$
	$0.7 \leq X_{H_2O} \leq 0.74$
	Remainder Nitrogen
Gas Velocity, cm/s	$0.7 \leq U_G \leq 3.8$
Catalyst Concentration, wt%	$1.5 \leq C_{cat} \leq 10.45$ (14.28*)
Pressure, kPa	900
Temperature, K	523, 543, 563

* Value for a few experimental runs

TABLE IV [15]

Operating Conditions of Synthesis Runs

Pressure = 1.2MPa

Run No.	T,K	$(CO/H_2)_I$	SV, h^{-1}
1-7	555	1.63-1.69	430-875
8-13	561	1.85	363-710
14-24	566	1.61	258-1150
25-32	571	1.68	258-1180
33-41	576	1.73	340-1650
42-49	576	1.35	237-1620
50-59	576	2.25-2.29	340-1010
60-69	576	0.73	335-1240