Fischer-Tropsch Run III at the LaPorte Alternative Fuels Development Unit

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ABSTRACT

During October 1996, operations were carried out at DOE's Alternative Fuels Development Unit (AFDU) in LaPorte, Texas, to evaluate further improvements to the slurry process for Fischer-Tropsch synthesis. Earlier work at LaPorte in 1992 and 1994, had established proof-of-concept status for the slurry phase process. This third campaign aimed at aggressively extending the productivity and operability of the slurry reactor using an improved catalyst.

Catalyst activation proceeded well and stable operation with uniform temperatures and excellent heat transfer was achieved after the introduction of synthesis gas. The specially designed gas introduction device appeared to work well, and the mixing and fluid dynamics of the bubble column were satisfactory. Unfortunately, the catalyst-wax separation unit external to the reactor did not permit operations to continue for more than a week due to filtration problems. Catalyst productivity was stable around the 50 g/hr of hydrocarbons per litre of slurry. It did attain 200 g/hr per litre later in the run although only for short periods as conditions were somewhat transient due to the worsening separation problem. Methane yields were higher than expected.

Improvements in the interplay between catalyst, slurry pump and filters are all in hand, and we expect to reconvene and complete the run early 1998.

INTRODUCTION

During October 1996, operations were carried out at DOE's Alternative Fuels Development Unit (AFDU) in LaPorte, Texas, to evaluate further improvements to the slurry process for Fischer-Tropsch synthesis. Earlier work at LaPorte in 1992 and 1994, had established proof-of-concept status for the slurry phase process. The first campaign in 1992 was a 19-day run demonstration of the technology at 1 T/D product scale and addressed scale-up issues such as catalyst activation, catalyst performance and hydrodynamics (1). A very high level of reactor productivity (more than five times the F-T I productivity) was demonstrated for slurry phase Fischer-Tropsch synthesis in 1994 (2). Reactor productivity of 136 grams of HC/hr - litre of slurry volume was achieved, which was within the target of 120-150. The productivity was constrained by mass transfer limitations, due to slurry thickening. With an improved catalyst, if carbon formation can be avoided, there appeared to be significant room for further improvements. The third campaign, in 1996, aimed at aggressively extending the operability of the slurry reactor using an improved catalyst.

OBJECTIVES

The principal objective of this run was to conduct Fischer-Tropsch synthesis in a large diameter bubble column and demonstrate: (1) Sustainable high productivity - a space time yield of 150 grams hydrocarbon per hour per litre of reactor volume; (2) Activity and selectivity of Shell's proprietary catalyst; (3) Catalyst-wax separation by external cross-flow filtration; (4) In-situ catalyst activation. The run would also allow the participants to study other issues such as large scale fluid dynamics, erosion, catalyst stability and catalyst attrition.

ENGINEERING AND MODIFICATIONS

A new high pressure (1000 psig) filtration system was installed in order to conduct filtration close to reactor pressure and avoid catalyst attrition at pressure let down. The filtration system included cross-flow filters, a catalyst-wax slurry circulation pump, a slurry cooler and a slurry degasser. The Fischer-Tropsch train was connected to the recycle compressor to allow gas recycle. The Fischer-Tropsch reactor was modified to accommodate Shell's proprietary sparger and optical fibre probe. Additionally, radial thermocouples and differential pressure transmitters were added to the reactor.

RESULTS AND DISCUSSION

The run plan included a process variable scan at nine different conditions. Key parameters to be studied were feed compositions, recycle ratio and conversion levels (see Table 1). This matrix of process variables spanned through a large range and approached the plant limits of recycle compression and heat removal capacity. In addition, a high catalyst loading of about 40 wt% would push slurry F-T technology to its limit. Due to the earlier-than-anticipated termination of operations, the significant results and observations made are presented below in the form of a short summary. Progress made in tests following the run is also summarised. Operations had to be terminated after seven days on-stream as the external filter membranes (sintered metal) became irreversibly plugged with catalyst fines. However, significant advances to slurry-phase F-T processing were achieved in this short period, as described below:

Catalyst Activation

In-situ catalyst activation was well controlled using gas recycle. The water concentration level was maintained below the maximum allowed at all times. Increasing methane production led to a decision to terminate activation which may have been premature as, later in the run, there was evidence of further activation. When temperatures were raised to go to the high productivity condition, a significant amount of CO_2 was detected in the reactor effluent, suggesting reduction of the catalyst by CO. The two water measurement techniques used during activation, Panametric measurements and adsorption with P_2O_5, did not agree. The Panametric indicated 90% completion while the P_2O_5 suggested 40% completion (see Figure 1). This confirms that the P_2O_5 adsorption is a better water measurement technique.

Catalyst Performance

Mass balances were performed for two data periods during run condition AF-R15.1. A hydrocarbon productivity of about 45 g/hr of HC per litre of slurry was achieved at a reactor temperature of 227°C. However, it appeared that the alpha of the catalyst was lower than expected (high methane, low wax). When conditions were changed to high productivity (run AF-R15.2), significantly higher conversions and heat of reaction were observed. Although accurate estimates were difficult, as conditions were transient during this period, productivities in the range 100 to 200 g/hr of HC per litre of slurry were achieved. Also, heat of reaction consistent with the above productivities (1.8 to 3.1 MMBtu/hr) was observed during the period.

Reactor Performance

The reactor showed excellent temperature uniformity and even gas and catalyst distribution. Axially, the temperatures ranged from 225 to 228°C during the operations at the start-up condition (Run # AF-R15.1). The radial variation was only 0.4°C. Nuclear density readings taken in the two phase slurry during a dynamic gas disengagement test indicated that the catalyst was uniformly distributed axially. The specially designed gas introduction device appeared to work well over all conditions. Also, no erosion was evident in the reactor as indicated by erosion test pieces.

Gas Hold-up and Catalyst Concentration Estimates

The average gas hold-up calculated from nuclear density gauge (NDG) readings compared well with that calculated from differential pressure (DP) readings. The gas hold-up was in the range of 34 to 37 vol% during run AF-R15.1. Gas hold-up was also measured using the optical fibre probe during catalyst drying and early activation. Gas hold-up indicated by the probe was generally lower than that estimated by the other methods. Catalyst concentrations in the reactor were estimated in the 37 to 41 wt% range based on both NDG and DP readings. Slurry and wax density measurements in the filter loop agreed very well with these estimates.

Heat Transfer and Heat Balance in the Reactor

Heat transfer coefficients were calculated based on the data obtained for the run AF-R15.1. The measured overall coefficient (U) was estimated to be 92.3 Btu/hr-ft2-°F as compared to the prediction of 89.3. Measured slurry-side coefficient was estimated at 285 Btu/hr-ft2-°F compared with the prediction of 258. The heat transfer in the reactor was slightly better than expected. Heat loss from the reactor was estimated at about 35,000 Btu/hr from data obtained during drying. Heat balance during the run AF-R15.1 was in the 96 to 97% range based on the heat of reaction.

Dynamic Gas Disengagement and Reactor Temperature Control

Differential pressure data were acquired on a proprietary fast data logger during the dynamic gas disengagement test conducted at the end of the run. The data are being analysed to estimate bubble size distribution. Measurements were also made to evaluate the response time of the revised reactor temperature control system. With the re-alignment of the utility oil system carried out prior to the run,

the control system was judged to be adequate for the high productivity condition achieved during run AF-R15.2.

Filtration Loop

The filtration loop included a degasser to protect the slurry pump from gas and eliminate further any reaction in the loop. The degasser functioned as designed. It effectively removed gas from the slurry going to the slurry pump when proper level in the reactor was maintained. The slurry cooler provided sufficient cooling; there was no evidence of any reaction in the filter loop. The slurry pump provided steady head and flow in the filtration loop. No erosion was found in the loop, however, inspection of the pump internals showed evidence of erosion.

Cross-Flow Filters

After initial start-up challenges, the filters operated normally at the low productivity condition. However, after two days on stream, the longitudinal as well as the membrane differential pressures started rising. After five days on stream, under conditions of high productivity, there was a large increase in the pressure drop across the filters and the filters were not able to keep up with wax production rate. Backflushing the system seemed to increase the pressure drop further. The filters were taken apart and backflushed with steam and nitrogen resulting in removal of some solids. However, a subsequent clean oil flux test revealed a significantly higher than expected pressure drop across the membranes. It seems that while we were successful in removing the filter cake, the membrane remained blocked with particles. Particle size analysis of spent slurry samples showed a bi-modal distribution indicating unexpected level of particle breakdown.

Post-run Testing

Extensive testing was started at Shell Research & Technology Centre, Amsterdam (SRTCA) to identify and solve the catalyst-wax separation issues. Successful slurry pump testing has been completed. An improved proprietary catalyst was activated in situ and showed greater strength than the one used in the F-T III run. Initially in the test, slurry circulation was started at high pump velocity to create severe starting conditions for particle attrition and to enable effective testing of the pump for erosion. Reliable and steady operation was obtained with negligible sign of pump erosion. For that purpose, a more erosion resistant material - manganese alloy - was used for the pump internals. At the same time, the observed catalyst attrition also proved to be limited.

For filtration a new type of woven metal filter elements were tested. These elements are most promising as, in contrast to the filters used in F-T III, the openings are uniform and the smallest opening is in the first layer at the process side, minimising the possibility of retaining fines in the filter. It was successfully shown that these filters have an operating window, where sustainable filtration is possible. Mechanical strength (number of woven layers) versus the resulting cross membrane filtration pressure is still a development consideration. The required longitudinal velocity (and consequently the resulting longitudinal DP) is at the high side for the LaPorte test facility. A new series of tests is now underway to establish the best operation scheme for the LaPorte run. One of the variables is the slurry

concentration (20 - 30 vol %), while some alteration of the filter pore size may also be considered in an alternative scenario. Anticipating success in the laboratory tests, a continuing run is planned for spring 98 at LaPorte.

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Table 1 - Fischer-Tropsch III Demonstration Run Plan

Shell's Proprietary Catalyst Charge: 1043 lbs,
Shell's SX-70 Wax: 1489 lbs
Pressure Range: 520 - 710 psig
Temperature Range: 210 - 250°C

Run No.	Description	H2/CO in Reactor Feed	Sup. Gas Vel (in), ft/sec	Plant CO Conv. mole%	Reactor Prod., g HC/lit-hr	Wax Production gpd	Days on-stream
AF-A11	Activation		0.31				1
AF-R15.1	Start-up	1.18	0.41	80	75	664	2.5
AF-R15.2	Baseline	1.44	0.34	80	150	1327	2.5
AF-R15.3 to AF-R15.9	Process Variables	0.65 to 2.07	0.32 to 0.85	80 to 90	150	1327	17.5
AF-R15.10	Baseline Repeat	1.44	0.34	80	150	1327	2.5
AF-R15.11 to AF-R15.12	Tracer Studies	1.19 to 1.44	0.34 to 0.73	80	150	1327	3
AF-R15.13 to AF-R15.14	Dynamic Gas Disengagement Tests	1.19 to 1.44	0.34 to 0.73	80	150	1327	2
AF-R15.15	Filter Tests w/o Syngas						3

Figure 1: Fischer-Tropsch III Activation Results