DOE/PC/92108--T13

FINAL REPORT

TECHNOLOGY DEVELOPMENT FOR COBALT F-T CATALYSTS

Contract No. DE-AC22-92PC92108

QUARTERLY TECHNICAL PROGRESS REPORT NO. 11

Covering the Period April 1, 1995 to June 30, 1995

Prepared for:
U.S. Department of Energy
Pittsburgh Energy Technology Center
PETC Project Manager: Richard E. Tischer
P. O. Box 10940
Pittsburgh, PA 15236-0940

Submitted by:
Principal Investigator: Alan H. Singleton
Energy International Corporation
135 William Pitt Way
Pittsburgh, PA 15238

October 25, 1995

EXECUTIVE SUMMARY

Preliminary results on the effect of reaction temperature on the performance of Co catalysts during F-T synthesis obtained during the last quarter confirmed that Co catalysts were very sensitive to temperature and deactivated significantly at temperatures above 240°C both in the fixed bed and the slurry bubble column reactors. Following this preliminary investigation, a series of tests were carried out during this period in order to elucidate the nature of this deactivation process as well as determine possible means of preventing it. In order to elucidate the nature of this deactivation process, the catalysts which had undergone significant deactivation after high temperature (280°C) reaction in either the fixed bed reactor or the slurry bubble column reactor were regenerated and retested in the fixed bed reactor. In both cases the catalysts recovered completely their initial activity. In addition, reactions at very high H_2/CO ratios and high temperatures showed very little deactivation, suggesting that the deactivation of the Co catalysts during F-T synthesis at high temperatures was mainly due carbon formation via the Boudouard reaction. Due to the unreactive nature of this carbon, it could only be removed by calcination.

A second series of experiments was carried out to investigate the effect of certain promoters (Zr, La, Cr, and Re) as well as the effect of another support such as silica on the deactivation characteristics of Co catalysts during F-T synthesis at high temperature. The choice of these promoters was based on previous results from the slurry bubble column reactor, which indicated that catalysts with these promoters had undergone relatively lower deactivation under standard F-T synthesis runs. In addition, a series of new catalysts were formulated with a choice of promoters based on their intrinsic ability to enhance the hydrogenation reactions while slowing down the Boudouard reaction under the conditions used in F-T synthesis. The results suggest that the

deactivation process and rate for most of these catalysts are similar to those of the alumina-supported catalysts tested previously (Co.005 and Co.053), and that none of the promoters helps to slow down the rate of carbon formation at high temperatures above 240°C.. The only exception may be the use of Pd as promoter, although the amount added remains to be optimized since high concentrations result in low activity and high selectivity for methane. Further investigations of the effect of some of these promoters on preventing the deactivation of Co catalysts are still being carried out.

Several slurry bubble column reactor runs during this reporting period have also focussed on the effect of certain promoters on the general performance of the Co catalysts as well as their resistance to deactivation at high temperature. The results indicate that only the addition of Cr or Fe to cobalt catalysts can prevent their fast deactivation at high temperature. However, both promoters result in low overall activity catalysts with high selectivities for methane.

After the satisfactory performance tests carried out in the last quarter with the three 1 kg catalyst batches prepared by Calsicat, the 1000 hour aging test was carried out with one of these catalysts. The test was carried out under the standard conditions used in most of the previous runs, i.e., 450 psi and 240°C. As a result of this high temperature, the catalyst experienced excessive deactivation with the conversion dropping steadily over the first 600 hours from ca. 28% before leveling off for the remainder of the run at ca. 6.5%. A second shorter aging run (ca. 500 h) was carried out at lower temperature (212°C). Very little deactivation was observed under these conditions, confirming again the temperature sensitive nature of Co F-T catalysts.

TABLE OF CONTENT

LIST of TABLES