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## Feasibility Study of Separating Fischer-Tropsch Wax from Catalyst Using Supercritical Fluid Extraction

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**Abstract:** The technical feasibility of a method of separating Fischer-Tropsch (F-T) catalysts from the viscous output slurry of F-T bubble column reactor, where the slurry comprises fine catalyst particles with average size of  $3\mu$  and heavy hydrocarbon products was studied. The method comprises contacting a compressed solvent, here defined as hexane, at supercritical condition, with the output slurry at a temperature and pressure wherein the liquid hydrocarbon product is soluble in the solvent to form a concentrated slurry phase containing the catalyst particles and an enriched solvent phase containing liquid hydrocarbon product. This study was accomplished by making comparison between such new method and the conventional method using no hexane for extracting 10 wt% cobalt catalysts in wax, using a pilot-scale batch apparatus including filtration as extraction unit. This study revealed the advantages of applying the novel method in comparison with the conventional filtration method itself; by achieving high amounts of extracted catalyst. Further, the effect of pressure, temperature and hexane to wax ratio on the process was investigated. The analysis of results showed that; first, catalyst extraction would increase by raising the pressure; second, catalyst recovery was first increased by raising the temperature but by more temperature increase the catalyst recovery got downward trend; third, mounting the hexane to wax ratio from 1 to 3, increased the amounts of recovered catalyst noticeably.

**Key words:** Fischer-tropsch, separation, filtration, supercritical, catalyst

### INTRODUCTION

Since extensive reserves of coal and natural gas exist in most parts of the world that lack of sufficient petroleum, there is a significant incentive to convert readily available solid and gaseous fuels into liquids (Leung, 1995; Rahmim, 2003). The Fischer-Tropsch synthesis is one reasonable way to carry out this conversion through the Gas to Liquid (GTL) technology. In such synthesis, carbon dioxides are reacted with hydrogen to form higher hydrocarbons, mixture of paraffins, olefins and alcohols of different carbon numbers, defined as liquid clean fuels (Satterfield, 1991; Lunsford, 2000). This issue is frequently referred in honor of the pioneering work of Fisher and Tropsch (1930) in the early 1920's. All large scale F-T reactors built to date have utilized either fixed-bed or fluidized-bed reactors. However, slurry bubble column reactors (SBC) have been the focus of recent development (Zhou, 1991; White *et al.*, 1996) for its distinct advantages over the fixed and fluidized beds. Some of these advantages are generic, e.g., a very close approach to

isothermal operation, simple construction leading to low capital cost and the ability to continuously withdraw and add catalyst in order to maintain a constant level catalyst activity in the reactor. A major advantage that is specific to F-T chemistry and related reactions is the ability of SBC reactors to operate with a feed gas containing a high ratio of carbon monoxide to hydrogen. However, the main obstacle, which must be overcome before SBC reactors can be widely used, is that the catalyst fines suspended in the F-T reactor liquid phase withdrawal from the reactor, must be separated and recycled back to it to maintain required conversion and to avoid the catalyst loss. Catalyst/wax separation is also necessary from the standpoint of wax upgrading, since the catalyst fines may foul the catalysts in subsequent wax processing steps (Zhou, 1991, White *et al.*, 1996; Biales *et al.*, 1999). Many techniques have been studied and conceivably performed for wax/catalyst separating with different degrees of success including, vacuum distillation, thermal cracking of vacuum bottoms, sedimentation, various forms of centrifugation, filtration, high gradient magnetic

separation (HGMS), solvent-assisted catalyst/wax separation and chemical methods (Zhou, 1991). Historically, pressurized filtration has received the most attention but it has been plagued with operational problems such as filter plugging, which has caused significant downtime and raised serious questions concerning the technical feasibility of filtration as a catalyst/wax separation technique (Zhou, 1991). In overall, experimental researches concluded that no single technology was entirely satisfactory and recommended certain hybrid approaches. Totally, the high wax viscosity of 2-5 Cp at 200°C and the fine catalyst particles below 3 μ (Patel *et al.*, 1990) made this solid/liquid separation a difficult task, so that there was a continued need for new low-cost, continuous and highly efficient method and apparatus for wax/catalyst separation. More recently, a near-critical fluid extraction process was proposed by White *et al.* (1996) for the separation of F-T catalysts and wax. This process shown schematically in Figure 1, involved continuously removing catalyst/wax slurry from the SBC reactor and contacting it in the extraction unit with a light hydrocarbon solvent near its critical point. The extraction unit consisted of any conventional methods, mentioned before. In such condition, some of the heavy liquids in the slurry were extracted into the light phase and some of the light solvent dissolved into the slurry. The light and heavy phases were separated and the slurry which contained concentrated catalyst, was then recycled to the reactor. The light phase passed to a recovery unit, which operated at a different pressure and/or temperature, so that the heavy phase formed the end product and the remaining light phase was recycled to the extraction unit.

The process simulation using Aspen Plus program (Biales *et al.*, 1999) and some experimental studies have been carried out by Robert and co-workers (Roberts and Kilpartick, 2001) to produce catalyst free wax (< 0.1 wt%) from the slurry of F-T reactor.

The objective of this study project is to evaluate the feasibility and potential of supercritical fluid extraction for

F-T catalyst/wax separation using a pilot-scale batch apparatus, including filtration as extraction unit. This issue is studied by making comparison between such method and the conventional filtration method and analysis the factors influence the process such as, pressure, temperature and hexane to wax ratio.

## MATERIALS AND METHODS

A pilot-scale batch apparatus was used to conduct experiments at Research Institute of Petroleum Industry-Iran during 2005-2006. The feed to the semi-batch extractor was slurry of catalyst/wax mixture containing about 10 wt% catalysts (average particle size of 3 μm) from a recent slurry-phase Fischer-Tropsch reaction performed in the GTL unit at R.I.P.I.

The major task was first selecting a proper solvent for conducting experiments. Preliminary process simulation calculations indicated that any hydrocarbon with number of carbons within 4-8 could be as a choice. However, in the present case, the process would be most effective at temperatures near the slurry reactor operating condition (200-250°C) because of reducing the additional utility costs such as heating and pressurizing the reactor's slurry. Therefore, a solvent whose critical temperature is within this range was primary interest for use as the supercritical solvent. A logical alternative was hexane ( $T_c = 234.4^\circ\text{C}$ ;  $P_c = 30.25\text{ bar}$ ); also being a product of the F-T reaction, inexpensive and readily available. The pilot-scale batch apparatus is shown in Figure 2. The apparatus comprised a vessel as feeder tank for receiving and preheating feed containing catalyst/wax mixture; a hexane tank as solvent storage either used in process or system washing; a so-called contactor which was a high pressure/temperature cylinder having the height to diameter ratio of 10, the inner volume of 400 cc which was equipped with a mechanical seal mixer used for slurry/hexane mixing to prevent the catalysts settle down in contactor; a sintered-metal filter with stainless steel membranes of 0.1 μm pore size used as first-stage separator and a flash tank vessel used as the second-stage separator and for solvent recovery if needed. Three main pipelines named headers were installed including, nitrogen header for purging and pressurizing, solvent header for hexane treatment and the ventilation header. System heating was conducted applying electrical belts wound around the vessels while each temperature's stage was independently controlled by a PLC system. Safety was a major emphasis in the design of the apparatus. In order to prevent the possibility of explosion (in case of leaks, for example), the hot sections were kept in the

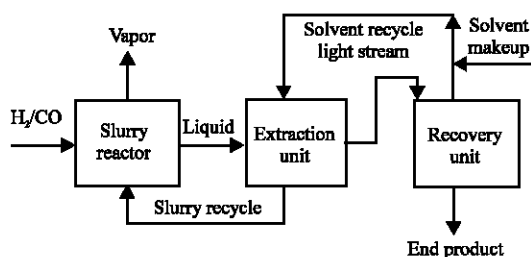


Fig. 1: Schematic diagram for F-T catalyst/wax separation using critical extraction process

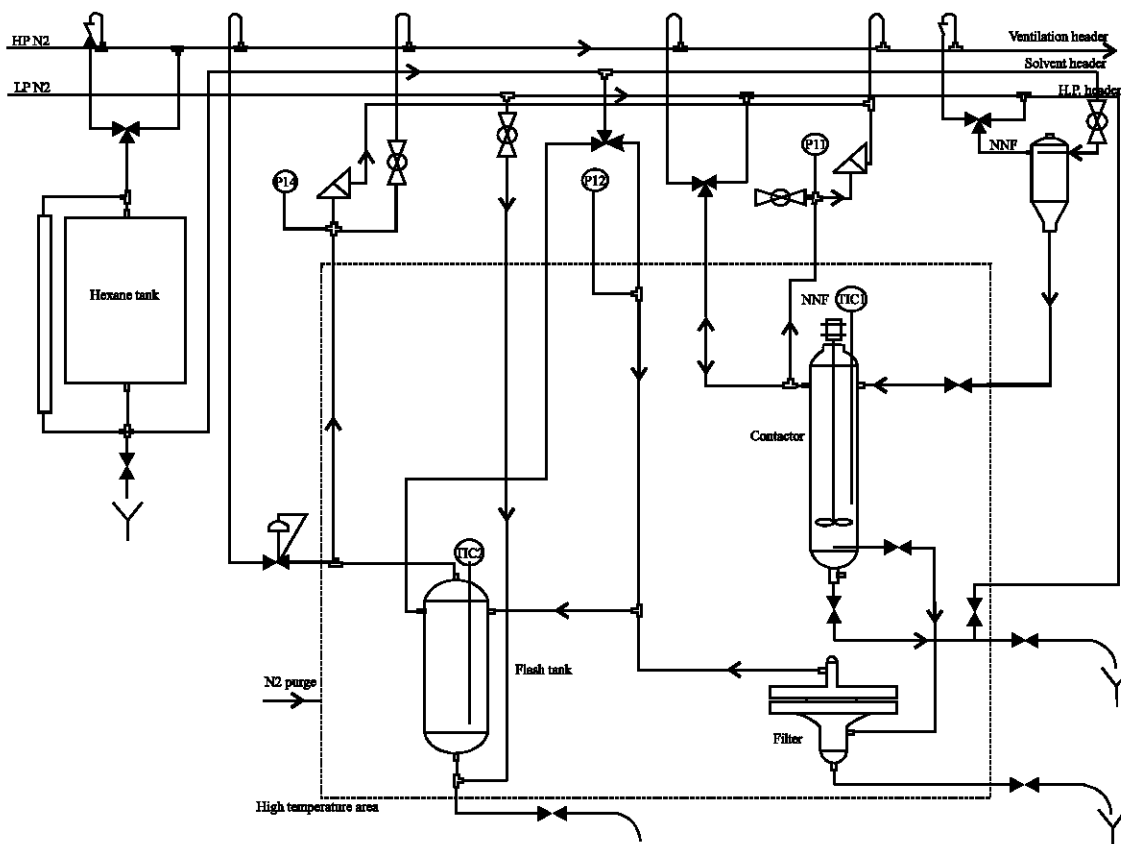


Fig. 2: Pilot-scale batch apparatus for catalyst/wax separation

sealed case under a constant nitrogen purge, so that the oxygen content was kept under 2 mol%. Similar purging was carried out before the system startup.

**Process description:** After purging the system by high pressure nitrogen, wax containing 10% by weight catalyst particles was introduced to the contactor, following the feed section in conjunction with preheating. A fixed amount of hexane (adjusted by a level indicator) was then brought into the contactor through the solvent header and mixed with slurry applying the mixer of 400 rpm. The amount of hexane used in each test was adjusted, so that the contactor would be pressurized to the expected value, regarding contactor volume and its operating temperature of supercritical hexane. This could be accomplished by using VTPR EOS (Lin and Duan, 2005). The amount of needed slurry in each test was then weighted proportional to the hexane to wax ratio amount applied in the related experiment.

At supercritical hexane operating condition, most of the wax components dissolved in hexane, so the density and viscosity of wax media noticeably came down. After achieving the expected operating condition at contactor, the mixture conducted to the filter media, used as

separation stage. In this stage, having the similar operating condition of contactor, the concentrated catalyst and some insoluble wax constituents remained in this stage, while the light stream containing a few amounts of catalyst introduced into the flash tank with lower temperature and pressure adjusted by a back pressure regulator. When the pressure was reduced, the supercritical solvent became a low-density gas and loosed its solubility properties, causing the dissolved wax to precipitate in the second-stage separator. The low-density gas was vented to the safe zone through the ventilation header, while in a commercial system it would be collected, repressurized and used.

In the case of conventional filtration, the stages pressurizing was carried out using HP nitrogen through its related header.

At the end of each experiment, the system was cooled and slowly depressurized. The contents of each separator were removed and weighted. Then, the vessels were cleaned and the filter was back flushed by warm.

The amount of catalyst in each sample was determined by ashing the sample. The samples were weighted into crucibles and ashed at 750°C for 2 h. Any hydrocarbon wax product was burnt off at these

temperatures and any catalysts remained in the crucible. The crucible was then weighted on an analytical balance before and after ashing. The difference in weigh between the empty crucible and its weight after ashing was the amount of catalyst in the sample. So, the separation efficiency of each stage was obtained, regarding the catalysts amount presented in each experiment's inlet feed.

## RESULTS AND DISCUSSION

Four series of experiments were conducted in order to investigate several concepts. The main objective was studying the feasibility of F-T catalyst and wax separation using supercritical hexane, either by making comparison between this method and the used conventional one, or by the analysis of factors influence on the process including; operating conditions, such extraction temperature, extraction pressure and solvent to wax ratio (S/W).

Initially, the results of catalyst/wax separation were compared via the two methods, first, supercritical extraction using hexane, second the conventional method with no hexane use. As mentioned before, filtration was used as the first stage extraction in both two methods, settling was known as its second stage and in fact performed as a receiver for catalyst particles not separated from wax at filtration stage.

Experiments were carried out for different extraction stage operating conditions, all within hexane supercritical region. These conditions were arranged either by varying temperature at constant pressure shown in Table 1, or by varying pressure at constant temperature, shown in Table 2. In all experiments, the second stage temperature was adjusted so as the first stage for the related experiment, however its pressure was kept at 15 bar to allow simply flow between the two stages and also to vent hexane as low-density gas.

To analyze the results, it is good to define <sup>a</sup> as weight percent of catalyst feed material which was recovered from the first-stage separator; <sup>b</sup> weight percent of catalyst feed material which was recovered from the second-stage

separator; <sup>c</sup>sum of the catalyst weight recovered from the first and second stages of separation, all in using supercritical hexane extraction method. While, <sup>d,e</sup> and <sup>f</sup> represent the similar definitions when using the conventional method in absence of hexane.

Difference between total catalysts recovered and the initial catalyst feed demonstrates the catalyst amounts, which were not separated through the separators and in fact were lost in the process. These amounts were collected from the system by washing treatment after each experiment in order not to interfere the next test results.

As results in Table 1 and 2 indicate, not only the amounts of catalyst extracted in the first-stage separator through the supercritical hexane extraction were much higher than the opponent ones without hexane use, but also the total recovery of catalyst, showed higher values. Such trend was observed for all experiments, in different temperatures and pressures. It means that by using supercritical hexane in extraction unit, not only the filter efficiency was raised and its related problems, including filter clogging, low separation rate, back flushing and emergency shot downs were reduced, but the overall catalyst lost through vessels, valves and pipelines approached to negligible values. It shows that the wax/catalyst separation worked more efficient via the new method of supercritical extraction. This fact would be more noticeable when working commercial scales.

Other point is, the higher the weight percent catalyst in the first-stage separator, the better separation and the less need to more separation stages. This subject can be seen within the stages' separation results. By using supercritical hexane, most of the catalysts were separated in the first-stage and only small need of approximate 10-15 by wt%, in comparison with 55-60 wt% for other conventional method, exists for applying other separation stage. However, there would be no need of such stages by applying higher amounts of hexane, known as hexane to wax ratio. So, some other experiments were executed, either to demonstrate this truth, or to investigate influence of pressure/temperature raise on catalyst recovery, regarding, higher amount of hexane to wax ratio. Results are presented in Table 3 and 4.

Comparison between the Table 1 and 3 also Table 2 and 4 shows that regarding same operating conditions of temperature and pressure for each experiment, mounting the hexane to wax ratio from 1 to 3, increased the catalyst recovery through the extraction unit. This result can be attributed by more density/viscosity decrease via the hexane concentration raise within wax media and resulting in higher filtration efficiency.

Table 1: Results of catalyst recovery at various temperatures; comparison of two method Extraction temp: 260°C; S/W=1; 2nd stage pressure: 15 bar; Exp. data: (Amiri, 2006)

Supercritical extraction method				Conventional used method		
1st sep temp. (°C)	1st sep catalyst <sup>a</sup> (%)	2nd sep catalyst <sup>b</sup> (%)	Total catalyst rec <sup>c</sup> (%)	1st sep catalyst <sup>d</sup> (%)	2nd sep catalyst <sup>e</sup> (%)	Total catalyst rec <sup>f</sup> (%)
240	82.60	14.5	97.1	36.93	34.86	71.79
250	83.91	13.65	97.56	38.11	33.71	71.82
260	85.82	12.01	97.83	40.32	31.71	72.03
270	83.87	13.70	97.57	42.68	29.52	72.20
280	82.11	15.10	97.21	44.24	27.98	72.22

Table 2: Results of catalyst recovery at various pressures; comparison of two methods Extraction temp.: 260°C; S/W=1; 2nd stage pressure: 15 bar Exp. data: (Amiri, 2006)

Supercritical extraction method				Conventional used method		
1st sep pressure (bar)	1st sep catalyst (%)	2nd sep catalyst (%)	Total catalyst rec <sup>c</sup> (%)	1st sep catalyst (%)	2nd sep catalyst (%)	Total catalyst rec <sup>f</sup> (%)
31	85.02	12.89	97.91	39.01	33.00	72.01
33	85.82	12.01	97.83	40.32	31.71	72.03
35	86.43	11.34	97.77	41.01	31.09	72.21
37	86.91	10.52	97.43	41.85	30.57	72.42

Table 3: Results of catalyst recovery at various temperatures, extraction pressure: 33 bar; S/W = 3; Exp. data: (Amiri, 2006)

Extraction temp.(°C)	250	260	270	280	285	290	
% catalyst recovery (Filtration)		88.56	91.52	94.77	93.21	91.89	90.10

Table 4: Results of catalyst recovery at various pressures, extraction temp.: 260°C; S/W = 3; Exp. data: (Amiri, 2006)

Extraction pressure (bar)	31	33	35	37	
% catalyst recovery (Filtration)		90.89	91.52	92.11	92.95

According to Table 1 and Table 3, in supercritical extraction method, catalyst recovery in filter was first increased by raising the extraction temperature within supercritical hexane region. This increase was limited by the temperature of 260°C for solvent to wax ratio of 1 and 270°C for solvent to wax ratio of 3. In the other hand, by more temperature increase the catalyst recovery got downward trend. The reason of such trend can be interpreted by declining the supercritical solvent solubility because of its concentration decrease within wax/hexane mixture. This matter is because of separating portion of hexane from hexane/wax mixture as gaseous state which thermodynamically stems from entering two-phase region in wax/hexane envelope through further temperature raise. This fact is so important when using supercritical solvent extraction in separation processes.

Similar studying was carried out to investigate the effect of pressure raise on the process efficiency. The results of such study are observed in Table 2 and Table 4. According to these results, the catalyst recovery had upward trend through the pressure raise. This fact could be attributed from increasing effect of pressure raise on supercritical solvating power. However, this increase occurred with a smooth slope, in comparison with temperature raise.

The above results were some generals obtained for F-T wax/catalyst separation using supercritical extraction. Detailed thermodynamic analysis of the factors which influence this process can be conducted in future. In addition, feed wax recovery in conjunction with hexane recovery via the flash operation, also identifying its related effective factors and their analysis was not studied in this research which they are matter of importance for more practice in future.

## CONCLUSIONS

The technical feasibility of a method of separating Fischer-Tropsch (F-T) catalysts from the viscous output slurry of F-T bubble column reactor supercritical hexane as solvent and filtration as extraction stage, was studied. The major points could be arranged as following:

- In summary, supercritical extraction method used with filtration was more effective for separating fine catalyst particles from wax achieving 94.77 wt% catalyst recoveries, in comparison with 44.24% by the conventional filtration.
- By using supercritical hexane in extraction unit, not only the filter efficiency was raised, but also its related problems, including filter clogging, low separation rate, back flushing and emergency shot downs were reduced, but the overall catalyst lost through vessels, valves and pipelines approaches to negligible values.
- Less need to more separation stages was observed via supercritical extraction method.
- Mounting the hexane to wax ratio from 1 to 3, increased the catalyst recovery through the extraction unit.
- Solubility power of supercritical hexane and therefore the catalyst recovery was first increased up to the temperature of 260°C for solvent to wax ratio of 1 and 270°C for solvent to wax ratio of 3. In the other hand, by more temperature increase the catalyst recovery got downward
- The catalyst recovery had upward trend having smooth slope through the pressure raise.
- Further thermodynamically analysis of process, feed wax recovery in conjunction with hexane recovery via the flash operation, also identifying its related effective factors and their analysis are matter of importance for more practice in future.

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