2. INTRODUCTION

Three broad principles of combustion, gasification and liquefaction are generally employed to generate desired sources of energy from coal. Liquefaction methods are classified in three categories of pyrolysis, direct liquefaction and indirect liquefaction [1]. In pyrolysis, coal is converted in a non-oxidizing environment by the application of heat to gases, liquids and solid char. Liquid yields can be enhanced in a hydrogen environment by the proper selection of operating conditions and solid char is the major product. In direct liquefation, coal reacts at an elevated temperature and pressure with gaseous hydrogen and a hydrogen- donor solvent with or without the presence of a catalyst. The principal products are high molecular mass fuels, distillate fuel oils, gasoline or chemical feed- stocks. In indirect liquefaction, coal is gasified at a high temperature in the presence of oxygen and steam to produce a raw mixture of carbon monoxide and hydrogen known as synthesis gas or syn gas. After purification, the clean syn gas is catalytically converted to a wide range of products, such as hydrocarbons, alcohols, aldehydes ketones and acids. The Fischer- Tropsch Synthesis is the name given to the commercial process involving the conversion of coal into Substitute Natural Gas (SNG), gasoline, diesel oil, wax and alcohols.

The products of both direct and indirect liquefaction processes have a higher energy content than coal which typically contains 60 weight percent of the heating value of the liquefied products [1]. The total efficiecy of the direct liquefaction process is improved to over 60 percent. However, the chemical composition of the liquid products produced in the two methods are very different. The products of direct liquefaction are highly aromatic such as high-octane gasoline and excellent feedstock for aromatic chemicals. On the other hand, the indirect liquefaction provides saturated hydrocarbon liquids such as high quality diesel fuel and intermediates for olefin production [1]. Indirect liquefaction is considered as being more flexible than direct liquefaction as regards to the types of coal that can be used and the end products that can be produced

A variant of the Fischer - Tropsch Synthesis is the production of methanol in high yields [1, 2], approaching 100 percent unlike the hydrocarbon synthesis [1]. Methanol is suitable for direct use as a turbine and transport fuel, although its energy content on a volume basis is only half that of gasoline [1]. It can also be used as a feedstock to produce high octane gasoline by employing the Mobil Methanol- to - Gasoline (MTG) process which uses a highly shape selective, synthetic zeolite ZSM - 5 catalysts [3-5]. The Technology of Liquid Phase Methanol (LPMEOH), a trademark of Chem System Inc., has been developed in recent years by Air Products and Chemicals Inc., and is considered to have the potential to be a lower cost conversion route to methanol-from-coal than the current gas-phase processes. These continuing developements are reported in a series of articles [6-14]. This report deals with the process developments work related to the indirect coal liquification technology only. The general flow sheet schematic of the indirect coal liquification process is discussed by many authors such as Derbyshire and Gray [1], Schultz [15], and O'Hara et al. [16].

Both direct and indirect coal liquefacation processes were developed in Germany in 1913 and 1925 respectively [17], and historical developments of major related technical details of the technolgies are chronologically listed by Derbyshire and Gray [1]. However, these early developments of oil-from-coal technology were held back and progress slowed down considerably due to the decline in the price of oil during the 1950's and 1960's. The only exception to this global trend was South Africa, and it is considered to be a special case. The reason being the vast availability of cheap coal, inexpensive labor, and because this undertaking is subsidised by the state as a strategic defense against embargoes from middle-east countries [17]. The science and technology of Fischer-Tropsch synthesis is involved and challenging, and is dealt in detail from different perspectives by a number of researchers [18-27].

Several reactor configurations have been developed to produce liquid products by Fischer - Tropsch synthesis. The reactor systems used are: fixed-bed reactor (ARGE), tube-wall reactor, hot-gas-recycle system, oil-circulation process, entrained-bed reactor, fixed-fluidized-bed reactor, and slurry bubble column reactor. These reactor systems are briefly mentioned in the following. A comparative discussion of several of these reactor systems and their relative characteristics is presented by several workers such as Thyrion [17], Dry [19], Derbyshire and Gray [1], Schultz [15], Baird et al. [23], Deckwer [27], Field et al. [21], Riekena [28], and Satterfield et al. [29].

The original fixed-bed reactors comprised of catalyst pellets and operated at temperatures in the range 473-543 K and produced liquid products that consisted of about half gasoline and half heavier hydrocarbons [17]. Proper temperature control was difficult to accomplish and resulting hot spots deactivated the catalyst and its carbonization. Catalyst regeneration necessitated process interuption. The fixed bed-reactors were developed jointly by Lurgi and Ruhrchemie and an improved multitubular fixed- bed Fischer - Tropsch reactor design (ARGE) has been commercialized in South Africa at Sasolburg in what is commonly known as Sasol One Plant [19, 20]. The Sasol one reactors are 3m in diameter and 13m in height [1], and each one contains 2050 tubes, 50 mm internal diameter and 12 m long. Each tube is packed with about 20 liters of catalyst. The tubes are surrounded by boiling water and the reactor temperature is maintained at the desired level in the range 493-523 K by controlling the steam pressure above the water. The normal operating pressure is about 27 atmospheres [19,1]. The Fischer - Tropsch Synthesis is extremely exothermic, about 36 kcal per reacted carbon atom. About 20 percent of the energy of the incoming synthesis gas is dissipated as reaction heat. The reaction heat is removed from the reactor through its wall into the surrounding water and also by maintaining a high velocity of gas through the catalyst bed. Part of the tail gas is recycled, and typically recycle/fresh feed volume ratio is about two. The synthesis gas enters at the top of the reactor tubes and a large fraction of the hydrocarbon product is in the liquid phase. The present yield of about 18,000 tons per year which can be increased to 70,000 tons per year by increasing the number of tubes, their diameter and length, by raising the operating pressure and feed - flow rate, and recycle flow [27].

The tube-wall reactor was developed at the Pittsburgh Energy Technology Center (PETC) [23]. It is essentialy a shell and tube heat exchanger with catalyst applied to the outer wall of the inner pipe, usually referred to as the catalyst support tube. The reactor consisted of two carbon steel pipes, the outer one 1.5 in. external diameter and 35 in. in length and the inner one 0.75 in. external diameter and 24 in. long. The catalyst was sprayed over the support tube over its entire length to a thickness of 0.023 in. The exothermic heat of synthesis reaction was removed by boiling Dowtherm contained within the support tube. Dowtherm vapor passed to the top section of the reactor where it was condensed and the same was circulated back to the bottom of the support tube via a dip tube. The temperature of the catalyst bed or the rate of the heat removal was maintained by controlling the Dowtherm vapor pressure. The general performance of the bench scale tube -wall reactor was investigated for reactor temperatures in the range 255 - 342°C, at pressures in the range 300 - 1000 psi, using different catalyst and spray procedures. These data indicated that the flame-spraying operation is better than the plasma-spraying technique to produce active catalysts. The major hydrocarbon products were light gases (C_1+ C_2), and the maximum selectivity to raw gasoline was 24% of all the hydrocarbons produced. Ralph M. Parsons have undertaken studies dealing with Fischer - Tropsch economics and conceptual plant design [16, 30].

Riekena et al. [28] of UOP Inc. , presented a conceptual design of the tube - wall reactor based on the R.M. Parsons Co. findings [30] but suitably modified it in the light of information generated at PETC [23,31], the kinetic model of Thompson et al. [32], and other engineering considerations. The catalyst was flame-sprayed on the inside surface of the 5 cm diameter inner pipe unlike the PETC design [23]. This modification made it possible to replace the catalyst without completely dismantling the reactor. This is an important modification as the expected catalyst life is only six months. It is also mentioned that the minimum diameter that can be flame-sprayed with the existing techniques is 5 cm. Further, this size resulted in extremely large reactors for the required catalyst surface area. The operating parameters were chosen as 338°C, 2,760 kPa, no recycle gas , hydrogen to carbon monoxide ratio of 2.0, and a space velocity " J " factor of 9 SCFH per ft^2 of catalyst surface area. To minimize reactor size, a high operating temperature was essential but at these conditions formation of free carbon was a serious problem. For the design rate of 793×10^3 standard m^3/h ($CO+H_2$) converted, four parallel trains of 13 tubes-wall reactors were necessary. Each reactor was 4.9 m in diameter and 19 m long. The heat of reaction was removed by boiling oil on the shell side of the exchanger and this resulted in nearly isothermal operation. In a separate heat exchanger, steam was generated at 42,000 kPa by heat exchange against the hot oil and this removed 85% of the heat of reaction. The final reactor effluent was robbed of its sensible heat and cooled to 104°C by heat exchange against the fresh reactor feed. This thermal transfer amounted to 15% of the heat of reaction.

The major advantages of the tube-wall reactor are: isothermal operation, high thermal efficiency, and efficient utilization of a small amount of catalyst; while its major disadvantages are: the high cost, the lack of a proven flame-sprayed catalyst, and free carbon formation at higher temperatures. Hence it follows that the tube - wall reactor configuration is not an attractive choice for the Fischer - Tropsch Synthesis.

The hot gas recycle process was investigated in Germany and reported by Faragher and Foucher [33]. In this process a fixed bed of ammonia-type catalyst in the form of 1cm cubes was used through which large volumes of recycle gas was circulated to remove the heat of reaction as sensible heat. The major operating difficulties were catalyst attrition, carbon deposition and a high resistance to gas flow [34], and were eliminated in the PETC effort [23] by employing active lathe turning catalyst. Fixed beds of steel wool and parallel - plate assemblies containing active catalyst coatings were investigated [23]. The reactor consisted of a 3 in. schedule 80 pipe, 12 ft in length and was electrically heated to maintain adiabatic operation. The total feed gas, consisted of fresh and recyclable gases, and were passed downward through the catalyst bed at a superficial linear velocity of about 4 to 5 ft/s. The gas leaving the reactor entered a gas to gas heat exchanger and was cooled to 200°C. Recycle gas and fresh feed was heated in gas preheater, gas to gas exchanger and a Dowtherm jacketed gas heater before entering the reactor. The influence of operating variables was investigated on product distribution. The decrease in the reactant temperature, H_2/CO ratio, space velocity, H_2O and CO_2 content in the recycle stream, could shift the product distribution toward heavier hydrocarbons.

The oil circulation process was first investigated in Germany [23 , 25, 27, 35] . In this process, CO, H_2 and recycle oil are passed over an iron catalyst to produce hydrocarbons ranging from methane to high molecular weight solids.The heat of reaction is removed by recycle oil which is externally cooled and then returned to the reactor. In early experiments at the Bureau of Mines, a flow of oil was trickled through the catalyst bed, but in later work better temperature control and hence smoother operation was obtained by submerging the catalyst bed completely in oil [35]. Unfortunately, in this operation the catalyst particle crumbled and matted together. This catalyst particle agglomeration caused a gradual increase in the bed pressure drop across the bed and thereby making it inoperable. This led to the development of a new operating method, the moving or jiggling catalyst bed [25, 35, 36]. The upward linear velocity of the cooling oil was increased sufficiently so that the catalyst bed (particle diameter 0.4 to 2mm) expanded by about 5 to 30% above its settled height. This expanded bed operation which paralleled a three-phase fluidized bed performed successfully for several months without cementation of the bed. The gasoline fraction obtained in the liquid products was more than 50 percent. The heavy distillate and wax cuts could be readily cracked to the diesel or gasoline fractions. Thus as much as 85 percent of the liquid products obtained were transportation fuels.

The entrained - bed reactor process was developed in the United States by the M.W. Kellog Co. [27]. Such reactors are also referred to as the fluidized-bed or entrained fluidized - bed or transported or circulating fluidized-bed or synthol reactors [1, 15, 17, 19 20]. The Synthol reactors have a much higher gas throughput than the fixed bed reactors and for this reason Sasol Two and Sasol Three employ only Synthol reactors [19]. The throughputs of the individual reactors were increased about threefold by increasing the reactor diameters, as well as by raising the operating pressure .

The overall height of Synthol reactors is about 50 m [19]. The reactor feed comprising of fresh feed and recycle is introduced at the bottom of the reactor at about 165°C where it contacts hot catalyst stream flowing down the standpipe. This preheats the gas to its ignition temperature. The hot gas and catalyst particles flow up through another limb of the reactor equipped with two banks of heat exchangers. These remove 30 - 40% of the heat of reaction, the rest is removed by the recycle and product gases [1]. These exiting gases are at about 340°C and are separated from the catalyst in the disengaging section by cyclones.

The catalyst settles in the hopper and flows down the standpipe to be swept back into the reactor again by the incoming gas. About 78% of the liquids are naphtha, 7% are heavier oils, and the rest are alcohols, acids, etc [17].

In fixed - fluidized - bed reactor systems the catalyst bed is expanded and remains in the fixed mode without circulation, unlike Synthol reactors. The heat of reaction is mainly recovered by steam generation in an appropriate tube bundle, mounted in the interior of the reactor [15, 21]. Hydrocarbon Research Inc. [25, 27] developed Hydrocol process to convert natural gas-to-gasoline which consisted of the conversion of a natural gas to a mixture of CO and H_2, followed by catalytic reaction to produce liquid hydrocarbons boiling substantially within the range of gasoline. The first commercial application of the Hydrocol process [24] was made by Catharge Hydrocol Inc. at Brownsville, Texas, engineered by Hydrocarbon Research Inc., in the early 1950's. This production unit was based on two fluidized - bed reactors

A fluidized - bed reactor system was evaluated by the U.S. Bureau of Mines [23] using nitrided fused iron catalyst particles 120 to 230 mesh. The reactor consisted of a 1 in, schedule 30, stainless steel pipe, 6 ft. in length, and was jacketed by a 3 in schedule 40 pipe. A 3/8 in. outer diameter baffle tube having external fins was installed in the center of the reactor to help disperse the catalyst and to aid in fluidization. The carry over of catalyst particles was prevented by using two porous stainless steel filters at the top of the reactor.

At Sasol [19], the fluidization characteristics of its heavy iron catalyst were investigated in large plexiglas models in view of the great potential of the fixed fluidized bed reactors. An effective gas distribution nozzle system was developed, and the quality of fluidization was improved by adding charcoal powder. A 5 cm internal diameter pilot-plant fixed fluidized-bed reactor system was operated at a pressure of about 80 atm. The percentage of gas conversion was found to be independent of pressure, and no reaction heat exchange problems were encountered. The fresh feed and recycle flows were always increased in proportion to the increase in pressure. Thus, when going from 20 to 80 atm, the actual hydrocarbon production rate also increased four fold. Such reactors have a potential for increased synthesis gas throughputs. Conversions of about 85 mole percent were achieved.

The three-phase slurry bubble column reactor was developed by Kolbel and coworkers in Germany as an alternative to the fixed-bed reactor in view of its several notable disadvantages viz., poor heat of reaction removal capability, nonuniform catalyst loading, need to use hydrogen rich synthesis gases, and low conversion efficiency [1, 17, 23, 27-29]. Several distinct advantages of the slurry bubble column have been recognized [22, 23, 27]. These are uniform temperature of the reactor and absence of local overheating of the catalyst particles, high catalyst and reactor productivity, a catalyst efficiency of about one, good heat transfer, catalyst handling is easy and catalyst regeneration is accomplished under favorable conditions, a low H_2/CO ratio synthesis gas can be used without carbon deposition on the catalyst, reactor design is simple and hence the initial capital costs are relatively low, no attrition and erosion problems, high single pass conversion, high yield of C_{3+} products, large content of transportation fuels in C_{3+} products, and low methane formation.

The slurry bubble column is claimed to have great flexibility with respect to product distribution [27]. It is accomplished mainly by the choice of catalyst and such important operating variables such as temperature, pressure, H_2/CO ratio in the feed gas and space velocity. For instance, a low H_2/CO ratio gas at high temperatures can be fed to a slurry bubble column which would result in bed plugging due to carbon laydown in the case of a fixed bed reactor; or at low temperatures which would result in defluidization due to wax laydown in the case of a fluidized-bed reactor [17]. Sasol has compared all the three systems, fixed, fluidized and slurry, in a 5 cm internal diameter pilot-scale reactors [19, 37]. In the low-temperature wax-producing mode, the fixed and slurry bed reactors performed equally well. In the high-temperature gasoline producing mode, the fluidized-bed reactor had a much higher conversion than the slurry-bed reactor. However, the slurry-bed operation has been investigated at Sasol mainly because of its simple construction and lower cost in relation to multitube fixed-bed reactors. It is also recognized that in the slurry-bed reactor operation geared towards wax production it is necessary to have a successful technique for the separation of finely divided catalyst from the product wax.

It is to be noted that the residence time behavior of the liquid phase and partly also that of the gas phase in a simple bubble column is practically equivalent to the behavior encountered in an ideal stirred tank reactor [22]. This causes difficulties when higher selectives are to be obtained. However, it is claimed [22] that such problems can be partially avoided by the use of bubble column cascades in the multistage process or by building elements in the reactor. In 1953, a slurry-phase Fischer-Tropsch pilot-plant was operated with an effective reactor volume of about 10 m^3, under the direction of Kolbel and Ackermann in Germany, with a production capacity of 11.5 tons of hydrocarbons per day. The primary goal was the production of fuels as well as products for further chemical processing. The operating conditions of the slurry process gave a high single-pass conversion of about 90 percent. Under the chosen operating conditions, the main goal of the demonstration plant was accomplished of the maximum value for the gasoline fraction in the product distribution. Only about 4% of the total hydrocarbons produced were in the form of methane and ethane. Kobel and Ralek [22] have given other examples of maximizing the fractions of lower and higher hydrocarbons.

The three-phase slurry reactor system of Rheinpreussen-Koppers plant included a pressure-resistant steel cylinder with a diameter of 1.55 m and a height of 8.6 m, and equipped with an internal heat-exchanger which ended about 1.3 m above the gas distributor. The three-phase reactor technology for the synthesis of gases to produce liquid products have been investigated in many countries by several investigators. In Germany, in addition to the earlier efforts of Kolbel and coworkers; in recent years, Deckwer and coworkers [38, 39] have investigated the related process details in a pilot-plant operation. Other important works are of Schlesinger et al. [40, 41] in this country; Hall and Taylor [42], Farley and Ray [43], and Calderbank et al. [44] in England; Mitra and Roy [45] in India; and Sakai and Kunugi [46] in Japan. All these investigations have been discussed and compared with each other to bring out the overall assessment of this technology in a review article by Saxena [47].

In the above we have mentioned the different reactor configurations which have been employed to produce different transportation fuels based on the use of coal. Several comparative studies made of these reactor operations [17, 19, 22, 26, 27 - 29] have concluded that the three-phase slurry bubble column operation be investigated in detail to understand and establish its distinct and unique potential for this important technological application. It is this motivation which prompted this research activity, under the sponsership of the U. S. Department of Energy, to investigate the heat transfer process in slurry bubble columns to immersed surfaces and thereby optimize the heat exchanger configuration and design. To this end, two slurry bubble columns of different diameters have been designed, fabricated, installed and tested under a variety of process variables. These include solids of different physical properties, powders of different mean particle sizes and particle size distributions, and forming slurries of different concentrations. As liquid phase two liquids of widely different viscosities have been used. Air and nitrogen have been employed to simulate the gas phase. Column temperatures have been varied over a wide range from ambient to 250^{0}C. The gas velocity is varied to bring about different hydrodynamic regimes. As heat transfer surfaces, single tubes of different diameters, and tube bundles of different sizes and configurations have been employed.