DE-AC22-90PC90043--12
(6510)

Novel Approaches To The Production of Higher Alcohols From Synthesis Gas

Quarterly Report
July 1 - September 30, 1993

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Work Performed Under Contract No.: DE-AC22-90PC90043

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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.
Task 4.	Synthesis of Higher Alcohols via Acid-Base Catalysis.
Task 5.	Technology Evaluation.

SUMMARY

- Under Task 2

Severe catalyst deactivation due to iron and nickel contamination was experienced during another set of methanol synthesis runs. X-ray photoelectron spectroscopy analysis revealed high levels of carbon on methanol catalysts from the April, 1993 synthesis runs. A fourth high temperature oil test was conducted, but no oil remained in the reactor.

- Under Task 3

Experimental work was concluded. In the future, work on data analysis and documentation of procedures and results will be reported under Task 1.

TECHNICAL PROGRESS

- Task 2:

Methanol Synthesis Runs

Another series of methanol synthesis tests was conducted, as shown in Table 1. During the seventh day of continuous operation, the tests were terminated prematurely during the third set of process conditions. Inlet gas flow was lost when the building air compressor was taken off line, causing equipment to shut down. Operation could not be restarted due to a blockage in the reactor feed line. This blockage was caused by massive carbon formation in the carbonyl trap.

Table 1
Process Conditions for the Methanol Verification Runs

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

The first two sets of process conditions were completed without incident. However, as shown in Table 2, the spent catalyst at the end of the operation contained 980 ppm iron and 527 ppm nickel. Therefore, the catalyst was almost certainly substantially deactivated by the end of the operation.

Table 2

Inductive Coupled Plasma Analysis of Spent and Fresh BASF S3-86 Cu/ZnO Catalyst

September, 1993 Methanol Synthesis Run

(All values are based on mass)

Analyte	Spent Catalyst	Fresh Catalyst
Aluminum	3.43%	4.12%
Copper	72.07%	71.34%
Zinc	24.18%	24.43%
Iron	980 ppm	34 ppm
Nickel	527 ppm	56 ppm
Chromium	27 ppm	2 ppm
Magnesium	113 ppm	111 ppm

One possible source of iron carbonyl was from the steel wool in the gas/liquid separator above the reactor. The steel wool is used for demisting the reactor exit gas of mineral oil. This steel wool was found to be magnetic, after operation was terminated, indicating that it is not stainless steel, despite contrary labeling. Carbonyls could have formed in the separator, which typically operated at 100 °C, and returned to the reactor with the mineral oil. High temperature glass wool will be used in subsequent runs.

Preliminary mass balance results indicate that methanol production decreased by a factor of 4 during the course of the first two runs. However, the mass balances are not complete due to inaccurate gas standards obtained from National Specialty Gases. These gas standards are currently being reanalyzed. Final analysis of all data will be completed in October.

Catalyst Poisoning

X-ray photoelectron spectroscopy (XPS) was conducted on fresh (unreduced) and spent BASF S3-86 (Cu/Zn/Al_2O_3) catalyst samples from the April, 1993 methanol synthesis run. XPS is considered a surface composition analysis, but this instrument also had "sputtering" capabilities, i.e. surface atoms could be removed at a rate of 100 A/min for analysis of sub-surface layers. After two minutes of sputtering, most extraneous species that are adsorbed on the catalyst surface should be removed, and a more accurate surface composition can be determined. The results are shown in Table 3.

Table 3

XPS Analysis Results for Fresh and Spent BASF S3-86 Catalyst Samples from the April, 1993 Methanol Synthesis Run

(Values in Atomic Percent)

	Fresh Catalyst Sample		Spent Catalyst Sample	
Total Sputter Time:	2 min	12 min	2 min	12 min
Cu	25.95	29.52	14.81	24.15
Zn	15.88	17.52	15.70	15.12
C	0.00	0.00	30.01	26.05
O	58.17	52.95	39.48	34.69

The most striking result is the high level of carbon present on the spent catalyst, especially since the fresh catalyst had none. The carbon could have come from two sources: 1) residual mineral oil or cyclohexane from the cleaning process, and/or; 2) carbon formation on the catalyst surface during the reaction run. Carbon formation could result from the Boudouard reaction, catalyzed by iron and/or nickel atoms deposited from metal carbonyl decomposition. Earlier elemental analysis showed 2280 ppm Fe in the bulk spent catalyst, as compared with 19 ppm Fe in the fresh catalyst. Carbon formation on the catalyst surface due to the presence of iron could explain why very low iron and nickel concentrations effectively poison the Cu/ZnO catalyst, since the carbon would easily block active sites.

To help determine whether the carbon is an artifact of the catalyst washing/drying procedure, fresh catalyst will be reduced in the stirred autoclave and then removed, washed and dried per the procedure established with the spent catalyst, and then analyzed with XPS.

High Temperature Mineral Oil Test

A fourth high temperature test of the Drakeol 34 mineral oil was conducted in the stirred autoclave. No oil remained in the reactor upon completion. A summary of this run is listed below.

Oil Screening Test #4

Based on results from the previous three tests, the process modifications made prior to this run included:

- Replacing all NPT fittings in the oil recycle loop with Swagelok fittings to reduce the possibility of leaks;
- Verifying all internal thermocouples;
- Relocating traps for capturing mineral oil that might be leaving the reactor/separator loop to the inlet of the wet test meter so that the wet test meter would not "capture" reactor oil. Also, the traps were submerged in liquid nitrogen to condense oil.

Table 4

Conditions for Oil Screening Test 4

REACTOR CONDITIONS

DATE	Press (psig)	Temp (°C)	Slurry	Oil Left (mL)	GAS FEED
7/15 - 7/16	1000	400	200 mL Drakeol 34 - no catalyst	> 5 mL	H_2 only, 3300 sccm

Results/Explanation

- No oil remained in the reactor at the end of two days of operation;
- About 30 mL of oil was trapped downstream of the reactor in the oil traps;
- The gas/liquid separator gas inlet temperature was above 200°C during the first few hours, despite operation of the cooling loop;
- After achieving 400°C, the reactor appeared to "percolate", i.e., the reactor pressure would increase about 10-20 psi quickly, then the gas temperatures in and out of the separator would increase 5-10°, and then the reactor temperature would decrease suddenly. This phenomena was not observed during the previous runs, but the reactor contained only 175 mL of oil during those runs as well;
- No mist or vapor was observed coming from any fittings in the oil recycle loop;
- A fine grit was present at the bottom of the reactor. Elemental analysis showed ppm levels of iron, copper, nickel, and zinc. The main constituent could not be identified by the analysis, suggesting a carbonaceous material. The grit could have originated from the graphite bearings around the drive shaft of the reactor agitator. The bearings did display some degradation when inspected after the run. This grit has not been observed previously.

Three possible explanations for the oil disappearance have been formulated:

- Under high temperature conditions, the oil/gas mixing generates a two phase "foam" which carries liquid out of the reactor and through the gas/liquid separator. This concept will be tested in laboratory glassware, similar to the thermal stability testing apparatus used in November 1992;

- The mineral oil is decomposing rapidly to more volatile hydrocarbons due to high temperature coupled with high hydrogen pressure. Previous high temperature testing in glassware did not show noticeable decomposition, but N_2 instead of H_2 was used to purge the apparatus, and the test ran at atmospheric conditions;
- If the pressure drop between the reactor gas exit and the gas/liquid separator exceeded 0.5 psi, then the condensed oil collected in the separator could not return to the reactor, i.e. the liquid head of oil generated would not be sufficient to overcome the pressure drop. The consequence would be condensed oil carried out the separator gas exit. Although calculations indicate that pressure drop should not be a problem for steady state operation, a 0.5 psi tolerance is probably too small for "real" operation. This phenomena could have easily occurred during the "percolation" observed at the beginning of the run.

- Task 3

Experimental research on catalyst development has been completed. Current effort is focused on data analysis and on documenting and reporting all results.