EXECUTIVE SUMMARY

Significance of Slurry Fischer-Tropsch (F-T) Catalyst/Wax Separation

The advantages of slurry bubble column F-T reactors, such as effective heat-transfer, uniform reaction temperature, free of local-overheating of the catalyst, simple reactor construction and low capital cost, can be realized commercially only if a continuous and cost-effective technique for catalyst/wax separation could be developed to achieve:

a. A continuous stream of product wax essentially free of solids suitable for further upgrading. It is recommended that the solids content in the clean wax product be limited to below 1-2 ppm to protect the catalyst bed from fouling during wax processing, and

b. Recovery and recycle of catalyst fines back to the reactor to maintain required conversion and to avoid catalyst loss.

It is reasonable that a continuous separation facility be used for purifying the product wax during normal operation, and an intermittent separation device (usually a centrifuge) be provided for separating the deactivated catalyst from the reactor liquid medium at the end of the run.

Difficulties in slurry catalyst/wax separation arise from (1) the small particle size, which is usually less than 3 microns down to submicron size, and (2) the high viscosity of the reactor wax, which ranges approximately from 4 to 8 cP (at 200°C). An ideal catalyst/wax separation method must be able to recover a clean wax virtually solids-free at a capacity suitable for large-scale production, and its capital and operational costs must be justified for commercialization.

Catalyst/Wax Separation Inside the Reactor

Internal filters immersed in the reactor slurry, as used in some bench-scale or pilot-scale units, do not work successfully due to operational difficulties. A reactor with a section of its wall as a filter may be operable for a pilot plant but is not practicable for commercial reactors. Internal filters are subject to plugging risks, which may cause premature termination of the run, and commercial plants are not allowed to take chances.

The high gradient magnetic separation technique may be applicable to F-T catalyst/wax separation inside the reactor and is discussed later.

Vacuum Distillation and Thermal Cracking of Vacuum Bottoms

Due to the high boiling points and cracking tendency of the waxes, only a small

amount of solids-free paraffin wax can be obtained by vacuum distillation as an overhead product. A part of the paraffin wax and all the hard wax remain in the vacuum bottoms containing all the catalyst fines, therefore the vacuum distillation is by no means a catalyst/wax separation method. Thermal cracking of the vacuum bottoms yields a significant amount of cracked gas and unsaturated liquid products, while the catalyst is lost along with coke deposition if the total conversion is high. Hence, thermal cracking is also an unsatisfactory technology for wax processing.

Chemical Conversion of Iron Catalyst

The very little work done on chemical conversion of F-T iron catalysts, such as converting it into iron carbonyl, was unsuccessful. Generally, chemical recovery methods are complicated, expensive, and might create waste disposal problems. Physical and mechanical techniques should be favored unless very cost-efficient chemical methods are found.

Sedimentation by Gravity or Centrifugal force

Gravity sedimentation or settling is a commonly used, simple and inexpensive method for F-T catalyst/wax separation, but a long settling time of 1 to 3 hours is required to reduce solids content of the reactor wax down to 0.1 wt%. The British Greenwich F-T pilot plant operated a gravity settling system fairly well. Mobil used an on-line catalyst settling system, and believes that it was demonstrated. However, basic understanding regarding the settling characteristics of the catalyst/wax slurry with respect to particle size, wax viscosity, effects of solvent (to reduce liquid viscosity), and/or coagulants (to increase particle size) is indeed necessary.

Hydroclones offer a relatively simple and inexpensive means for solid/liquid separation. Although not yet demonstrated in F-T slurry system, hydroclones have been successfully employed in similar applications in the petroleum refining industry. Hydroclones were adopted in Mobil's conceptual process design, and improved performance over gravity settlers is expected. The hydroclones should be tested in pilot-scale F-T units.

Centrifuges have so far been used only for separating deactivated catalyst from reactor wax when the on-stream period is over, so that the catalyst can be regenerated or disposed of and the wax reutilized.

It may be difficult to achieve very low solids content, e.g., 1-2 ppm, for the wax by means of settlers and hydroclones. However, they can be a good preliminary separation step to recover most of the catalyst particles from the slurry in the form of a concentrated catalyst underflow for recycling back to the reactor. The 'clarified' wax overflow can subsequently be processed by more efficient but usually expensive techniques, such as pressure filtration and magnetic separation to required low solids content.

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Pressure Filtration

Bench-scale slurry filtration tests were not successful (UOP). The withdrawal rate was limited because of the high wax viscosity coupled with the small particle size of the catalyst (British Greenwich slurry F-T pilot plant). Pressure filtration may give higher withdrawal rates necessary for commercial operation, as demonstrated in a German F-T pilot plant. Pressure filters can be used to process reactor slurry (Rheinpreussen Demonstration Plant), treat concentrated catalyst slurry after settling (Sasol II), or remove residual catalyst fines from the clarified wax, which had been separated from most of the solid particles by settling or centrifuging, as in Mobil's conceptual process design. Here again, a combination of two separation techniques seems to be appropriate.

Pressure filtration should be studied on a pilot scale that would focus on filter construction, operation performance with respect to slurry viscosity and particle size, and mechanical maintenance.

Magnetic Separation

High gradient magnetic separation (HGMS) has been tested on F-T catalyst/wax slurry, and preliminary successful results have been obtained in reducing the solids content down to less than 0.015 wt%. Parametric studies should be completed to further reduce the solids content down to a few ppm to meet the requirements set forth by hydrocracking. This technique has a potential to be used inside the slurry reactor, conceivably as a section of the slurry recycle line surrounded by an external electromagnet. The magnetic filament matrix has a packing porosity of around 95%, so the pressure drop is low. High flow rates are achievable for highly magnetic particles such as F-T iron catalyst. Cyclic HGMS operation in alternate feeding and flushing modes is claimed to be reliable.

The magnet structure is expensive, but the operation and maintenance costs are low. HGMS also happens to be the first entry for the superconducting technology into conventional commercial applications, which operates more economically and offers larger capacity.

Suggestions

Based on the above review of the current R&D status of slurry catalyst/wax separation technologies, the following suggestions are made:

1. The criterion of catalyst/wax separation should be set at a solids content of the clean wax below 1-2 ppm to meet the requirements for catalytic wax processing such as hydrocracking. Catalyst recovery should be determined by the cost efficiency of the technology.

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2. Separating the catalyst fines from the reactor wax inside the reactor is the simplest way, if a reliable technology can be found. However, internal filters have not been successful and are probably not practicable for commercial applications. High gradient magnetic separation (HGMS) has a potential of being used inside the reactor, conceivably as a section of a slurry recycle line attached to the reactor, and is worthy of investigation.

3. External catalyst/wax separation may be more reliable and flexible, and techniques like sedimentation, pressure filtration, centrifugation, and magnetic separation are available. They have been studied and tested with different degrees of success.

4. Basic research on settling characteristics of catalyst particles and parametric studies on HGMS technology prior to engineering studies on gravity sedimentation, pressure filtration, centrifugation, and HGMS are necessary. The target is to accelerate gravity settling, improve hydroclone efficiency, increase capacity, and obtain 'solids-free' waxes from pressure filters and magnetic separators. Bench-scale research on performance characteristics of sedimentation and magnetic separation should precede pilot tests, while pilot-scale testing is necessary for hydroclones and pressure filters.

5. Gravity settlers and hydroclones are relatively inexpensive, but obtaining solids-free waxes by these techniques may be impractical or uneconomical. Pressure filters and magnetic separators are able to give clean waxes, but they are costly and the former needs mechanical maintenance. As a consequence, efforts to obtain a very clean wax and a complete catalyst recovery by any single technique may not be justified, and a combination of two different techniques is probably advantageous. A less costly but less efficient method, such as gravity settling or centrifuging by hydroclones, could be used as the first-stage separation, mainly to recover the bulk of the catalyst particles and obtain a concentrated catalyst slurry for recycling. A clarified wax containing around 0.1 wt% solids could be processed in the second stage of separation or wax finishing. The wax-finishing stage may consist of pressure filtration or magnetic separation, reducing the solids content of the reactor wax down to 1-2 ppm. Economic evaluation of different combinations of separation technologies are hence needed.

STATUS REVIEW OF FISCHER-TROPSCH
SLURRY REACTOR CATALYST/WAX SEPARATION TECHNIQUES

I. INTRODUCTION

1. Background

The Fischer-Tropsch (F-T) reaction is one of the major components of indirect coal liquefaction. In this process, hydrogen and carbon monoxide in the synthesis gas are rebuilt into a wide spectrum of hydrocarbons and oxygenates with a carbon number ranging from C_1 up to about C_{200}, depending on the catalyst, temperature, and type of process employed.

Recent research efforts have focused on the development of slurry bubble column reactors for the F-T process. Due to the unique features of the three-phase bubble column reactor, a uniform temperature can be maintained in the reactor at the favorable level, and local overheating of the catalyst can be avoided. It has a high catalyst efficiency and reactor productivity. High single-pass $H_2 + CO$ conversion can be achieved using synthesis gas with an H_2/CO molar ratio as low as 0.6-0.7, obtainable from advanced coal gasification systems, provided the F-T catalyst has water-gas shift reaction activity. Low capital and operating costs are anticipated with slurry reactors due to their simple construction.

Because of the non-selective nature of F-T reaction, a large amount of waxy material is produced when the catalyst, reactor configuration, and operations favor long chain growth. This is particularly true when low H_2/CO ratio synthesis gas is used in low $C_1 + C_2$ gas yield, or high reactor wax mode, operation in slurry F-T reactors. As high $H_2 + CO$ conversions (80-85 mol%) are reached, a reactor wax yield of 50-65 wt% is obtained [1]. This wax can be refined to produce premium transportation fuels.

The catalyst fines, suspended in the F-T reactor liquid phase withdrawn from the reactor, must be separated and recycled back to the reactor to maintain required conversion and to avoid catalyst loss. Catalyst/wax separation is also necessary from the standpoint of wax upgrading, since the catalyst fines may foul the catalyst in subsequent wax processing. For commercial-scale operation, a continuous and cost-effective catalyst/wax separation technique is an absolute necessity.

Slurry F-T catalyst/wax separation can conceivably be performed inside or outside the reactor. In the current R&D stage of the slurry F-T process, catalyst/wax separation has been practiced by filtration inside the reactor, and/or by gravity settling, batchwise, periodically, or continuously, outside the reactor. Other commercially proven solid/liquid separation techniques including filtration, centrifugation, and magnetic separation have been tested for the application to F-T reactor wax-catalyst slurry.

Vacuum distillation of the slurry and chemical treatments, such as thermal cracking of the reactor wax and converting iron into iron carbonyl, have also been explored. Some of the tests encountered difficulties or were not successful, and some others have been promising but results to date are not yet conclusive. Because of various uncertainties involved in these techniques, Sasol is testing and comparing different methods (gravity settling, filtration, centrifugation and electric precipitation) for solid/liquid separation in its 1-m diameter slurry F-T reactor unit. Conclusions are yet to be drawn [2].

To delineate further R&D needs for catalyst/wax separation techniques, it is necessary to review the current status of these technologies and to identify the achievements and existing problems.

2. Scope of Report

The objective of this review is to survey the solid/liquid separation technologies suitable for slurry F-T reactor catalyst/wax separation that have been studied, or being investigated, or proposed. As an accomplishment, relevant information was collected and studied.

Related properties of the slurry wax and the suspended catalyst are first discussed, since they virtually determine the performance of the separation techniques applied to them. Subsequently, this review summarizes techniques previously tested or currently under development or testing, including physical, mechanical, electromagnetic, and chemical methods. Technologies that may find their way to F-T catalyst/wax separation, such as solvent dilution, are also explored and discussed. Finally, this report concludes with comments and research suggestions.

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II. RELATED PROPERTIES OF WAX SLURRIES FROM FISCHER-TROPSCH REACTORS

It is essential in the slurried F-T operation to establish an appropriate liquid phase in direct contact with the catalyst to substantially suspend the particles and maintain predetermined and desired temperature control, thus limiting the buildup of coke on the catalyst particles. The liquid medium used for the suspension of the catalyst is preferably a hydrocarbon product of an appropriate boiling range, which under reaction conditions will not appreciably volatize.

The success of the catalyst/wax separation is dependent upon the soundness of the technology as well as the property of the reactor slurry. The efficiency of catalyst/wax separation methods is influenced not only by the property (i.e., density, viscosity, etc.) of the liquid, but also by the property of the solids (particle size, density, etc.).

1. Reactor Wax

In the actual slurry F-T synthesis, the liquid phase (or the reactor wax) does not only contain starting wax but is mixed with reaction products. It should be in both chemical and phase equilibria with the residual gas after a steady-state is established, whatever the starting liquid may be. The reactor wax is therefore a wide-boiling fraction of F-T products, which remain in liquid state in the reactor. It usually ranges from C_{10} to C_{200} approximately. For instance, a Union Carbide F-T wax sample (cobalt catalyzed) was analyzed and its carbon number distribution was found to range from C_{12} to C_{196} with an average carbon number 28-29 [3]. The portion of the reactor wax that boils above 450°C (roughly equivalent to C_{32+}) is usually called the hard wax, and the 320-450°C fraction (roughly equivalent to C_{18}-C_{32}) is referred to as paraffin slack wax. A small amount of distillate below 320°C is also present in the reactor liquid phase.

The wax yield is somewhat a function of methane selectivity. At low methane + ethane yield (<6.0 wt%), the reactor wax yield ranges from 35 to 65 wt% [1]. In order to minimize methane + ethane yield and maximize liquid fuel (gasoline and distillate) yields, it is necessary to increase the reactor wax yield from the F-T reactor. For instance, when the methane + ethane yield dropped from 10 wt% of the total hydrocarbons produced to 4 wt%, the reactor-wax yield increased from 8 to 50 wt%. A further drop of the methane + ethane yield to 2 wt% increased the wax yield to 80 wt% [4].

Mobil workers [4] used an improved gas chromatographic method to analyze some reactor wax samples, and results are summarized in Table 1. Waxes from high reactor-wax operations contain a large fraction of hydrocarbons heavier than C_{55}.

Field Ionization Mass Spectrometry (FIMS) was found to give the most complete carbon-number distribution, reaching as high as C_{150}. In heavy reactor waxes, as much as 75 wt%

of the material is above C_{55}. The distributions show that the amounts of the components larger than C_{18} are substantially higher than those predicted by a normal Schulz-Flory mechanism. The raw FIMS spectrum for a Mobil reactor wax is illustrated in Figure 1. The FIMS spectrum for reactor wax from another Mobil run shows a similar pattern, but the bimodal carbon-number distribution is more clearly revealed with a second hump at a carbon number of about 150 [1].

The F-T reactor waxes also contain a certain amount of oxygenates and the quantity mainly depends upon the catalyst and operating conditions used in the process. The oxygenates content in Co-catalyzed F-T waxes is usually lower than that in waxes obtained with Fe catalysts (Table 2 [5]). Analyzed by high temperature liquid chromatography method, the reactor wax produced in a gasoline-mode operation (low reactor-wax mode) with an iron-based catalyst has an oxygenate content of 13 wt%. A sample from a high reactor-wax mode operation with the same type of catalyst shows 22 wt% oxygenates, though the total oxygen content was only about 1.0 wt% [1]. As a general trend, when operated in the high reactor-wax mode, the reaction produces more reactor-wax with higher average molecular weight, and more oxygenates.

Composition data of four waxes in Table 2 and their carbon number distribution have been determined using a Gel Permeation Chromatography (GPC) technique, as shown in Figure 2 [5]. The Mobil and commercial Arge waxes have the highest average carbon number, followed by the Union Carbide and Air Products waxes. IR spectra of these waxes are very similar, with long chain paraffins being the major component. Carbon-13 NMR spectra show that the major component in the commercial Arge wax is linear paraffins. Quantitative spectra from these four waxes on an expanded scale show peaks characteristic of terminal dimethyl groups, indicating that most of the branching occurs at the terminus of the molecule. The Union Carbide and Air Products waxes have the highest concentration of paraffins at about 90 wt%, and they also have a high degree of branching (13 and 44%). The Arge commercial wax has the lowest amount of branching with only 2.3% of the molecules being branched. The lower branching in the Arge wax may be explained by the iron catalyst, as compared with the cobalt catalyst used in producing the Union Carbide and Air Products waxes. This may also be a factor in the lower average carbon number seen for these two waxes [5].

The lowest concentration of olefins (and cycloparaffins, if any) (5.6 wt%) was present in the commercial Arge wax. Air Products wax has 7.0 wt% and Union Carbide wax has 6.2 wt%. Mobil wax has by far the highest concentration of olefins/cycloparaffins with 23.2 wt%. This observation is consistent with the low H_2/CO ratio of 0.7 used in the Mobil F-T reactor. Although MS analysis could not differentiate between cycloparaffins and mono-olefins, both IR and NMR data showed mono-olefins and not the cycloparaffins to be the more prevalent species in the Arge wax. Also, it is probably true for other F-T waxes. The average carbon number of the olefins is also believed to be similar to that of the paraffins for each wax, but that is currently difficult to establish. The diolefins and aromatics are present in too low a concentration to be characterized.

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However, the mass spectral fragment ions detected suggest long chain alkylbenzenes [5].

The Mobil wax has the highest concentration of total oxygenates around 10 wt%, followed by Arge wax with 6 wt%, and the other two waxes in the range of 2-3 wt%. The IR and NMR data suggest that primary aliphatic alcohols are the major oxygenates present in each wax. Double oxygenated compounds are also detected and extend to about C_{35}. The IR spectra suggest that esters are the major dioxygenates present in these waxes [5].

Tables 3-5 list some physical property data of F-T slurry bubble-column mediums [1,5,6]. For a variety of similar waxes, the surface tension values are between 0.021 and 0.027 N/m under typical F-T process conditions [7]. The density of Krupp wax at 270°C was reported to be 0.68 g/cm^3 by Calderbank et al. [8], and its viscosity at 270°C was estimated to be 0.33 cp [9]. Data for paraffinic oils have been compiled by Bland and Davidson [10].

Obviously, density and viscosity of the reactor liquid medium are two important properties that affect solid/liquid separation. The higher the density and viscosity of the reactor wax, the more difficult the separation. In this respect, high-wax mode operation of the F-T process is disadvantageous to the catalyst/wax separation.

As pointed out by Kolbel and Ackermann [11], the formation of higher-molecular weight products is favored by low operating temperature and a high alkali content of high-activity iron precipitation catalyst, as well as by the chain-extending molecular buildup of the hydrocarbons present in the catalyst suspension or recycled into it. Mobil workers also observed further chain growth of large molecules, presumably through readsorbing onto the active catalyst sites [1]. In the high-molecular products operating mode at Rheinpreussen, the reactor liquid, after pressure filtration, was distilled, and the fraction boiling up to 320°C together with 1/3 of the 260-320°C fraction was recycled back into the reactor. As a result, 75 wt% of the total product was paraffin and hard wax, and 1/3 of the waxes were formed through molecular building of the fraction recycled to the reactor, and the remaining 2/3 were synthesized from the feed gas. About 80% of the recycled fraction was involved in the molecule enlargement [12]. It is noteworthy that, in this operation, only the distillate (<320°C) and no wax was recycled back to the reactor. If wax, instead of the distillate had been recycled, probably more and heavier waxes would have been formed. It might be necessary to study the effect of recycle composition on the steady-state composition and property of the reactor slurry, since it may have impact on catalyst/wax separation, as well as on overall product distribution.

2. Catalyst Particles

If a low-ratio synthesis gas (H_2/CO ratio of 1.1 or less) is charged, carbon monoxide hydrogenation catalyst used must include water-gas shift activity or characteristics so that steam formed in the F-T operation by conversion of the low-ratio synthesis gas will react

with charged CO to form H_2. Examples of F-T catalysts comprising shift activity are iron alone, or iron, cobalt, or ruthenium provided with an added shift catalyst component. Shift catalysts suitable for the purpose include those containing the elements Fe, Cr, Zn, or Cu.

The catalyst concentration in suspension is usually around 10 wt% in terms of iron present in the catalyst. Lower concentrations reduce the reactor efficiency, whereas higher concentrations increase the viscosity of the slurry. An optimum equilibrium should be established among catalyst concentration, gas throughput, and operating temperature [12].

The suspended catalyst particles retained in the slurry phase may be selected from within the range of about 1 to 50 microns, thereby providing a larger amount of surface-active sites than obtainable with larger size catalyst particles or extrudates used in fluid and fixed catalyst bed systems. According to Deckwer et al. [13], if 50-micron particles are applied, the catalyst is uniformly distributed over the reactor volume even for the lowest gas velocities used. Since the particles of the commonly applied precipitated catalysts are usually smaller than 50 micron, this indicates that catalyst sedimentation and liquid-solid mass transfer resistances would not be a problem in the slurry F-T process.

The catalyst particle size distribution in the reactor slurry is essential for determining the catalyst settling characteristics. In contrast to other types of reactors, mechanical strength of the catalyst is not required in slurry F-T reaction systems. On the contrary, it is advantageous to have the catalyst particles break up during the reaction as a result of carbide formation, because this leads to a good dispersion in the liquid [12]. It had been shown that the particle size of a precipitated iron oxide catalyst (incorporating small amount of potassium and copper oxides as promoters) in the slurry reactor decreased with time on synthesis to a relatively uniform size of 1-3 microns [14]. Clearly, smaller particle size makes solid separation from liquid more difficult.

Mobil identified a particle size analyzer (Sedigraph 5000E), which can be applied to fresh slurry F-T catalysts. This analyzer uses a low-intensity X-ray beam to measure the size of solid particles settling in a liquid. Analytical results of a sample of fresh F-T catalyst $(Fe/Cu/K_2CO_3)$ is shown in Figure 3. The mean particle size is 4.2 microns, the range being 0.15-40 microns. After 86 days of operation, a sample of spent catalyst was separated from reactor-wax by centrifuging in toluene. Preliminary analytical results show that the particles were smaller than 3 microns and a significant portion was in the submicron range. It appeared that there was substantial disintegration during that run. However, this catalyst could not be analyzed for detailed particle size distribution. The major difficulty in analyzing spent F-T catalyst is to separate the catalyst from the reactor wax without changing the particle size distribution [1].

III. BASIC REQUIREMENTS OF SLURRY CATALYST/WAX SEPARATION

In the high-wax mode F-T operation, the wax slurry in the reactor has to be continuously withdrawn to maintain the desired liquid level, and a steady-state operation mandates that a certain amount of reactor wax be withdrawn as products. The catalyst, dispersed in the liquid phase, is required to remain in the reactor to maintain certain productivity. Therefore, the catalyst and the reactor wax must be separated, and there are two ways of performing this solid/liquid separation. One way is to separate them inside the reactor so that only clear liquid is withdrawn and catalyst is left in the reactor. The other way is to draw the reactor slurry containing a certain amount of catalyst, and separate the catalyst from the liquid in another device. The liquid stream is then further processed, and the catalyst, usually in the form of a concentrated slurry, is recycled back to the reactor. In either way, a part of the reactor liquid is recycled back to the reactor according to process requirements.

Wherever the separation is done, the catalyst particles should be recovered as complete as possible to reduce the operating cost of the slurry F-T process. As the wax is to be refined into transportation fuels through catalytic processes such as hydrocracking, solid particles left in the clarified wax must be limited to an acceptable extent so that the wax would not foul the catalyst bed during wax refining. When the solid/liquid separation is conducted outside the reactor, the catalyst concentration in the underflow does not have to be very high, since the underflow is to be recycled back to the synthesis reactor. In fact, a certain amount of liquid must be retained in the underflow for the sake of pumpapability of the catalyst concentrate and/or process recycle requirement.

As a consequence, the basic technical requirements for slurry catalyst/wax separation are (1) high solids separation efficiency, and (2) low solids content of the product wax. It is likely that the refining catalyst is more expensive than the F-T iron catalyst, hence a solids content limit for the wax product should be the first requirement, and the separation efficiency is correspondingly determined. The underflow catalyst concentration is in turn determined by the transferability of the underflow and the maintenance of the catalyst concentration and liquid level in the reactor. These technical requirements are important because they serve as the criteria for judging the effectiveness of the catalyst/wax separation technologies.

As the acceptable solids content of the product wax is concerned, there is only one experiment available to date. The hydrocracking test of a wax containing 133 ppm of iron did show that at least 50% of the iron in the feed processed remained in the hydrocracking reactor. Although no catalyst deactivation was observed in that period, the preheater section was stuck together in solid chunks [5]. Reactor plugging and catalyst poisoning may be causes for plant shutdown. For instance, hydrocracking catalyst run time may be decreased by irreversible poisoning caused by metals such as vanadium in the feedstock, and therefore the heavy metals content should be kept below 2.5 ppm for the Linde hydroconverter [15]. For a hydrocracking fixed catalyst bed, Unocal specifies a maximum particulates content of 2-5 ppm [16].

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It is reasonable to limit the solids content of the F-T product wax to a few ppm, preferrably below 2 ppm, and a further investigation into this problem seems to be necessary. With respect to the pumpability of the solids concentrate, certain tests are also required.

Available catalyst/wax separation techniques are discussed in the following sections.

IV. CATALYST/WAX SEPARATION INSIDE THE SLURRY REACTOR

Collecting and quantifying the high-molecular-weight products, which accumulate in the reactor during the F-T synthesis, and separating the fine catalyst particles from the reactor wax are considered to be disadvantages of slurry reactors [17]. The liquid-phase F-T process would be greatly simplified if the high-boiling products, which do not vaporize and escape with the residual gas under operating conditions, can be withdrawn from the reactor free of suspended solids.

Farley and Ray [14] described the early laboratory tests to find a method of wax removal from a F-T reactor capable of high withdrawal rates that would leave the catalyst available for reuse. Various magnetic, sintered-metal, and woven-wire cloth filters were shown to be unsuitable for the conditions of temperature, pressure or particle size utilized, and none of the filtering methods investigated gave adequate throughputs.

In laboratory research, as withdrawal of the wax without simultaneous withdrawal of the suspended catalyst fines turned out to be very difficult, some researchers let the product wax accumulate in the slurry reactor [18]. A common practice is to allow wax to accumulate in the reactor for the experimental period and then remove it from the reactor after each mass balance period [17]. This is by no means a satisfactory method, even for laboratory research, since it restricts the length of the run and a steady state could never be reached. This is also unacceptable for commercial operation.

Efforts have been made to withdraw a clean wax stream from and leave the catalyst fines in bench- and pilot-scale slurry reactors.

At the Fuel Research Station in England, the liquid level in a laboratory-scale slurry F-T reactor was maintained constant either by withdrawing liquid medium via a filter immersed in the slurry or by returning heavy oil and wax from the partial-condenser receiver [19]. Workers at PETC, Mobil, UOP, and Texas A&M use similar filters (e.g., porous metal filters with pore diameters ranging from 0.5 to about 10 microns) inside a reactor for withdrawal of solids-free reactor liquids. Maintaining certain differential pressure across the filter helps to obtain a flow of the filtrate reactor wax, and back-flushing could clean the clogged-up filters when necessary. However, the operation of an internal filter has not been continuous and satisfactory. Since difficulties have been experienced and hard to overcome, it is therefore deemed necessary to perform the solid/liquid separation outside the reactor for commercial-scale operations [20-22].

Regarding the wax reflux from the partial condenser as mentioned in the case of British Fuel Research Station, it is not possible that a significant amount of wax would volatize under reactor conditions to avoid wax accumulation. In high-wax mode operation, therefore, this method can not provide a product wax stream.

Internal filters of different forms were also tested inside reactors of larger sizes. In the

fifties, the U. S. Bureau of Mines (BOM) had operated three different slurry F-T systems [23]. Figure 4 is a diagrammatic sketch of one BOM pilot-scale reactor system with slurry circulated by natural convection. The reactor was a 3-inch pipe, a, 10 feet high. A parallel 1.5-inch slurry recycle line, b, was attached to the reactor with two valved crossover lines, g, at the 5- and 10-foot levels and a 1-inch return line to the bottom of the reactor. A constant liquid level was maintained above the 10-foot crossover line by withdrawing the excess oil through a porous metal filter, f, installed in the recycle leg. The recycle line was found to be completely plugged after 330 hrs of operation, probably because of catalyst settling and deposition in the leg due to lack of agitation [24].

In a later version of the BOM slurry reactor of the same size, a short section of porous bronze tube having the same diameter as the steel reactor and surrounded by a pressure-retaining jacket was welded into the wall of the reactor tube, as shown in Figure 5. Through this section, excess heavy products could be withdrawn, while the accumulated catalyst was flushed back into the slurry by the motion of the bed. Excess reactor wax was drained off periodically. Experiments were run continuously from 900 to 3200 hrs and no forced shutdown due to filter plugging was reported [25].

The relative success of the last method can be attributed to its larger filter surface, which is readily accessible to the motion of the slurry bed. This kind of filter structure, however, is not realistic for commercial reactor designs. Even if other filter designs may be successful, the reactor is subject to the risk of filter plugging, which would result in an involuntary shutdown of the system. An external catalyst/wax separation facility can be flushed or cleaned whenever necessary without interrupting the run, if a surge tank or a standby filter is available.

Other solid/liquid separation techniques are not known to have been tested for catalyst/wax separation inside the slurry reactor. With the development of high gradient magnetic separation (HGMS, Section XI), it may be possible to apply this technique to the removal of catalyst fines from the reactor wax in a slurry recycle line attached to the reactor, in a way similar to that shown in Figure 4. Instead of a filter, a section of the line can be filled with filaments magnetized by a magnetic field generated outside the line. The purified wax can be withdrawn from the recycle line. When it is necessary to clean the filament matrix, the magnet is deenergized and the particle fines trapped or held in the matrix are flushed off the filter elements and returned back to the reactor. The details of the HGMS system will be discussed in Section XI.

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V. VACUUM DISTILLATION

As mentioned earlier, the reactor wax is a wide-boiling mixture, and it has to be fractionated to obtain products of different boiling ranges. Vacuum distillation is a conventional means to separate high-boiling fractions from non-volatile components, and it was explored as a technique to obtain a solids-free wax stream.

A scoping vacuum fractionation of a reactor-wax containing 0.1-0.18 wt% catalyst fines (after catalyst/wax separation) was conducted by Mobil [1]. The vacuum distillation was terminated when a small amount of wax was found in the condenser. A gradual vacuum loss was experienced, which is believed to indicate some cracking of the wax during fractionation. The cut temperature was 461°C and overhead fractions amount to 17 wt%, which are very clean, of course, and do not contain any catalyst fines. If a cut point of 566°C (roughly equivalent to a paraffin of C_{47}) could be achieved, about 30 wt.% of the reactor-wax would appear as overhead fractions.

Vacuum distillation of the slurry wax does give solids-free distillates including a part of the paraffin wax, but the yield is limited due to cracking. Commercial vacuum distillation in petroleum refining industry usually gives a cut point around 500°C. This implies that almost 80 % of the reactor wax is left as the vacuum bottoms, and essentially no solids-free hard wax products can be obtained. If the reactor slurry is vacuum distilled without prior catalyst separation, then the vacuum bottoms must be further processed to separate catalyst particles from wax and to recycle the catalyst. Recycling all of the vacuum bottoms is impractical since there is no outlet for the heavy waxes.

In short, vacuum distillation is not a technique for catalyst/wax separation. Unless the feedstock to the vacuum distillation column does not contain catalyst fines, there is no way of getting solids-free heavy waxes by vacuum distillation.

VI. THERMAL CRACKING OF VACUUM BOTTOMS

The paraffinic nature of F-T waxes suggests that vacuum bottoms of reactor waxes are excellent feedstocks for thermal cracking. Five scoping batch runs of thermal cracking of reactor-wax vacuum bottoms using a laboratory "shaker bomb" setup were done by Mobil. The vacuum bottoms were obtained from vacuum distillation of reactor waxes containing 0.1-0.18 wt% catalyst fines as described in the previous section. The thermally cracked materials are supposed to be recycled to the vacuum distillation column, and the solids-free overhead fraction would be an excellent feedstock for further upgrading to light fuel products. The results are listed in Table 6 [1].

Problems with thermal cracking of slurry wax vacuum bottoms are the following: First, the highest conversion of $C_{47}+$, as reported by Mobil, is less than 50%. Recycle cracking could increase the total conversion, but severe deposition of solid particles along with coke formation would occur. If the vacuum distillation is undertaken without previous catalyst/wax separation, the heavy deposition of solids would soon plug up the cracking tubes. The on-stream time would be extremely short, and all the catalyst would be lost. Finally, the thermal cracking product, mostly unsaturated, has to be further refined by hydroprocessing. Therefore, thermal cracking also is not a technology for catalyst/wax separation. If the reactor wax is already freed of solids, then hydrocracking is a much better technology for wax processing than the obsolete thermal cracking.

VII. SEDIMENTATION

Gravity causes solids to settle out from a slurry, whereupon they can be removed continuously or intermittently. This settling of solids is referred to as sedimentation, and sedimentation devices are usually economical when flow rates are large. However, the sedimentation depends on several factors, such as the amount of solids entrained by the liquid, and the settling characteristics of the solids, including particle-size analysis, specific gravity relative to that of the liquid, and response to chemical additives. It is advisable to perform settling tests in the laboratory or in pilot equipment to determine the settling rates, limits of concentration of the settled slurry, or clarity of supernatant liquid. Often the settling rate of solids is enhanced by flocculants or coagulants, which work best on 74 microns or smaller particles [26].

In many laboratory and pilot studies on slurry F-T process, settling has been a major method for separating catalyst solids from the wax. Settling usually takes 45 minutes to a few hours and the clean wax after settling contains solids up to 0.1 wt% or more.

A gravity separation system was devised for the Greenwich F-T pilot plant, as shown in Figure 6 [14]. The slurry entered the sedimentation vessel via the filter loop and sedimentation limb, all of which were maintained at plant pressure. The height of the slurry was controlled by the level of the outlet drain pipe. The system remained static for the required time of sedimentation, and the settled catalyst flowed via the sedimentation limb to the filter vesssel, from where it was returned to the reactor by the natural circulation of the slurry. It was found that the rate of catalyst sedimentation was not rapid enough to control the slurry level within the reactor. Simple model experiments had shown that, in the type of system employed in the plant, there were only two zones in the sedimentation vessel, i.e., the clear (solids-free) zone at the top and a zone of uniform concentration. In the conical portion at the bottom of the vessel, however, the particles that settled on the surface coagulated until their combined weight exceeded the viscous and surface-friction drag, and then they slid down the surface as a dense layer. Sloping surfaces were therefore designed and inserted into the sedimentation vessel to reduce to a minimum the height any particle had to fall. Thus, if 1 inch of liquid appeared clear in 1 hr with simple sedimentation, then filling the vessel with sloping surfaces 1 inch apart would theoretically result in the whole vessel being cleared in 1 hr. The solids that fell on the sloping surfaces would slide off as agglomerates.

Different forms of inserts were tested in a model apparatus and results are compared in Table 7 [14]. Elliptical plates bent along the main axis to an internal angle of 60° were found to be the most efficient system. The dense phase fell from the lower edges of the plates and replacement liquid was able to flow unhindered up the line of apexes of the plates. The disadvantage of the conical plates was that the agglomerates falling from the lower edges always met resistance from and were re-dispersed by the upflowing liquid. Typical results obtained from a run on the plant are shown in Figure 7 and indicate a relatively high initial loss of catalyst in the wax drainings, which, during the first 80 hrs, amounted to 8.6 wt.% of the catalyst loading. Calculations indicated that, after 35 hrs, 20% of the catalyst in the

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sedimentation vessel had a particle size below 3.5 microns, while after 80 hrs, only 1% was below 3.5 microns. The less efficient separation of catalyst from the slurry observed initially was considered to be due to hindered agglomeration because of the wider size range of the primary particles. The mechanical difficulties of operating this British pilot plant were mainly those of efficient separation of catalyst and wax to maintain a constant level in the reactor. These difficulties were not successfully overcome until the program was due to be terminated.

Mobil previously used a batch settling system. The settling pot is a 300 cm³ pressure vessel with a dip-tube extending halfway down for decanting the wax. The pot was situated 30 cm below the level of the reactor bottom. Slurry was brought from a drain at the 1.5 m level to fill the pot. When settling was completed (usually 45 minutes), the upper layer of the wax was decanted and the remainder pressurized quickly back into the reactor bottom [1].

Mobil's on-line slurry catalyst/wax separation system can continuously withdraw up to 7 kg of clean (<0.1 wt% solids) reactor wax per day. A schematic of this system is shown in Figure 8 [1]. During normal operation, slurry is withdrawn continuously from the F-T reactor and entrained gas is disengaged in a small disengager pot, which is connected to the reactor top. The gas-free slurry is passed through a dip-tube into a two-liter settling pot. The dip-tube length is designed to maintain 80% of the settling pot volume above its tip. The concentrated slurry exits the settling pot through a conical section and is pumped back to the slurry reactor through a positive-displacement slurry pump. The pump is inverted, i.e., feed enters at the top and effluent exits at the bottom. This prevents catalyst settling in the feed line to the pump. The clean reactor-wax is withdrawn from the top of the settling pot either semi-continuously by periodically opening a valve, or it can be withdrawn continuously by using a metering valve. The residence time in the settler is less than 3 hours for separating the wax from the catalyst achieving less than 0.1 wt% residual catalyst in the wax.

Mobil believes that this reactor-wax removal system was successfully demonstrated. Nevertheless, catalyst settling in the reactor suggests a problem. In Mobil Run CT-256-11, before catalyst settling, a 5-micron particle size is sufficient to match the catalyst concentration profile, while, after catalyst settling, a 13-micron particle size is needed to match the steep profile. This suggests a strong possibility that the catalyst may have increased in size either by agglomeration or by the growth of heavy polymers on the outside of the catalyst particle. Photographs comparing fresh and end-of-run (CT-256-13) catalysts are shown in Figure 9. The tremendous increase in apparent particle size is clearly evident, which is contrary to what was observed elsewhere [14], as described in Section II. The large particles do appear to be aggregates, but a mechanism for their formation remains unknown [1].

Although gravity settling can remove the bulk of catalyst fines from liquid hydrocarbon products, a complete removal of catalyst particles could take an unacceptably long time. Essentially no study was specifically done on settling performance of the slurry F-T catalyst/wax system. A basic understanding is necessary regarding the settling characteristics of the catalyst/wax slurry with respect to the viscosity of F-T wax under operating conditions and the effect of flocculants and/or coagulants.

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VIII. FILTRATION

In early German work on slurry F-T reactors, it was stated that those experiments led to the installation of a filtering equipment permitting the removal of a catalyst-free, liquid paraffin from the reactor while the suspended state of the catalyst was maintained [27]. However, UOP workers [5] reported that bench-scale filtration techniques did not work because of the high wax viscosity coupled with the small size of the iron particles. A portion of the catalyst fines are smaller than 1 micron in size, which makes ordinary filtration ineffective for fines removal. Filtration using filtering aids is time prohibitive and will not permit catalyst recovery.

In the initial design of the British Fischer-Tropsch slurry reactor pilot plant at Greenwich in the late fifties, the slurry level in the reactor was controlled by withdrawing wax through a filter unit attached to the reactor. This plant was designed for a throughput of 2500 SCF/hr to produce 70-100 gal of product/day with operating pressures up to 20 atm gauge and reaction temperatures to 300°C. During operation, slurry circulated around the "filter loop" by thermosyphon, and wax was filtered from the slurry through five streamline-type filter candles inserted in the filter vessel. However, the withdrawal rate was limited, so the slurry level rose rapidly [14].

Pressurized filtration may give higher withdrawal rates necessary for a commercial size plant. In the German semi-industrial demonstration plant with a slurry bubble column F-T reactor, catalyst/wax separation was realized by filtration. When running the plant for the predominant production of high molecular products, the contents of the reactor were continuously passed through a special pressure filter where part of the liquid medium was separated and recovered, while the bulk of the suspension flowed back into the reactor [28,29]. The flow chart of the Rheinpreussen-Koppers Demonstration Plant (1952-53), the first pilot plant of liquid phase F-T process, is shown in Figure 10 [12]. No filter was used inside the reactor. The slurry was withdrawn by means of a pump through nozzles at the bottom of the reactor which has a diameter of 1.55 m and a height of 8.6 m. The catalyst was continuously separated from the high-molecular-weight products in a pressure filter n.

Sasol II mainly employs filtration in solids removal from heavy F-T liquids streams [30]. The tars and oils separated from the gas liquor and the residual pitch obtained in the Phenosolvan unit are recombined and the combined stream contains virtually all the fine entrained coal and ash that left the gasifier. The solid residue is recovered by filtration. Also, the heavy oil (970°F+) from the Synthol reactor effluents contains the carryover catalyst, which is pumped into a large decanter with a rotating rake. Catalyst solids settle and the clean oil is decanted. The concentrated catalyst slurry is pumped through a pressure filter and the filtrate of cleaned oil is subject to further processing. Therefore, it is a combination of settling and filtration for catalyst/wax separation. In Sasol's 1 m diameter slurry F-T reactor unit, filtration is also employed as one of the options for catalyst/wax separation [2]. However, no details about the filters are available.

Another application of filtration is to remove the residual catalyst fines from the "clean" wax that had been separated from most of the solid particles, as Mobil did in its conceptual process design, again a combination of two different techniques. In this design, the wax from the hydroclones and the wax recovered from the deactivated slurry are processed through the wax cleanup system. From the surge vessel, the wax containing less than 0.1 wt% catalyst is filtered through a vertical leaf filter precoated with filter-aid material to remove traces of the F-T catalyst, which may otherwise affect the performance of the downstream reactor-wax upgrading units. At the end of the filtration cycle, the filter cake is broken loose from the leaf and collected by a screen conveyor system into a cake hopper for disposal. A total of 8 horizontal tank, vertical leaf filters are required for a plant processing synthesis gas at a rate of 106,782 lb-mol/hr [1]. However, its operability needs to be demonstrated and its economics justified.

Generally, as a solid/liquid separation technique, the advantages of filtration are (1) high efficiency of solids separation with reasonable particle size, and (2) minimum liquid product loss. While the disadvantages are (1) poor mechanical history, (2) high capital and operating costs, (3) intermittent operation, (4) environmental problems, and (5) difficulty in catalyst recovery if filtering aid is used. When more cost-efficient techniques are not available, it is advisable to proceed pilot-scale tests to obtain fundamental understanding. Settling and filtration may be a reasonable and economical combination, with the filters handling the clarified wax from settling.