SEPARATION OF CATALYST PARTICLES AND WAX FROM EFFLUENT OF A FISCHER–TROPSCH SLURRY REACTOR USING SUPERCRITICAL HEXANE

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Abstract: The separation of a catalyst/wax mixture from Fischer–Tropsch (F-T) synthesis products in a slurry bubble column reactor is one of the most important challenges in the development of F-T slurry reactors. So far, various techniques such as internal and external filtration, gravity and forced sedimentation and high gradient magnetic separation have been proposed. The technique must be able to separate the catalyst (with a size distribution of 1–60 microns) effectively and quickly in a continuous process and the catalyst content in the separated wax should become less than 2 ppm, economically speaking.

In the present work, a number of experiments using normal hexane in its supercritical and subcritical states were carried out for separation and it showed that this technique was highly effective and quick. Since hexane in its supercritical state can reduce the wax viscosity, separation of the catalyst will be easy and fast. A settler was initially used to remove the main portion of catalyst content (i.e., up to 90%) and a filter as the secondary step of separation to remove remaining solid content of the wax. N-hexane was used as the solvent and contacted to the wax with different solvent/wax mass ratio of 1/1 to 5/1 and different residence time of 60–240 s. The catalyst content in the purified wax was lower than 2 ppm.

Keywords: catalyst; wax; separations; filtration; slurry reactor; supercritical fluid.

INTRODUCTION

The growing demand for clean liquid fuels (i.e., zero sulphur) with the increase in natural gas reserves has triggered an international effort to develop methods for production and commercialization of these valuable energy resources. The conversion of natural gas to liquid hydrocarbon products, GTL, is an attractive process for monetization of natural gas. The process includes production of synthesis gas, Fisher–Tropsch (F-T) reaction and upgrading the final product (Corke, 1998).

Different reactor configurations such as ARGE fixed-bed, synthol circulating fluidized-bed, advanced synthol fixed fluidized-bed and slurry bubble column (SBC) reactors have been developed to produce liquid products by F-T reaction (Anderson *et al.*, 1984; Krishna and Sie, 2000).

Several problems, such as removing the large amounts of heat released during the reaction, low conversion rate, local overheating of catalyst and low catalyst lifetime have been encountered with fixed and fluidized bed reactors. As a direct result of these problems, other reactor types, namely slurry or three-phase reactors, were developed. It is less tedious to control the reaction heat by using a SBC since the reaction is carried out isothermally; local overheating of the catalyst (hot spots) and catalyst deactivation can be prevented. The other advantages offered by SBCs include: high liquid (slurry) phase content for reactions to take place, reasonable inter-phase mass transfer rates at low energy input, high selectivity and conversion per pass, and online catalyst addition and withdrawal. Also, there is a low maintenance requirement due to simplicity in construction and absence of any moving parts (Dry, 2002; Gandhi *et al.*, 1999; Patel *et al.*, 1990; Shah *et al.*, 1982).

One major problem with the slurry bubble column reactor is the need for catalyst/wax separation of the product. An efficient and cost-effective technique can yet make the SBC reactor a more attractive process for commercialization (Pham *et al.*, 1999; Saxena, 1995).

REVIEW OF THE CONVENTIONAL TECHNIQUES IN CATALYST/WAX SEPARATION

During the past 50 years, a great deal of effort has been made to develop methods

for catalyst/wax separation from the products of the F-T slurry reactors (Zhou and Srivastava, 1991). As a result, a number of techniques, such as internal and external filtration, natural and forced sedimentation, magnetic separation, vacuum distillation and chemical conversion have been used. Implementation of these techniques has encountered problems as discussed below:

Catalyst/wax separation using internal and external filtration are two of the oldest techniques used in F-T process (Engel and Van Der Honing, 1999). Due to the high viscosity of the catalyst/wax mixture, filtration under pressure, performed inside or outside the reactor, cannot keep the liquid level of the reactor at a desired value. In addition, internal filtration always has the plugging risk, which may lead to reactor shutdown. The low separation rate which is caused by the high viscosity of the wax, and also being obliged to use catalysts of relatively large particles size range (about 30–60 microns) to improve the filtration efficiency, results in the low efficiency of the reactor and its low conversion performance.

Techniques such as natural and forced sedimentation of catalyst/wax separation, performed in batch or intermittent mode in settlers and centrifuges cannot be regarded as reliable techniques due to inefficient sedimentation time of the catalyst and will not result in favorable particle concentrations (1–2 ppm). Other techniques, such as addition of agglomeration and surface tension reduction agents to improve settling time, have not been useful either because of the problems of settling techniques and separation of the added reagents (Bohn and Siebarth, 2004).

Magnetic separation technique for catalyst/wax mixture shows a catalyst loss of about 100–900 ppm. Other techniques such as high gradient magnetic separation (HGMS) are relatively efficient, but very expensive, because of the high costs of superconductor as well as high annual operating costs (Fletcher, 1986; Hirschbein et al., 1982; Oberteuffer, 1974).

The advantages of slurry bubble column reactors have resulted in their wide spread application by researchers in F-T process. In this type of reactor, catalyst/wax separation is carried out either by internal, external and/or combined internal and external filtration. This technique has two disadvantages; firstly, large catalyst particles (30–60 μm) are used which gives lower efficiency and secondly, due to the high wax viscosity, filters with a large pore size are used to avoid plugging. These inevitably cause a significant catalyst loss (Fletcher, 1986; Oberteuffer, 1974). By taking these problems into consideration, new techniques such as the use of supercritical fluids are thought to be the right solution for catalyst/wax separation in SBC F-T reactors (Biales et al., 1999; Joyce, 1998; White et al., 1996).

Liquid–liquid and solid–liquid extractions using supercritical fluids have found wide applications in separation during the last few years (Hartono et al., 1999, Martineli et al., 1991). In recent years, this technique has been used in the chemical, petrochemical, pharmaceutical and food industries. Supercritical fluids (SCF) with their unique properties such as high diffusivity, low viscosity and low surface tension are highly suitable for extraction. Mixing of SCF and hydrocarbon wax causes a decrease in the mixture viscosity and settling time of the catalyst fine particles. SCF can be also fractionated and separated easily from SCF-wax mixture by changing the pressure and temperature.

Figure 1 shows the location of the catalyst separation system relative to the FT reactor. As it is shown in Figure 1, the catalyst and wax products mixture (the slurry) leave the reactor to separate catalyst from the wax. The slurry is sent to the catalyst separation section to contact with the supercritical solvent and produce concentrated catalyst stream and catalyst-free stream. The concentrated catalyst stream, which predominantly contains the catalyst, is recycled to the FT reactor and the catalyst-free stream comprising of the solvent and the wax, with a catalyst concentration of 1–5 ppm, is sent to the solvent recovery section to separate the solvent from the wax. The recovered solvent is recycled to the catalyst separation section and the wax will be subjected to operations such as hydrocracking, hydrotreating and several fractionations in order to produce FT liquid products, in the up-grading unit. The make up solvent for the catalyst separation section could be supplied from the up-grading unit.

Catalyst/wax separation using SCF depends on several factors, i.e., temperature, pressure, SCF/wax ratio, catalyst particles size and settling time. In order to make the process more practicable for commercial scale, the pressure and temperature of the selected solvent at its supercritical state (SCF) must be similar to those of the FT reactor, which operate at about 240–270°C and 3000–4000 kPa pressure. In this work, n-hexane was used as the solvent for catalyst/wax separation since its critical temperature is 234.7°C and its critical pressure is 3030 kPa. N-hexane viscosity at the FT reactor conditions is about 10^{-5}–10^{-4} Pa · s while the wax viscosity at this condition is between 10^{-3} and 4×10^{-2} Pa · s (according to the product distribution in the reactor) (Patel et al., 1990). Therefore, the viscosity of the solvent–wax mixture is dramatically decreased and catalyst–wax separation may be done easily in a settler by using supercritical n-hexane solvent.

Biales et al. (1999) have analysed the technical feasibility of a near-critical fluid extraction process for the recovery of heavy normal paraffins from a F-T slurry reactor. Process simulations and phase behavior studies were carried out using the ASPEN PLUS program over a wide range of operating conditions such as temperature, pressure, solvent/non-solvent ratios, and the number of recovery units. This study has not been intended to produce an optimized process design. In fact, one finding of this research is that the existing database of physical properties and vapour/liquid equilibrium models is not sufficient to support an optimum, or even reliable process design. Rather, the intent of these simulations was to assess the basic technical feasibility of the near-critical fluid extraction process concept and to define the technical issues that require additional study.
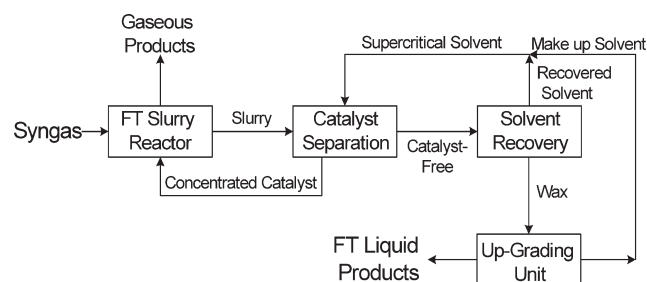

Figure 1. Location of the catalyst separation system relative to the FT reactor.