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FT catalyst performance: comparison between pilot-scale SBCR and CSTR systems

J.K. Neathery*, B.H. Davis

Center for Applied Energy Research, University of Kentucky, 2540 Research Park Drive, Lexington, KY 40511-8410, USA

Abstract

A considerable interest has been expressed in using slurry bubble column reactors (SBCRs) to carry out FT synthesis, particularly for the conversion of stranded natural gas into liquids. Historically, wall effects in small-scale SBCR reactors (diameters less than 30 cm) have presented many challenges with regard to interpretation of kinetic/conversion data for process scale-up. In this paper, we describe a novel 5 cm diameter SBCR system that incorporates a natural slurry recirculation loop that minimizes wall effects and promotes plug-flow behavior in the liquid phase. Conversion performance, activity decline, and attrition of a precipitated Fe/K Fischer–Tropsch synthesis (FTS) catalyst in the SBCR is compared to that of a continuous stirred tank reactor (CSTR) run using the same catalyst and operating conditions.

1. Introduction

The prototype integrated process unit (PIPU) is a pilot plant system built in the early 1980s at the University of Kentucky for studying a multitude of synthetic fuel/chemical processes. Recently, a direct coal liquefaction reactor within the PIPU plant was reconfigured as a slurry bubble column reactor (SBCR) for Fischer–Tropsch synthesis (FTS) studies (see Fig. 1).

Early attempts to operate the pilot-scale reactor in a FT mode were successful in that a clear wax product could be obtained. However, the initial activity observed in the bubble column was about 10–15% less than that of comparable continuous stirred tank reactor (CSTR) runs. It was hypothesized that catalyst was depleted due to the hold-up in the wax/catalyst separation system.

Consequently, the CAER SBCR plant was overhauled and redesigned to incorporate automatic slurry level control and wax filtration systems. These design changes allowed for a more constant inventory of the catalyst to be maintained in the reactor while reducing slurry hold-up in the catalyst/wax separation system. In addition, the wax filtration system was rearranged to accept a variety of filter elements.

In the following discussion, we will detail the results and operational experiences of a shakedown run with the enhanced SBCR system. Objectives of the shakedown were to: compare the performance of a precipitated Fe/K Fischer–Tropsch synthesis catalyst in the enhanced SBCR and a continuous stirred tank reactor; and determine change of the catalyst distribution within the reactor system due to particle attrition effects.

2. Experimental

All FTS runs were conducted in either CSTR or SBCR systems. A precipitated iron catalyst having atomic composition of 100 Fe/4.4 Si/1 K was used

* Corresponding author. Tel.: +1-859-257-0259.
E-mail address: neathery@caer.uky.edu (J.K. Neathery).

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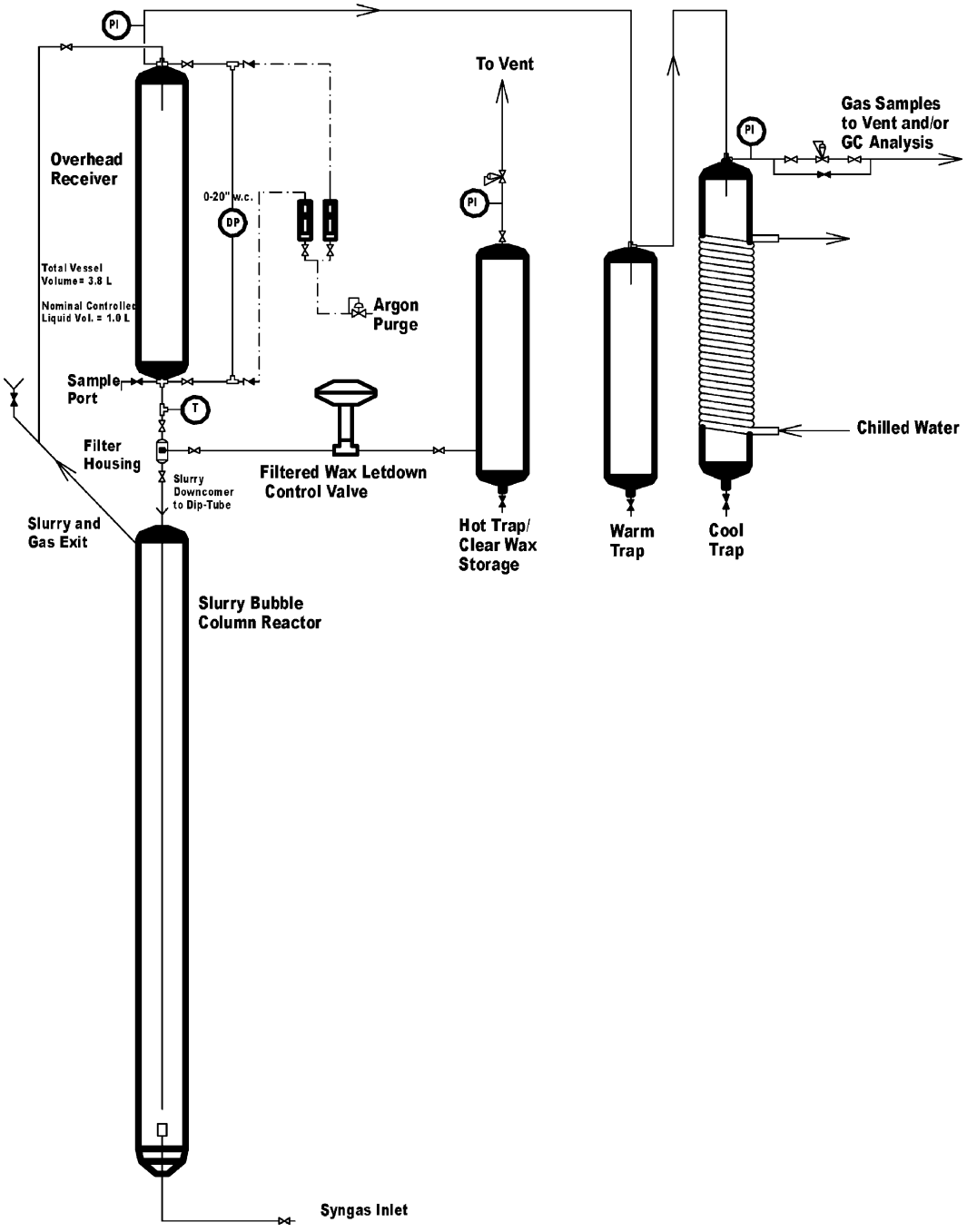

Fig. 1. Schematic of the SBCR pilot-scale apparatus.

for this series of experiments. All reactor runs were performed at a space velocity of 5 slpm/g Fe at 270 °C and 1.21 MPa.

2.1. CSTR apparatus

The 1 l CSTR used in this study has been described in detail in the literature [1,2]. The following is a brief description of the reactor system.

The synthesis gas was delivered to the catalyst slurry via a sparger tube located below an impeller blade turning at 750 rpm. The reactor effluent exited the reactor and passed sequentially through two traps maintained at 333 and 273 K.

2.2. SBCR apparatus

A schematic of the SBCR apparatus is shown in Fig. 1. In the current configuration, the bubble column has a 5.08 cm diameter and a 2 m height with an effective reactor volume of 3.7 l. The synthesis gas was passed continuously through the reactor and distributed by a sparger near the bottom of the reactor vessel. The product gas and slurry exit the top of the reactor and pass through an overhead receiver vessel where the slurry was disengaged from the gas phase. Vapor products and unreacted syngas exit the overhead vessel, enter a warm trap (333 K) followed by a cold trap (273 K).

A dip tube was added to the reactor vessel so that the FT catalyst slurry could be recycled internally via a natural convection loop. The unreacted syngas, FT products, and slurry exited into a side port near the top of the reactor vessel and entered a riser tube. The dip tube provided a downward flow path for the slurry without interfering with the upward flow of the turbulent syngas slurry mixture. Thus, to some degree, back mixing of the slurry phase and wall effects in the narrow reactor [3] tube were minimized.

An automatic level controller was added to the overhead slurry/gas separation tank. This insured a constant inventory of catalyst particles was being maintained in the reactor vessel if the superficial gas velocity within the column was constant. Slurry volume within the receiver was controlled to be no more than 1.3 l by removing wax from the reactor system via the level control valve. The unfiltered slurry flowed back to the reactor via a natural convection loop through a dip tube exiting near the bottom of a reactor.

Samples of the unfiltered slurry were taken from the bottom of the reactor vessel and the overhead receiver tank on a daily basis. Wax products were Soxhlet extracted according to the method of McCartney et al. [4]. The particle size distributions of the extracted catalyst particles were quantified using a light scattering technique by a Cilas 1064 liquid/particle analyzer.

3. Results and discussion

3.1. SBCR shakedown/conversion comparisons between CSTR and SBCR runs

One of the objectives of the shakedown run was to compare the performance of the enhanced SBCR with that of a CSTR configuration.

The CO gas conversions versus time-on-stream (TOS) for the SBCR and CSTR systems are displayed in Fig. 2. The CO conversion for the enhanced SBCR with level control reached a maximum of 78% after 72 h time-on-stream. After this catalyst initiation period, the gas conversion started to steadily decline to about 72% after 192 h TOS.

Slurry back mixing in the SBCR is significantly reduced by the addition of the down-comer/dip-tube flow path; consequently, the gas and liquid phases likely exhibited more “plug-flow” behavior. Thus, for a given space velocity, the enhanced SBCR should yield a higher conversion than that of a CSTR.

3.2. SBCR catalyst attrition

Achieving an efficient wax product separation from the catalyst is one of the most challenging technical problems associated with slurry-phase FT. The breakdown of the catalyst particles and the production of heavy wax using high alpha catalysts can further exasperate the filtration problem. Thus, designing a physically robust catalyst without compromising activity is an important factor for a stable and economical FT process. However, small-scale catalyst attrition tests may not be adequate in simulating the environment within a bubble column reactor. In previous studies [5,6] by Jothimurgean et al. and Zhao et al. an air-jet attrition tester as outlined in the ASTM-D-5757-95

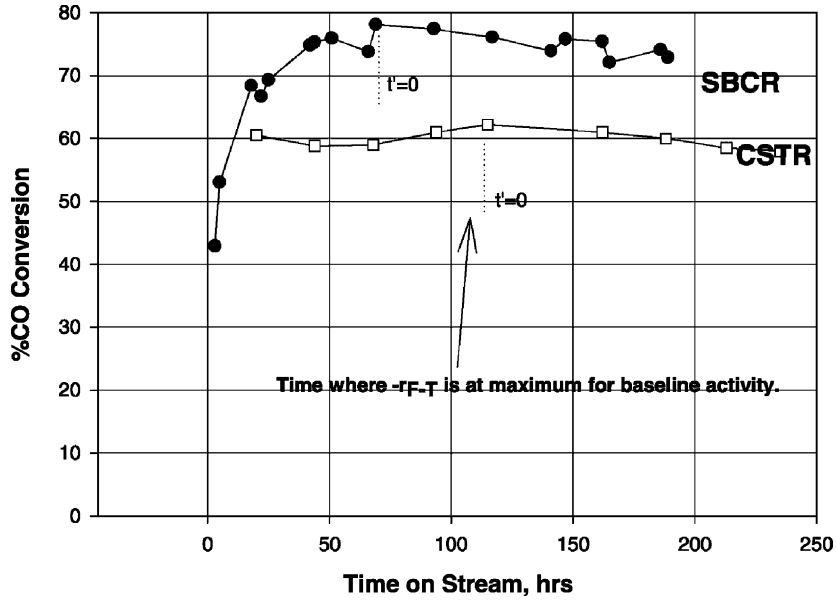

Fig. 2. CO conversion comparison between reactor types.

test method was used to compare the relative breakdown resistance of catalysts. This method is useful in comparing the relative strength between catalyst candidates; however, it does not yield information as to the rate of attrition during synthesis. Attrition data in CSTR systems are compromised by the extreme impact and shear forces from the impeller blade on catalyst particles. In contrast, the SBCR unit does not

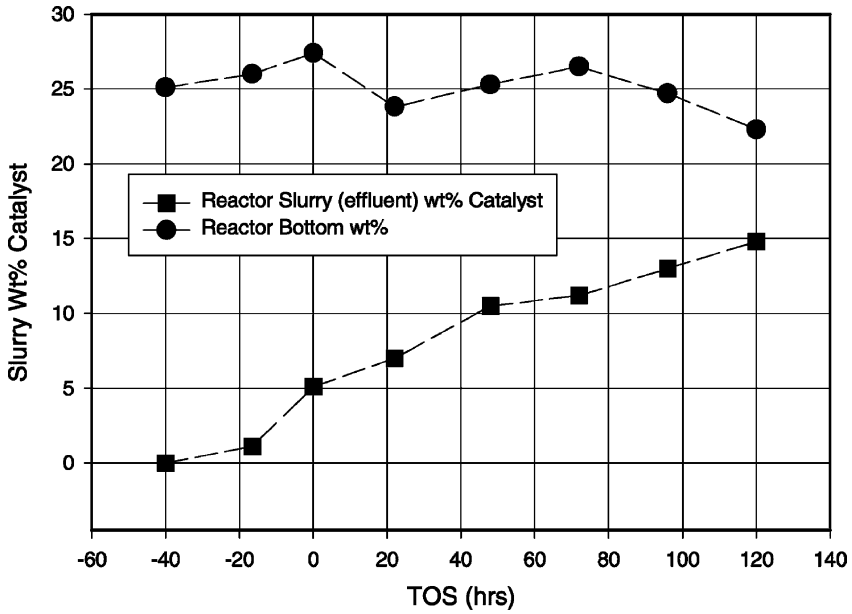

Fig. 3. Catalyst solids distribution (reactor and reactor effluent) vs. time-on-stream.

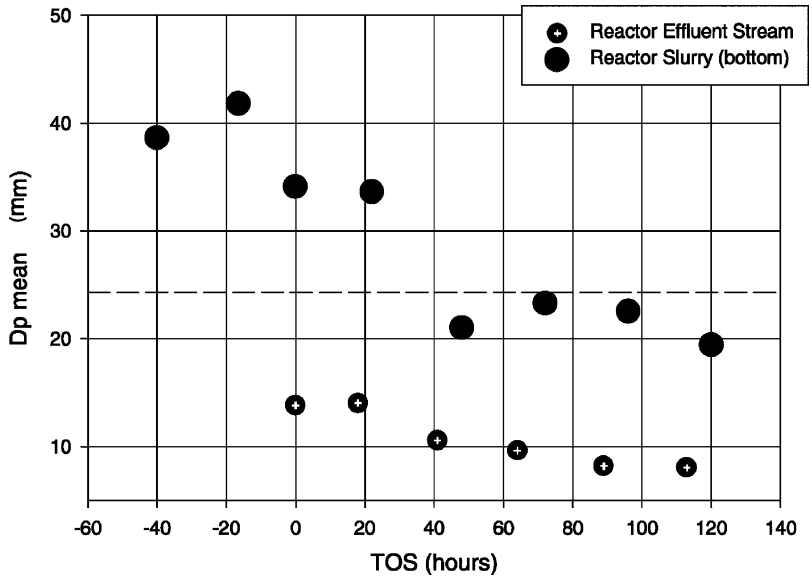

Fig. 4. Mean particle size in the catalyst slurry vs. time-on-stream (reactor and reactor effluent).

utilize any mechanical pumping devices that could alter the size distribution of the catalyst. Consequently, SBCR particle attrition will depend mainly on chemical changes within particles and perhaps some particle/wall or particle/particle mechanical abrasion.

Fig. 3 shows the changing distribution of catalyst concentration with TOS. During the start of activation, only a small fraction of catalyst fines were detected in the reactor effluent stream. However, near the bottom of the reactor the concentration of catalyst particles was greater than 25 wt.%. This indicated the liquid recirculation rate was not sufficient enough to fully entrain the largest (>23 mm) catalyst particles. As the activation process was completed (TOS = 0), the slurry effluent contained about 5 wt.% of catalyst fines. Thereafter, the solids concentration of the reactor effluent increased linearly with TOS.

The mean particle size of the reactor bottom and effluent streams are shown in Fig. 4. The dotted horizontal line represents the initial mean particle size of the raw catalyst. Physical classification of the catalyst particles was apparent as evidenced by the mean particle size of slurry in the bottom being greater than that of the raw catalyst. As the synthesis progressed, the mean particle size in the reactor dropped below the baseline (23 mm) after only 40 h TOS. In summary, the data shown in Figs. 3 and 4 indicate that a significant portion of the catalyst exited the reactor system due to particle attrition after 40 h of TOS. Considering the slurry hold-up outside the reactor was maintained at less than 1 l, the percentage of catalyst lost after 40 h TOS was less than 20 wt.%. Therefore, this lost catalyst must be considered when calculating the space velocity.

4. Conclusions

Tight control of catalyst distribution within SBCRs must be maintained in order to quantify activity decline, especially for small pilot plant systems. Transient problems with previous SBCR experiments were caused by a maldistribution of catalyst between the reactor and slurry filtration system. The level indication/control system installed in an enhanced SBCR was robust and effective in maintaining a steady inventory of catalyst slurry in contact with the gas phase. Measured deactivation rates in the enhanced SBCR system were comparable to that of CSTR experiments under similar conditions.

Attrition tests in the SBCR system indicated that the most of the catalyst breakdown occurred during catalyst activation and the initial synthesis stage; however, further research will be required to investigate the

possibility of particle size classification/segregation at the sampling points. After activation, the catalyst particle mean diameter decreased in an exponential decay fashion.

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