The Indian Effort

The work conducted at the Indian Institute of Technology, Kharagpur, [33] paid special attention to ensuring that the slurry is uniform throughout the reactor volume implying that solid catalyst particles were uniformly dispersed in the liquid phase. If it was not so, uniform bubbling was not accomplished, heat transfer rate between the cooling tubes and slurry was low, conversion of synthesis gas to desired products was reduced, and the catalyst activity was diminished. The activity was defined as the liters of (CO_2 + H_2) converted per hour per 100 g of the catalyst. This uniform bubbling was accomplished by the incorporation of an ejector as a pump for agitation and recirculation of slurry in the recator design. The dimensions of the ejector pump were optimized in a separate model apparatus with air-air, air-liquid, and air-liquid-solid systems. The slurry reactor system for the F-T synthesis comprising of the following four major components: (i) cylindrical reactor with slurry recycle line and an external Dowtherm heating arrangement, (ii) conical header for the separation of gas and slurry, (iii) an ejector pump assembly, and (iv) a slurry storage vessel, is shown in Figure 9 and is described here briefly.

The mild steel cylindrical reactor tube 1, 5.08 cm in diameter and 304.8 cm high, was fitted at the bottom end to the divergent section of the ejector, 2, via a flange joint. The top end of the reactor was flanged into the header, 3. The use of these flange joints enabled easy replacement and installation of reactors of varing heights, 2.13 or 3.05 m. Three thermo-couples, T_1, T_2, and T_3, were provided to monitor the reactor temperature. The reactor was jacketed with a 12.7 cm internal diameter tube, 4, communicating with a Dowtherm boiler, 5, 20.32 cm in diameter and 60.96 cm high. The latter was provided with cooling coils, 6, made of 6.35 mm standard mild steel tubings, and with a level gauge 7.

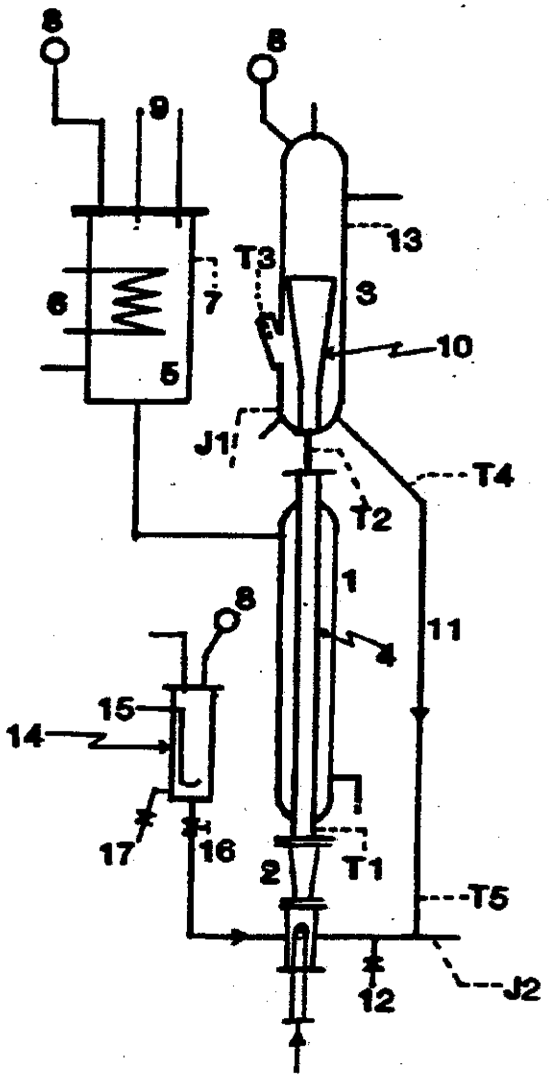

Figure 9. The Slurry Bubble Column and Associated Units of Mitra and Roy [33]. 1: Reactor Tube, 2: Ejector, 3: Header, 4: Reactor Jacket, 5: Dowtherm Boiler, 6: Cooling Coils, 7: Level Gauge, 8: Pressure Gauge, 9: Valve, 10: Perforated Funnel, 11: Slurry Recycle Line, 12: Sampling Valve, 13: Level Indicator, 14: Slurry Storage Vessel, 15: Nitrogen Bubbler, 16: One-Way Valve, 17: Sampling Valves, T_1, T_2, T_3, T_4, T_5: Thermocouples, and J_1, J_2: Jets.

The pressure gauge, 8, and valves, 9, were installed at the top plate of the flange.

The header, 3, 15.24 cm in diameter and 76.0 cm high, was provided with a perforated funnel, 10. A slurry recycle line, 11, connects the hemispherical shaped bottom of the header to the reactor through the ejector assembly. To overcome any catalyst settling problems, two jets J_1 and J_2 were provided which could sweep away any catalyst deposit either from the bottom of the header or directly from the slurry recycle line. The slurry recycle line was provided with an outlet valve, 12, to sample the slurry during the course of operation. Thermocouples T_4 and T_5 measured the temperatures of slurry in the line. The header was equipped with a pressure gauge, 8, a safety valve, a pressure release valve, and a level indicator, 13.

The ejector assembly, 2, consisted of a spherical duct of 6.35 cm diameter communicating into a parallel mixing length having the dimensions of 2.06 cm diameter and 12.7 cm long with a well rounded entrance, a 24.13 cm long divergent tail piece with a 10 degrees divergence angle and a nozzle of 1.4 mm diameter aligned with diffuser axis. The storage vessel, 14, for slurry, 10.16 cm in diameter and 60.96 cm in height, was equipped with a tube, 15, for bubbling nitrogen to keep slurry in suspension. It communicated with the ejector by means of a 2.54 cm standard mild steel pipe with a one-way valve, 16, in the line. A valve, 17, enabled the sampling of the slurry. The top flange plate of the storage tank was fitted with a pressure gauge and a pressure release valve.

The synthesis gas used in these investigations was obtained by the gasification of coke in a standard gas generator. Its percentage composition was: 5.6 CO_2, 0.8 O_2, 37.6 CO, 50.0 H_2, 0.0 CH_4, and 6.0 N_2. It corresponded to CO to H_2 ratio of 0.75. A number of inert and injurious impurities such as dust, tar, gum-formers, hydrogen sulfide, organic sulfur etc. were contained in the raw water-gas. It was therefore subjected to an elaborate purification process to bring down the dust and gum-formers to 1 grain per 2832 ℓ of gas and to remove the other impurities. Hydrogen Sulfide was removed by reaction with moist ferric oxide, organic sulfur compound particularly thiophene was removed by adsorption over activated carbon, and any residual organic sulfur was removed by passing the hot gas at 553K through a granular iron-oxide tower.

The reaction products left the reactor at the top and passed through a trap where heavy oils were collected. The pressure of the effluent stream was reduced to atmospheric pressure by a regulating valve and was then cooled to ice temperature when most of the products were condensed. Next the water vapor was removed by passing the gas stream through a $CaCl_2$ tower. Volatile hydrocarbons and residual oxygenated compounds were condensed in traps maintained at dry-ice acetone temperature, 193K. Lastly, the tail gas was metered and stored in a gas holder. At the steady state for a particular operating condition, the liquid products were collected for a period of fortyeight hours. The tail gas samples were periodically collected and analysed. After the operation it was found that the high boiling oil medium used for slurry preparation had turned into wax due to the continous formation of high boiling products during synthesis.

The performance of the reactor was found highly satisfactory with respect to slurry agitation, slurry circulation through the side tubes, removal of products and temperature control. The maximum temperature difference between the top and bottom of the reactor was always less than 1 K. No settling of the catalyst particles was observed. The replacement of spent catalyst with fresh catalyst could be easily accomplished.

Following the initial exploratory investigations in a 213.4 cm tall reactor, a 304.8 cm reactor was used in most of the measurements. The reactor was charged with slurry containing 16 to 18 percent by weight of catalyst. The synthesis reaction was carried out at presures of 100, 125, and 150 psig at 513, 523, and 533 K using space velocities of 100 and 150 vol. of gas/vol. of suspension hr. A precipitated iron support catalyst of the following composition was used: Fe: Cu: MgO: CaO: diatomaceous earth as 100: 10: 4: 3·5: 50. Some of the important results of these investigations are summarized below.

It was found that the increase in pressure increased the concentration of the reactants in the liquid medium by increasing their solubilities, and also enhanced the formation of larger molecules and both the factors favored greater conversion. The experiments revealed that at a given pressure, the CO and $CO + H_2$ conversion increased with temperature. This was explained by the fact that increase in temperature increased both the reaction rate as well as the concentration of reactants. The catalyst activity or conversion of $CO + H_2$ increased with increase in space velocity. This was explanined by the fact that at a higher space velocity the gas bubbles and the catalyst particles come closer at a greater frequency. Conversion of reactants CO and H_2 involves their transport by solution and diffusion through the liquid medium from gas bubbles to the catalyst surface. Reaction on the surface will produce concentration gradient which will promote diffusion. The usage ratio was approximately constant in this temperature range but increased with increase in pressure. A maximum CO conversion of 94 percent per pass was achieved with a specific yield of 174 g of liquid products $/m^3$ of $(CO + H_2)$ feed. The yield of methane was low and varied from 1.5 to 6 g $/m^3$ of $(CO + H_2)$

feed. The authors also found that the activity and selectivity of precipitated catalyst was much higher than that of the sintered catalyst and this was explained on the basis of much larger internal surface area per unit volume of the catalyst of the former as compared to the latter.

THE JAPANESE EFFORT

The motivation of this effort was to find a useful application for the converter furnace gases which were produced from steel manufacturing plants as a side product. This gas contained a high percentage of carbon monoxide and a typical volume composition was: $CO - 72.9\%$, $CO_2 - 18.3\%$, $N_2 - 7.2\%$, $H_2 - 1.3\%$ and $O_2 - 0.3\%$. Its heating value was estimated as 3,250 $kcal/Nm^3$. The aim was to develop the slurry bubble column technology using the converter furnace gases to produce straight chain high molecular weight olefins and high melting point waxes. A comprehensive well organized effort was initiated in 1961 at the Kogyo Kaihatsi Research Laboratory with the support of Yaiwata Steel and Fuji Steel, and technical cooperation of Professor Kolbel. In parallel with this developmental study, a basic research program was conducted for over five years at the Faculty of Engineering, Tokyo University to understand the principles behind the chemical reactions, catalysis and product pattern control. A brief description of these investigations was reported by Sakai and Kunugi[34] and is described in what follows.

A distinct advantage of the F-T synthesis method was felt over the socalled Bergius coal liquefaction method which produced oils rich in aromatic compounds while former method yielded almost all straight chain aliphatic hydrocarbons. A further incentive for developing the F-T process was in recognition of the advancements being made in the underground coal gasification technology.

The basic research related to the process was conducted in a small size cylindrical slurry reactor having an inside diameter of 37 mm and a height of 1 m, while the development work was performed in a cylindrical reactor of 50 mm inside diameter and a height of 6 m, and was called as

"Franz reaktor". The flow sheet of the large slurry column reaction system is shown in Figure 10. The catalysts used in the slurry column were prepared by the sedimentation method having a composition of Fe, Cu and K_2CO_3 in the proportion by weight as 100, 0.3 and 0.6 to 1.2 respectively. The catalyst with a high alkaline content was found to gave high activity at low temperature and was used to produce high melting point wax. Copper which was present in only very small quantities, was believed to catalyse the oxidation-reduction of the catalyst and it suppressed the formation of carbide. The iron catalyst was mixed with the F-T synthetic oil to produce a suspension liquid and had an average diameter of 1 mm and a concentration of about 10% in Fe. The slurry in the column reactor was preheated to 543-573K while nitrogen was bubbled from the bottom. Nitrogen was switched to synthetic gas and the reduction reaction was started. After the reduction was completed, the temperature was lowered to 503-533 K and the F-T synthesis reaction was initiated. The system pressure was maintained at 10-20 kg/cm^2.

The feed gas consisted of a mixture of CO and H_2. The carbon monoxide was obtained from a gas generator, 3, and was mixed with hydrogen from a storage vessel, 2, in the desired proportion varying from 0.5 to 2.0. The feed gas was then passed through a gas trap,4, and was metered using a wet flow meter,6, before being compressed to the desired level of pressure by compressor,5. The impurities in the feed gas stream were removed by passing it successively through columns of silica gel, 10, and active charcoal,9, before being stored in a storage vessel,7. The gas from the pressurized storage vesel,7, was utilized as desired. The withdrawn gas was passed through a strainer,13, and the pressure corresponding to the desired inlet conditions was adjusted using the pressure control valves, 11, and was then metered by a rotameter,8. This metered flow of feed gas was then preheated in the preheater, 12, before being fed at the bottom of the reactor, 14. The reactor consisted of two coaxial cylindrical tubes, the inner being the reaction vessel and the outer annulus for cooling the reactor. The reactor was provided with several outlet ports along its length to facilitate withdrawl of the slurry samples. The slurry charged into the reactor was stored separately, 18, and was fed into the reactor with the help of a slurry pump, 17. The exit gases from the reactor were not recycled, and the slurry level inside the column was maintained constant by either removing the excess liquid products formed or by pumping more slurry from the storage tank, 18. The exit gases were then passed through the separator, 15, where most of the condensation products were collected. The remaining uncondensed gases were vented after they were metered by the wet gas flow meter, 16.

The products of synthesis were classified as gas, high quality oil, and heavy oil. All these heavy quality oils remained in the liquid form and as a result the volume of slurry in the reactor increased with time. The catalyst was separated from the overflowing slurry from the column and was returned to the reactor. The authors have reported the chromatograms of the product gas, light and heavy oils. Table VII lists the results of the catalyst activity, yields and products distribution as a function of time. During this time, the sampling of the heavy oil was done as catalyst slurry and therefore the concentration of iron in the catalyst slurry decreased with the passage of time while the catalyst activity was approximately constant. The reason for the apparent change in the distribution of carbon numbers in hydrocarbons was that initially the slurry was prepared from a commericially obtained Gatsch fraction of paraffin mixture which was slowly replaced by the synthesized oil in a period of about 100 hours. In the last sample of Table VII, the Gatsch was considered to have been completely replaced by synthesis oil. The distribution of hydrocarbon products up to C_{18} remained almost constant while the fractions C_{19-27}, and C_{28} and over showed a large variation with time. The authors have also conducted separate experiments in small size slurry columns with a view to compare their results with those obtained in fixed beds using the same catalyst. These workers found that the catalyst activity while deteriorated sharply in the fixed-bed reactors it remained constant in the slurry column. This was explained by the fact that the metallic catalyst carbonized in the fixed bed configuration as the synthesis reaction started and the catalyst activity continuously decreased. An uncarbonized catalyst promotes the C-C bond rather than the hydrogenation reaction. Hence the higher molecular weight and olefin rich hydrocarbons were produced in the slurry column. The constancy of the catalyst activity in the slurry column was explained on the basis of maintenance of the metal state of the catalyst. The over-all activation energy was estimated to be 18.9 kcal/mole in the fixed-bed method and 5-7 kcal/mole in the slurry method. The differences in the catalyst activities and selectivities of the products in the two methods were attributed to the difference in the activation energies of the two methods. It was mentioned that the metallic state of the catalyst was the reason why the slurry column method produced products with a larger number of carbons and which were relatively rich in olefins.

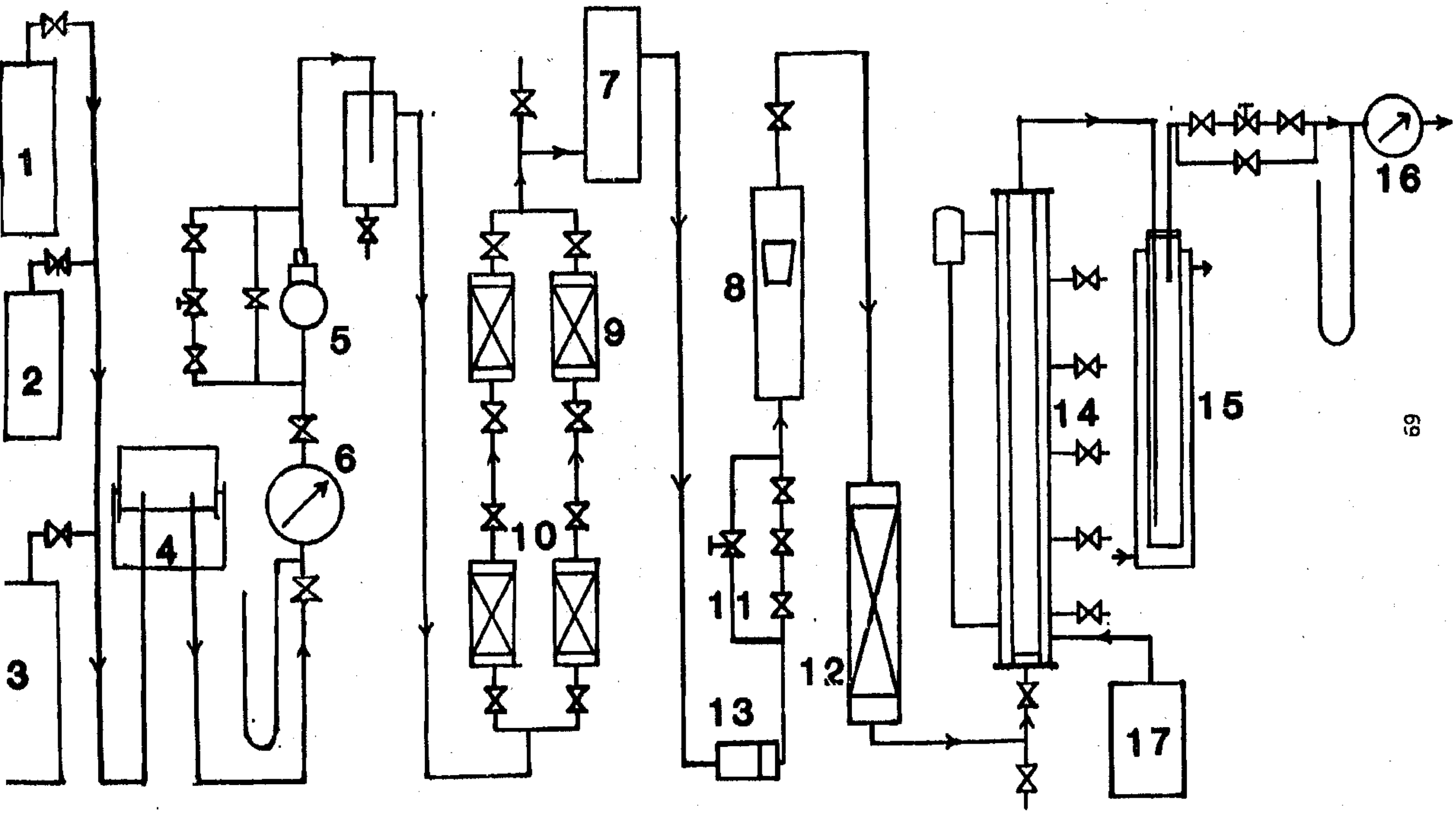

Figure 10. The Slurry Bubble Column Arrangement of Sakai and Kunugi [28]. 1: Nitrogen Tank, 2: Hydrogen Tank, 3: Gas Tank, 4: Gas Trap, 5: Compressor, 6: Wet Flow Meter, 7: Feed Gas Tank, 8: Rotameter, 9: Gas Purification Columns Using Active Charcoal, 10: Gas Purification Columns Using Silica Gel, 11: Pressure Control Valves, 12: Preheater, 13: Strainer, 14: Reactor, 15: Separator, 16: Wet Flow Meter, and 17: Slurry Storage Tank.

TABLE VII [34]

Some Pertinent Results of the Slurry Column Operation

Synthesis Reaction Elapsed Time, h	17.9	36.3	67.7	98.3
CO/H_2 Mole Ratio	1.7	1.9	1.7	1.9
Temperature, K	534	529	539	543
Pressure (gauge) kPa	9.8	10.6	10.1	10.6
Fe Catalyst in Slurry, Wt. %	7.3	4.9	3.2	2.6
Gas Flow Rate, ℓ/h at NTP	1,500	1,520	1,500	1,490
Amount of Catalyst, Nℓ/gFe/hr	4.18	6.37	10.0	12.7
CO Conversion Rate, %	96.5	89.9	80.0	78.5
Yield of Gaseous Products, g/Nm^3 of $(CO + H_2)$	14.0	14.6	16.5	18.6
Yield of Light Liquid Product g/Nm^3 of $(CO + H_2)$	20.2	20.0	31.6	37.3
Yield of Heavy Liquid Product g/Nm^3 of $(CO + H_2)$	111.4	146.2	98.6	99.2
Distribution of Products, wt %				
C1	2.9	2.3	-	2.7
C2	4.3	3.4	-	2.6
C3 - C4	7.0	5.8	-	5.1
C5 - C9	4.7	4.1	-	4.3
C10 - C18	16.0	11.1	-	12.1
C19 - C27	50.8	42.8	-	5.2
C28 and over	12.7	28.7	-	62.7
Oxygen Containing Compounds				
Carbonic Acid	0.2	0.1	-	1.4
Alcohol	0.6	0.6	-	1.5
Ester	0.3	0.5	-	1.7
Carbonyl Compound	0.5	0.6	-	1.7

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