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NOVEL APPROACHES TO THE PRODUCTION OF HIGHER ALCOHOLS FROM SYNTHESIS GAS

Quarterly Technical Progress Report No. 15

For The Period April 1, 1994 to June 30, 1994

Contractor

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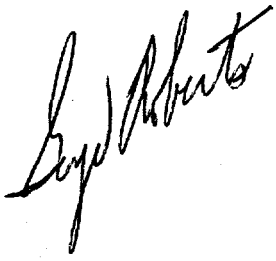

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CONTRACT OBJECTIVES

Task 1. Program Management.

Task 2. Liquid-Phase, Higher Alcohol Process with Recycle of Lower Alcohols.

Task 3. Novel Catalysts for Synthesis of Higher Alcohols. (Complete)

Task 4. Synthesis of Higher Alcohols via Acid-Base Catalysis.

Task 5. Technology Evaluation. (Complete)

SUMMARY

• Under Task 2:

Four sets of methanol synthesis runs were conducted with BASF S3-86 "low pressure", Cu/ZnO methanol synthesis catalyst. The objectives were: 1) to reproduce the data obtained with this catalyst by researchers at Air Products and Chemicals, Inc., and; (2) to determine whether the previously-observed problem of catalyst poisoning by metal carbonyls had been eliminated.

The catalyst poisoning problem appears too be resolved, although there is a need for additional data on the capacity of activated carbon for iron and nickel carbonyl adsorption. However, under apparently comparable conditions, the activity of the BASF S3-86 catalyst in the present experiments was lower than the activity measured at Air Products. The difference tentatively has been attributed to differences in the catalyst activation procedure.

Problems with reliability of the experimental equipment were experienced; these problems limited the quality and quantity of the experimental data.

TECHNICAL DETAILS

Task 2

A. Methanol Synthesis Runs

Four sets of methanol synthesis tests were conducted during the quarter. The specific operating conditions that were investigated during these tests are shown in Table 1. All of these runs were conducted with CO-rich synthesis gas (35 mole % H_2, 51 mole % CO and 14 mole % CO_2). Drakeol® 10 was the slurry liquid and a catalyst concentration of 20 weight % was used in all runs.

Table 1

Process Conditions for Methanol Synthesis Runs

Run	Pressure (psig)	Reactor Temp. (°C)	GHSV (sl/kg cat - hr)
1 *	750	250	5000
2	750	250	10000
3	2500	250	16500
4	750	250	5000

*referred to as "standard conditions"

April Operations:

One set of runs was conducted during April. The first three conditions, as shown in Table 1, were completed successfully. However, upon starting the fourth run, the Haskel gas compressor was no longer able to maintain flow to the reactor. The failure was caused by leaking seals around the piston shaft, allowing the process gases to leak into the vent ports. The compressor was probably leaking throughout the whole series of runs, since the reactor inlet and outlet flows decreased as the series progressed. These flow variations caused major discrepancies in the mass balances. However, the data may be of some value if the losses due to the leaking compressor can be quantified.

The new Vespel seats in the back pressure regular (BPR) were not responsive for control purposes during and after the third run, probably due to exposure to high gas outlet temperature, caused by the higher flow rate of hot gases through the overhead system. Once this problem appeared, the BPR allowed the reactor pressure to drift as much as 250

psig and also leaked process gas through the BPR. By the time the compressor failed, the BPR could only maintain 500 psig in the reactor due to leakage. Upon disassembly, it was determined that the new Vespel seats had not melted, but had become rigid. Unused Vespel seats are much softer and pliable. Another alternate material is being sought.

The reactor contained only 65 mL of slurry after shutdown, a loss of 118 mL. This is somewhat surprising since no major reactor upsets occurred during operation. The liquid-level indicator in the overhead system indicated high levels towards the end of Run 3 and during Run 4, making it likely that some oil was blown out through the BPR. This speculation was confirmed by the presence of mineral oil in the back pressure regulator at the end of the series of runs. In addition, during the third run, the high gas flow rate and the lower mole fraction of oil may have made condensation more difficult in the overhead system.

As with the methanol synthesis runs conducted during March, the catalyst was highly active throughout the April runs. Because of the failure of the BPR, a representative sample of the spent catalyst could not be obtained to send for elemental analysis, hopefully to confirm the absence of metal poisons.

May Operations - Overview:

Two sets of methanol synthesis runs were carried out in May. During the first set, only Runs 1 and 2, as shown in Table 1, were conducted. During the second set, only Run 1 was carried out.

May Operations (1):

Run #1 was completed satisfactorily, without any mechanical problem. During Run #2, the Autoclave Engineers gas compressor began leaking process gas through the seals, requiring a system shutdown. This compressor failure, and that of the Haskel compressor during April, were probably caused by high concentrations of water in the compressed air that drives both compressors.

The catalyst productivity for the first set of process conditions (Run #1) ranged from 11.4 to 13.0 moles methanol/kg catalyst/hr, as compared to 17 to 19 mol/kg/hr reported by Air Products for the same catalyst and operating conditions. However, the reactor thermocouple and temperature controller were calibrated after shutdown. The temperature controller showed a +10°C deviation at 250°C, i.e., when the controller read 250°C,

the actual reactor temperature was 240°C. When the catalyst rate constants were adjusted from 240°C to 250°C, the resulting adjusted productivities ranged from 13.2 to 14.6 mol/kg-hr, still about 15% to 25% below Air Products' results. This productivity difference suggests that the catalyst was not fully active.

May Operations (2);

Only Run #1 was executed during this operating period. The catalyst productivities were less than 9.4 mol/kg/hr, well below those of the previous standard run. The internal reactor temperature was controlled at 250°C, i.e., the temperature controller compensated for the temperature deviation mentioned earlier.

The catalyst productivities and rate constants decreased with time, as if the catalyst was being poisoned. Estimates of the capacity of the activated carbon carbonyl trap suggested that the trap might have become saturated during the run. Therefore, one possible explanation for the poor catalyst performance is catalyst poisoning, although this hypothesis was not confirmed by iron and nickel analysis of the used catalyst. The results are discussed in Section B of this report.

June Operations:

A single methanol synthesis run was conducted at standard conditions (Run #1 in Table 1). The run was terminated after 121 hours due to low catalyst activity. Catalyst productivities varied over time between 6.2 and 9.4 moles methanol/kg catalyst/hour. These values are less than one half of the expected productivities based on Air Products' results. Thorough review of the process conditions, gas chromatographic standards, data collection procedures, etc. during this run gave no insights that might explain the low catalyst activity. Fresh activated carbon traps for metal carbonyl removal from the reactor gas feed had been installed prior to the run, so poisoning of the catalyst by metal carbonyls was not likely.

The only plausible explanation for the low catalyst activity is that catalyst activation was somehow inadequate. Comparison of the procedure used for the June synthesis run with the procedure utilized by Air Products revealed some subtle differences, primarily in gas flowrates and system pressure. There is a possibility that the catalyst was "over reduced", i.e. the copper was reduced from Cu^{+2} to Cu^{0}, which is believed

to be inactive for methanol synthesis. Current theory holds that the Cu^{+1} sites are the active methanol synthesis sites on the Cu/ZnO catalyst.

In future methanol synthesis runs using the BASF Cu/ZnO catalyst, the exact reduction procedure used by Air Products will be followed.

B. Catalyst Analyses

Table 2 shows the results of analyses for iron and nickel on several catalysts.

Table 2

Analyses of BASF S3-86 Catalyst

Sample Identification	Fe (ppm)	Ni (ppm)
Fresh (Unreduced)	19	28
Used - March, '94	332	26
Used - May, '94 (Period 1)	65	43
Used - May, '94 (Period 1)	38	43

When the weight loss that occurs upon reduction of the fresh catalyst is taken into account, these results show no significant accumulation of nickel on the catalyst during operation. There does appear to be an accumulation of iron, especially during the March, 1994 period. However, there was no evidence of catalyst deactivation during the course of that operation, as discussed in detail in Quarterly Technical Progress Report No. 14 for the period January 1, 1994 to March 31, 1994. On balance, it does not appear that catalyst poisoning via iron and/or nickel deposition can account for the difference between the catalyst activities measured by Air Products and those reported herein.