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Overview of reactors for liquid phase Fischer–Tropsch synthesis

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Abstract

The following overview is divided roughly into three sections. The first section covers the period from the late 1920s when the first liquid phase synthesis was first conducted until about 1960 when the interest in Fischer–Tropsch synthesis (FTS) declined because of the renewed view of an abundance of petroleum at a low price. The second period includes the activity that resulted from the oil shortage due to the Arab embargo in 1972 and covers from about 1960 to 1985 when the period of gloomy projections for rapidly increasing prices for crude had faded away. The third section covers the period from when the interest in FTS was no longer driven by the projected supply and/or price of petroleum but by the desire to monetize stranded natural gas and/or terminate flaring the gas associated with petroleum production and other environmental concerns (1985 to date). These sections are followed by a brief overview of the current status of the scientific and engineering understanding of slurry bubble column reactors. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Reactors; Fischer–Tropsch synthesis; Petroleum

1. Introduction

Petroleum refining adjusted its production from kerosine to gasoline following the introduction and rapid acceptance of the auto for personal transportation. In these early years of petroleum usage, the United States was the principal exporter of petroleum crude and refined products [1]. During World War I (WWI), the Allies had sufficient petroleum supplies for the war effort that was becoming increasingly mechanized; however, Germany was very poor in oil resources and this greatly handicapped their effort. Following the end of WWI, German officials were determined to develop an independent source of transportation fuels that was based on their abundant brown coal resource. The introduction of the Haber process for the high pressure synthesis of ammonia provided Germany with a leadership role in high pressure process, especially those involving hydrogen. The importance and the scientific advances associated with the ammonia synthesis were recognized and Haber was awarded the Nobel Prize in 1918.

After much research and development work, the first commercial success in 1925 was with the direct hydrogenation of coal (especially German brown coal) at high-pressure, high-temperature conditions to produce liquids that could be utilized as transportation fuels. This was the Bergius Process and its discoverer, Friedrich Bergius, was awarded the Nobel Prize in 1931. Bergius was led to this effort by his desire to be an entrepreneur and a desire to free Germany from dependence upon external oil supplies for their transportation fuels. I.G. Farbenindustrie (Farben) purchased the rights to the Bergius Process. Farben was attracted to this process requiring severe conditions, at least in part, because of the expertise they had developed with other high-pressure processes. By 1925, Carl Bosch had risen to a high leadership position in Farben following his successful efforts to

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commercialize first the ammonia synthesis process, discovered in 1908 by Nobel Laureate Fritz Haber, and then the successful conversion of synthesis gas to methanol. In this work, Farben had become recognized for its ability to produce and utilize hydrogen at high pressures. For his leadership role in developing high-pressure processes and the materials of fabrication that was needed for the processes, Bosch was awarded the Nobel Prize together the Bergius in 1931. In addition to the technical contributions, Bosch was involved in extensive negotiations with the German government that would provide them with the support necessary to conduct the development of their synfuels industry. In addition to his business activities in Germany, Bosch was active at the international levels. The details of his negotiations with the organization that became Exxon are described in some detail in various sources (e.g., 2,3). In addition Bosch was in a delicate situation as he negotiated with Nazi government officials as he sought to establish Farben as the lead organization for government contracts for the production of fuels by both their direct and indirect coal liquefaction processes since he did not join the party.

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The first major work on the hydrogenation of carbon monoxide was by Sabatier and his co-workers, and this work was recognized by Sabatier being awarded the Nobel Prize in 1912. In 1923, Fischer and Tropsch discovered the production of liquid hydrocarbons from synthesis gas $(CO + H_2)$ that could be produced by gasifying coal. Following its discovery, the major advances in the Fischer–Tropsch synthesis (FTS) technology and scientific understanding emanated from Germany. The advances in FTS were concentrated initially in the Kaiser-Wilhelm-Institut (KWI) and then in the German companies selected by the government to commercialize the processes associated with FTS. The companies were supported by the government with a guarantee of a minimum price for the products.

The historical accounts of FTS are far too extensive to be covered adequately in a book, let alone a review paper. Hence, the following will provide a limited survey of the development of the reactors that were used to conduct the reaction in the liquid phase.

“Since 1921 the KWI had been engaged in intensive investigations of the area of gas synthesis, with the goal of producing liquid hydrocarbons. One of the reasons for this activity was the fact that Rhineland-Westphalian heavy industries, a source of financial support for the Institute, were interested in finding ways of utilizing their excess coke-oven off-gases [3].” Fischer and Tropsch were studying as one possible starting point the catalytic preparation of “Synthol,” a mixture of liquid hydrocarbon- and oxygen-containing oils described in prewar patents issued to BASF [4,5]. Schuster [6] later identified Mittasch and Schmidt as the inventors of these products derived from the reaction of carbon monoxide with hydrogen under high pressure. Much of the initial work was directed toward mechanistic aspects of the process (the “formate theory”). Nevertheless, Fischer and Tropsch [7] failed to develop a satisfactory scientific explanation of the synthesis, remarking simply in their first publication:

> ‘We wish therefore to conclude this section regarding the theory of Synthol formation by noting that for the time being we are giving first priority, relative to other possible explanations, to the notion of synthesis through carbon monoxide addition to alcohols, albeit without claiming that we have definitely proven this to be the mechanism.’

The initial mechanism that was widely accepted involved the formation of the metal carbide followed by the hydrogenation of the carbide to produce hydrocarbons. This mechanism became associated with Fischer even though he probably had less to do with its acceptance than others working in the area. By 1950, the bulk carbide mechanism had been shown to be invalid and was replaced by a mechanism that involved a surface oxygenate intermediate. This mechanism received strong support from the results of studies at

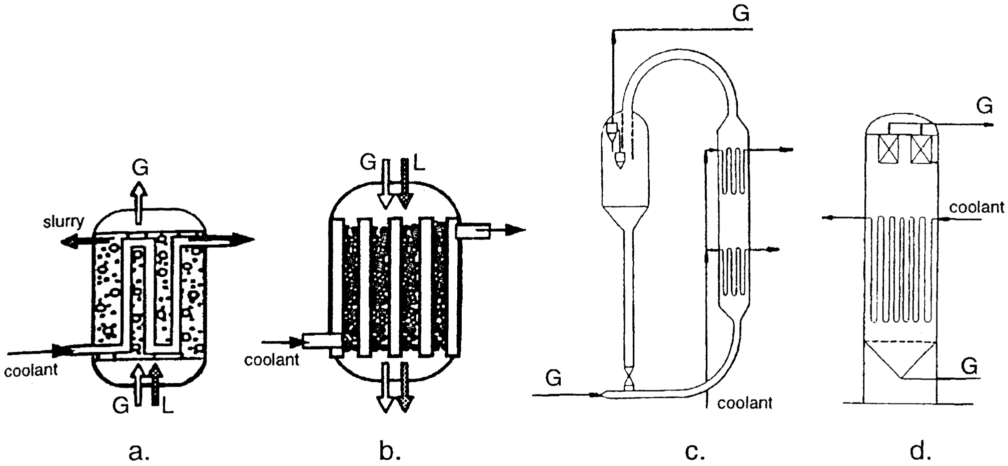

Fig. 1. Possible reactors for FTS: (a) slurry bubble column reactor; (b) multi-tubular trickle bed reactor; (c) circulating; (d) fluidized-bed reactor [G, gas; L, liquid].

the U.S. Bureau of Mines and the ^{14}C tracer studies of Emmett and co-workers. By 1980, the results produced using a variety of surface sensitive instruments led to the abandonment of the oxygenate mechanism and the revival of the carbide mechanism which now was limited to carbide formation of a surface carbon species. This surface carbide mechanism was so strongly supported that it was reproduced on the cover of an issue of Chemical & Engineering News on October 21, 1981. More recently the results of ^{14}C tracer studies indicate that the oxygenate mechanism is more appropriate, at least for the iron catalyst.

In their explanation of the course of the reaction leading to Synthol, Fischer and Tropsch assumed that methane and formaldehyde arose as intermediates, which is a reason why Fischer and co-workers (including the young doctoral candidate Otto Roelen) carried out an extensive series of experiments related to methane combustion and the formation and decomposition of formaldehyde [8]. Despite these efforts, Fischer and his co-workers never succeeded in detecting more than traces of the presumed intermediates [9].

Primarily because of the influence of the management of Farben with the German government and because its ownership of the Bergius direct liquefaction process, the early plants to produce synfuels were for the Bergius process, and not FTS [10,11].

Three reactor types have been utilized for FTS: fixed-bed, fluid bed and slurry bubble columns (Fig. 1). The fluid bed reactor must be a two phase, solid and gas, system for FTS; if this is not the case liquid will lead to solid agglomeration and loss of the fluid phase. The slurry-phase will always be a three-phase system for FTS. However, the tray columns never received widespread application. Biardi and Baldi [12] have recently reviewed briefly three-phase catalytic reactors and conclude that trickle bed and slurry reactors are the most important. Another review considers the advantages and prospects for FTS in a fixed-bed and slurry reactor but does not conclude that either is the preferred one [13]. Reactive distillation tray columns are receiving much attention for some applications (e.g., [14,15]) and, in at least a variation, have been applied to FTS. The early commercial plants that were operated in Germany utilized fixed-bed reactors; however, other reactor types were investigated. The Brownsville, Texas plant utilized a fixed fluid-bed reactor. While the Brownsville plant encountered and overcame many operational problems, it remained for Sasol to develop the circulating fluid-bed reactors to the point where its operation was reliable. More recently Sasol has replaced the circulating fluid bed reactors with fixed fluid bed reactors. Sasol also operates fixed-bed reactors but on a smaller scale that the fluid bed reactors.

2. Period I: 1929–1965

2.1. Work in Germany

Conversions in the liquid phase were initiated in Germany shortly after the discovery of the reaction. The developments progressed from the initial effort at atmospheric pressure to work in a bubble column reactor operated at atmospheric pressure to a large medium-pressure pilot plant that was operated during the 1940–1950 period. The German efforts were extensive and involved work by several companies. These companies added to the complexity faced by a reviewer because of their joint ventures with organizations located outside Germany. Thus, a complete and detailed coverage of the German work is outside the scope of the present manuscript.

2.1.1. Kaiser-Wilhelm-Instituts für Kohlenforschung

The Institute, founded in 1913 with Fischer as the director, was established to concentrate its efforts on fundamental studies of coal and its conversion [16]. The onset of WWI within months following Fischer's arrival and Germany's need for synfuels led the institute toward more practical accomplishments. Both direct and indirect coal liquefaction studies were undertaken. The indirect approach eventually led to the low-pressure synthesis of predominantly hydrocarbon products, the FTS. The exothermicity of the reaction and the need to provide a uniform temperature in the reactor were quickly recognized.

Fischer and co-workers turned to synthesis in the liquid phase soon after they discovered the FTS reaction. Fischer and Peters [17] evaluated the use of a bubble column reactor (Fig. 2) that was operated at atmospheric pressure for the hydrogenation and oligomerization of acetylene and for the hydrogenation of carbon monoxide using a supported nickel catalyst. They indicated that the use of the catalyst in liquid media for these exothermic reactions is advantageous for laboratory and commercial operations because it makes possible close control of temperature and eliminates overheating as is encountered in fixed-bed reactors. In November 1930, the pilot plant

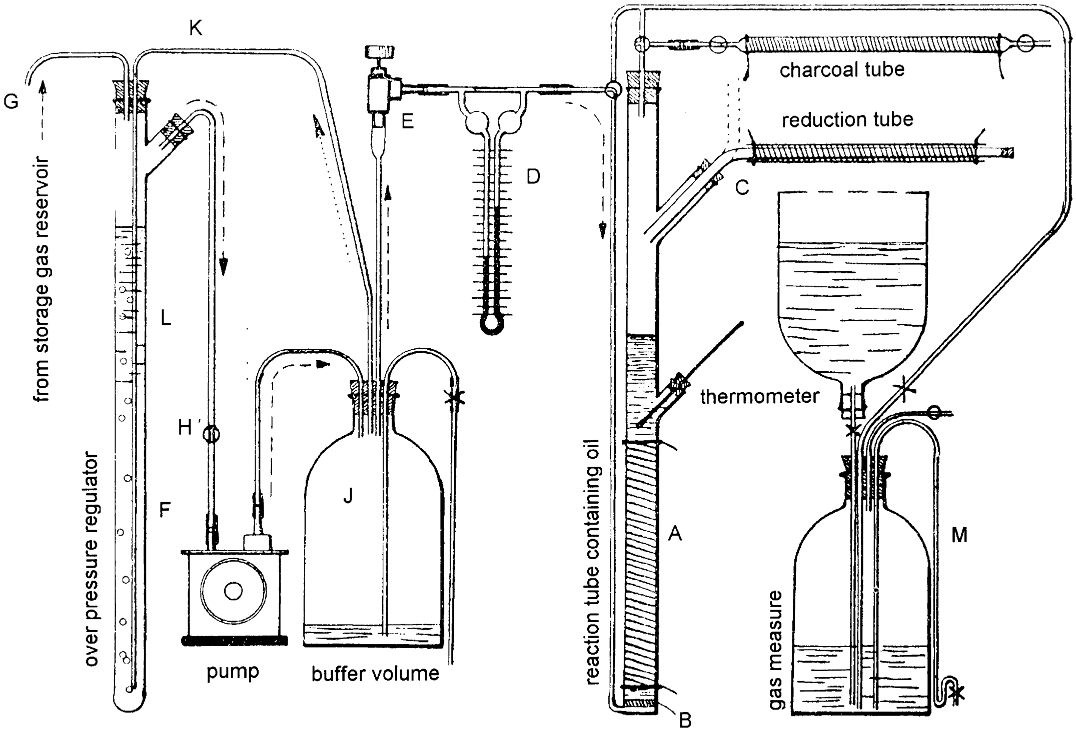

Fig. 2. Schematic of first slurry-phase catalytic reactor for FTS [17].

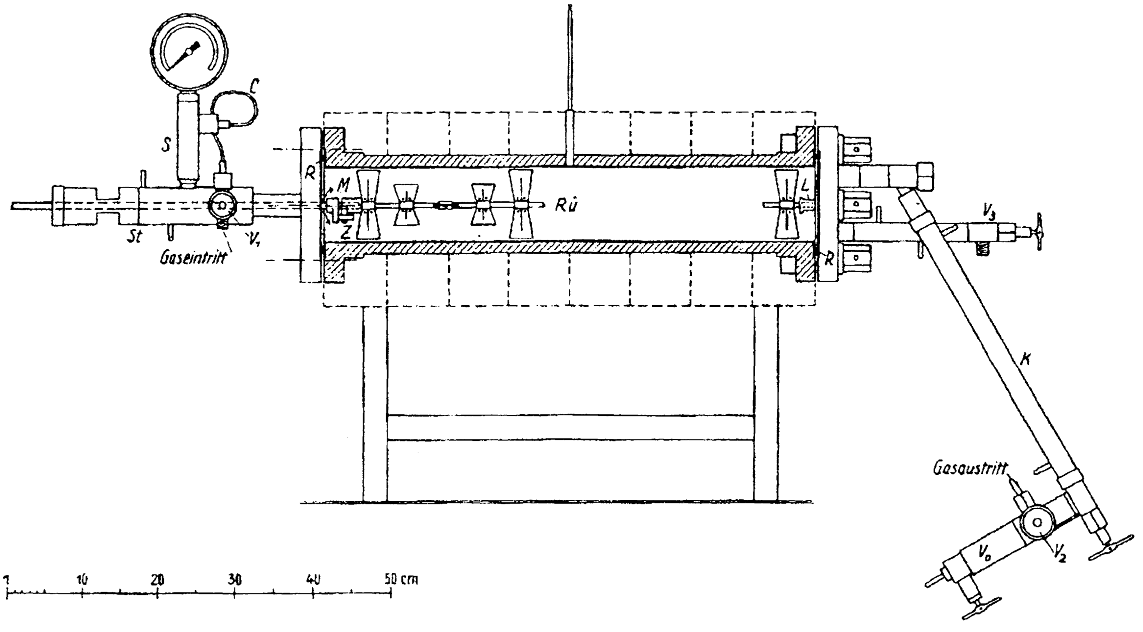

Fig. 3. Tubular stirred autoclave with silver cladding [18].

staff attempted to run the F.-T. in the liquid phase, and they were successful in solving the heat flow problem. Fischer and Küster [18] reported results to identify the influence of temperature and pressure on the synthesis. A horizontal stirred silver-lined autoclave was utilized for these studies (Fig. 3). The authors found that higher temperatures were needed for liquid phase synthesis because there was no hotspot as was the present for fixed-bed operations. They utilized a catalyst with a composition of 9Co:2Th:1Cu:0.25Ce with an equal mass of Kieselgur as support. However, the typical catalysts of that day had an activity that was too low to have practical commercial interest. They also reported that pressures near atmospheric were preferred since "Synthol" (alcohols, acids, aldehydes, ketones, etc.) was formed at higher pressures.

Fischer and Pichler [19] indicated that four approaches were suitable for removing the heat of reaction and for maintaining a uniform temperature in the reactor: (1) circulating oil outside the tube with the catalyst, (2) suspending the catalyst in oil, (3) circulating superheated water outside the catalyst space (e.g., 180 °C and 10 atm (1.01 MPa)) and (4) the suspension of the catalyst in superheated water. Interestingly, they referred to middle-pressure synthesis not as FTS but, the Fischer–Pichler middle-pressure synthesis. They utilized four catalysts (Ni, Co, Fe and Ru) in a study of middle pressure synthesis in an aqueous phase utilizing a stirred-horizontal autoclave, similar to the one in Fig. 3, to effect the synthesis. They found that only Co and Ru were suitable for synthesis since Ni formed the carbonyl and was carried from the vessel while the iron catalyst was too active for the water-gas shift reaction. The best catalyst was Ru, which was active below 200 °C. The amount and kind of products for both Ru and Co were similar to those of the dry synthesis. It was noted that water was effective in removing the heat of reaction and in providing a uniform temperature; this was based on the fact that the fixed-bed catalyst in a reaction tube of the diameter they used would have not produced useful products (i.e., higher hydrocarbons). They indicated that work in the aqueous phase was not suited for scale-up because: (1) the results are not better than operating in the dry phase, (2) a larger reactor volume is needed, (3) the apparatus is more expensive due to the need for an acid resistant reactor liner, (4) considerable expenditure of energy is necessary for stirring to provide the vigorous agitation and (5) the reaction products are not easily removed from the reactor.

Thus, Fischer and co-workers were successful in using liquid phase synthesis to control the temperature but the reaction velocity with their catalysts was too slow to be of commercial interest. In 1931, they returned to the gas phase reaction and experiments were conducted with the so-called "moving catalyst" where the catalyst was transported through the heated zone with a screw conveyor. This research was also led to results that were unsatisfactory [20].

2.1.2. I.G. Farbenindustrie A.G. (Farben)

Farben utilized two general types of liquid phase operations: (1) a fixed-bed of solid catalysts with liquid and syngas circulating concurrently over the catalyst and (2) a suspension of fine catalyst particles due to the fine bubbles formed when the syngas passed through a ceramic bottom plate with slurry circulation through an external vessel for heat removal. In some versions, they also utilized stirring as a means to maintain the catalyst suspension. Only the fixed-bed version was developed beyond the laboratory scale.

The foam process was one variation of the liquid phase synthesis [21–26]. During 1939–1944, Farben was developing a liquid phase operation in which iron powder, prepared from iron carbonyl, was mixed with oil and the gas contacted with the liquid suspension [27,28] using a process scheme as outlined in Fig. 4.

Michael [28] reports that laboratory reactors of 3 m height and 6.6 and 16.5 cm i.d. were utilized. These reactors were fitted with an internal central tube along the axis of the reactor. Because the gas bubbles rose in the annular space between the reactor wall and the inner tube, the density of the slurry in the annular space was lower than the essentially gas free slurry inside the smaller tube. The difference in density caused rapid circulation of the slurry within the reactor. In today's language, the inner tube would be a downcomer tube. When they constructed a pilot plant reactor identical to the laboratory reactors except that the volume was 300 l (2.0 m diameter), difficulties were encountered. If the circulation was interrupted for some reason, the catalyst would settle and, upon restarting, the gas flow was insufficient to cause the catalyst to become uniformly suspended. The concentration of the catalyst at the lower portion of the annular space of the reactor provided a density that was greater than the slurry in the downcomer so that circulation could never be restarted. For this reason, a pump was installed and, for convenience of maintenance, placed outside the reactor vessel as shown in Fig. 4. A reactor of this design with a 0.5 m diameter and 8 m tall (1.5 m^3 volume) was constructed and operated satisfactorily. A larger 1.5 m diameter and 8 m tall (14 m^3 volume) reactor was constructed but was not operated because of a shortage of synthesis gas because of wartime problems.

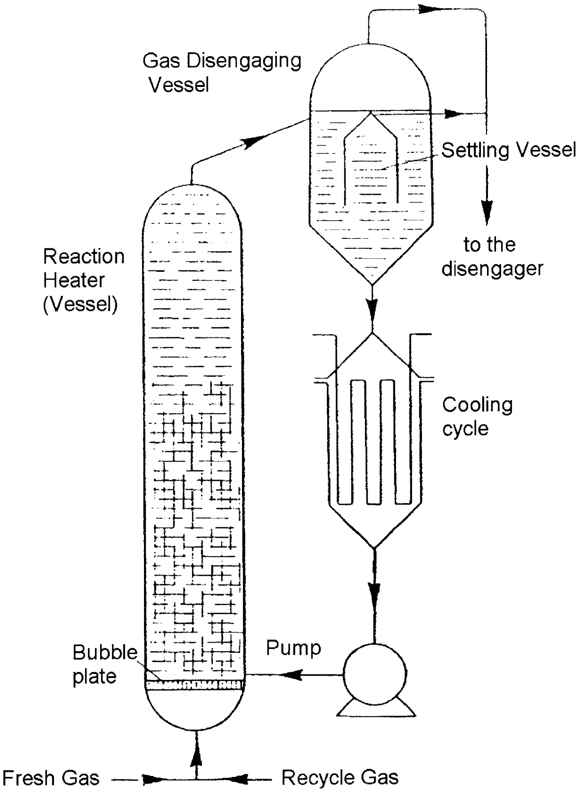

Fig. 4. Schematic of the FTS reactor unit for the foam process [28].

It was found to be difficult to operate the suspended catalyst because the formation of high molecular weight products of limited solubility caused the catalyst particles to agglomerate and settle [21,29]. Frequently they experienced thick deposits of iron catalyst around the wall of the reaction vessel, and especially in the upper portions of the reactor.

2.1.2.1. Duftschmid process. One Farben development [30–32] consisted of an oil recycle process in which a cooling oil was passed concurrent with the synthesis gas over granules of an iron catalyst (fused or sintered iron that was doubly promoted with aluminum and potassium oxides, or with titanium, manganese and potassium oxides). Cooling was effected by recycling the oil heated by the exothermic reaction through an external heat exchanger. The process was operated at a pressure of 20–25 atm (2.02–2.53 MPa) and a temperature of 260–300 °C in the first stage, and 280–330 °C in the second stage if one was used. The throughput of synthesis gas ($H_2/CO = 0.8$) was controlled to yield about 0.5 kg of total product per liter of catalyst per day. The yield of C_3^+ hydrocarbons was about 150 g per cubic meter of synthesis gas ($H_2/CO = 1$) and was distributed as follows: 16% C_3 and C_4 (85% olefin), 40% gasoline boiling to 200 °C (50% olefins), 20% gas oil (25% olefins), 20% paraffin wax and 4% alcohols, largely methanol and ethanol. The crude gasoline had a research octane number of 62–65 and the gas oil a cetane number above 70. Some of these patents were assigned to the Standard Catalytic Company. The Standard Catalytic Company, formed by six of the US petroleum companies that were formed when the courts divided the original Standard Oil Company, was established to develop processes for the production of synthetic fuels, and included an agreement with Farben. Following WWII, legal actions divided the holdings of the company. Standard (Jersey) received complete possession of 544 patents and ownership of Standard Catalytic Company. Jersey retained half-ownership of another 254 patents.

Benson et al. [33] report that, after the preliminary work by Duftschmid et al., as described above, a pilot plant with a reactor of 0.2 m diameter and 6 m height (about 200 l) was constructed during 1936 and 1937 and that it was operated, first at pressures of 100 atm (10.1 MPa) and then at 15–20 atm (1.5–2.0 MPa). In 1938, a larger plant with a 0.5 m diameter and 6 m height (1500 l) was operated. The recirculation rate was high, 9–12 reactor volumes of catalyst/oil was recirculated each hour [34]. At the end of the war they were planning a 40,000 tonnes per year (860 bbl per day) plant for this process [34].

The Duftschmid process was consider to be different from the one developed by Ruhrchemie (described below) since the entire bed of solid catalyst is immersed in oil [33]. However, Farben obtained a patent [35] in which oil was sprayed onto the catalyst in a fixed-bed (Fig. 5). The liquid passed in the same direction as the gas. They indicated that, while it was desirable to always have a thin layer of liquid present on the surface of the catalyst, it may be advantageous to temporarily interrupt the trickling in order to cause a brief increase in the temperature of the catalyst, in effect, a catalyst rejuvenation step.

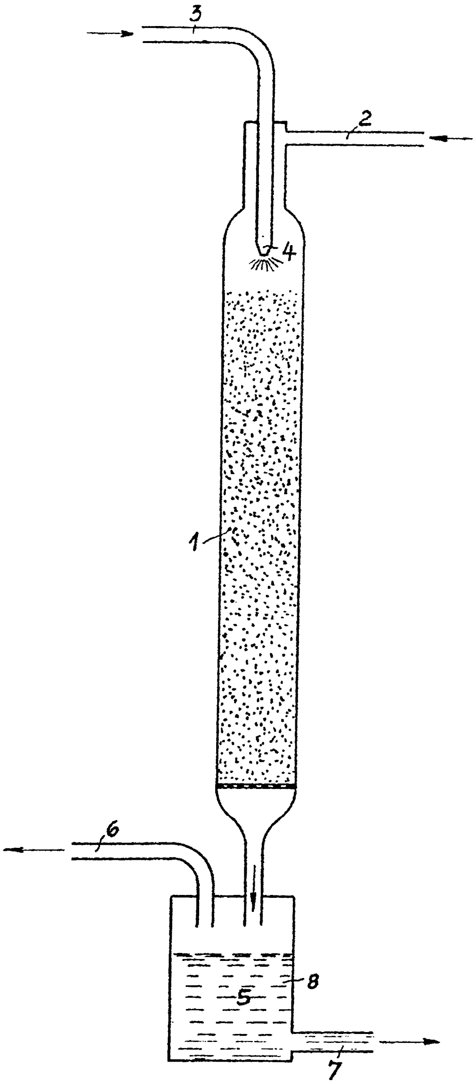

Fig. 5. Farben fixed-bed FTS reactor with oil sprayer for cooling [35].

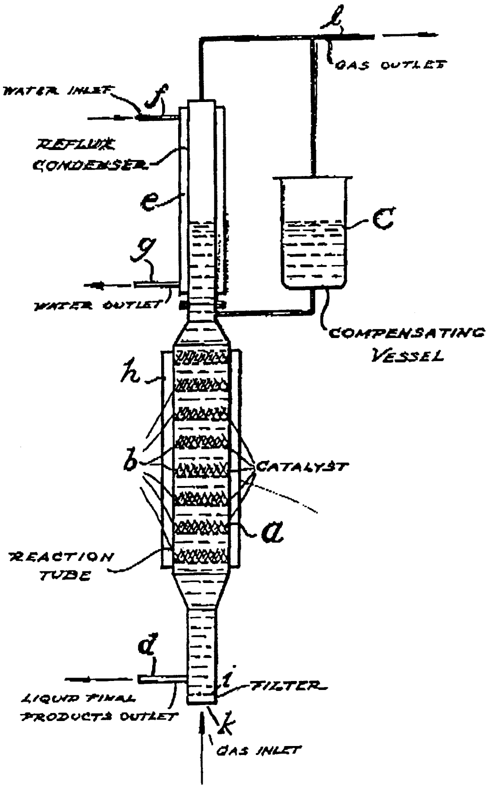

Fig. 6. Schematic reactor fitted with catalyst trays for the preparation of hydrocarbons from synthesis gas in slurry reactor [36].

An early German liquid phase reactor involved an arrangement of trays, each containing catalyst particles, that were contained in a cylindrical vertical reactor that was fitted at the top with a reflux condenser and an arrangement for removal of liquid at the bottom of the reactor (Fig. 6) [32,36]. Experiments were conducted in a seven-tray reactor, 4.5 cm diameter and 60 cm tall, with up-flow of the reactant gas.

Another variation of the liquid phase fixed-bed reactor was developed as shown in Fig. 7 [30]. A catalyst, K, is placed in an inner tube, which is surrounded by an outside tube. In the example, the reactor was 15 cm in diameter and 5.8 m tall; it was surrounded by a shell that was 20 cm in diameter. An inert liquid from FTS is circulated by a pump, P, through a preheater, H, where, it is heated to 240 °C and then added through L to the reactor shell held at 120 atm (12.1 MPa). Syngas is preheated by passing through T and then enters through N located below the reactor. Products and recycle solvent exit the top of the reactor and pass through a cooler, S, where liquid products, including water, condense and enter a holding vessel, B. Water and product are withdrawn through D and the oil is recycled. In the example about 6 l of liquid products are formed per hour while 0.75 m^3 of oil is recycled per hour. If the separation vessel, B, has about the volume of the reactor, the recycle volume/reactor volume would be about 10 and the material being withdrawn would contain only about 10% liquid products. It would therefore appear that separation would present major operational problems at the commercial-scale. In addition to the reactor configuration shown (Fig. 7 (1, 1a)), two other versions were shown: in one the location of the catalyst bed is reversed (Fig. 7 (2, 2a)) and in the other multiple catalyst tubes are located within the shell (Fig. 7 (3, 3a)). The US patent covering this reactor configuration [30] was assigned to Standard Catalytic Company.

2.1.3. Ruhrchemie

A general license for the FT process was assigned to Ruhrchemie A.G. in Oberhausen-Holten on 27 October 1934. Independent of this licensing agreement, Ruhrchemie has started construction of a pilot plant on their own and had acquired the services of Otto Roelen, who was glad to leave the KWI since his relationship with Fischer was not entirely satisfactory [16]. Roelen is credited with much of the experimental success at both KWI and Ruhrchemie. In addition to his excellent experimental capabilities, Roelen had outstanding scientific and technical abilities. His keen intellectual curiosity led him to discover the oxo process by concluding, correctly and in contrast to the views of others, that the recirculation of ethene to the FT reactor led to the formation of additional C_3-products, especially C_3-oxygenates. This observation led him to the discovery of the oxo process.

Their reactors had a vertical tube 6 m in height that was inside a larger tube where oil circulated to remove the heat of reaction (Fig. 8). The reactor volume of one was 55 l and a second reactor had 85 l of slurry volume. Because significant quantities of oil were carried over, even with a wider head at the top of the larger reactor, a reflux condenser was operated to return heavier oil to the reactor. Heavy products were withdrawn from the reactor through a filter stick immersed in the slurry. Initially a ceramic plate was used to generate

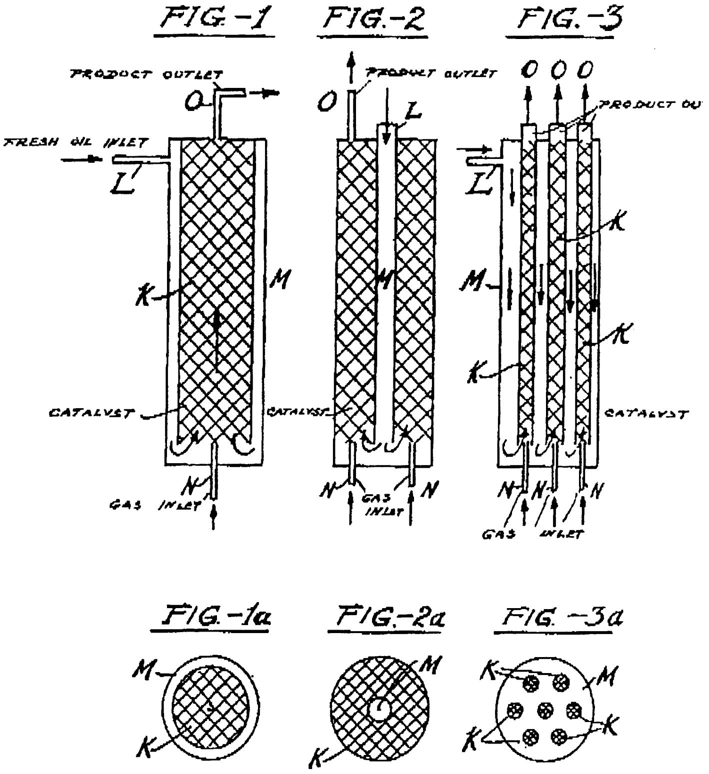

Fig. 7. Schematic of slurry reactor tube subdivided into cells to modify liquid flow patterns [30].

small gas bubbles of feed gas, but the catalyst settled and plugged the plate when the operation had to be interrupted, even temporarily. The plate was replaced by a simple copper capillary tube which never blocked and, based on the conversion, operated to produce fine bubbles of syngas just as well as the ceramic plate.

They indicated that, on a large commercial-scale operation, it would be better to limit the conversion in the stage I reactor and to use reactors in series. This operational mode was claimed to limit methane formation and to extend catalyst life.

The usage ratio (the ratio of H_2/CO converted) when CO conversion was in the 70–75% range, as when operating a single stage, was usually 1.4–1.5; however, if the reactor was operated at lower conversion levels the usage ratio could be reduced to about 0.9. With two stages together, the usage ratio was 1.24–1.28, which was essentially that of the feed syngas. They had an objective of making the feed and usage ratio the same for each reactor in the series, but apparently never attained this goal. We have reported that this goal can be easily accomplished with a low H_2/CO ratio syngas when using an iron catalyst but that it may be more difficult to accomplish with a high H_2/CO ratio [37].

Ruhrchemie [38] worked to develop a modified liquid phase process in which finely divided cobalt–thoria–magnesia–kieselguhr catalyst was suspended in oil boiling between 240 and 300 °C. During the synthesis, water was injected into the slurry where it vaporized to maintain control of the slurry temperature. The presence of a high water partial pressure, as must be present in this operation, implies that oxidation of their cobalt catalyst did not occur to an extent that it was a problem. An alternative explanation is that the activity of the catalyst was so low that the change could not be detected. With $H_2/CO = 2$, 10 atm (1.01 MPa) and 2.5 l/g Co/h at 190–210 °C, 172 g of liquid and solid hydrocarbons per cubic meter were produced, with 90% of the liquid product boiling below 300 °C. By the end of the war, the work

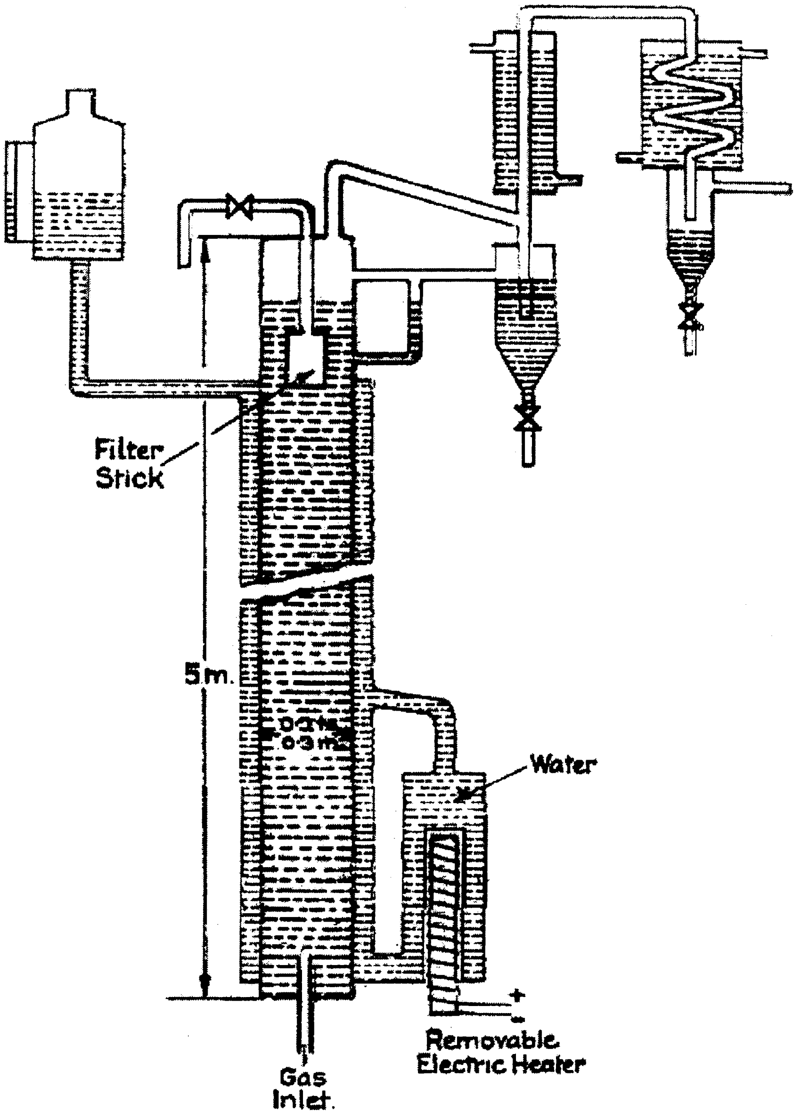

Fig. 8. Liquid phase synthesis apparatus [34].

had not progressed to the large-scale pilot plant stage [39].

Ruhrchemie workers also developed a version of the oil recirculation process. Their process utilized a fixed-bed of catalyst that was sprayed continuously with an oil that was added through a device that was designed to provide a uniform distribution of oil across the radial dimension of the catalyst. The intent was to have the oil maintain the catalyst free of wax and to remove the heat of reaction by the latent heat of vaporization of the added oil [34]. It was not made clear how the added oil could wash the wax from the catalyst through the bottom of the reactor and, at the same time, evaporated to maintain the temperature.

2.1.4. Rheinpreussen

This company began work on the liquid phase synthesis about 1937. Most of the work was under the direction of Kölbel and the work conducted up to 1945 was summarized by him [34]. The composition of most of the catalysts used by Kölbel and co-workers in this early work, as well as in the later pilot plant studies, had a composition of Fe:Cu:$K_2O = 100{:}0.2–0.5{:}1.0$ and was activated 10–20 °C above the synthesis temperature. They used a suspension of 10–20% Fe, a syngas with $H_2/CO = 0.5$ and a space velocity of $75\,h^{-1}$, a very low value. The early experiments were conducted in a vessel with 15 cm i.d. and 3–4 m height with cooling coils either inside or outside. They reported an utilization ratio of 0.5, as it was reported that no water was present in the products. In this and other work, Kölbel reported that diesel and the product olefins, and even paraffins, reincorporated extensively to produce heavier products. Excluding the mass of product formed from the diesel recycle fluid, 180 g product was formed from a m^3 of synthesis gas. With this catalyst they reported that no methane was not formed. The synthesis products were obtained by withdrawing oil and catalyst, filtering, and returning the remaining catalyst slurry to the reactor, all operations being conducted under synthesis gas [34].

The claim of even paraffin reincorporation is astounding but the data that are reported seem consistent with this claim. Kölbel reported that the great freedom present in the fluid phase process is the reason why we cannot approach the large variation with respect to the primary product, with respect to the variables (temperature, gas composition, catalyst, pressure, residence time, etc.) (Table 1) [40], with other reactors. In addition, it is possible that doing the synthesis in the reactor, liquid hydrocarbons which were added (recycled is allowed with this German word) to the reactor, through molecular (reincorporation) of the liquid hydrocarbon that is added back to the reactor, to form hard paraffins [41,42]. For this reason, there is no need to treat the primary product in a secondary process, such as, in general, cracking. This type of process allows one to change the molecular size, according to Kölbel.

Kölbel and Ackermann [43,44] obtained patents for an apparatus for carrying out gaseous catalytic reactions in liquid medium. The reactions included FTS. It was stated that the (Fischer–Tropsch) synthesis according to known processes is feasible without trouble in a reaction space of up to 20 cm (7.9 in.) diameter. With increasing horizontal diameter of the reaction space the amount of gas conversion decreases and it is always more difficult to maintain a constant gas conversion. The larger the horizontal diameter of the reaction space, the more the liquid substance leans toward changing from stationary state to a state of vertical rotation. Vertical rotation occurs when the liquid flows downwardly along the surface of the wall and flows along the bottom to the middle of the reaction space, whereby it is drawn out by the gas bubbles leaving at the middle of the bottom. The compressed central gas stream flows along with the liquid toward the top whereby the firmly compressed gas bubbles combine to form large elongated gas bubbles. Only at the upper reversal point of the liquid, in the vicinity of the surface of the column of liquid, does the gas spread out horizontally across the transverse section and the large gas particles are partially decomposed (Fig. 9).

Table 1
Flexibility of product composition by liquid phase synthesis [40][a]

	Synthesis based on molecular size			
	Low	Low	Medium	High
Hydrocarbon product—$C_3{}^+$ (g/m^3 CO + H_2)	162	166	175	182
$C_3 + C_4$ (wt.%)	29.6	18.1	6.9	2.2
C_5^+to190 °C (C_5–C_9) (wt.%)	63.0	68.0	40.0	7.1
190–310 °C (C_9–C_{17}) (wt.%)	6.2	10.9	25.7	8.3
320–450 °C (C_{17}–C_{31}) (wt.%)	1.2	2.4	18.3	33.0
>450 °C ($C_{31}{}^+$) (wt.%)	–	0.6	9.1	49.4
Alpha values[b] (wt.%)	α_1, 0.68	α_1, 0.68	α_1, 0.69; α_2, 0.92	α_1, 0.40; α_2, 0.95
Fraction of product from α_2 (wt.%)	–	–	0.17	0.50

[a] Calculated by author from data above.

[b] Calculated by author assuming two alpha distributions with α_2 representing the higher carbon number products.

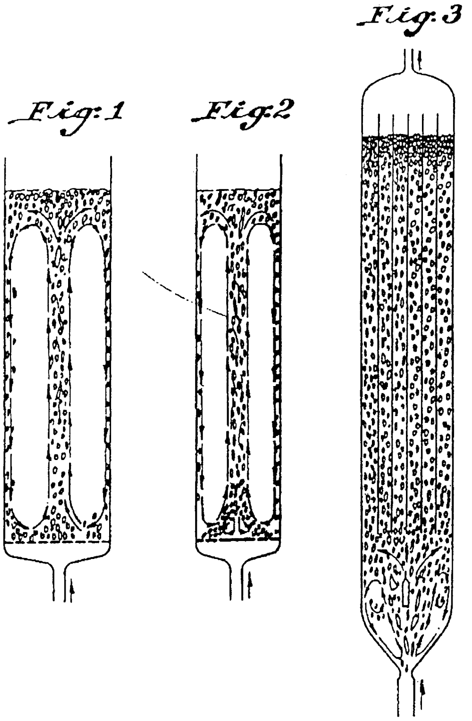

Fig. 9. Schematic of oil recirculation within slurry reactor (Figs. 1 and 2) and the elimination of recirculation by adding shafts (tubes) (Fig. 3) [43].

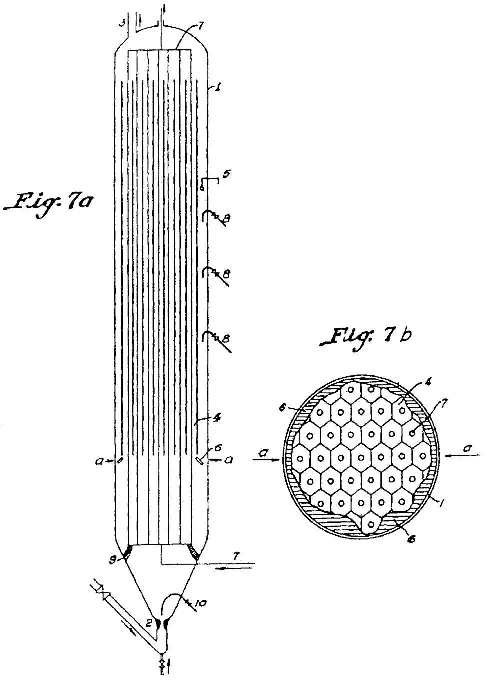

Fig. 10. Schematic of slurry reactor with shafts (open at top and bottom) to subdivide reactor shell to establish reactor zone with stationary catalyst and liquid condition [44].

As Kölbel and Ackermann illustrate (Fig. 9), the liquid flows upwardly in the interior of the reactor tube and flows downward along the wall side of the reactor. They indicated several disadvantages that accrue from this situation, including: (1) decreased gas conversion, (2) occurrence of secondary reactions, (3) increased catalyst damage, and (4) increased catalyst aging.

These authors state that, for reactions like FTS where the gas composition changes with conversion and where the products admix with the unconverted gas, "... the gas conversion should be complete as possible on passing the gas through once ..." The authors indicate that, prior to their patent, none of the available operations permit "... maintaining the liquid medium and the suspended catalyst stationary and nevertheless permitting the gas bubbles in uniform size and distribution to pass vertically through the liquid medium at equalized velocity ..." The authors indicate that the disadvantages of the liquid and catalyst circulation, as shown in Fig. 9 (Fig. 1, left), can be overcome in a cylindrical reactor with a horizontal diameter of more than 30 cm and up to 3 m or more and more than 1.5 m in height, and a gas head space above the liquid at least as large as the reactor diameter. To provide within the reaction zone a stationary catalyst and liquid condition, the large reactor shell is subdivided into similar, vertical shafts which are open at top and bottom that have liquid-tight casings and a diameter of at least 5 cm (Fig. 10). The shafts should terminate above the expanded liquid level; i.e., in the free-board gas space. Because of the flows in the bottom of the reactor, it is stated that each of the shafts, in the center as well as at the wall region, receive the same amount gas. While there is circulation of the liquid in the sump (bottom of reactor in Fig. 10), "... there are formed in the shafts extremely stationary liquid columns whose expansion depends on the amount of gas."

The authors indicate that in certain cases, as in the Fischer–Tropsch reaction, it may be an advantage to allow the temperature to rise toward the top of the reactor, and provisions are described which would allow for this to occur. Thus, as the partial pressure of the reactants decrease, the higher temperature will be able to compensate, completely or partially, by having the rate increase to compensate for the partial pressure decrease.

Kölbel and co-workers operated a large demonstration plant with a reactor that was 1.55 m in diameter and 8.6 m in height. Until the start-up of the slurry reactor by Sasol, the Rheinpreussen-Koppers demonstration plant was the largest slurry reactor that had been operated successfully. Kölbel states that at the time that most work was conducted using the demonstration plant (1952–1953), the operation was confined almost exclusively to the production of gasoline [45]. The results of the operation of this plant and the smaller laboratory scale slurry-phase reactor produced data that have become the "standard" that is used to compare with other slurry-phase studies. As indicated above, a typical catalyst used by Kölbel in this plant would have a composition of $Fe:Cu:K_2O = 100:0.1:0.05–0.5$; thus, it would be consistent with the objective of producing gasoline range material, and not high molecular weight reactor wax. The catalyst used by Kölbel would be similar to a low-alpha iron catalyst described in Mobil patents [46,47] and government reports for the Mobil work [48,49] and, except for a much lower copper content, the one used for LaPorte Run II [50].

At the conversion level shown in Table 2, only 178 g of hydrocarbons were produced per cubic meter gas (from the original paper in German, it is not possible for even a native German to tell whether this volume of gas refers to the amount of gas fed or to the amount of gas converted). Even, if it is taken as the amount fed, at the 90% conversion level, more than 178 g of hydrocarbons should have been produced. For example, in the Mobil runs more than 200 g hydrocarbon were produced. Sasol workers indicate that they could not repeat Kölbel's results in their early studies [51]. Kölbel et al. report that through polymerization of lower olefins, about 18 g of alkylate gasoline can be produced for each meter cube of syngas that was converted. When this was mixed with the reformed gasoline ($112\ g/N\,m^3\ CO+H_2$), $130\ g/N\,m^3\ CO+H_2$ of finished gasoline could be produced. For a CO conversion of 91%, the $H_2 + CO$ conversion was 89%; the feed gas ratio was $H_2/CO = 0.67$. With this gas

Table 2
Operating data and results of liquid phase synthesis for one-step operation with a single passage of the gas over iron catalysts [45]

	Demonstration plant (a)	Laboratory plant (b)
Effective reaction space (volume suspension including dispersed gas) (l)	10000	6
Catalyst (kg Fe)	800	0.4
Synthesis gas pressure (bar)	12	11
Synthesis gas (volume ratio, $CO:H_2$)	1.5	1.5
Quantity of synthesis gas ($N\,m^3/h$)	2700	1.3
Linear velocity of the compressed gases at operating temperature referred to the free reactor cross-section (cm/s)	9.5	3.5
Total $CO + H_2$ used ($N\,m^3/h$)	2300	1.1
Per meter cube of reaction chamber ($N\,m^3/h$)	230	183
Per kilogram of Fe ($N\,m^3/h$)	2.6	2.45
Average synthesis temperature (°C)	268	266
CO conversion (%)	91	90
$CO + H_2$ conversion (%)	89	88
Synthesis products referred to $CO + H_2$ used		
Hydrocarbons C_1^+ ($g/N\,m^3$)	178	176
Hydrocarbons $C_1 + C_3$ ($g/N\,m^3$)	12	11
Hydrocarbons C_3^+ ($g/N\,m^3$)	166	165
O-containing products in the synthesis water ($g/N\,m^3$)	3	2
Space time yield of C_3^+ products including O-products in 24 h (kg/m^3 of reaction chamber)	930	740

ratio, based upon our results, the only way that Kölbel could have obtained such similar high CO and $CO + H_2$ conversions would be to operate so that the single pass conversion was 50–60% and to recycle the unconverted gas. It has not been widely appreciated that much of the work that Kölbel reports has been conducted under conditions designed to produce gasoline; in this mode the demand on wax/catalyst separation is minimal. Thus, much of Kölbel's work can be viewed as being conducted under conditions that make the operation of a slurry reactor much easier than the current goal of operating to maximize the reactor wax fraction to subsequently hydrocrack to produce diesel fuel.

Kölbel stressed that the low viscosity and surface tension of the liquid was crucial for maintaining the small bubble size needed to maintain gas–liquid mass transfer. Kölbel maintained the view that it was necessary to establish upper limits upon the solids content of the slurry in order to maintain a low viscosity. Kölbel and co-workers obtained very low methane for the distribution of the other products that they reported. This is illustrated in Fig. 11 where the Kölbel data are compared by the author with data obtained by others using bubble column slurry reactors [49]. In spite of the question regarding mass balance, Kölbel and co-workers provided a strong scientific and engineering basis for further work.

Another reactor type was constructed along the lines of a modern multi-tray bubble cap distillation tower. Thus, a reactor is fitted with a number of trays that contain catalyst and are fitted with bubble caps arranged to allow vapors, unconverted feed gases and vapor phase products, to be distributed to keep the catalyst in suspension (Figs. 12 and 13) [52]. Some bubble caps are fitted with downcomers that allow non-volatile liquid to descent to the bottom of the reactor. In an example, 0.34 kg lb of catalyst was suspended in one gallon of oil (about 10% slurry) and charged to a reaction chamber containing 50 bubble trays. Other variations were provided (Figs. 14 and 15) [31]. In these versions, the cooling liquid could be added at several levels in the reactor to maintain a better control of temperature during startup and synthesis.

2.2. The Netherlands

2.2.1. International Hydrocarbon Synthesis (N.V. Internationale Koolwaterstoffen Syntheses Maatschappij, The Hague, The Netherlands)

This company was reported to employ a form of the recycle technique that utilized vapor-phase synthesis

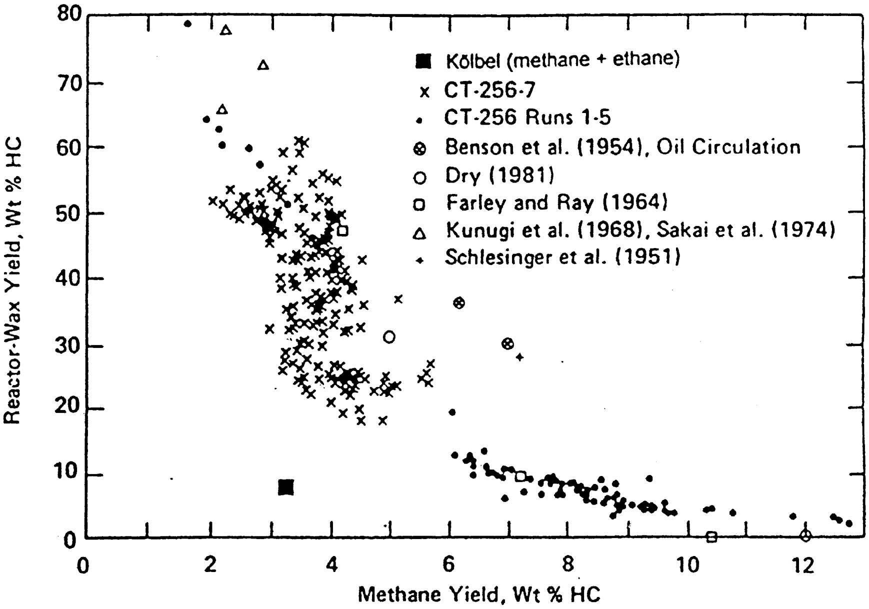

Fig. 11. Reactor wax yield vs. methane yield with data from [45,49] (redrawn by author).

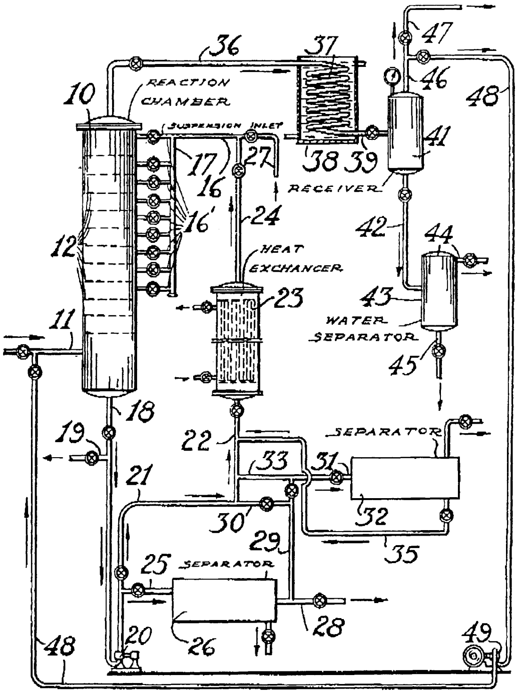

Fig. 12. Reactor fitted with catalyst trays, each containing bottle caps, to effect slurry-phase synthesis of hydrocarbons [52].

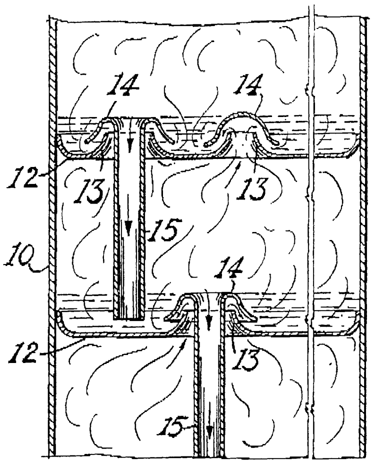

Fig. 13. Schematic of bubble caps and gas transport columns for trays in reactor shown in Fig. 12 [52].

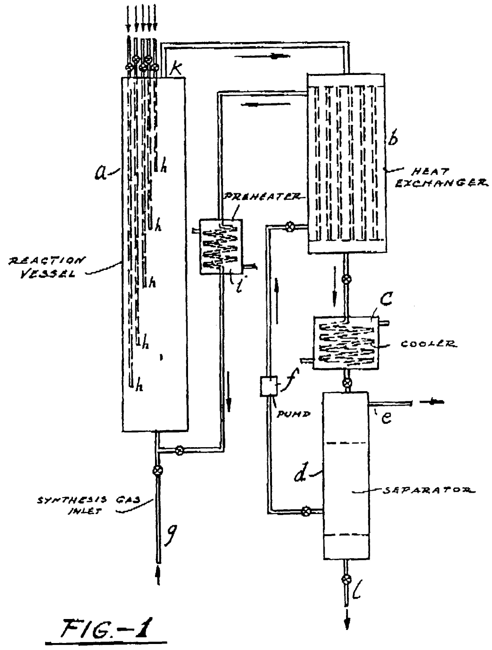

Fig. 14. Schematic of slurry reactor with capability of adding preheated liquid as several levels within the reactor [31].

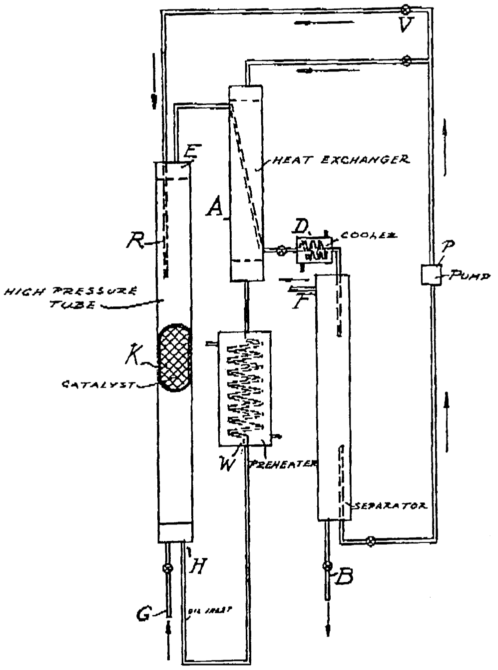

Fig. 15. Schematic of slurry reactor with recycle of oil to the reactor [31].

in the first stage and this stage was followed by a liquid phase operation that utilized a catalyst suspended in oil. The two reactors were separated by a product condensation unit [53]. However, the reference given for this work appears to apply only for an oil recirculation liquid phase process that has the features of those described above [54]. This company obtained many patents covering FTS during the 1930s but only a limited number apply to liquid phase synthesis.

2.3. United Kingdom

The Fuel Research Station first utilized fixed-bed reactors that had a reaction space up to 50 l volume and in 1947 began work on the fluidized bed reactor. In 1949 work began on the liquid phase technique. Hall et al. [55] compared fixed-bed, fluid-bed and liquid-phase reactors and in 1952 concluded that the maximum selectivity and flexibility could be obtained with the liquid phase system. The decision was made to construct a pilot plant, based primarily on the fact that the liquid phase reactor was the only one that could be operated with the CO-rich gas produced in a slagging coal gasifier. The plant was to produce up to 385 l of product per day and to operate at pressures up to 20 atm (2.02 MPa) and reaction temperatures to 300 °C. The reactor had a 9.75 in. (23.5 cm) internal diameter and was 28 ft tall (8.5 m), allowing a reactor volume of 273 l. Initial problems were encountered in the settling method they used for wax separation from the catalyst slurry and from carbon formation which increased the viscosity of the reactor contents to the point of near-gellation.

The operation of the British plant was terminated about the time that they had solved most of the operating problems and considered themselves to be at a point where they could operate to produce reliable data. The operation became a causility due to the discovery of a plentiful supply of petroleum in the Middle East. Low catalyst activity and rapid catalyst aging were problems that limited the usefulness of the data produced during the period of operation of the plant.

Dreyfus [56,57], a British citizen who assigned his US patents to the Celenese Corp., described a liquid phase synthesis for FTS. In his version a catalyst was immersed in a liquid medium which boils at about the temperature of the desired reaction. Syngas is bubbled through the liquid containing the catalyst and fitted with a reflux condenser to maintain the liquid phase. While the inventor indicated that the reaction could be conducted at high pressure, he indicated that it had the greatest value when applied to the synthesis of hydrocarbons under atmospheric pressure. Cobalt catalysts were utilized at a temperature of about 180–200 °C and an iron catalyst at a temperature of about 250 °C. The example utilized a cobalt catalyst that was promoted with thoria. Excess liquid products are drawn off by an overflow at the desired level, fitted with a liquid seal.

Dreyfus also described the use of liquid phase synthesis in the range of sub-atmospheric to about 5 atm (5.05 MPa) of pressure [57,58]. A feature of this patent was the use of a metal active for FTS that was present in a reduced form and at a low concentration. A salt of a reducible metal (especially Co, Ni or Fe) that is soluble in the reaction medium was indicated. A salt of a fatty acid is especially preferred since is very soluble in the organic medium. Promoters may be included as part of the catalyst system. The metal is reduced in a few hours at the reaction temperature, e.g., 200 °C, prior to the synthesis.

2.4. United States liquid phase work

2.4.1. US Bureau of Mines

The US Bureau of Mines constructed and operated a pilot plant that utilized oil-recycle in a reactor that was 3 in. (7.6 cm) and 8 ft (2.44 m) tall [33]. After several runs during 1946–1947 with co-current downflow of gas and liquid over cobalt catalysts, a run was made with the cobalt catalyst completely submerged in liquid and co-current upflow of gas and liquid. After it had been demonstrated that the unit could be operated with the cobalt catalyst, the later runs were made with an iron catalyst. The composition of the cobalt catalyst was Co:ThO_2:MgO:kieselguhr = 100:7:12:200. The cobalt catalyst was reduced at atmospheric pressure (0.101 MPa) in the reactor. The temperature was raised to 360 °C as rapidly as possible using a hydrogen flow of 10 ft^3/h (1.05 m^3/h) and then the hydrogen flow was increased to 200–400 ft^3/h (21–42 m^3/h) and the reduction continued for 4 h. Since the catalyst bed occupied about 0.25 ft^3 (0.026 m^3), the GHSV was about 800–1600 h^{-1} during the reduction at 360 °C. Following reduction, the hydrogen flow was reduced to 5 ft^3/h (0.53 m^3/h) and the temperature reduced to

150 °C. Nitrogen replaced hydrogen at this point and the pressure was increased to 40 psig (0.28 MPa). Oil was then admitted to the reactor. After the oil was added, syngas flow (GHSV = 100) was started. The temperature was slowly increased from 150 °C while increasing the pressure in small increments, which decreased the rate of evaporation of the cooling oil. The temperature was maintained below 175 °C, maintaining a gas contraction of less than 50%, during 48 h. The temperature was increased to 180 °C during the next 24 h, after which the induction was considered complete. The conditions were then adjusted as required to obtain maximum productivity.

The US Bureau of Mines also operated a larger 8 in. (20.3 cm) diameter reactor in the oil-recycle mode (Fig. 16) [59]. These units were operated with a precipitated and a fused iron catalyst that has a very low activity compared to the high surface area precipitated iron catalyst. The fused catalyst was used because it was hard and seemed to have the physical strength needed for slurry operation. Some experimental operating problems made it difficult to maintain constant temperature during significant portions of the runs. While it was demonstrated that this mode of operation was viable, little else was obtained that merit further consideration here.

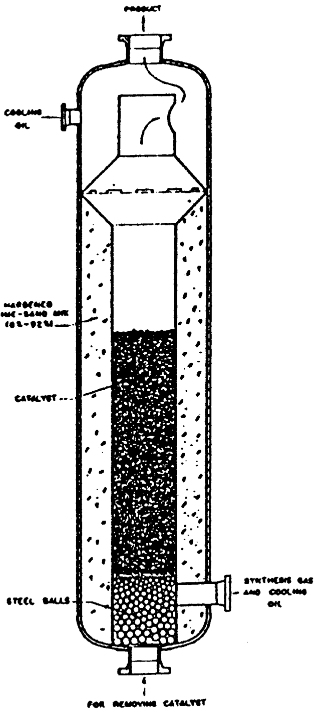

Fig. 16. Synthesis reactor at US Bureau of Mines, Louisiana, Missouri plan [59].

2.4.2. Standard Oil Development Company (Jersey) (now Exxon Mobil)

In the 1920s, it became necessary for Farben to seek funding from partners that were located outside of Germany. One company that was targeted by Bosch, then head of the company, was Exxon. When the top management of Exxon visited the research facilities where Farben was working on the Bergius process and other high pressure hydrogenation and hydroconversion processes, they were sufficiently impressed to enter quickly into a joint effort that was centered on hydrogenation. In the early 1930s, Exxon abandoned research on hydrogenation although they had spent more than $ 30 million on experimental and commercial plants and an additional $ 35 million payment in Jersey stock to Farben. Larson et al. [60] conclude that, “Perhaps the most important result of the early work in hydrogenation was the interest it stimulated among Jersey researchers in catalysis and catalytic processing... Catalysis research also aroused the company’s interest in the synthesis of hydrocarbons from carbon monoxide and hydrogen derived from natural gas or coal... Thus, Jersey sought still other methods (than direct hydrogenation) for making motor fuels of high quality. For example, it investigated the Fischer–Tropsch hydrocarbon synthesis process, developed by Ruhrchemie, which converted brown coal into liquid fuel. In 1938 and 1939, patents for this process outside Germany were transferred by Ruhrchemie to Hydrocarbon Synthesis, in which Standard Oil Development (now Exxon Mobil) took 680 shares, Shell and Kellogg 425 each, and Farben 170. Both UK and France considered the building of plants using this synthetic process for providing aviation gasoline, but they had been unable to accomplish anything definite by the time the war broke out in Europe in 1939.”

It was recognized soon after the discovery of the FTS that a reactor employing the catalyst in direct contact with a cooling oil was an attractive approach to maintain temperature control of the exothermic reaction. US patents were obtained by Farben, Standard

Oil Development Company and Standard Catalytic Company. The Standard Catalytic Company was established by six US petroleum companies to develop processes for the production of synthetic fuels, and included an agreement with Farben. Following WWII, legal actions divided the holdings of the Standard Catalytic Company.

A procedure designed to facilitate removal of the reaction product was to pass the preheated synthesis gas into a 50-bubble tray tower at the rate of 105 m^3/h. A suspension containing about 0.34 kg of finely divided nickel catalyst activated with magnesium and aluminum oxides per 3.8 l of sulfur-free paraffin was charged through the tower at the rate of 20 l/min. The reaction produced about 385 l of liquid hydrocarbons for each 105 m^3 of gas charged [61].

2.4.3. Texaco

Most of Texaco's attention during this period was directed toward fluid bed operations such as was utilized at the Brownsville plant. The Brownsville plant was developed by a group of companies and utilized a fixed-fluid bed reactor. The driving force for this plant was Dobie Keith who founded Hydrocarbon Research, Inc. [62]. During WWII, Keith was assigned the responsibility for developing the barrier for the separation of the uranium isotopes and the construction for the gaseous diffusion plant at Oak Ridge. He developed an interest in the Fischer-Tropsch synthesis during his work on the Manhattan Project. Three drivers for the Brownsville plant were: (1) the anticipated shortage of petroleum crude, (2) the lack of a pipeline to deliver natural gas to markets, and (3) the development of plants that could be used to produce oxygen for preparing the syngas. The discovery of vast quantities of Mid-East oil removed the major driving force for the plant just as many of the operating difficulties for the plant were overcome. The scale of the operation was small by today's standards: 6000 bbl/day gasoline, 900 bbl/day of diesel, 200 bbl/day of fuel oil and 300,000 lb/day of chemicals [63]. Texaco obtained a patent which provided much insight into the operation of a slurry bubble column reactor (Fig. 17) [64]. While the process equipment and its operation are described in much detail, neither experimental data nor examples are given; thus, it is not certain whether the patent presents a detailed conception or whether it describes equipment that was constructed and operated. Discussions with people who were employed with Texaco during this period did not resolve this question. The reactor can be viewed as a grouping of tubes inside a shell. The catalyst slurry is circulated through the tubes while the cooling fluid is circulated in the space between the tubes and the shell. Moore cautioned that the height/cross-sectional area should be large and provide an example where the height may range from about 10 to 40 ft (3.1 to 12.2 m) and have an inside diameter of 1–6 in. (2.54–15.2 cm). Moore taught that the flow of gas should be sufficient such that the "flooding velocity" is exceeded and that diluent gases may be used to accomplish this objective. It was indicated that a light olefin product, e.g., propene, may be used as the diluent and that a portion of the olefin may enter into the conversion, presumably by chain initiation, reincorporation or by hydrogenation. The gas feed rate may be adjusted to give turbulent flow within the tubular reactor tubes. The recycled slurry and dispersed gas flow can be adjusted to give rise through the reactors in "tubular flow". Presumably, tubular flow can be considered to be equivalent to plug flow, as this term is used today. A variety of catalyst formulations were presented, including supported or unsupported cobalt and iron. Separation of wax from the slurry was accomplished external to the reactor and could be operated so that separation was accomplished continuously or by filtering the entire catalyst inventory at one time. The entire recovered catalyst could be regenerated and returned to the reactor or, as an alternative, regeneration could be effected by discontinuing the CO feed while continuing the H_2 feed to the reactor while the system was held at some elevated temperature.

In another variation, the liquid phase synthesis is effected in a reactor similar to the one in the above patent but materials are added to alter the surface tension to permit the formation of a froth or foam [65]. This was claimed to increase the rate of synthesis by materially increasing the area of the liquid–gas interface. In one variation, water is introduced into the reactor above the entrance of the catalyst/slurry oil entrance. The steam will evaporate and form a foam which will fill the reactor. The foam, after leaving the reactor, is broken and the slurry is separated from the products and recycled.

Another variation of the Texaco liquid phase synthesis [66] is similar to the Duftschmid process. As

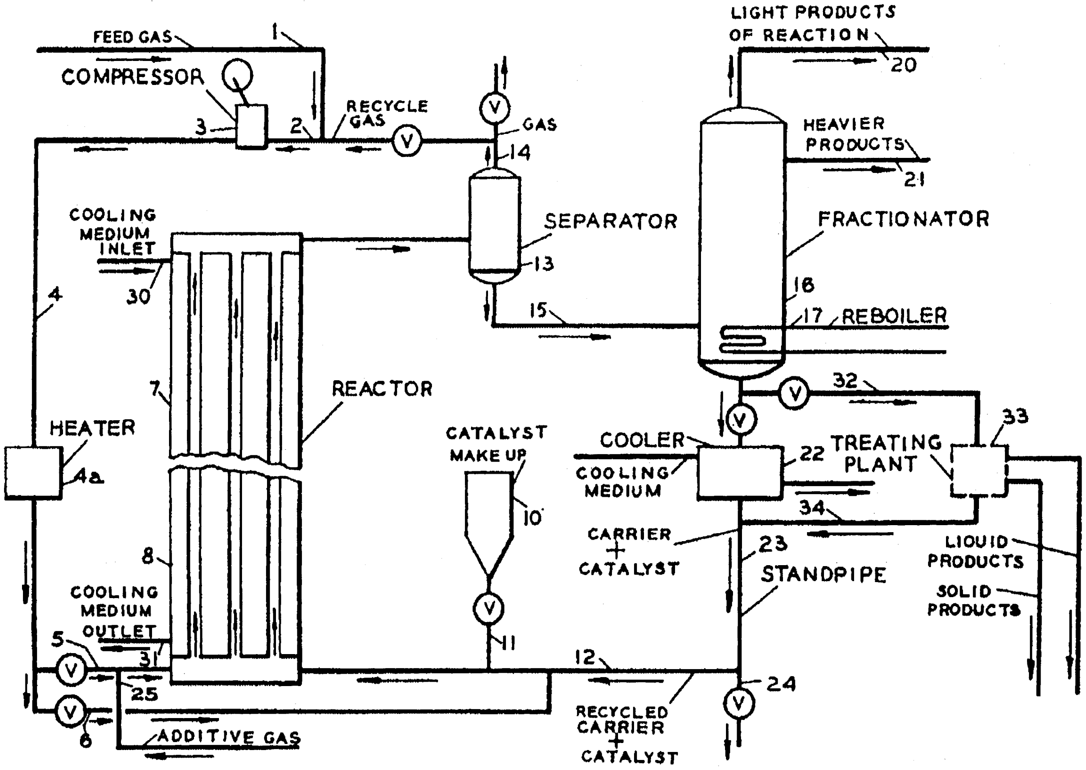

Fig. 17. Texaco method of effecting catalytic reactions [64].

shown in Fig. 18, a solvent is injected between the catalyst layers of alternating catalyst and non-catalyst solids. Above each stage in the reactor, there is a device for injecting a fluid which, by partial evaporation, effectively removes the heat of the synthesis reaction.

2.4.4. Gulf

Cornell and Cotton [67] patented a reactor that was dramatically different from the others described above. First, the reactor was oriented with its length horizontally rather than vertically (Fig. 19). A catalyst bed is located within a tube in a tube (cross-section shown in Fig. 20). Located above the catalyst bed and at locations along the length of the reactor are openings to allow syngas to be fed [12] and fans to provide the pressure needed to force the liquid and syngas through the catalyst bed. Along the bottom of the vessel a number of openings allow for the removal of liquid products. Tubes [29] are located below the catalyst bed so that a coolant can be added and withdrawn through openings 31 and 32. A portion of the liquid phase is recirculated around the catalyst through the space between the tube shell containing the catalyst and the outer shell which depends upon the pressure difference across the catalyst bed that is generated by the series of blowers at near the top of the reactor. This reactor configuration would have intellectual appeal, especially where the height of a reactor is important, as it may be if the reactor is located on a barge. However, it appears that the operation of this plant in a steady-state condition would be an exceptionally demanding task.

In viewing the reactors described for this period, one should keep in mind that the Brownsville plant, at about 7000 bbl/day, was very large for its time. However, today one thinks of 20–50,000 bbl/day plants so that a design that was reasonable to consider for this period may be impractical when projected to the reactor size needed today.

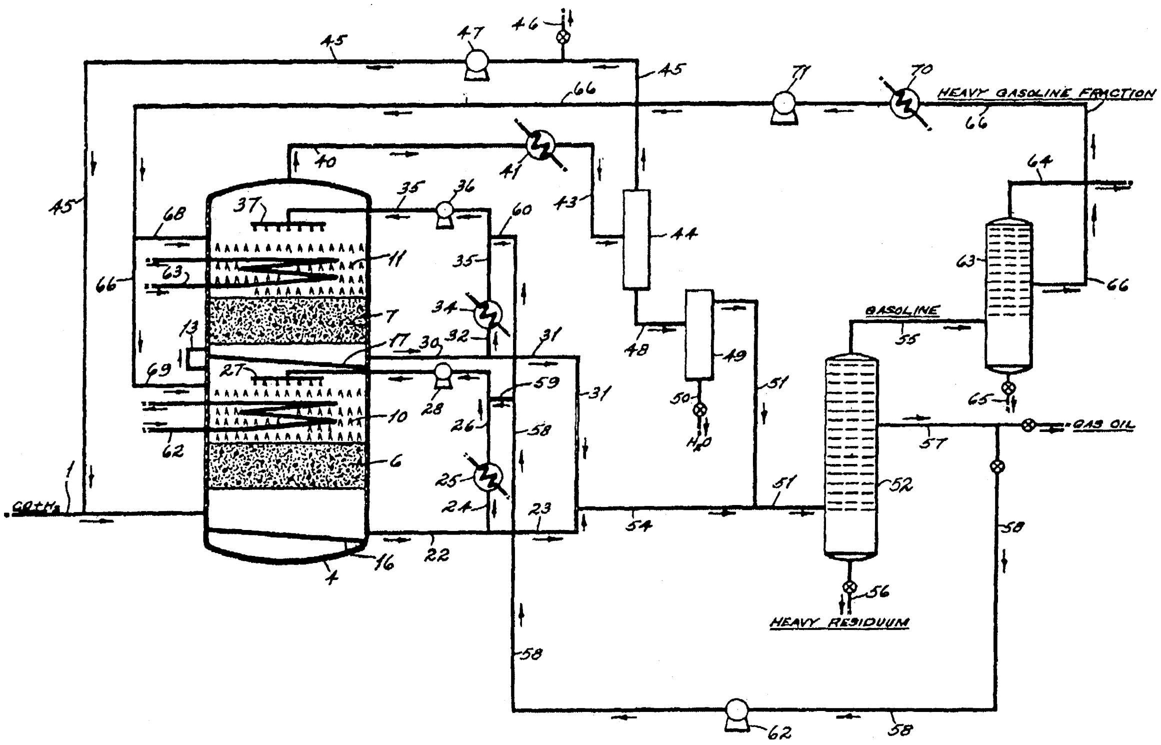

Fig. 18. Method for synthesizing hydrocarbons and the like [66].

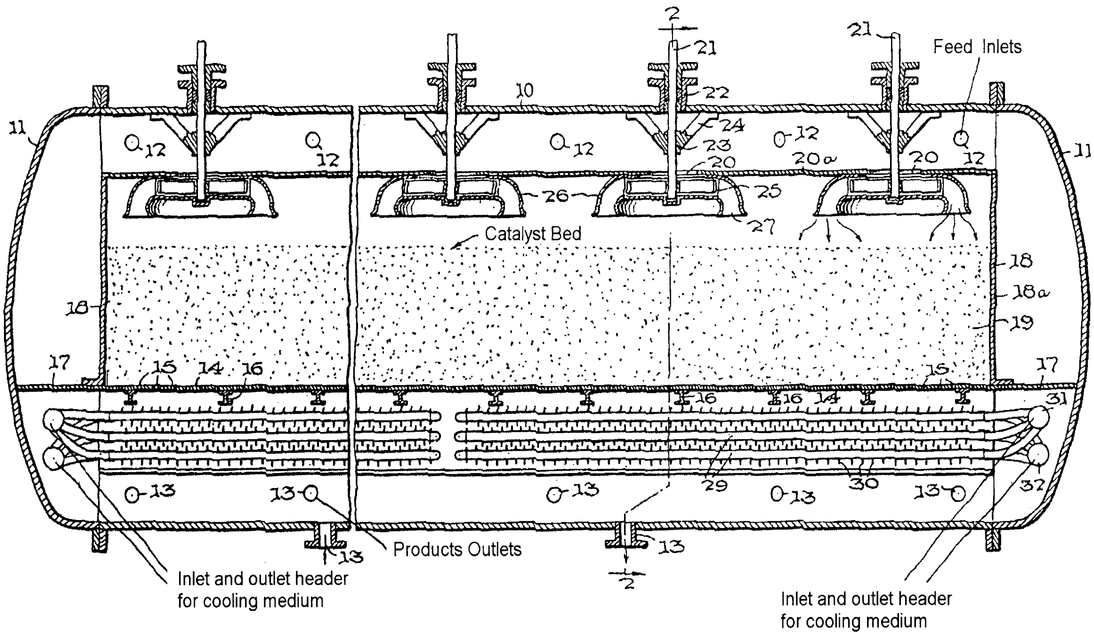

Fig. 19. Catalytic reactor for liquid phase synthesis [67].

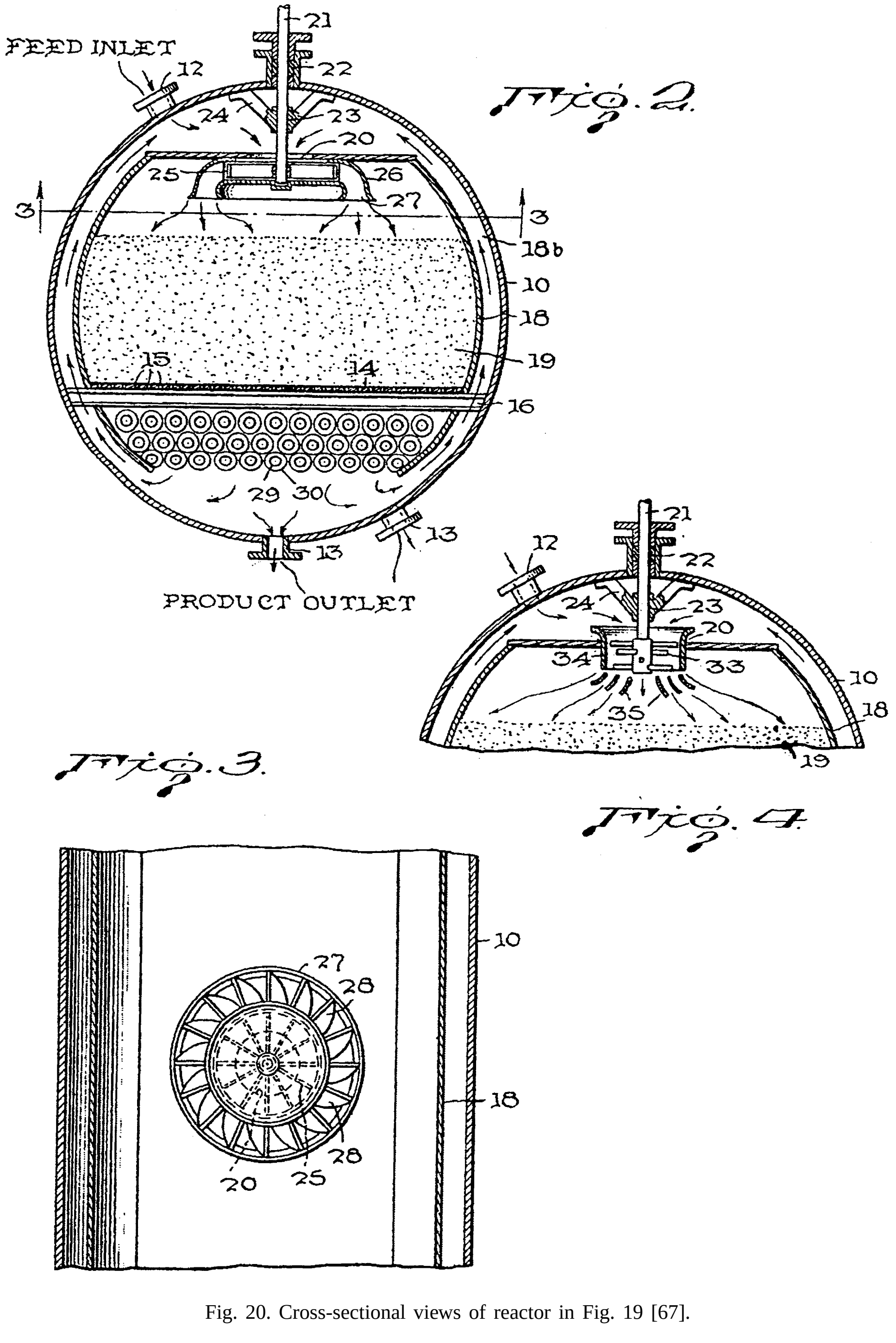

Fig. 20. Cross-sectional views of reactor in Fig. 19 [67].

3. Period II: 1960–1985

3.1. UOP

UOP workers [68] made a comparison of the entrained bed reactor, designed by Kellogg [69] and operated commercially by Sasol, a tube-wall reactor developed by US DOE [70], a slurry reactor, designed by Kölbel and Ralek [45] and operated on a semi-commercial-scale at Rheinpreussen-Koppers, and the ebullating bed reactor, developed by the US Bureau of Mines [33] and utilized by Chem Systems [71].

It was concluded that, since the FT reactor represents only a small part of the total cost of an indirect liquefaction plant, the value of the products is of primary importance in the selection of a particular reactor [72]. These authors also concluded that in spite of uncertainties in the yield structures that have been reported for some reactor systems, the differences in comparing the above reactor systems are large enough to indicate clear advantages for the slurry reactor as it has the lowest investment and catalyst costs. It was expected to give the highest gasoline yields and thermal efficiencies [72]. While the slurry reactor seems to be the one currently being considered by most organizations, it appears that it will be operated to maximize wax yield which will be cracked to diesel fuel with the goal of minimizing the gasoline yields.

3.2. Exxon

The patent history indicates that Exxon has exhibited a renewed interest in converting synthesis gas to hydrocarbons. The early work during this period contains numerous examples of syngas conversion at ambient pressures. More recently the data reflect a more sophisticated evaluation of catalysts and a long string of patents that relate to improvements in equipment and its operation. The latter are a result of the operation of a sizable fully integrated pilot facility (200 bbl per day) at their Baton Rouge Laboratory for their AGC-21 process. Because the Exxon work overlaps Periods II and III, and, since there is no logical break in the reports, their work during both periods will be covered in this section.

3.2.1. Slurry bubble column reactor design

3.2.1.1. Modified gas inlet system. Patents provide claims of methods to improve the axial distribution of catalyst and the mixing of particulate catalyst in the slurry. The methods include adding a secondary gas into the column at locations above, as well as the commonly practiced addition below, the gas distributor plate. The basis of this design is that since solids distribution along the axis of a column is a function of gas velocity in the column, by increasing gas velocity, solids distribution will decrease in the lower part of the column and increase in the upper part. A key to the method disclosed in patents is that introducing a disproportionate share of the gases at an inlet point source close to but above the distributor inlet will reduce the concentration of solids in that particular portion of the reactor and result in an increase in solids concentration in other portions of the reactor. The overall result is a more even distribution of solids in an axial direction.

3.2.1.2. Downcomers. The patents make a variety of claims regarding the utilization of downcomers to effect catalyst redistribution and/or catalyst rejuvenation. The downcomer is specified as a vertical conduit which is open at both ends, fully submerged in the slurry with the bottom near the bottom of the reactor and the top near the top surface of the slurry. A patent issued to Behrmann et al. [73] claims a method for redistributing catalyst in a slurry reactor by use of a downcomer. The bottom of the downcomer is shielded by a baffle plate to divert gases from rising from the bottom and gas free slurry enters at the top and passes down the conduit and out at the bottom. Most, if not all, Exxon patents utilize downcomers with some attachment to the bottom of the conduit and this feature presumably relates to some finer technical and/or legal features. The preferred cross-sectional area of the downcomer should be no more than 2% of the total cross-sectional area of the entire reactor. An example is provided using the same equipment described under Pedrick et al. [74] in which the bubble column was run both with and without a downcomer in operation. In both cases rejuvenation tubes were operated in an equivalent manner. The results showed that axial distribution of the catalyst was more uniform when the downcomer was in operation, as shown in Fig. 21.

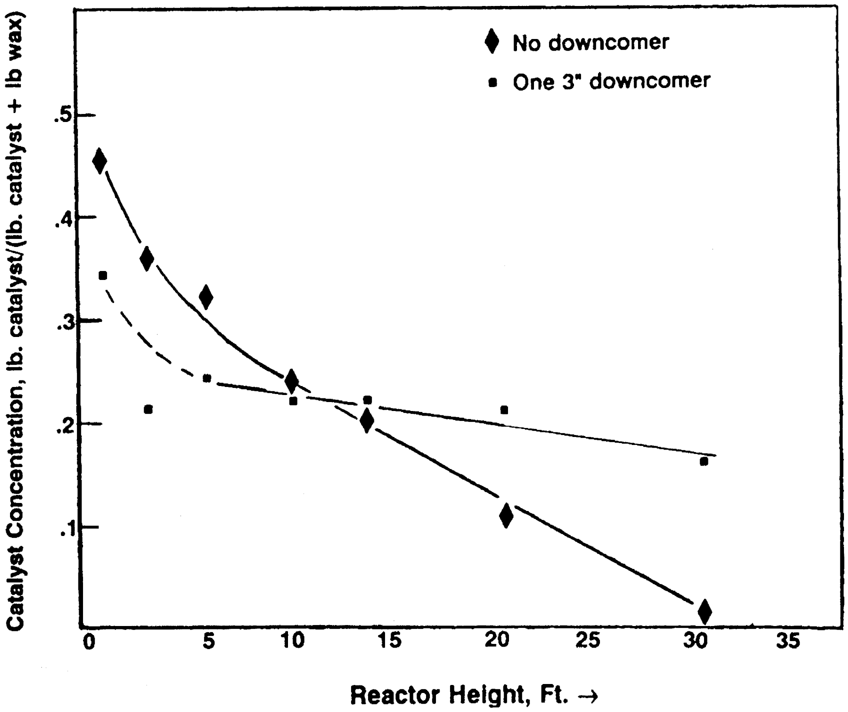

Fig. 21. Catalyst concentration vs. reactor height for no downcomer (♦) and for one 3 in. downcomer (■) [74].

A patent issued to Chang [75] claims a slurry bubble column reactor design incorporating a peripheral downcomer. The reactor comprises a double walled vessel wherein the inner vessel serves as the main reactor zone and the peripheral circumferential top rim of the inner vessel wall, having attached to it an inverted channel having an apex and two edges, being attached to the inner wall along the outer edge of the inverted channels. The second edge of the inverted channel extends over the main reaction zone creating a gas space within its inverted contour with a gas vent extending upward from the inverted channel. A liquid by-pass pipe extends from below the top of the liquid level interface through the inverted channel between the attachment of the inverted channel to the inner reactor wall and the apex of the channel providing a means through which slurry flows into the peripheral downcomer section. This design is shown in Fig. 22 wherein the outer edge 8A of the inverted channel is attached to the top of the inner vessel wall. The innermost edge is in contact with the slurry in the main reaction zone. Gas disengaging from the slurry trapped in the inverted channel exits into the gas disengagement space 5 through line 12 and slurry exits through line 13 onto the top of an inverted channel outside the apex 10 through line 13 into the downcomer section 4. The higher density in the downcomer section promotes flow from the top of the vessel to the bottom. A more complete description of this invention can be obtained by referring to the patent specification.

3.2.1.3. Heat transfer system. This is illustrated by a patent issued to Stark [76] which claims a method for removing heat from an FT reactor which comprises passing pentane through the tube-side of cooling tubes, vaporizing the pentane to a pressure greater than the pressure in the reaction zone and recovering the vaporized cooling medium. In a preferred embodiment of this invention the vaporized pentane is sent to an expander where the high pressure energy is recovered. The low pressure vapor leaving the expander is fed to a condenser where it is liquified and then

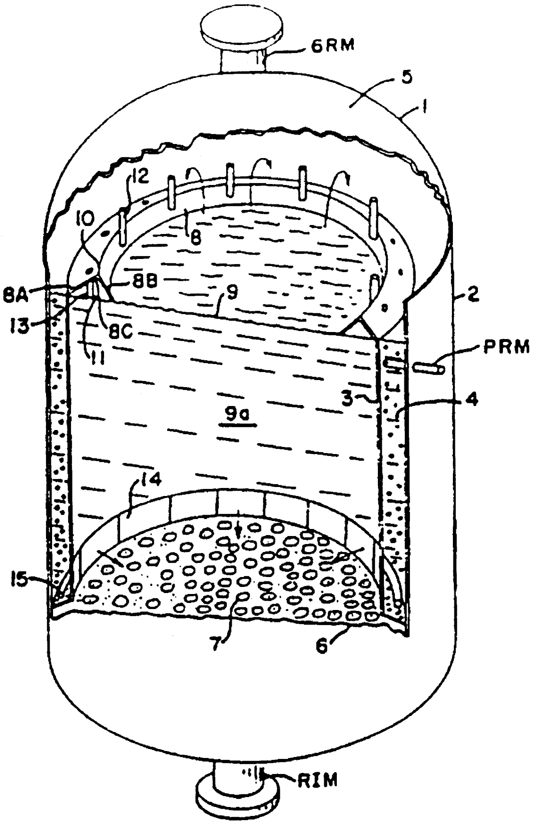

Fig. 22. Schematic of reactor for enhanced gas separation for bubble column draft tubes [75].

pumped up to pressure and fed back to the reactor. The recovered energy can be used to drive compressors for an air separation plant or turbogenerators to generate electricity. A goal is to replace steam so that if a leak develops the cooling fluid will be an inert which will not damage the catalyst whereas steam would in nearly all cases be harmful to the catalyst.

3.2.1.4. Tube-in-shell reactor. A patent issued to Koros [77] claims a slurry FT reactor wherein the slurry catalyst is disposed in a plurality of vertically arranged tubes having a length/diameter ratio of at least 10 with each tube surrounded by a common heat transfer medium disposed within the shell of a shell and tube reactor, the heat transfer medium not in fluid communication with the slurry liquid. The description of the operation of a reactor comprising a 5.76 in. (114.6 cm) i.d. × 50 ft (1.52 m) long pipe mounted in a 12 in. pipe cooling jacket was provided. Liquid heights varied between 12 and 32 ft (3.66 and 9.75 m) with linear gas velocities up to 7.9 cm/s. For a 2.1/1 H_2/CO synthesis gas mixture at a superficial velocity of 5 cm/s, 2200 GHSV, reactor pressure of 285 psig (1.96 MPa), and steam jacket pressure of 140 psig (0.96 MPa), CO conversions in excess of 50% were obtained. The temperature of this run was not given.

3.2.2. Reactor operation

3.2.2.1. Setting operating conditions. A patent issued to Herbolzheimer and Iglesia [78] claims a method for operating a solid–liquid–gas bubble column having a diameter >15 cm for FT synthesis over a supported cobalt catalyst in which the solids are fluidized by the gas. The invention comprises:

1. Injecting gas at an average gas velocity >2 cm/s.
2. Fluidizing the particulate catalyst having an average diameter >5 μm in an expanded liquid column >3 m in height and a particle settling velocity U_s (cm/s) and a dispersion coefficient D, such that (H, expanded slurry height)

   $$0.5(U_s - U_L) \leq \frac{D}{H}, \quad H > 3\,\text{m}$$

   where

   $$U_s = \frac{1}{18} d_p^2 \frac{\rho_s - \rho_l}{\mu} g f(C_p), \quad d_p > 5\,\mu\text{m}$$

3. Operating at plug flow at a gas velocity U_g, expanded liquid height H, and dispersion coefficient D such that

   $$U_g \geq 0.2\frac{D}{H}, \quad H > 3\,\text{m}, \; U_g > 2\,\text{cm/s}$$

   In one example using a Co–Re/TiO_2 catalyst having a density of 2.7 g/cm^3, a liquid density of 0.7 g/cm^3, and a wax viscosity of 0.01 g cm/s, the particle settling velocity is

   $$U_s(\text{cm/s}) = 1.1 \times 10^{-4}[d_p(\mu\text{m})^2]$$

   For a 60 μm average particle, $U_s = 0.39$ cm/s. For a liquid velocity of $0.5U_s$, and a column height of 3 m, a gas velocity of 2 cm/s provides a Peclet number of 10, which is the minimum gas velocity allowed that would maintain suspension of the solids

> in the column and maintain a plugflow operation in the column.

This patent and its European counterpart have attracted enormous attention, both technically and in the courts. It appears that enforcement of the patent would prohibit the use of a cobalt catalyst in a slurry bubble column reactor for any conditions that would have appeal for a commercial operation.

3.2.3. Catalyst activation and rejuvenation

A patent issued to Mitchell [79] claims a method for activating a fresh, reduced cobalt containing FT catalyst by treating the catalyst with H_2 in hydrocarbon liquids for a period sufficient to increase catalyst productivity. A patent having an identical specification issued to Mitchell [80] claims a process using the method of catalyst activation that is run under FT conditions. The method applies specifically to treating catalysts that had been previously reduced ex situ and exposed to the atmosphere before introduction into a slurry system. Such catalysts are suspended in a slurry and treated with H_2 at hydrocarbon synthesis temperature and pressure with temperatures no lower than 40 °C below hydrocarbon synthesis temperature. Another patent issued to Mitchell [81] claims a method for rejuvenating partially deactivated catalysts which is essentially the same procedure described above. An example for activating a 12% Co–1% Re on a 94% TiO_2–5% Al_2O_3 support by reducing the catalyst with H_2 was given. Following reduction, catalyst was passivated with a H_2/CO stream. This passivated catalyst was combined with wax in a slurry reactor and treated with H_2. Synthesis gas productivity over the treated catalyst increased to 100% relative to 25–60% productivity for the non-H_2 treated catalyst. The effect of several periods of catalyst rejuvenation during a 50-day run on catalyst productivity following this method is shown in Fig. 23.

A patent issued to Pedrick et al. [74] claims a method by which reversibly deactivated particulate hydrocarbon synthesis catalyst in a gas–slurry reactor is rejuvenated and more uniformly distributed in the reactor. A hydrogen rich gas, injected into the bottom of a vertical draft tube which is fully immersed in the slurry, forces the catalyst up the draft tube

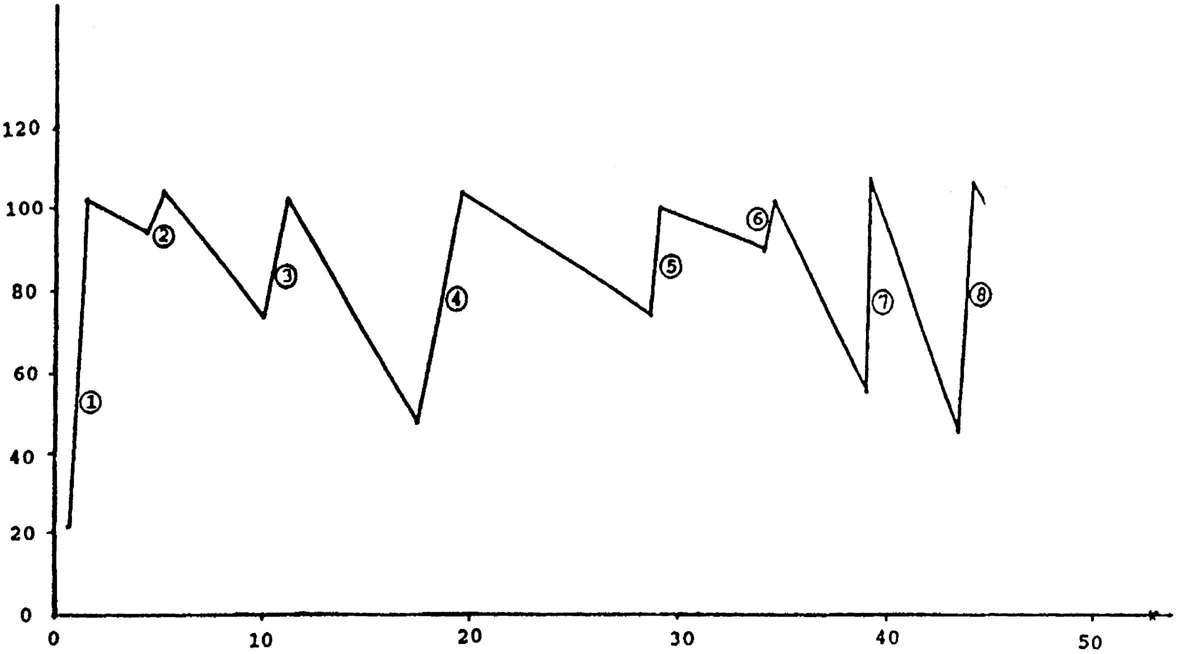

Fig. 23. Relative volumetric productivity represented by activity versus days-on-stream with intervals of hydrogen rejuvenation (12 wt.% Co on titania with 6 wt.% Al_2O_3 as binder [81].

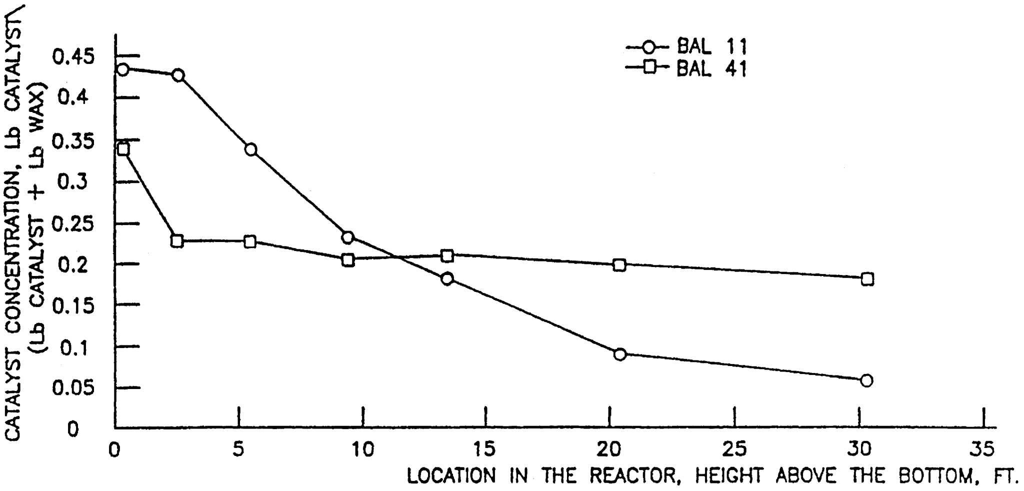

Fig. 24. Catalyst concentration vs. elevation in the reactor with (□) and without (○) use of draft tubes [74].

while concomitantly reactivating the catalyst, which is discharged from the top into the upper portion of the slurry-phase. The examples contained results from a series of balances made during a run in a 4 ft (0.12 m) diameter by 35 ft (10.7 m) high reactor that show both activation and axial redistribution of the catalyst. During the run, various combinations of draft tubes fed with H_2, which were commonly referred to as rejuvenation tubes, and draft tubes fed with tail gas, were employed. The maximum flue-gas fed draft tube plus rejuvenation tube cross-sectional area for any of the run conditions was 2.6% of the cross-sectional area of the reactor. A feed gas mixture comprizing 56% H_2/26% CO/13% CO_2/5% CH_4, by volume, was fed to the reactor containing a 12% Co–1% Re on a 94% TiO_2–5% Al_2O_3 slurry catalyst at 210–230 °C and 20 atm (2.02 MPa). When operating the reactor with two 2 in. (5.08 cm) diameter and two 4 in. (10.2 cm) diameter flue-gas fed draft tubes and one 3 in. (7.62 cm) diameter rejuvenation tube, the superficial velocities in the respective locations were: inlet, 12–14 cm/s; outlet, 10.5–12.1 cm/s; draft tubes, 58–60 cm/s; rejuvenation tubes, 40–70 cm/s. Under these conditions the axial dispersion of the catalyst in the reactor improved significantly (Fig. 24) and productivity increased from 41 to 69 (vol. CO/h/vol. slurry). The overall reactor temperature differentials from the bottom to the top of the reactor for the individual balances using both lift and rejuvenation tubes was only a couple of degrees.

The effect of rejuvenation tubes on catalyst activity is shown in runs where both flue-gas fed draft tubes as well as rejuvenation tubes were used [81]. In a run sequence shown in Fig. 25, the decline in activity of catalyst was followed for a period of 3 days after which one 3 in. (7.62 cm) rejuvenation tube was brought on line. Immediately upon addition of H_2 an exotherm was observed followed by an immediate increase in catalyst activity recovering its initial activity in 1–2 days, after which it remained constant. After line-out, adding another rejuvenation tube provided no additional benefit. The exotherm in the rejuvenation tube was also used as a method to determine the degree of aging of the catalyst.

The beneficial effect of heating the rejuvenation tube to a temperature higher than the surrounding slurry was also demonstrated. Although, the temperature in the rejuvenation tube is typically a few degrees higher than the surrounding slurry, through insulation of the tube and heating with steam, even higher temperatures can be attained. During one period in which the rejuvenation tube was heated sufficiently to raise the temperature an additional 5.6 °C, CO conversion in the reactor increased from 26 to 36% over a 24 h period whereas in a prior balance period without ex-

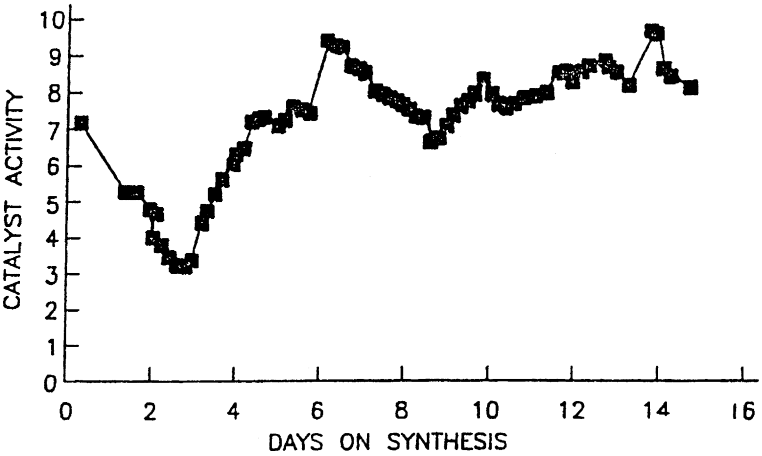

Fig. 25. Conversion using hydrogenation rejuvenation (to day 3 no rejuvenation; rejuvenation after day 3) [82].

ternal heating being applied to the rejuvenation tube, CO conversion had dropped from 32 to 26% over a 12 h period, as shown in Table 3 [82].

Exxon patents have covered a variety of procedures to effect catalyst rejuvenation that utilize operations within as well as external to the reactor. A number of patents pertain to catalyst rejuvenations that mirror the operations utilized for fluid cracking units. An example is a patent issued to Hsia [83] claims an FT process comprising a slurry reactor design coupled with a continuous rejuvenation reactor. Deactivated catalyst is reactivated and rejuvenated using an external rejuvenation reactor vessel to which catalyst from the synthesis reactor is continuously fed via a downcomer from the top of the slurry bed in the synthesis reactor to the bottom of a slurry bed in the external rejuvenation reactor vessel (see Fig. 26). Likewise, rejuvenated catalyst is fed to the synthesis reactor via a downcomer from the top of the slurry bed in the rejuvenation reactor to the bottom of the slurry bed in the synthesis reactor. Slurry flow from synthesis reactor vessel to the rejuvenation vessel and the flow of rejuvenated catalyst back to the synthesis reactor vessel are driven by gravity since both vessels are under the same pressure. A drawing is included but no examples are given.

3.2.4. Removal of catalyst fines

A patent issued to Hsu and Robbins [84] claims a method for removing <1 μm particles adhering to catalyst particles containing a Group VIII metal supported on an inorganic refractory oxide. The removal of fines is important for wax separations. The method comprises dispersing the particles to which the <1 μm particles adhere in a liquid comprising a Fischer–Tropsch derived wax, agitating the dispersion and concentrating the <1 μm particles in the supernatant liquid and separating the <1 μm particles by decanting this layer from the larger particle containing phase. Although examples are given in which

Table 3
Effect of heating rejuvenation tubes on catalyst activation [82])

Heat addition	No	Yes
Gas rate in tube (scfh)	5100	4800
Average reactor temperature (°F)	427	427
Average rejuvenation temperature (°F)	430	440
CO conversion, start to end of run (%)	32–26 (over 12 h)	26–36 (over 24 h)
Conversion (change per day)	−12.4	+10.4

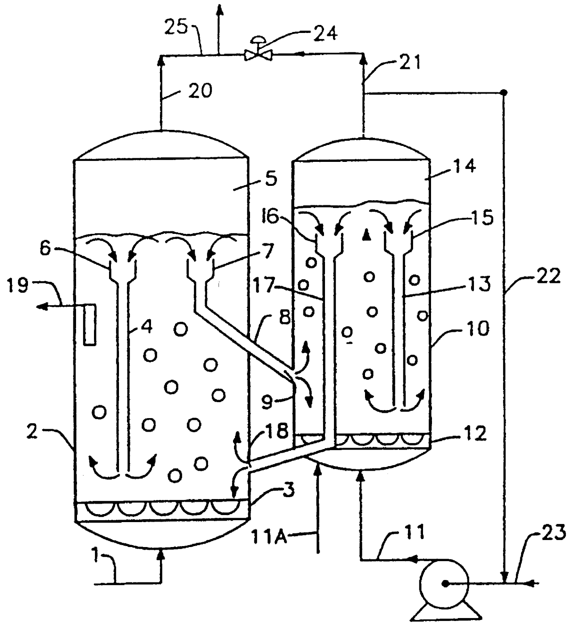

Fig. 26. Schematic of multiple vessels for catalyst rejuvenation [83].

the liquid used in the particle classification step includes solvents other than Fischer–Tropsch derived wax, the claims only apply to the latter (see Table 4). Catalysts stirred with FT wax at 130 °C gave initially a filtration rate of 0.024 l/cm^2/min which decreased to 1.2 cm^2/cm^2/min after stirring for 44 h. Using the method of this invention of extended stirring and separating the decant after 3 cycles, the filtration rate improved to 0.06 l/cm^2/min.

3.2.5. Apparatus for substantially plug-flow slurry-phase synthesis

Koros [77] has patented a slurry apparatus that permits a substantially plug-flow slurry-phase operation in an arrangement of multiple tube reactors in a shell. Thus, the concept of the mechanical part of the tube and shell reactor resembles a Sasol Arge reactor; however, numerous additional features are incorporated to permit slurry-phase operation.

Table 4
Improvement in catalyst/wax separation in slurry FT processes by removal of catalyst fines [84])

Classification solvent	Catalyst/solvent (wt./wt.)	Other	Cycles	Acetone cycles	Filter time	Filter rate (g/min)	Filter rate (gal/ft^2/min)
Millipore filter paper (0.45 μm)							
Blank	–	–	–	–	95.0	0.5	
Water	15/85	–	6	2	0.9	55.0	
i-C_3H_6OH/n-C_7H_{16} (1/9)	10/150	1% oleic acid added	7	2	1.0	50.0	
i-C_3H_6OH/n-C_7H_{16} (1/9)	10/150	1% aerosol OT-100 added	7	2	1.0	50.0	
Glass fiber filter (0.3 μm)							
FT wax at 130 °C	2/98	Stirred 5 min	None	None	–	–	5.8 at 14 psig
		Stirred 44 h	None	None	–	–	0.05 at 14 psig
FT wax at 120 °C	2/98	Stirring per cycle 19/48/24	3	None	–	–	14.5 at 14 psig

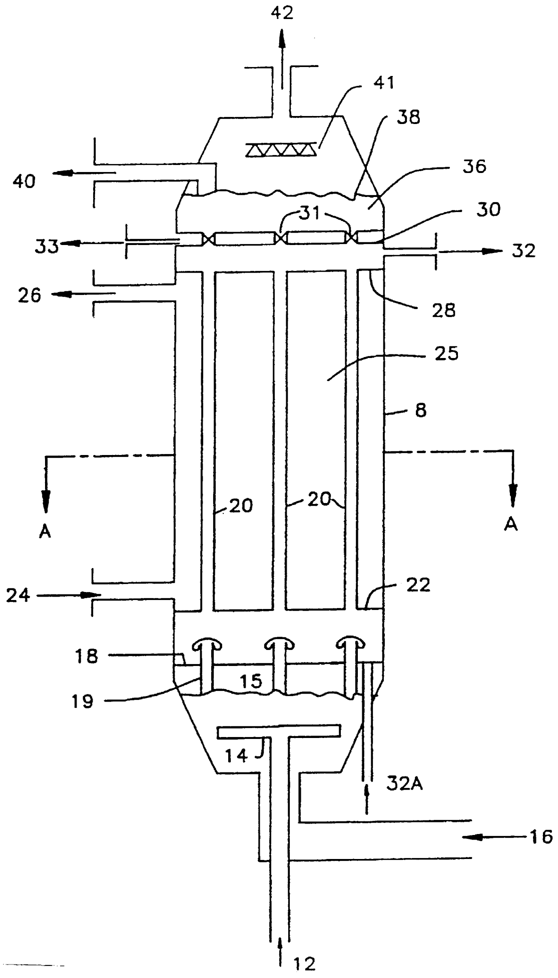

Fig. 27. Elevation of a shell and tube reactor arrangement showing the gas, liquid, catalyst interconnection both above and below the upper and lower tube sheets [77].

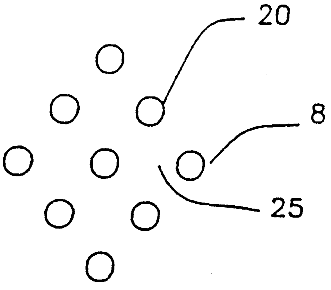

Fig. 28. Horizontal section A—a through the elevation of Fig. 29 showing a possible arrangement of tubes, i.e., reaction zones [77].

In Fig. 27, the syngas is added through 12 and is dispersed through sparger 14 into the liquid slurry medium, held at a level so as to maintain a gas–liquid interface, with the gas held in the space between 15, the slurry–gas interface and 18, a distributor tray.

A series of reactor zones, 20, are arranged within the shell, such as the ones shown by the example in Fig. 28.

The reactor tubes are held in place by lower, 22, and upper, 28, tube sheets. The space between the distributor plate, 18, and the lower tube sheet, 22, may or may not contain catalyst in addition to the slurry liquid. A detail of the distribution zone is provided in Fig. 29. The bubbly liquid from area 9 enters the tube/bubble cap 19A/19B. The bubble cap is aligned vertically with the reaction zone tube 20. The bubble cap is sized to give a pressure drop and injection velocity sufficient to decrease the size of the bubbles and to suspend the catalyst in the reaction zone (injection velocity about 20–100 ft/s (6–30 m/s)). The gas to liquid transfer rates are at least equal to the conversion rate of the syngas gas.

Preferred slurry materials are stated to be Fischer–Tropsch waxes and C_{16}–C_{18} hydrocarbons. The con-

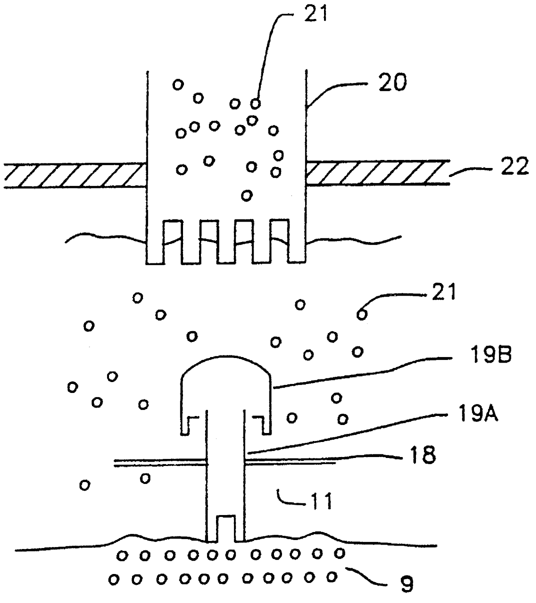

Fig. 29. Detail of a possible distribution zone for one reaction tube/zone [77].

centration of solids are usually about 10–50 wt.%, preferably 30–40 wt.% solids.

Catalyst/slurry addition/withdrawal may be effected through line 32. The region between tube sheets, 28 and 30, allows interconnection between the upper ends of the reaction zones for gas, liquid and catalyst. Tube sheet 30 holds filter cartridges, 31, which may be manufactured from sintered metal mesh, woven metal fibers, glass fibers, cloth or fibrous carbon, which can retain the catalyst particles while allowing the wax to pass. The filter cartridges are aligned vertically above each reaction zone. A gas–liquid disengagement zone lies above the filter cartridge tube sheet, and liquid product, separated from catalyst, can be withdrawn through tube 40 and/or 33. A demister, 41, separates gas from liquid droplets; residual gases are withdrawn through tube 42.

During operation the catalyst, 21, is preferably located in the reaction zone although some catalyst may be found in the liquid zones above or below the upper and lower tube sheets.

The catalyst most preferred is cobalt on titania (primarily in the rutile form) with less than about 70 m^2/g. Preferred promoters are stated to be rhenium and hafnium.

It is stated that "... catalyst particle size is not critical ... " but is preferably in the 20–150 μm size range.

The example described the operation of a single reactor (6 in. o.d., 5.76 in. i.d. (15.24 cm o.d.; 14.63 cm i.d.)) about 50 ft (15.2 m) tall mounted inside a 12 in. (30 cm) pipe to serve as a cooling jacket. Feed gas to the reactor was preheated.

The catalyst was prepared by impregnation cobalt onto titania extrudates which were crushed and screened to give ca. 30 μm diameter particles (presumably the catalyst contained promoters). The catalyst was reduced in hydrogen in a fluidized bed, and then the slurry wax was introduced. Following a prescribed procedure of start-up, they attained a CO conversion in excess of 50% at GHSV = 2800. Following a brief reactor upset, the unit was restarted at a higher steam jacket pressure (140 psig; 0.96 MPa) and higher reactor pressure (285 psig, 2.0 MPa at the reactor gas outlet). The reactor maintained CO conversion of 60–70% (2800–3600 h^{-1}) for nearly 7 days of synthesis. This material was stated to be a "... very

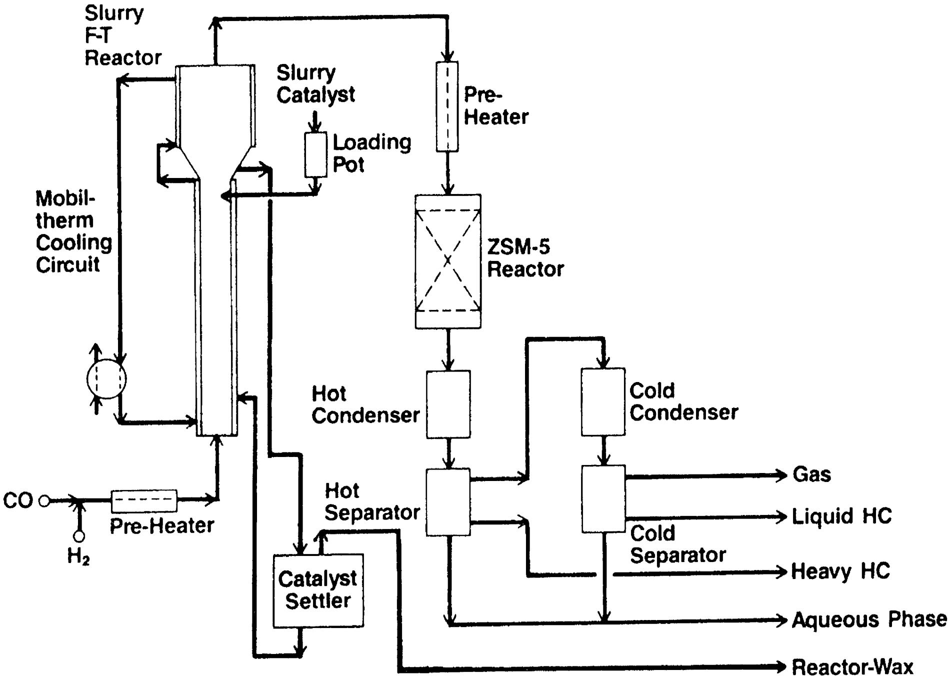

Fig. 30. Simplified flow diagram of the Mobil Oil two-stage plant for synthesis gas conversion [48].

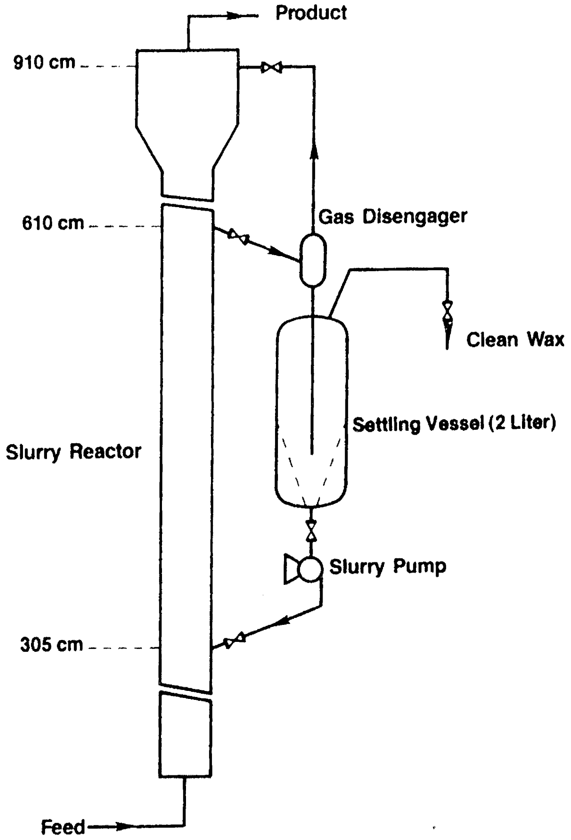

Fig. 31. Schematic diagram of the continuous settling system for catalyst/wax separation [48].

active HCS catalyst.” Methane selectivities were in the range of 2.7–3.2%. Assuming the steam jacket pressure represents steam/water, this corresponds to 354 °F (178 °C); presumably the reactor side would not be at a much higher temperature.

3.3. Mobil (now Exxon Mobil)

The initial runs in the pilot plant (Figs. 30 and 31) at Mobil Oil [48,49], based upon the catalyst compositions in Mobil’s patents, utilized a catalyst with a composition that resembles the one reported for Kölbel’s work and the catalyst used for the LaPorte Run II (low, not high, Cu content). Mobil’s data from work funded by DOE have become the “standard” for both economic (e.g., [85]) and technological evaluations (e.g., [86]). The first three runs in the Mobil plant were conducted using a catalyst that produced low molecular weight materials; during the third run a potassium salt was added at 81 days-on-stream and this decreased the methane + ethane production from about 13 to 18 wt.% without significantly lowering the CO conversion; however, operational upsets prevented a valid assessment of the impact of the added alkali [49]. The later runs were in the high molecular weight product mode (wax mode). In most runs, Mobil operated with about a 20 wt.% slurry catalyst loading. In run 8, the aging rate of the iron catalyst operated at 250 °C, 1.48 MPa and 1.4 NL/gFe h was such that half the activity would be lost during 24 days; later in the run the catalyst half-life was 13 days when the temperature and pressure were increased. Mobil workers indicate that the catalyst used in this run was not acceptable because of its high aging rate. In run 9, a surprisingly low methane + ethane make (about 5.4 wt.%) was obtained. The catalyst was the “same” as had been used in a prior run where this was not observed; the only difference noted was that the low methane + ethane catalyst had a lower surface area. An operational upset terminated the effective operation at day 10. In run 10, Mobil workers reported that the catalyst could not be fully activated at synthesis conditions.

Run 12 was operated for 17 days at constant conditions and “This period represented the finest example of low methane + ethane (4.1 wt.%) mode operation we have ever produced in the pilot plant.” Wax production was about 60 wt.%. An operational upset occurred on day 17 and afterwards catalyst settling and low catalyst activity were problems that could not be overcome.

Run 13 was a repeat of run 12 and good operation was accomplished for 35 days-on-stream, after which catalyst settling became a problem. Viewing the pictures of the catalyst, Mobil was utilizing particles in the 1–5 μm range, and the final catalyst particles were considerably larger following removal from the reactor. It is not clear whether this is due to catalyst particle growth or, more likely, cementing together several particles by reactor wax. It is not clear, if wax caused the particle size increase, whether this occurred in the reactor itself or was an artifact introduced during catalyst collection and subsequent treatment.

As stated above, the Mobil data have replaced the Kölbel data as the “standard” for slurry F.-T. operation. Data for reactor wax yield of 46 wt.% are shown in

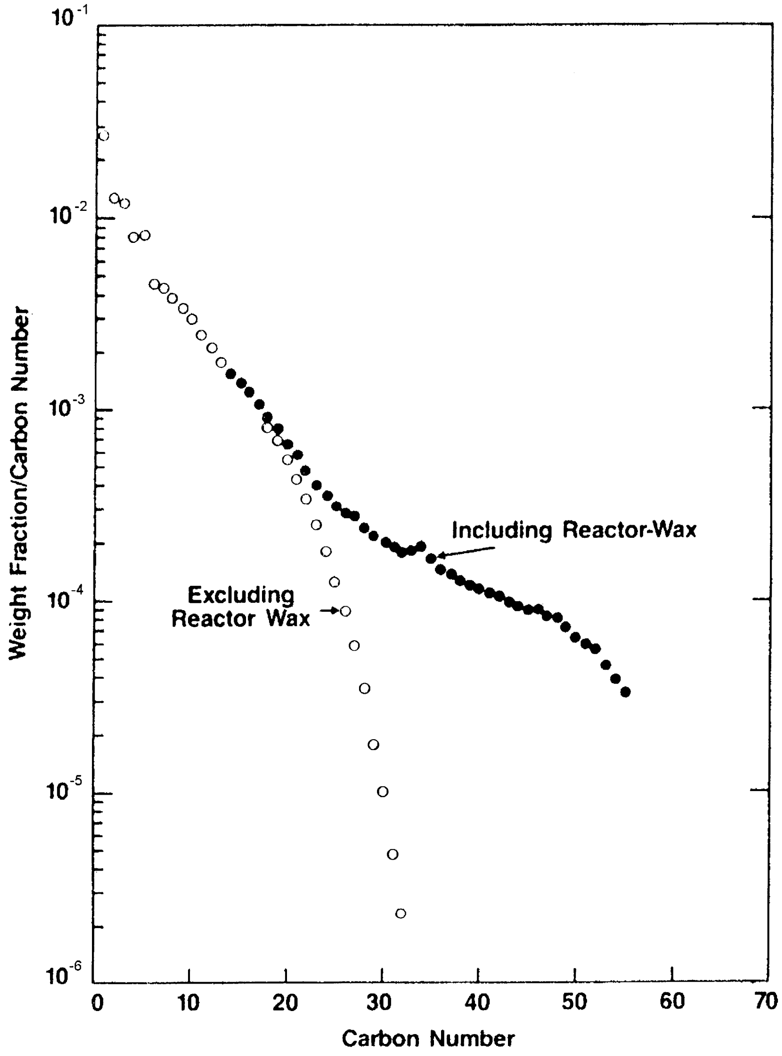

Fig. 32. Schulz–Flory distribution for the first stage Fischer–Tropsch products obtained by Mobil Oil at a reactor wax yield of 46 wt.% [49].

Fig. 32. This data has been utilized by Bechtel for their analysis of slurry F.-T. operations. They consider the data to consist of three regions: methane (α_1) that is higher than ASF; C_2–C_4 (α_2) and reactor wax (α_3). Theoretical curves for reactor wax make of 9.49 wt.% (low alpha data), 46.02 (intermediate alpha data) and 75.95 (high alpha data) are shown in Fig. 33.

Thus, the Mobil data, in spite of operational problems, represents the best data that is available in the open literature in sufficient detail that its quality can be adequately judged.

3.4. Gulf Oil (now part of Chevron)

During this period Gulf Oil conducted a major effort to develop processing that would enable them to convert natural gas to transportation fuels and to petrochemicals. Much of this work was devoted to the development of active catalysts and to the operation of fixed-bed reactors. An outgrowth of this effort was the development of the Gulf-Badger FTS process. Most, if not at all, of the rights to the Gulf FTS technology were obtained by Shell following the incorporation of

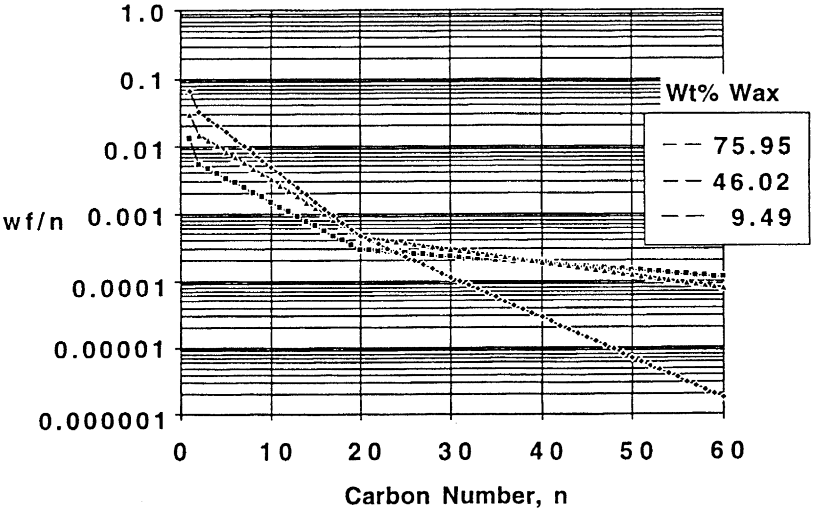

Fig. 33. Schulz–Flory distribution based on Mobil Oil data at low, intermediate and high alpha synthesis conditions [85].

Gulf Oil into Chevron. Gulf did some work using a slurry bubble column reactor that is described in the following.

A 1985 patent [87] obtained by Gulf Oil claimed a process for the conversion of synthesis gas using a finely divided catalyst (ca. 10–110 μm) dispersed in a fluid medium. The catalyst consisted essentially of cobalt and ruthenium on a support.

The process is outlined in Fig. 34 and does not differ significantly from one used by Kölbel and Ralek [45]. In the reactor, the catalyst particles are suspended in a liquid medium having sufficient viscosity to ensure that the particles remain in suspension and having a volatility that is low enough to avoid loss due to vaporization within the reactor. The catalyst is present in the slurry at concentrations from about 2 to 40 wt.%.

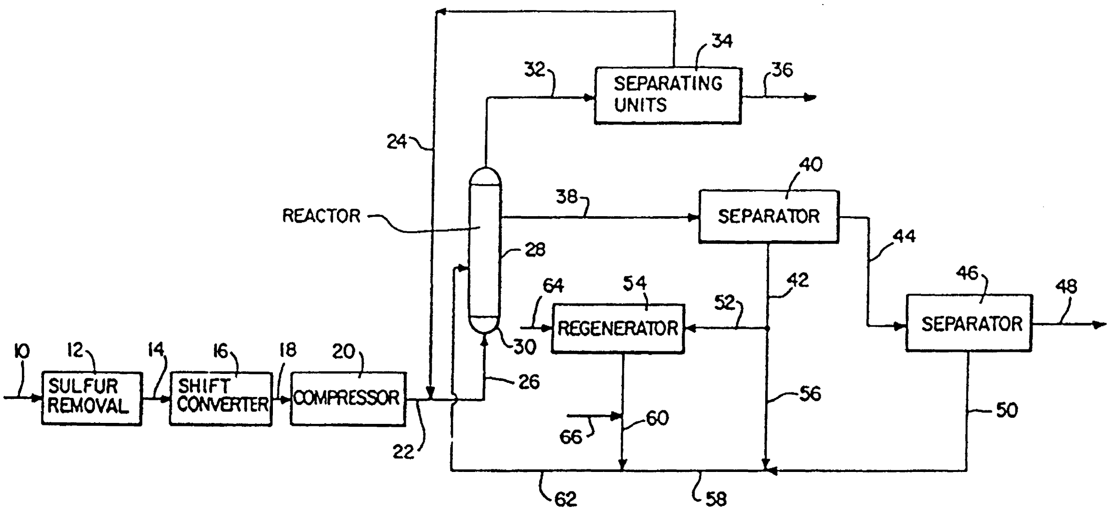

Fig. 34. Process schematic for slurry reactor system using cobalt catalyst [87].

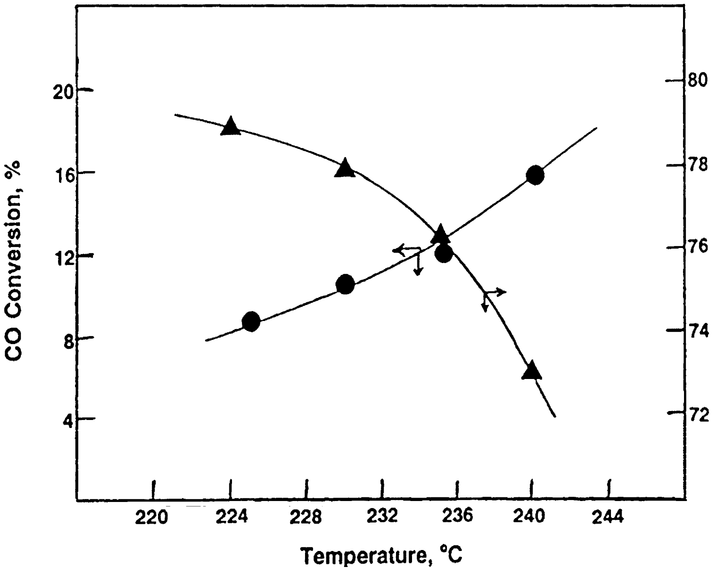

Fig. 35. CO conversion and $C_5{}^+$ product selectivity for FTS using slurry reactor and cobalt catalyst [87].

The catalyst density can be in the range of 0.25–0.90. The gas flow enters at a rate sufficient to suspend all of the catalyst particles in the system without settling. The gas flow rate will be selected depending upon the slurry concentration, catalyst density, suspending medium density and viscosity, and particular particle size utilized. Suitable gas flow rates include, e.g., from about 2 to 40, preferably from about 6 to 10 cm/s. The pressure range covered is from about 1 to 70 atm. Light hydrocarbon products, such as C_{20} and below, are withdrawn overhead through a line designated 32 in Fig. 34. A portion of the heavier products and catalyst slurry is withdrawn through line 38 and is passed to a separation zone. A concentrated catalyst/slurry fraction is returned to the reactor while a portion of the catalyst/slurry may be passed through a regeneration zone 54 before being returned to the reactor. Heavy products with low catalyst concentration are removed through line 44. Separation by filtration can be utilized for separating catalyst from the suspending liquid (vessel 40).

The data obtained in the slurry reactor were compared to a run in the fixed-bed reactor with the same catalyst formulation. Gas entered the reactor at the bottom through a stainless steel screen in the form of small bubbles. Hydrocarbon was removed from the top through a heated line. The pressure was 160 psig (1.08 MPa) and the gas flow with $H_2/CO = 1.95$ was 1826 cm/s. Initially the temperature was 225 °C but was increased and held at several higher temper-

Table 5
Conversion data for syngas conversion using fixed-bed and slurry reactors [87]

Test number	1	2	3	4	5
Reactor type	Fixed-bed	Slurry	Slurry	Slurry	Slurry
Temperature (°C)	215	225	230	235	240
CO conversion rate (ccCO/g/h)	215	649	808	992	1210
CO conversion (%)	45.3	8.4	10.4	12.8	15.6
Product yields, methane (wt.%)	26.6	10.5	11.5	12.5	14.0
C_5–C_{20} (mg/g/h)	67	325	400	478	560
$C_5{}^+$ (wt.%)	60.0	79.0	78.0	76.0	73.0

atures to obtain additional conversion data. The increase in conversion with increasing temperature gives an activation energy of 20.5 kcal/mol (85.7 kJ/mol). At 225 °C, methane is 8.4 wt.% of the product and increases to 15.6 wt.% at 240 °C. As the temperature increases, the C_5^+ fraction gradually decreases (Fig. 35) and the C_5–C_{20} fraction increases, indicating that the alpha value decreases with increasing temperature; however, there is not sufficient data to obtain reliable values of alpha (Table 5).

4. Period III: 1985–2000

4.1. Sasol

Sasol has reported general, but few specific, details about the development and operation of their slurry reactor operations. Sasol's work on a small scale began in the early 1980s [51]. In 1990, a slurry bed with a diameter of about 1 m was commissioned and the results confirmed their early expectations. In a bold move, Sasol decided to construct a commercial-scale slurry reactor (5 m diameter, 22 m high) rather than two 5000 tube tubular-fixed-bed reactors for the expansion of their low temperature operation. The commercial reactor was commissioned in May 1993 and has been reported to operate successfully since that time.

Sasol uses a separate catalyst pretreatment reactor in which hydrogen reduction (extent of reduction not specified) is used to activate an iron catalyst prior to its introduction into the slurry reactor. During operation, it is understood that an activated catalyst batch is on "stand-by" so that if a significant upset, such as a slug of sulfur to produce severe catalyst poisoning, causes a significant loss in productivity, the reactor is emptied and a fresh catalyst batch added during a short period of a few hours. On-line catalyst removal and additions are reported to be done without difficulty. Based upon reports of the extent of sulfur poisoning in the fixed-bed ARGE reactors, it should not be surprising if Sasol operators had made several replacements of the catalyst inventory during the 7 years of commercial operation.

The authors [51] describe the churning nature of the slurry–base bubble interactions, implying that the Sasol operation operates in the bubbly, rather than slug, flow condition. Because of the isothermal nature of the slurry reactor, the operating temperature can be much higher than in a fixed-bed tubular reactor without fear of hot spots leading to carbon formation and break-up of the catalyst. Hot-spots in the fixed-bed reactor presumably allows for the catalyst in the hot-spot to reach a temperature sufficiently above that of the reactor set-temperature so that carbon formation and rapid catalyst deactivation become possible.

It is reported that for an iron catalyst, the product slate is considerable affected by the age of the catalyst, with wax selectivities decreasing with time. However, "by proper scheduling of catalyst renewal, it is possible to maintain a steady selectivity profile for a single reactor while minimizing the catalyst consumption." It, therefore, appears that the Sasol operation involves a regular schedule of catalyst addition, presumably to replace catalyst that is intentionally withdrawn as well as that which is lost as catalyst fines due to catalyst attrition.

Foam was found to build up in the reactor under certain conditions but it was reported that this could be prevented by modifying operation procedures. "Separation of gas from the entrained slurry was another development that was easily resolved", implying that slurry carryover can be a problem if not handled properly.

Several approaches were tried at Sasol in order to effect wax separation form the catalyst containing slurry. These included close attention to the production of the catalyst and its physical characteristics as well as to the separation processes. The technique currently in use in the commercial operation for wax/slurry separation is considered to be proprietary information. The removal of wax, but not catalyst, is a critical aspect of bubble column reactor operation. While Sasol patents address this, the filter operation is poorly described in most of these.

4.2. China

The Chinese have operated a two stage process involving slurry F.-T. synthesis with an iron catalyst and fixed-bed cracking/oligomerization processing using a ZSM-5 catalyst to convert the F.-T. product to gasoline range fuels [88]. The F.-T. slurry reactor was 4 cm in diameter and 450 cm in height. The reactor, in a schematic form, is very similar to the one used by Mobil Oil (Figs. 30 and 31). They used an unsupported precipitated iron catalyst with a typical composition of Fe:Cu:K_2O = 99.5:0.5:0.29. The sample of catalyst used in the slurry reactor had obviously been calcined (based on our work, at temperatures of at least 300 °C) since the XRD analysis showed that the main crystal phase was α-Fe_2O_3. The authors indicate that diffusion effects could be neglected for their runs. It appears that they used a slurry that contained 12% catalyst. Most of the published data concerning runs with their pilot plant are for the product following processing with the ZSM-5 catalyst. However, based upon data presumed to be for the F.-T. only operation, the liquid phase is reported to have a composition of approximately 70% $C_{5\text{–}12}$, 27% $C_{13\text{–}22}$ and 3% $C_{22}{}^{+}$. Thus, based upon the catalyst composition, the product distribution would be considered to originate from a low-alpha mode of operation, and the composition of the catalyst is consistent with this. Furthermore, the low-alpha mode would probably be preferred for subsequent conversion of the F.-T. products with a ZSM-5 catalyst in the second stage.

The output during the course of a 1000 h (40 days) run declined due to loss of catalyst. From the data published for the Chinese F.-T. only operation, it is difficult to reach definitive conclusions on catalyst performance.

4.3. Syntroleum

While Syntroleum began work of FTS earlier than 1985, their visibility dates to this period. Much of the early work they reported did not involve liquid phase synthesis and will not be covered. The first significant public information for liquid phase synthesis was the construction and operation of a 70 bbl per day integrated pilot plant at ARCO's Cherry Point Refinery near Bellingham, Washington [89]. This project was led by ARCO's upstream technology unit. The individual process units were modular in design, were constructed in Tulsa, Oklahoma, and shipped to the site where they were erected [90]. A proprietary reactor design for the autothermal reformer was used to generate syngas from natural gas (actually a refinery dry gas stream substitute) and air. The return to the use of air for the generation of the synthesis gas is a unique feature of the Syntroleum process. For the FTS component, they tested their advanced reactor design and a proprietary cobalt microsphere catalyst. The system is described as, "... a moving bed system, where catalyst microspheres are suspended by the gas in circulating liquid." The catalyst is reported to have high activity, attrition resistance, excellent hydrodynamic properties and is readily separated from the hydrocarbon products. The plant is reported to operate in a turbulent mixing regime that is associated with commercial sized moving bed reactors. After several thousand hours of operation under widely varying conditions, there was no evidence of significant attrition within the unit while catalyst life and activity maintenance met or exceeded expectations.

A recent patent application describes a Syntroleum liquid phase system that utilizes a fixed catalyst bed [91]. To accomplish this, they employ a catalyst that has a voidage ratio greater than approximately 0.45 or 0.6; in another version of this they utilize a catalyst with a voidage ratio >0.4 and a catalyst concentration in the reactor volume of at least 10%. The catalyst is to have a productivity of 200–4000 vol. CO/volume catalyst/h or greater during at least a 600 h run. In one version, a saturator precedes the reactor to generate a syngas saturated liquid which is used as the feed to the fixed-bed liquid phase reactor. Another version utilizes a reactor consisting of tubes in a shell that receives the liquid feed that is saturated with syngas. In another version, the reactor may consist of any version from a single vessel with a length/diameter (L/D) >5 to a shell in a tube vessel with a high L/D that receives liquid and syngas feed streams. In another version, the single vessel reactor is filled with a fixed catalyst bed submerged in a liquid and the feed is only syngas. Another reactor resembles the Dortflund type reactor with a series of fixed catalyst beds within a reactor shell, with each reactor bed having the capability of receiving fresh liquid and syngas feed or not, as desired for the operation (Fig. 36). In another version the reactor is essentially the same as in a bubble column reactor except that a fixed catalyst bed is utilized.

4.4. Rentech

Rentech reports that they have operated during 1982–1983 a commercial-scale gas to liquids facility. This facility utilized a Pueblo, Colorado landfill to

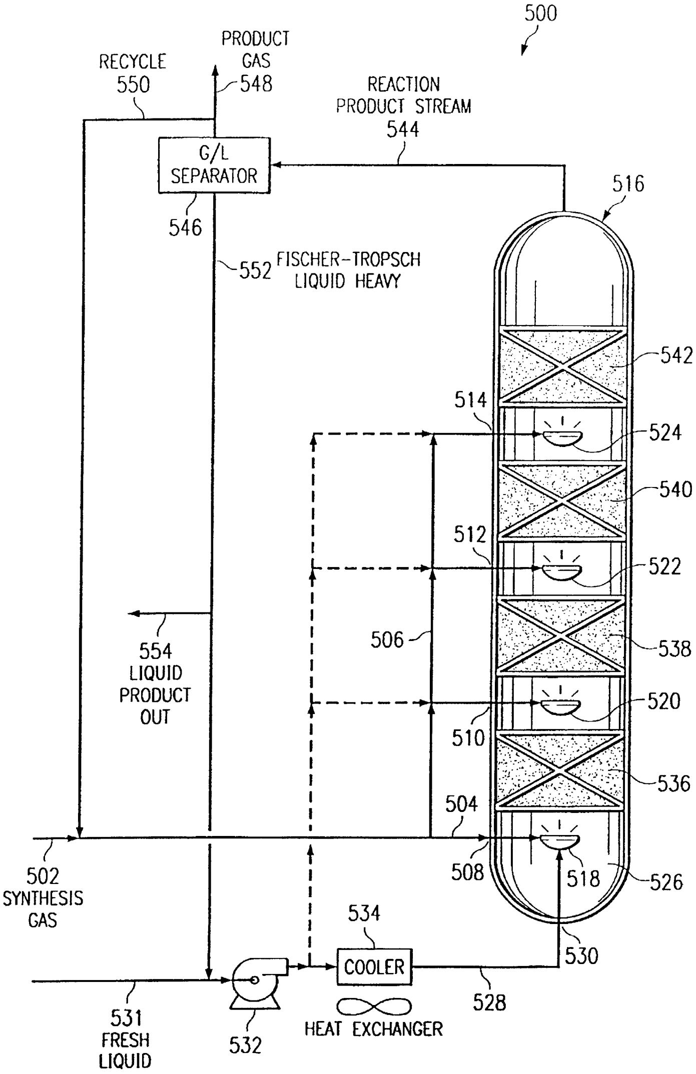

Fig. 36. Syntroleum liquid phase fixed catalyst bed reactor with gas and/or liquid addition at one or more catalyst trays [91].

produce gas sufficient for a plant with a capacity of about 235 bbl per day of liquid hydrocarbons. This plant has a capacity that is about the same as the reactor for the demonstration plant that Exxon operated at Baton Rouge, LA. It was soon learned that the landfill was unable to produce sufficient amounts of gas and the operation was discontinued within 3 months after attainment of full-scale production.

Rentech has at least nine patents to cover their technology. The bodies of most of these patents are either the same or very similar and provides a concise summary of FTS that can serve as an excellent introduction for the novice in this area. The claims are more modest in coverage than the body of the patents. Furthermore, it is sometimes difficult to discern when the cited examples are based on theoretical calculations and when they are based upon data obtained by Rentech.

Rentech has operated a 6 in. (0.15 m) diameter, 8 ft (2.54 m) tall slurry reactor with an iron catalyst. They report that they have designed, built and tested two 6 ft

(1.83 m) diameter slurry reactors and have produced catalysts batches of more than 7.5 ton (6810 kg) for use in these reactors [92]. The wax/slurry separation, as reported in 1992, was accomplished using an external cross-flow filter. Using this technique, separation was still a problem. They apparently utilized later in their pilot plant studies an external separator that involved gravity settling to concentrate a catalyst/wax slurry for return to the bottom of the reactor; this approach was apparently very similar in design to the one Mobil Oil utilized in the work they conducted for their DOE contracts.

4.5. US DOE, LaPorte

Air Products operated DOE's Alternative Fuels Development Unit, located in LaPorte, TX. The unit was initially designed to conduct methanol synthesis in the slurry-phase and was later expanded to include development work in FTS liquid phase operations starting in 1992. The methanol synthesis work was very successful and resulted in a commercial operation (reactor 7.5 ft (2.3 m) diameter and 70 ft (21.3 m) tall) at Tennessee Eastman in Kingsport, TN, and the initial commercial-scale has now been expanded in size.

Four runs for FTS have been described to date [93]. The bubble column reactor is 22.5 in. (0.57 m) and 28.3 ft (8.6 m) top to bottom. The actual slurry space is 20 ft (6.2 m) with the remainder serving as a space for vapor disengagement. One inch (2.54 cm) cooling tubes occupy <5% of the reactor cross-section (Fig. 37). The first two runs utilized iron catalysts: for Run I a high alpha catalyst was used and slurry/wax separation was a problem [94,95] and for Run II a low alpha catalyst was used [96]. Apart from the separations problem, Run I was successful. For Run II, the initial activation was attempted with a 44 wt.% catalyst concentration and the run had to be aborted due to slurry thickening due to carbon formation and particle agglomeration. The second portion of Run II utilized 29 wt.% catalyst concentration and both the activation and synthesis periods followed closely the results from work in a CSTR that were conducted at our lab.

4.5.1. Shell runs at LaPorte

Run III utilized Shell's proprietary catalyst and wax to make a slurry that contained 41.2 wt.% cobalt-based catalyst. During the run a number of operating conditions were to be tested: H_2/CO ratio of 1.18–2.07, inlet superficial gas velocity from 0.31 to 0.73 ft/s (9.5 to 22.3 cm/s), CO conversion of 80–90%, temperature from 210 to 250 °C, and pressure from 520 to 710 psig (3.6 to 4.9 MPa). Recycle was utilized to obtain the high total CO conversion levels. During Run III a productivity of 126 g hydrocarbon/h l slurry was obtained. Poor catalyst integrity caused slurry thickening and mass transfer limitations. Catalyst break-down limited the operational time for Run III. Run IV was a repeat of Run III but with a new catalyst formulation and a proprietary filtration system. Run IV was accomplished successfully and covered the period of time scheduled. It appears that the products were lighter than normally expected for a cobalt catalyst; methane was in the range of 20 wt.% of the products and the alpha value was in the 0.85–0.89 range. Using the planned operational conditions, we have estimated the productivity for the run. Assuming a slurry density of 2 g/cm^3 and the reactor productivity of 150 g hydrocarbon/l reactor volume/h, we calculate a productivity of 0.18 g hydrocarbon/g catalyst/h. The same productivity with a 29 wt.% catalyst slurry would provide a productivity of 0.27 g hydrocarbon/g catalyst/h. Assuming that the 29 wt.% slurry has a density of only 1 g/cm^3, the productivity would be 0.54 g hydrocarbon/g catalyst/h.

5. Products

5.1. Low temperature versus high temperature

The product distribution reported by Kölbel was typical of high temperature (low alpha) operation: C_{1-2}:C_{3-4}:gasoline (25–190 °C):diesel oil (190–310 °C):heavies (>310 °C) = 7:17:62:10:3 [97]. The olefin content of the C_{2-4}, gasoline and diesel fractions were 72, 74, and 45%, respectively. Kölbel reported in less detail on runs made to produce "medium" and "high" molecular weight products in addition to the ones described above. These products are shown in Table 6.

As noted, the production of hydrocarbons per cubic meter gas increases as the molecular weight of the products increases; however, in no instance does it approach the theoretical yield of 208 g/m^3. On the other hand, Mobil runs consistently produced greater

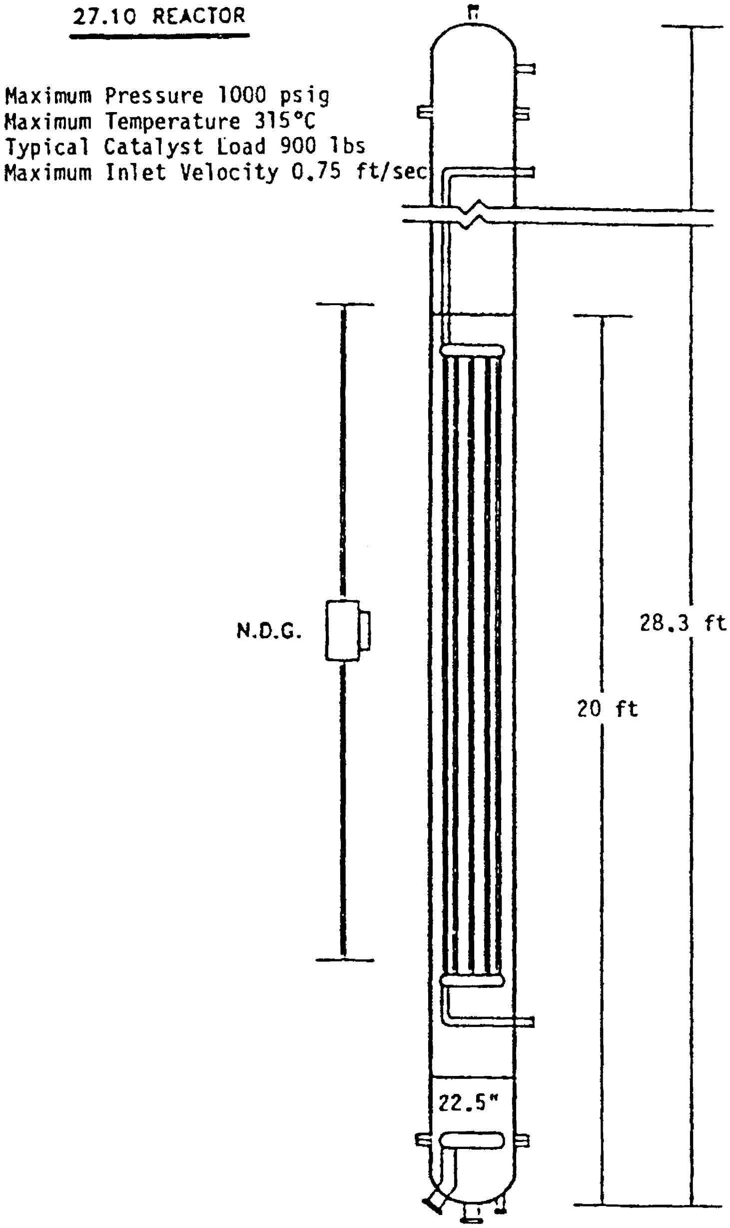

Fig. 37. Bubble column reactor (27.10) at LaPorte [93].

than 200 g/m^3. This low hydrocarbon productivity in Kölbel's work is apparently a problem that many investigators have struggled with.

The quality of a diesel fuel can vary considerably. Cetane number is used as one measure of the quality of a diesel fuel much in the same manner as octane number is used for gasoline. However, octane number and cetane may be viewed as opposites. Thus, highly branched paraffins, olefins and aromatics are desirable, and normal paraffins undesirable, components of

Table 6
Variations in product composition from the Kölbel reactor [40]

	Molecular weight goal		
	Low	Medium	High
Single-pass C_3^+ product yield (g/m^3 feed)[a]	166	175	182
Distribution of C_3^+ products (%)			
C_{3-4}	18	7	2
Gasoline (C_5–190 °C)	68	40	7
Diesel fuel (190–310 °C)	11	26	8
310–450 °C	2.5	18	33
>450 °C	0.5	9	50

a fuel if one wants a high octane number; on the other hand, *n*-paraffins are desirable and highly branched paraffins, olefins and aromatics are undesirable components for diesel fuel with a high cetane number. In viewing the high molecular weight product slate in Table 6, it is noted that 33% of the product is diesel and 50% is heavier molecular weight material that must ultimately be cracked to produce gasoline and diesel. As produced with an iron catalyst, the diesel fraction of the products (straight-run diesel) contains a significant amount of olefins, and consequently a relatively low cetane number. However, when this fraction is hydrogenated it will contain predominantly (90% or greater) *n*-paraffins, and this fraction will have a high cetane number (at or approaching 70). Because there is little difference in the ratio of *i*-/*n*-paraffin fraction of the hydrogenated straight-run diesel from an iron catalyst and the straight-run diesel from a cobalt catalyst, the straight run diesel produced by either catalyst will be the same, or very similar. Furthermore, it requires the same amount of hydrogen to produce a paraffin irrespective of whether it is produced indirectly by hydrogenating an initially formed olefin produced by iron catalysis or produced directly using a cobalt catalyst. Based upon straight-run diesel, there should therefore be no difference in the quality of the materials produced using either catalyst. Likewise, the >450 °C fraction of the iron and cobalt catalyst is composed essentially of *n*-paraffins, either before or following a hydrogenation step, so that, while the quality of the diesel fuel produced by hydrocracking may depend upon the hydrocracking process utilized, it should not depend upon whether the >450 °C fraction is obtained by iron or cobalt catalysis.

It cannot be overemphasized that diesel is not a sufficient specification to use to compare catalysts and/or processes. Straight-run diesel and diesel obtained from hydrocracking will not, in general, have the same properties even when both are composed only of paraffins. The major reason for this is that hydrocracking normally produces a significant fraction of monobranched paraffins; in fact, the classical bifunctional hydrocracking mechanism would produce an *i*-/*n*-paraffin ratio of 1 or even greater. Thus, it is important, when discussing cetane number, to specify whether one refers to what is straight-run diesel, diesel produced by hydrocracking or some blend of these two products. For blending with petroleum-derived diesel to produce a more environmentally friendly transportation fuel, it is desirable that the F.-T. product have the highest possible cetane number. From the point of view of obtaining a superior diesel for blending with petroleum-derived diesel, it appears that straight-run F.-T. diesel would be preferred over hydrocracked diesel when the decision is based on cetane number.

In considering the medium and high molecular weight cases shown above, an equal amount of blended diesel would be produced by combining the straight-run and hydrocracked diesel fraction only if the hydrocracking selectivity was such that it produced only 32% diesel fraction. The selectivity for hydrocracking is much greater than 32% so that it is obvious that more diesel will be produced from the “high” operation in Table 6. However, for a run at LaPorte to generate diesel to make a large-scale test, both straight-run and hydrocracked diesel could be produced using either the medium or high molecular weight mode of operation. For the medium molecular weight case the straight-run fraction would dominate over the hydrocracked diesel whereas the opposite would result from the high molecular weight mode of operation.

6. Wax/slurry separation

In general, there are two approaches to this task: in-reactor separators that retain the slurry while allowing clean wax to pass and external separators where slurry is removed from the reactor and separation is effected in an external separator. Both of these approaches were utilized by Kölbel in his work in the 1950s.

Wax/slurry separation is not needed for fluid-bed reactor operation since wax cannot form without causing agglomeration of the catalyst with loss of fluidization. Robust iron catalysts have been formulated for operation in fluid-beds and are in commercial operation at Sasol. Presumably supported cobalt catalysts could be operated in this reactor type since fluid catalytic cracking catalysts have been formulated with the necessary robustness and some form of these materials could be utilized as support for cobalt catalysts [98].

Separation of wax from supported cobalt catalysts is much easier than for an unsupported iron catalyst. A major reason for this is that the support material (alumina, silica, titania, etc.) can usually be prepared so that it has the attrition resistance that is required for operation in a fixed or slurry bubble column reactor. While there were problems with one supported cobalt catalyst during operations at the LaPorte facility, an improved version of the catalyst could be separated successfully in an external separator that utilized a cross-flow filter with slurry circulation using a pump [93]. However, operating the same plant with spray dried iron catalyst, the filter became plugged within a few hours or days of operation [99].

Mobil utilized an external system in which slurry is circulated by density differences and the time in the separator is sufficient for the slurry to settle so that solids-rich and nearly solids free zones are formed; the clean wax is removed from the solids free zone and the solids rich fraction is returned to the bottom of the column. A similar apparatus has been utilized by Rentech, at least in their smaller pilot plant. A number of external filtration systems as, e.g., [100] have been patented.

While separation devices have been described in the body of several patents, fewer patents describe filtration devices within the reactor. Most of the patents that describe a reactor mention internal or external separation but usually do not provide details. Statoil patents [101,102] describe a vertical cylindrical filter element in the form of a fine meshed screen, although alternatives could be used, located inside the reactor within the slurry. In the examples, models are used for the separation rather than a working reactor. Sasol has described in some detail their operation in a large pilot plant with a slurry bubble column reactor using a separation procedure, in one particular case, a spiral wound (candle) filter [103]. An improved candle filter has also been described [104].

A process for the separation of a catalyst from FT slurry has been patented by US DOE [105]. This process separates the catalyst from the wax product using a dense gas and/or liquid extraction in which the organic compounds in the wax are dissolved and carried away from the insoluble inorganic catalyst particles. This work utilized wax/slurry generated at the LaPorte facility and the separation work was conducted by Kerr-McGee [106]. The use of near-critical fluid extraction to remove wax product to provide a solids enriched stream to return to the reactor has also been studied and has shown promise [107]. For the latter technique, the extraction would likely be effected at temperatures above the reactor temperature and how this impacts the catalyst remains to be determined.

In summary, the separation of wax from a supported cobalt catalyst slurry will be much easier than from an unsupported iron catalyst. The unsupported iron catalyst rapidly attrits to produce small (1–3 μm) particles [108] that blind the pore openings of the filter. It would, therefore, be desirable to develop a filter material that can handle the 1–3 μm sized particles without blinding.

In the British work at Greenwich, the catalyst, after "break-in," was 1–3 μm in size. A liquid slip-stream was withdrawn continuously from the reactor and catalyst was recovered in a multiple-stage, gravity-settling apparatus. Because of the relatively rapid catalyst aging rates as well as significantly coke formation, reliable data for wax/catalyst separation is not available from this work.

A finely divided powder catalyst was utilized by Kölbel and Ralek [45]; the starting material has a particle size <30 μm but sizes during or after use are not provided. The liquid level in the reactor was maintained by a float-device. A slip-stream, utilized when excess liquid was produced, allowed for wax/catalyst separation by pressure filtration. Kölbel operated most of the times under conditions where the liquid inventory of the reactor could be maintained only by adding heavier liquid products along with the synthesis gas and wax/catalyst separation was not a problem. As an alternative, wax/catalyst separation could be effected by centrifugation. Capability for replacement of the catalyst was included in the process although catalyst replacement rates are not given. Data are not available to enable one to reach valid conclusions about the effectiveness of the wax/catalyst separation because of the lack of knowledge of catalyst addition rates. Based on the data in Table 6 for the “low” operating conditions, an upper limit of 15% reactor wax removal can be set, and in practice it should have been much lower.

7. Supercritical phase FTS

While supercritical phase synthesis is not strictly a liquid phase synthesis, it approaches liquid phase when operating at higher densities. It is claimed that three main advantages of the supercritical synthesis are: (1) rapid diffusion of reactants, (2) effective removal of reaction heat and (3) effective extraction of wax, α-olefins and water. Thus, the supercritical operation could, if item 3 is accomplished, decrease or eliminate secondary reactions.

Yokota et al. [109] compared the results of the operation of three types of reactors: fixed-bed, liquid and supercritical. In order to make an effective comparison the feed consisted of 22–36% synthesis gas with the remainder being diluent (nitrogen for the fixed-bed, hexadecane and nitrogen for the liquid, and *n*-hexane for the supercritical). An iron catalyst was utilized and had the following composition by weight fraction: Fe, 83.5; Ca, 2.1; Al, 1.5; Si, 0.4; K, 0.5 or Fe, 99; Cu, 0.3; K, 0.3. Thus, both iron catalysts were of the low alpha type utilized by Mobil Oil and LaPorte Run II. The total pressure was 5 MPa, 270 °C, $H_2/CO = 1$ and W/F $(CO + H_2) = 10$ g cat h/mol. Each run was conducted for 6 h. Under no circumstances should it be considered that a steady-state operation was attained.

The authors show the CO conversion, CO_2 yield and chain-growth probabilities for the fixed-bed, supercritical and slurry-phase reactors as 33.0, 30.2 and 27.9; 8.65, 7.52 and 9.15; and 0.84, 0.83 and 0.80, respectively. They considered these differences to be significant and attribute the lower CO_2 yield for the supercritical operation as being due to the increased removal of water from the reactor. The reported chain growth probabilities appear high for an iron catalyst that contains such a low level of potassium. These data may be viewed as suggestive.

Fujimoto et al. [110] report that the addition of a small amount of heavy 1-alkene in a supercritical-phase or liquid phase F.-T. reaction medium greatly enhanced the selectivity of wax products, along with increased CO conversion and suppressed methane selectivity. A cobalt–silica catalyst that contained La was used. The authors reported that the addition of 1-tetradecene or 1-hexadecene significantly decreased the hydrocarbon production for carbon number products lower than that of the added alkene, and increased significantly the production rate of the carbon number products with higher carbon numbers that the added alkene (Fig. 38). The data shown in Fig. 38 are astounding. When alkenes were not added the production rate of the products above carbon number 15 decreased with increasing carbon number; this is expected and observed in normal F.-T. synthesis. However, when the alkene is added, the hydrocarbon production with carbon numbers above that of the added alkene become essentially constant; i.e., independent of carbon number. It appears that this requires the added alkene to initiate chain growth that differs from that of the F.-T. reaction. If the only impact of the alkene was to initiate additional growing chains, the product distribution above the carbon number of the added alkene should be determined by the Anderson–Schulz–Flory distribution; i.e., the rate of production of all higher

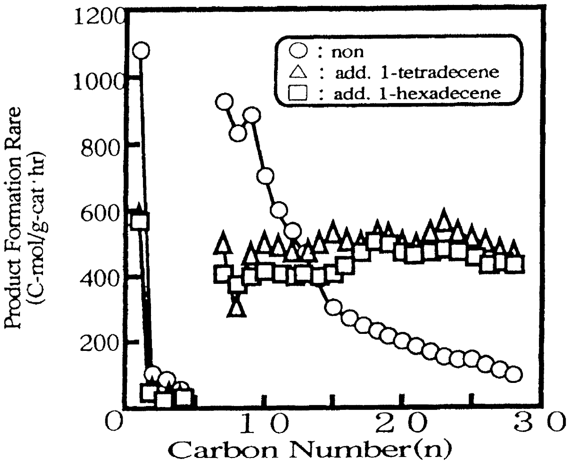

Fig. 38. Product distribution in the olefin-added supercritical phase FT reaction with a cobalt catalyst: (○) no olefin added; (△) 1-tetradecene added; (□) 1-hexadecene added [110].

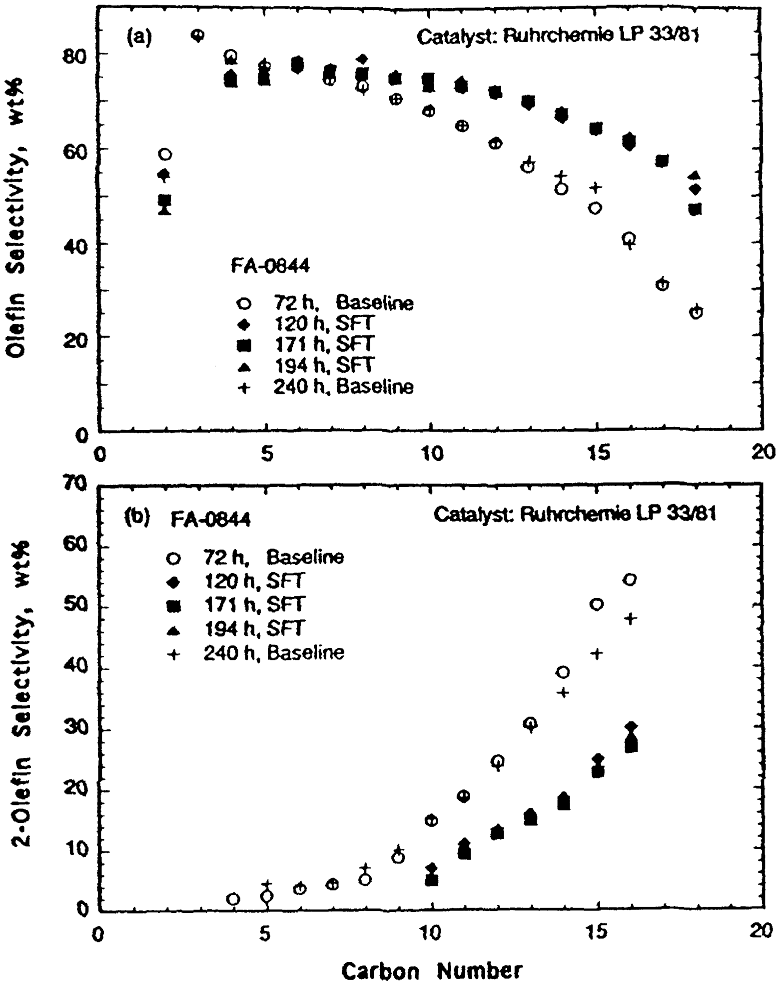

Fig. 39. Effect of supercritical FT synthesis on α-olefin (a) and 2-olefin (b) selectivity using an iron catalyst [111].

carbon number products may increase but the products should still be produced in the same ratio as they were when no alkene was added. Thus, the amounts of higher carbon number products may increase but the alpha value should be the same as when the alkene was not added. The data obtained when 1-heptene, in contrast to 1-tetradecene or 1-hexadecene, was added is in better agreement with the expectation.

Lang et al. [111] utilized a precipitated iron catalyst in a fixed-bed reactor and found that the catalyst activity and lumped hydrocarbon product distribution under the supercritical conditions were similar to those obtained during reaction at the baseline (non-supercritical) conditions. This is in contrast to the views expressed above. Lang et al. [111] reported slightly higher selectivities for the 1-alkenes during supercritical operation (Fig. 39). This suggests to them that the F.-T. reaction is not diffusionally limited under their reaction conditions. The higher alkene production during supercritical operation was due to higher diffusivities and desorption rates of the high molecular weight olefins relative to those under normal F.-T. conditions.

8. Summary

The major attention, both industrial and academic, during the past 10 years, has been given to the slurry bubble column reactor. The slurry-phase methanol process has been developed and operated in a commercial setting [112–114]. Deckwer [115] has published a major treatise on bubble column reactors. Saxena [116] has recently reviewed the use of bubble column reactors in FTS. The reader is referred to these for description of reactor details.

Two major types of slurry bubble column reactors are possible and these are illustrated in Fig. 40 [77,117]. The reactor containing cooling coils immersed in the slurry is the one that is most frequently encountered [77,78,92,104,117–122]. The concept of one type of reactor patented by Exxon has many similarities to the Arge fixed-bed reactor except the fixed catalyst bed has been replaced with a slurry catalyst; both utilize the "tube-in-a-shell" reactor concept [77].

As with the three-phase slurry reactor in other applications, the distributor plate is treated as a proprietary topic. Kölbel contends that when the bubble column reactor is operated in the proper gas flow range the bubbles within the reactor will be in dynamic equilibrium with the formation of larger bubbles and their spontaneous break-up.

For modeling, the bubbles within the slurry are usually considered to have a spherical shape, their size distribution taken as some average size, and their breakup and reformation are neglected. The work conducted at Ohio State show that the bubbles are clearly not spherical but are as shown in Fig. 41 [123]. The influence of elevated pressure and temperature on the shape and rise velocity of a single bubble in a liquid–solid suspension has been investigated in a unique experimental setup (e.g., [124]). For very low flows (gas velocity of 0.01 m/s) it is possible to have a reasonably uniform distribution of small (<5 mm) bubbles that rise vertically [125] and can be modeled

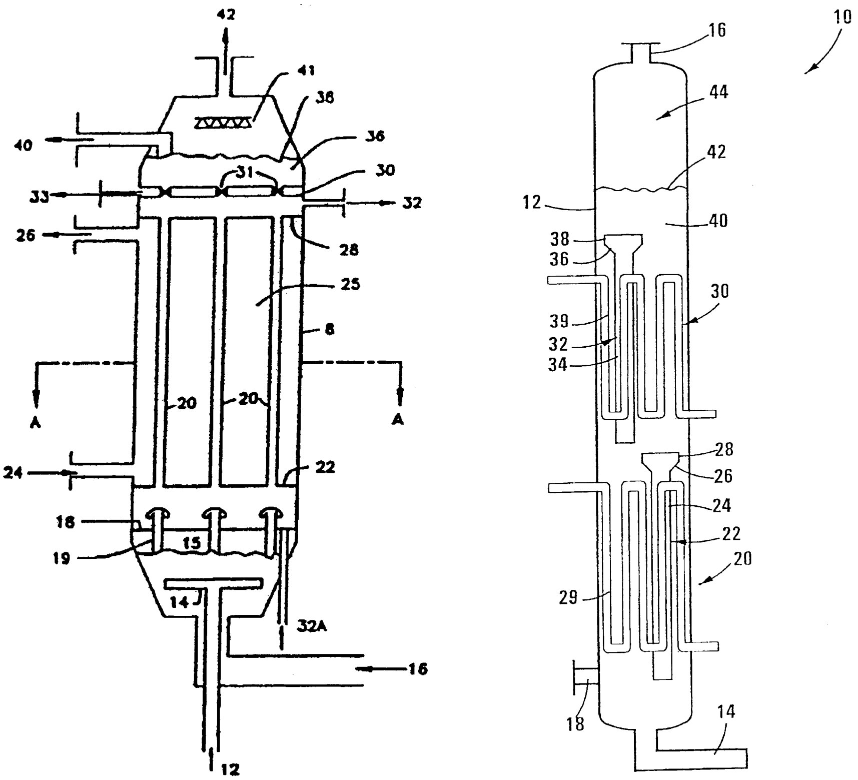

Fig. 40. (left) Schematic of Exxon slurry-phase reactor [77]; (right) schematic of Sasol slurry bubble column reactor [117].

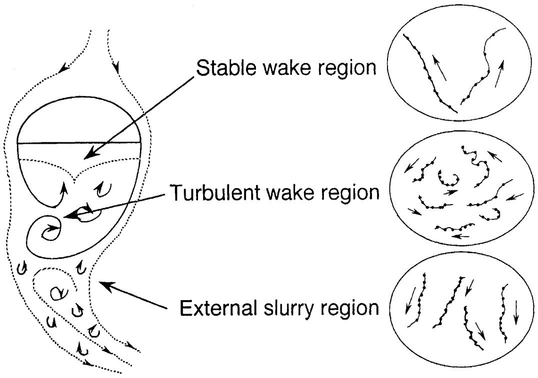

Fig. 41. Typical particle trajectories within three different flow regions around a rising bubble [123].

as plug flow. However, to operate in the small bubble, plug flow regime DeSwart et al. [125] calculates that it would require seventeen 11 m diameter reactors [17] to produce the same amount of product as could be produced in four 7.5 m diameter reactors that operate in the churn turbulent slurry regime.

It is found that the bubble rise velocity decreases with increasing pressure and with decreasing temperature. This is mainly due to the changes in the densities of the gas and the liquid velocity. Not only do the bubbles have a shape like a comet with a tail of smaller bubbles, they also do not rise straight to the vertical but exhibit a corkscrew path to the top of the reactor, leaving regions rich in bubbles and regions with a lower concentration (Fig. 42) [126]. The bubble shape is frequently modeled with variable aspect ratios as cross-sections of ellipsoids [127]. A representative status of the activities in this research area may be obtained from [123,128–139].

The US DOE has a major effort to understand the many variables affecting the performance of a bubble column reactor. Dudukovic and Toseland [140]

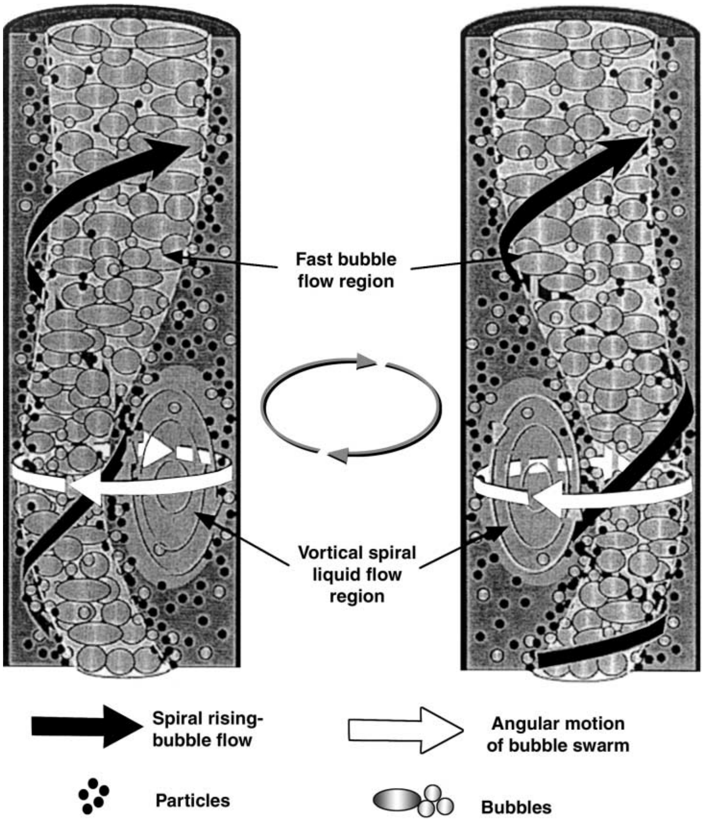

Fig. 42. Model of flow scheme in the slurry bubble column [126].

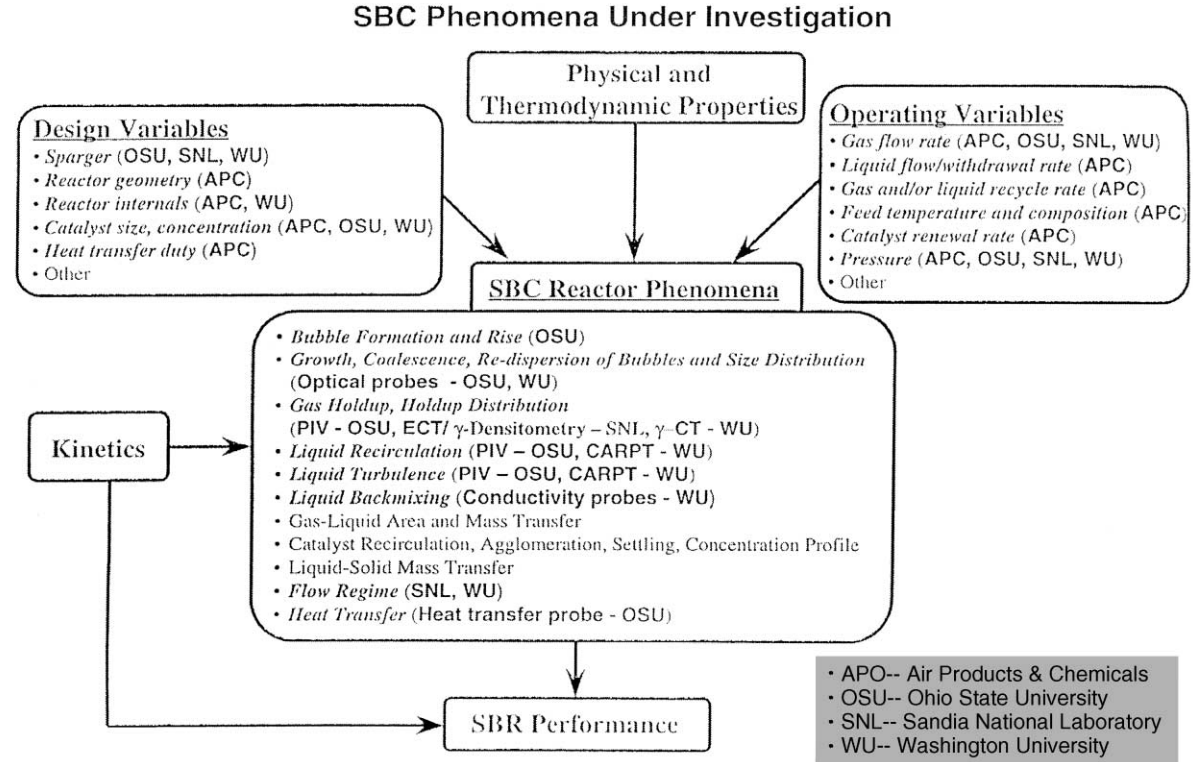

Fig. 43. SBC phenomena under investigation [140].

outlined the cooperative study by Air Products and Chemicals (APC), Ohio State University (OSU), Sandia National Laboratory (SNL) and Washington University (WU); this program is outlined in Fig. 43. The efforts of this group have developed valuable unique experimental techniques for the measurement of gas holdup, velocity and eddy diffusivities in bubble columns. They have obtained data that allow improved insight in churn-turbulent flow and have assessed the impact of various effects (internals, solids concentration, high gas velocity, pressure, etc.). General ideal flow pattern based models do not reflect bubble column reality; to date the models are based on a combination where some parameters are evaluated from first principles and some from the data base.

It has been observed that the time-dependent flow behavior in a cylindrical column is chaotic and not predictable. However, some periodic structures may be detected in the velocity time series in the axial and tangential direction the may lead to some kind of periodicity [141]. It has been reported that the transition from the homogeneous to the heterogeneous flow regime in bubble columns can be quantitatively found with high accuracy by analyzing the chaotic characteristics of the pressure fluctuation signal. A distinctive feature of the pressure signal from bubble columns is that it is composed of two different parts: a low frequency part resulting from the motion of the large bubbles and a high frequency part resulting from all other processes (coalescence, collapse, breakup, etc.) [142]. Delnoij [143] conducted an extensive study and concluded that their computed flow structures resembled the experimentally observed patterns although the time-dependent behavior predicted by the model differed from that observed in their bubble column.

The extensive theoretical and experimental data for bubble column reactors has been applied to situations that are applicable to FTS. Inga and Morsi [86,144] have constructed a 0.3 m diameter, 2.8 m tall slurry bubble column reactor and have operated this in the

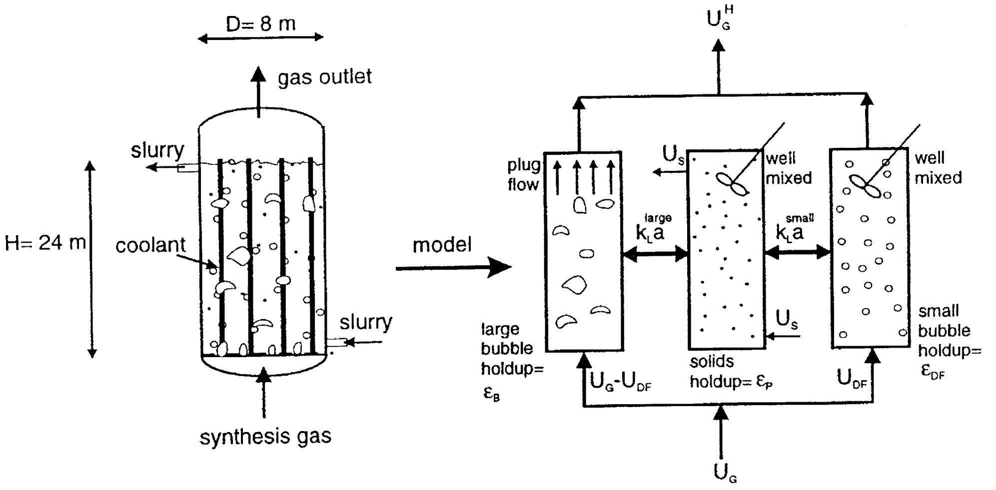

Fig. 44. Hydrodynamic model of slurry bubble column reactor in the heterogeneous flow regime [146].

churn-turbulent regime with catalyst concentrations up to 50 wt.% and pressures to 8 bar. The impact of gas velocity, pressure and catalyst concentration on gas holdup (V_G) has been determined and it was found that under given operating conditions, the gas bubbles can be classified into "small" and "large" bubbles [86,144]. The "large" bubbles exhibit plug flow behavior but the "small" bubbles recirculated with the liquid. The gas holdup (V_G) increases with superficial gas velocity and pressure and decreases with catalyst concentration. At high catalyst loading, coalescence of gas bubbles increased, reducing the number of small bubbles, and the gas interfacial area. The gas/liquid mass transfer coefficient ($k_i a$) values follow the trends of the gas/liquid interfacial area [145].

van der Laan [146] reported attempts to model FT in a bubble column reactor. His model exhibits well mixed liquid and two gas bubble regimes: small bubbles that are well mixed and large bubbles that exhibit plug flow behavior (Fig. 44). van der Laan also provides a summary of bubble column reactor models that others have utilized (Tables 7 and 8). He concluded that the FT SBCR is reaction controlled due to the low activity of the iron catalyst and the volumetric mass transfer coefficient of the large bubbles due to frequent bubble coalescence and breakup.

Groups are now beginning to apply multi-component reaction engineering models for FTS in bubble column reactors. Recent examples can be found in [146–148]. van der Laan [146] provides the following summary of slurry bubble column reactors:

> "A number of patents deal with modifications of Fischer–Tropsch slurry bubble column reactors to reduce the back-mixing of both the liquid and the gas phase [123,149–151] described the influence of various degrees of back-mixing on the selectivity and productivity based on kinetic data obtained over a Co/TiO$_2$ catalyst, both in plug flow (fixed-bed), bubble column and completely mixed reactors (CSTR). Arcuri [149] claimed that the productivity in a slurry bubble column is equal to or greater than for plug flow, and the same selectivity is obtained for the completely mixed system. Koros [150] reported the invention of a slurry bubble column multi-tubular slurry bubble column reactor with cooling medium around the tubes. The example presented shows a reaction tube of 0.15 m mounted inside a 0.30 m pipe that served as a cooling jacket. According to our opinion, this reactor configuration has several disadvantages: (1) possibility of slug flow conditions, (2) large gas holdup due to the influence of the column diameter on the large gas bubble holdup [152], (3) possibility of maldristribution of the gas, the liquid and the catalyst phases, and (4) low specific cooling area rel-

Table 7
Comparison of reaction engineering models for the FTS in slurry bubble column reactors [146]

Authors	Gas phase	Liquid phase	Catalyst distribution	Energy balance	Components	FT (Table 8)	WGS (Table 8)
Calderbank et al.	PF[a]	PF	Uniform	Isothermal	H_2	1	–
Satterfield et al.	PF	PM[b]	Uniform	Isothermal	H_2	1	–
Deckwer et al.	PF	PM	Uniform	Isothermal	H_2	1	–
Deckwer et al.	Ad[c]	AD	Non-uniform	Non-isothermal	H_2	1	–
Bukur	PF	PF, PM	Uniform	Isothermal	H_2	1	–
Stern et al.	PF	PM	Uniform	Isothermal	H_2, CO, CO_2, H_2O	1	–
Kuo	PF	PM, PF, AD	Non-uniform	Isothermal	C_5, H_{10}	1	
Kuo	PF	PF	Non-uniform	Isothermal	H_2	2	2
Stenger et al.	AD	AD	Non-uniform	Isothermal	H_2, CO, CO_2, H_2O, $C_{1–3}$	1	1
Prakash et al.	AD	AD	Non-uniform	Isothermal	H_2, CO, CO_2, H_2O, $C_{1–3}$	2	2
Prakash	AD	AD	Non-uniform	Isothermal		2	2
DeSwart[d]	AD	AD	Non-uniform	Non-isothermal	H_2	1	–
DeSwart[e]	PF	PM	Uniform	Isothermal	H_2	1	–
Mills et al.	AD	AD	Non-uniform	Non-isothermal	H_2	1	–
Inga et al.	PF	MC[f]	Uniform	Isothermal	H_2, CO, H_2O	1, 3	2
Krishna et al.[e]	PF	PM	Uniform	Isothermal	H_2, CO	3	–
Our model [145]	PF	PM	Uniform	Isothermal	H_2, CO, CO_2, H_2O, N_2, $C_{1–100}$		

[a] Plug flow.
[b] Perfectly mixed.
[c] Axial dispersion.
[d] Heterogeneous flow regime: large bubbles: PF, small bubbles and liquid: AD.
[e] Heterogeneous flow regime: large bubbles: PF, small bubbles and liquid: PM.
[f] Mixing cells.

Table 8
Kinetic models for Table 7 [146]

FT	Kinetic expressions	WGS	Kinetic expressions
1	$kC_{H_2,L}$	1	$k\left(C_{CO,L}C_{H_2O,L} - \frac{C_{CO_2,L}C_{H_2O,L}}{K_p}\right)$
2	$\frac{kC_{H_2,L}C_{CO,L}}{C_{CO,L} + \mathrm{a}C_{H_2O}}$	2	$\frac{k(C_{CO,L}C_{H_2O,L} - C_{CO_2,L}C_{H_2O,L}/K_p)}{P_{CO} + aP_{H_2O}}$
3	$\frac{kC_{H_2,L}C_{CO,L}}{(1 + aC_{CO,L})^2}$		

ative to, e.g., 1.5 in. cooling tubes. A better option is staging the slurry bubble column horizontally as proposed earlier by Graaf [153] for slurry-phase methanol synthesis. Maretto and Piccolo [151] reported the effect of staging a slurry bubble column. The temperature in each stage could be controlled separately. Their model assumed plug flow of the gas phase and complete mixing of the slurry in each stage. Maretto and Piccolo [151] claimed that the liquid phase in the multi-stage reactor may approach plug flow behavior, resulting in an increase of the synthesis gas conversion with increasing the number of stages. Our model can easily be extended to incorporate the effect of staging of a slurry bubble column. In addition to the study of Maretto and Piccolo [151], extension of the model presented will also predict the effect of staging on the product selectivity. Maretto and Piccolo [151] did not report on the engineering details of staging bubble columns. One of the possibilities would be the application of horizontal gauzes or perforated plates [154,155]. These plates decrease the bubble size of large gas bubbles and slugs which results in a higher gas holdup and improvement of the plug flow characteristics of the gas and liquid phase."

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