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**NOVEL APPROACHES TO THE PRODUCTION OF HIGHER
ALCOHOLS FROM SYNTHESIS GAS**

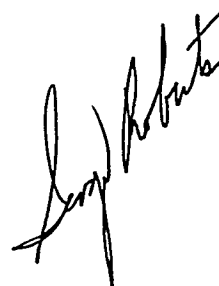
Quarterly Technical Progress Report No. 16

For The Period July 1, 1994 to
September 30, 1994

Contractor

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MASTER

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NOVEL APPROACHES TO THE PRODUCTION OF HIGHER ALCOHOLS FROM SYNTHESIS GAS

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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:

1) A new reactor overhead system design has significantly improved retention of slurry oil during reactor operation at high temperature, ca. 375°C. The most important changes to the overhead system were:

a) a positive displacement pump was installed in the liquid return line between the overhead condenser/separator and the reactor;

b) the area of the cooling loop in the condenser/separator was increased by a factor of five;

c) a ceramic foam demister was added prior to the gas exit line on the condenser/separator.

These changes have eliminated most of the oil loss associated with incomplete condensation in the overhead system and with liquid flow through the back pressure regulator. Losses of liquid during high

temperature operation now appear to reflect primarily the thermal stability (or lack thereof) of the slurry medium.

2) A series of "blank" (without catalyst) runs were made at 375°C to evaluate thermal stability of three potential slurry liquids: Drakeol® 34, Ethylflo® 180 and perhydrofluorene. The order of stability was: perhydrofluorene > Drakeol® > Ethylflo® 180.

3) The rate of methanol formation with the Cu/ZnO BASF S3-86 "low temperature" methanol synthesis catalyst was a strong function of stirrer speed at a "standard" set of operating conditions. This result suggests that the reaction rate is influenced or controlled by gas/liquid mass transfer, and may explain the previously-observed discrepancy between results from this laboratory and those from Air Products.

TECHNICAL DETAILS

Task 2

A. Reactor Overhead System Improvements

1. Metering Pump Installation

A positive displacement metering pump was installed in the liquid return line, between the gas/liquid separator and the reactor, to pump the mineral oil collected in the separator back to the reactor. This eliminates reliance on gravity to return vaporized and condensed oil to the reactor. The liquid return pump is a metering pump which allows a range of flow settings, depending upon what process conditions are being run, i.e., the rate of slurry liquid vaporization and condensation. The pump is self-priming, allowing it to go "dry" and then begin pumping again when oil returns. Pump performance appeared satisfactory during two high temperature "blank" runs at 375°C, which are described in the following section, since a significant amount of oil was retained in the reactor at the end of each run. In every previous high temperature "blank" run, there was very little oil in the reactor after only two days of operation.

2. Other Changes

Based on the results from the first "blank" run, the cooling loop in the gas/liquid separator was replaced with a new one that provided approximately 5 times the heat transfer area. A separate 1" diameter demisting "section" filled with ceramic foam was added prior to the separator gas exit. Finally, the thermocouple in the gas exit from the separator was relocated just downstream of the demisting section in a 1" diameter tube, essentially eliminating the possibility of touching the wall.

B. High Temperature Slurry Oil Tests

1. Drakeol® 34 (Test Number 1)

This "blank" run was conducted with Drakeol 34 mineral oil. The reactor was initially charged with 150 mL of oil and was run for about 60 hours. No catalyst was present in the reactor. Operating conditions were comparable to previous runs; 800 psig, 375°C, and an inlet gas flow of 3780 sccm hydrogen. After shutdown, 110 mL of oil remained in the reactor, i.e., 40 mL were lost. This result is far better than achieved in

any previous "blank" run at comparable conditions. Typically, less than 15 mL of oil was retained in the reactor in previous high temperature blank runs.

The possible reasons for oil loss were:

- Inadequate cooling of the reactor exit gas in the gas/liquid separator. The flow rate of coolant, ethylene glycol, to the cooling coil in the overhead system was substantially lower than the design value. The thermocouple measuring the gas exit temperature from the separator was probably reading low because it was touching the wall. Heat transfer and energy balance calculations supported these hypotheses.
- Mineral oil cracking. Light hydrocarbons were detected in the reactor exit gas via gas chromatography. The few measurements taken during the run showed that approximately 50% of the lost carbon atoms from the mineral oil were accounted for by methane, ethane and propane in the exit gas. Other hydrocarbon peaks were observed, but could not be identified due to the lack of required gas standards. This suggests that an even larger fraction of the lost carbon atoms could have left the reactor in the exit gas as light hydrocarbons.

The mineral oil retained in the reactor was a light blue-green color which is uncharacteristic of the spent mineral oil from previous autoclave runs and laboratory tests. The reactor contents might have been contaminated after the process was shut down by ethylene glycol that leaked from a fitting in the gas/liquid separator cooling coil. Based on this concern, the run was repeated.

2. Ethylflo® 180

Another high-temperature blank run was carried out using Ethylflo 180, which is hydrogenated poly-alpha-decene. The reactor was charged initially with 150 mL of Ethylflo and was operated without catalyst at 1000 psi, 375°C, and an inlet gas flow of 3780 sccm hydrogen. The run lasted 4 days. After shutdown, 56 mL of mineral oil remained in the reactor, less than the 110 mL of Drakeol 34 retained in the previous run, but still much better than other previous runs.

The principal reason for the higher loss appears to be that Ethylflo is inherently less thermally stable than Drakeol 34. Gas chromatographic analyses of the gas leaving the reactor showed that Ethylflo performed

similarly to Drakeol, eluting light hydrocarbons ($C_1 - C_6$) in the exit gas throughout the run. The light hydrocarbons accounted for about 40% of the oil loss. However, a noticeably larger unidentified peak appeared at 12 minutes retention time. This probably resulted from C_7-C_9 chains breaking off the polymerized structure. In addition, the Ethylflo 180 was more discolored after reactor shutdown than was the Drakeol 34, suggesting more extensive decomposition. The differences in behavior of the two oils probably lies in their chemical structure. Drakeol 34 is 68% paraffinic and 32% naphthenic, while the Ethylflo is 100% paraffinic, with substantial branching. The naphthenic structure appears to be inherently more thermally stable. This suggests that a 100% naphthenic oil should be tested for high temperature service.

3. Drakeol 34 (Test Number 2)

A second "blank" run was conducted with Drakeol 34 mineral oil, using a "standardized" test procedure. The procedure includes frequent analysis, via gas chromatography, of the gas leaving the reactor in order to estimate the amount of oil lost from the reactor due to oil decomposition.

After running for 70 hours, the reactor contained 64 mL of oil compared to the initial charge of 150 mL. Reactor conditions were comparable to previous runs; 1000 psig, 375°C, and an inlet gas flow of 3780 sccm hydrogen. There was no catalyst in the reactor. The analytical data for the reactor exit gas, integrated over the duration of the run, accounted for about 44 grams of a total of 75 grams of oil lost. However, the gas chromatograph (GC) configuration currently in use is not suited for detection of C_8+ compounds, so some peaks could have been overlooked. The GC results showed an initial "burst" of light hydrocarbons leaving the reactor once the internal reactor temperature passed 350°C. The loss rate decreased rapidly after about two hours at 375°C and then slowly decayed to a steady-state value of 0.10 grams/hour after about 70 hours of operation.

Compositional analyses will be performed on the spent oil from this and previous runs to help determine what structural changes occur during reactor operation.

4. Perhydrofluorene

Another high-temperature blank run was carried out using perhydrofluorene ($C_{13}H_{22}$), a fully hydrogenated version of fluorene ($C_{13}H_{10}$). Perhydrofluorene is a fused-ring naphthenic structure with no alkyl groups, so that this run tested the hypothesis that a non-alkylated naphthenic structure is inherently more thermally stable than a paraffinic structure. The reactor was charged with 146 grams of 97% perhydrofluorene and was operated at "standard" conditions: 1000 psig, 375°C, and an inlet gas flow of 3780 sccm hydrogen with no catalyst in the reactor. After running for 72 hours, 129 grams of perhydrofluorene remained in the reactor, a loss of only 17 grams.

Gas chromatographic analyses of the reactor exit gas showed a behavior similar to the mineral oils, i.e., an initial "burst" of the hydrocarbons which then decreased to lower values. However, the loss rate for perhydrofluorene quickly dropped to a "steady-state" value of < 0.1 grams/hour after only 5 hours. The rate of hydrocarbon loss for Drakeol 34 decreased much more slowly, eventually reaching a higher value after about 70 hours. Five of the 17 grams lost can probably be attributed to impurities in the original material since it was only 97% perhydrofluorene.

All things considered, the perhydrofluorene demonstrated far better thermal stability under the test conditions than any oil evaluated to date. This supports the hypothesis that the non-alkylated naphthenic structure is more thermally stable than its paraffinic counterpart.

5. Overall Evaluation

Table 1 summarizes the results of the thermal stability tests with Drakeol 34, Ethylflow 180 and perhydrofluorene.

TABLE 1
RESULTS OF THERMAL STABILITY TESTING OF
VARIOUS LIQUIDS AT STANDARD CONDITIONS¹

Liquid	Run Duration (hr.)	Molecular Weight ²			Rate of Liquid Loss (wt. % of initial charge/hr.)	
		Fresh	Spent	Reduction (%)	Maximum	Steady-State
Drakeol 34 (Test 1)	60	448	249	44	---	---
Drakeol 34 (Test 2)	69	405	264	35	1.2	0.10
Durasyn 180	65	1449	198	86	1.8	0.12
Perhydroflourene	71	230	232	(1)	0.44	0.044

1 - at a temperature of 375° C, H₂ pressure of 60 to 70 atm. and H₂ flow rate of 3.8 sL/min.

2 - by vapor phase osmometry

The molecular weights shown in Table 1 were measured at Galbraith Laboratories using the vapor phase osmometry technique (ASTM D1480). Based on the result for fresh perhydrofluorene, the technique does not appear to be accurate. The measured molecular weight of fresh perhydrofluorene was 230 compared to a theoretical value of 178. However, duplicate measurements suggest that the technique is reasonably precise, so that the measured changes in molecular weight may be useful indicators of liquid stability.

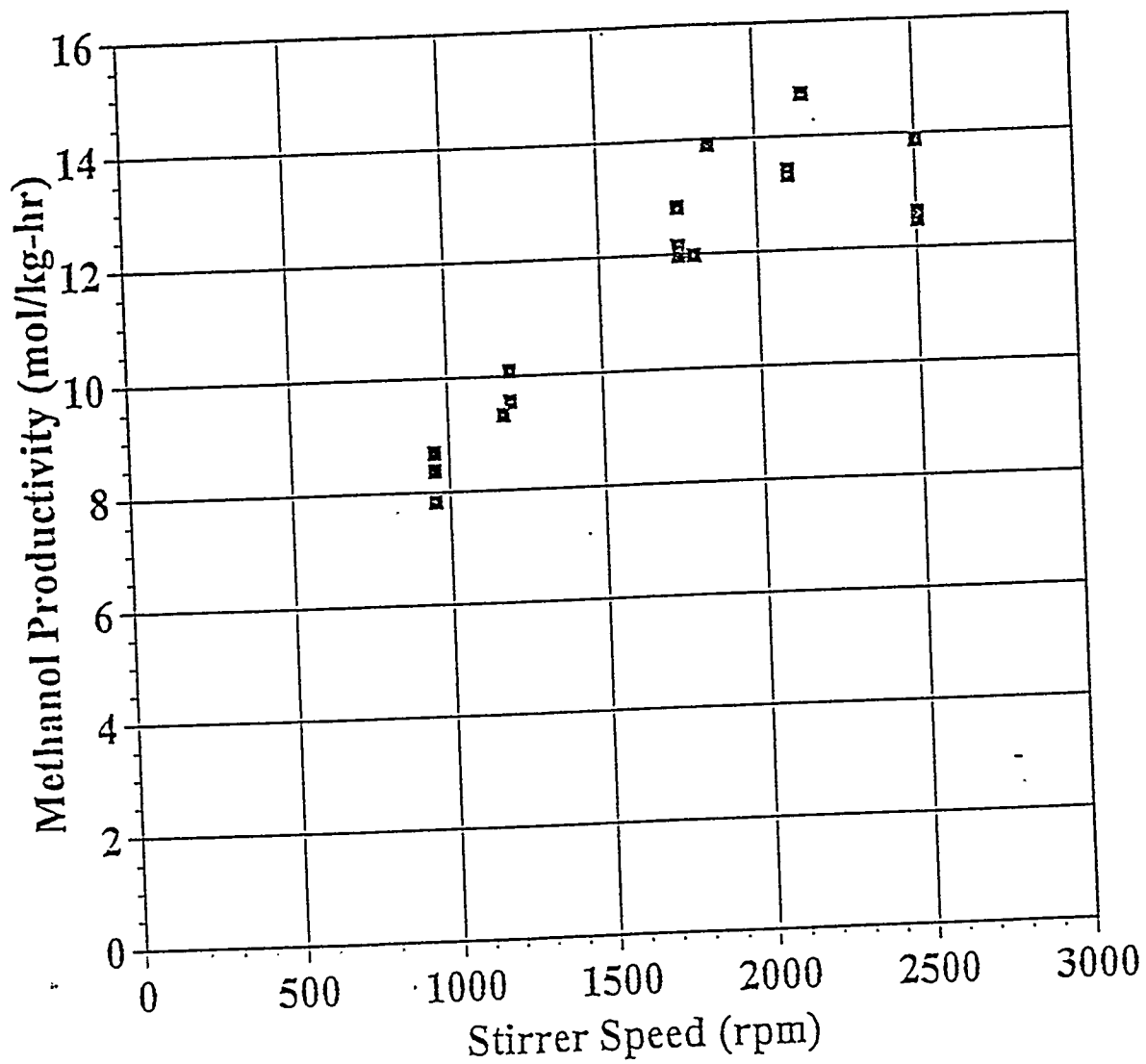
C. Methanol Synthesis

A methanol synthesis run using the BASF S3-86 Cu/ZnO catalyst was conducted. Drakeol[®] 10 was the slurry liquid. The charge was 130.4 gr. of liquid and 32.6 of catalyst. The initial plans for the run were to quantify the effects of reactor space velocity and pressure. However, the initial values of the methanol productivity were only 12 to 14 moles/kg catalyst/hr at 750 psig, 250°C and 5000 sl/kg/hr space velocity. Air Products typically reports productivities averaging about 17 mol/kg/hr under the same conditions. Based on these results, the experimental plan was modified to include a set of stirrer speed experiments to determine the influence of mass transfer on the reaction rate.

The stirrer speed was varied from 900 rpm to 2500 rpm over the course of the run. As shown in Figure 1, the methanol productivities depended on stirrer speed at the lower stirrer speeds. The data at a stirrer speed of 2500 rpm suggests that the reaction rate may have reached an asymptotic, but the scatter in the data prevents a definite conclusion. In any event, the data suggest that the reaction rate was influenced by gas/liquid mass transfer in the lower range of stirrer speed. Weimer, et. al. (1987) showed that their stirred autoclave system, which was very similar to the one used in these experiments, typically had mass transfer limitations only at stirrer speeds below 1000 rpm under these operating conditions. Possible causes of the observed mass transfer limitations include:

- The agitator shaft was plugged with catalyst and carbonaceous material from previous runs. Autoclave Engineers designed the hollow shaft to promote gas circulation by the pressure drop created by the rotation of the shaft/impeller assembly. Openings at the top and bottom of the hollow shaft allow gas to be drawn into the top and discharged through the impeller at the bottom. During this run, since the shaft was known to be plugged, the extra gas circulation benefits were not realized.

Figure 1
Effect of Stirrer Speed on Methanol Productivity
September 1994 Synthesis Run
5000 GHSV, 750 psig, 250 C



- The actual stirrer speed was much lower than indicated by the tachometer. This could be caused by an inaccurate tachometer or by the magnet inside the reactor shaft rotating more slowly than the outside drive unit.
- The slurry level during operation may have covered the top holes in the agitator shaft, thereby preventing gas flow through the shaft. Although the slurry volume can expand greatly during operation due to the agitation and gas flow, the slurry amounts that were used are consistent with those used by other researchers.
- The reactor gas inlet dip tube did not discharge in the mixing zone. The dip tube currently discharges about 1 cm above the impeller blades which should be well within the mixing zone.
- The cooling coil, which may act as a baffle, had been removed from the reactor.

The data for this run are presented in Appendix 1.

Modifications planned for the next synthesis run are:

- Cleaning the agitator shaft and ensuring that the agitator is rotating at all times while the reactor is assembled, This requires changes in operating procedures during pressure testing, etc., but the shaft must be spinning to ensure that it remains open.
- Verifying the tachometer reading with a strobe measurement device.

References

Weimer, R.F., Terry, R.M., and Stepanoff, P., "Laboratory Kinetics and Mass Transfer in the Liquid Phase Methanol Process", Presented at the A.I.Ch.E. Annual Meeting, November, 1987.

APPENDIX 1

Data Showing Effect of Stirrer Speed on Rate of Methanol Formation

<u>Experiment Number</u>	<u>Stirrer Speed Crpm</u>	<u>Methanol Formation Rate (moles/Kg. cat.-hr.)</u>
1	1800	12.0
2	1850	13.9
3	1750	12.0
4	1750	12.8
5	1750	12.1
6	2100	13.4
7	2100	13.3
8	2150	14.7
9	950	8.7
10	950	8.4
11	950	7.8
12	2500	12.5
13	2500	13.9
14	2500	12.6
15	1200	9.6
16	1200	10.1
17	1175	9.3

Liquid: Drakeol® 10

Catalyst: BASF S3-86

Catalyst Concentration: 20 weight percent

Total Pressure: 750 psig.

Temperature: 250°C

Space Velocity: 5000 sL/Kg.cat.-hr.