VII. Process Simulation Studies of UCC Fischer-Tropsch Catalysts in an ARGE-Type Fixed Bed, Tubular Reactor System

Introduction

It has been shown that, during the latter part of this contract, Union Carbide developed several cobalt based catalysts which demonstrated high C5+ yields and good catalyst stability. In order to evaluate these catalysts, the Department of Energy requested Union Carbide to provide adequate process design data so that a private contactor could perform a techno-economic evaluation of the Union Carbide catalysts.

Methodology Used to Obtain Process Design Data

Towards this end, Union Carbide correlated the test data already available on these catalysts to obtain expressions for (1) the syngas conversion rate, (2) the methane make, as weight percent of total hydrocarbon produced, and (3) the C2+ hydrocarbon distribution. This work has been reported in detail in the Fifteenth Quarterly Report.

Figure 77 shows how these three expressions were then used in a computer program which simulated an ARGE-type tubular reactor system operating at 270 C and 300 psig, at an overall 85 percent syngas conversion, and with a 2.3:1 recycle ratio for the non-condensed <C5 gases in the process configuration presented in Figure 78.

The output from this program was presented in

the form of a series of graphs, each depicting the space velocities and the H2:CO feed ratios required to obtain a fixed methane yield with Union Carbide catalysts having varying specific activities (their syngas consumption rate relative to the Co/UCC-101 catalyst measured during Run No. 10011-14 and reported in the Second Annual Report) and H2/CO usage ratios.

Design Curves for Private Contractor

Figures 79 and 80 are the two primary design curves generated for the Private Contractor. They show the feed H2:CO ratio/the catalyst specific activity/the usage ratio/and the feed space velocity relationships for an ARGE type reactor operating at 270 C and 300 psig, using a 2.3:1 recycle ratio, and having a packed catalyst density of 0.6 gm./cc to obtain an overall 85 % syngas conversion while producing hydrocarbon product containing either 12.3 weight percent methane (Figure 79) or 7.8 weight percent methane (Figure 80).

The use of these two figures is straight-forward. A single point is located for a catalyst having a definite specific activity and a definite usage ratio by using the right hand usage ordinate with the specific activity curves. The feed space velocity and the feed H2:CO ratio corresponding to that point (i.e., corresponding to that catalyst) are then read from the bottom ordinate and the left hand ordinate, respectively.

Comparison of the two figures shows that for a given catalyst (having a defined specific activity and usage

ratio) both the H2:CO feed ratio and the feed space velocity will be higher for the 12.3 weight % methane case than for the 7.8 % case. This is because the higher H2:CO feed ratio used to obtain the higher methane make (as dictated by the equation for the methane make) will cause the syngas conversion to increase (as dictated by the equation for the syngas conversion rate), and thus permit a higher space velocity to be used for the same overall 85 % syngas conversion.

Thus it can be seen that running the reactor with a high H2:CO ratio will ensure a desirably high space velocity, but will result in an undesirably high methane production rate.

The Independant Contractor decided to cost two cases. Case 1 would use a Union Carbide catalyst having a 1.6:1 usage ratio and a 2.68 specific activity, values which were considered readily achievable at the time. This catalyst would operate with a H2:CO feed ratio that would allow a high space velocity at the expense of a high (12.3 weight percent) methane make. Case 2 would use a Union Carbide catalyst having a 2.0:1 usage ratio (the increase in costs associated with the lower water gas shift activity was expected to be more than outweighed by the reduction of costs associated with the increased space velocity resulting from this higher usage ratio) and a 3.64 specific activity, values that were considered achievable over the course of an extended research effort. This higher

activity would operate at a leaner H2:CO feed ratio which would allow a low (7.8 weight percent) methane make at the expense of a lower space velocity (lower than would be required with a higher methane make). Case 2 would, in effect, use some of the anticipated increase in specific activity to reduce the methane make below that of Case 1.

When the Case 1 catalyst (having a usage ratio of 1.6:1 and a specific activity of 2.68) is located on Figure 79, the bottom and left hand ordinates indicate that the feed space velocity must be 300 vol./vol./hr. with a H2:CO feed ratio of 1.21:1. Similarly, when the Case 2 catalyst is located (having a usage ratio of 2.0:1 and a specific activity of 3.64) is located on Figure 79, the bottom and left hand coordinates indicate that the feed space velocity must be 360 vol./vol./hr. with a feed H2:CO ratio of 1.39:1.

Table 32 lists the compositions of the off-gas and liquid streams calculated by the FIXBD1 program for the two cases. Table 33 lists the characterization of the various components in the streams, for both cases.

It should be mentioned that the 0.11:1 and 0.17:1 H2:CO ratios in the off-gases of the cases shown in Table 32 are the ratios seen by the last section of the catalyst bed. These are far lower than the 0.68:1 and 0.39:1 ratios used in the correlations for the syngas conversion rate, methane make, and alpha. Consequently, the use of these

correlations in such extrapolations, particularly the one predicting the methane make, is certain to lead to significant errors.

It was assumed that such errors would be corrected in future correlation work for new, more promising F-T catalysts expected to be developed under a follow-up contract.