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CATALYST AND REACTOR DEVELOPMENT FOR A LIQUID PHASE FISCHER-TROPSCH PROCESS

QUARTERLY TECHNICAL PROGRESS REPORT

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PAUL N. DYER

RONALD PIERANTOZZI

BARRY W. BRIAN

JEFFREY V. BAUER

AIR PRODUCTS AND CHEMICALS, INC.

ALLENTOWN, PA 18105

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ABSTRACT

This report describes work carried out in the seventh quarter of a three year contract, begun October 1980, between Air Products and Chemicals, Inc. and the DOE: "Catalyst and Reactor Development for a Liquid Phase Fischer-Tropsch Process." Two major tasks are current in the program: (2) Slurry Catalyst Development, and (3) Slurry Reactor Design Studies.

In Task 2, seven supported conventional catalysts, prepared with different metal precursors, concentrations, calcination procedures and supports, were tested in the gas phase to determine the effect of these parameters on activity and selectivity.

A second slurry test of the baseline catalyst, sintered Fe_2O_3, utilized CO rich syngas to determine reactor mass transfer limitations. The product from 1.4:1 CO/H_2 approximated a straight line Schulz-Flory distribution, but higher CO/H_2 ratios gave increased high molecular weight material. Methane yields were low and high water gas shift activity gave a close match between syngas feed and usage ratios. At T >250°C some mass transfer effects were observed, and are being incorporated into a reactor model.

Six additional slurry tests used supported molecular cluster catalysts chosen from the Subtask 2d program. Initially in this series, slurry phase activities were low. A slurry test of one supported cluster showed marked deviations from the standard Schulz-Flory distribution in the C_{10}-C_{29} region, but at very low conversion. Thermal cracking of the slurry oil occurred at T >325°C however, contaminating the product.

Subsequent supported cluster catalyst tests led to a method of obtaining high slurry phase activities equal to the gas phase. A slurry test of another cluster catalyst utilizing this method gave high activity, but did not reproduce the product selectivity for C_{10}-C_{18} observed in its previous gas phase test. At higher pressure, 750 psig, and 280°C, however, methane yields decreased, becoming independent of the CO/H_2 ratio, and the Schulz-Flory product distribution became nonlinear with a definite cutoff at ~C_{28}.

Two supported cluster catalysts were prepared and seven were screened in the gas phase. One produced a high selectivity for oxygenates, e.g., >80% yields of CH_3OH and CH_3OCH_3 from 1:1 CO/H_2 at 280°C.

In Task 3, 5" column measurements concentrated on the water/0-5 μm silica and water/90-115 μm silica systems. Non-uniform gas holdup and solids dispersion profiles, dependent on solids loading and gas velocity, were observed in the larger silica system.

Mass transfer coefficients were found to decrease with increasing solid loading and with decreasing particle size. This may be due to variations in the gas/liquid interfacial area caused by solid dependent slurry viscosity and bubble size effects. Liquid dispersion coefficients were measured at several column positions. A higher value was determined at the distributor plate than elsewhere in the column, but this may be partially due to a feature of the model used to interpret the data.

Construction of the 12" column was completed.

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