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NOVEL APPROACHES TO THE PRODUCTION OF HIGHER ALCOHOLS FROM SYNTHESIS GAS

Quarterly Technical Progress Report No. 17

For The Period October 1, 1994 to December 31, 1994

Contractor

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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. (Complete)

Task 5. Technology Evaluation. (Complete)

SUMMARY

A series of experiments in which the stirrer speed was varied during a methanol synthesis run with BASF S3-86 catalyst showed that mass transfer limitations were present at 750 psig reactor pressure and at space velocities of 5000 and 10000 sl/kg(cat.)-hr.. There was no effect of stirrer speed on reaction rate at 2500 psig reactor pressure and 16500 sl/kg(cat.)-hr. space velocity. However, this was probably due to a close approach to equilibrium rather than to the lack of a mass transfer effect. The most plausible explanation for the presence of a mass transfer influence is the position of the gas feed dip tube relative to the agitator impeller.

A second set of stirrer speed experiments using the same catalyst showed that feeding into the reactor headspace produced much lower reaction rates, compared with gas feed through a dip tube. The headspace feed also showed a strong dependence on stirrer speed, consistent with the dip tube feed results.

In a "blank" run at 375°C with decahydronaphthalene, about 110 mL of the initial charge of 150 mL remained in the reactor after 73 hours of operation at 375°C and 850 psig of hydrogen. The rate of hydrocarbon evolution was low throughout the run. Decalin is the most stable liquid identified to date.

Three stirred autoclave runs with a commercial, high-pressure methanol synthesis catalyst (zinc chromite) slurried in decahydronaphthalene ended soon after the initial catalyst reduction due to failures of the liquid return pump in the overhead system. However, the catalyst appeared to be reduced and the liquid appeared to be stable.

TECHNICAL DETAILS

A. Diagnostic Experiments for Gas/Liquid Mass-Transfer Limitation

1. Methanol Synthesis Run - Stirrer Speed Experiments

A methanol synthesis run using the BASF S3-86 Cu/ZnO catalyst was conducted during October 1994. The run was designed to quantify the effects of stirrer speed, reactor space velocity, and total pressure on catalyst performance. Table 1 lists the reactor conditions tested.

Table 1
October Methanol Synthesis Run-
Reactor Conditions

Reactor Condition #	Stirrer Speed (rpm)	Pressure (psig)	GHSV (sl/kg-hr)
1A	1750	750	5000
1B	1000	750	5000
1C	2500	750	5000
2A	1750	750	1000
2B	1000	750	1000
2C	1250	750	1000
3A	1750	2500	16500
3B	1000	2500	16500
4A	1750	750	5000
4B	1000	750	5000

For all conditions, the reactor temperature was 250°C and the feed gas composition was 35% H_2, 51% CO, and 14% CO_2 (Texaco synthesis gas). Drakeol® 10 was used as the slurry liquid and the catalyst concentration was 20 weight percent.

Since an apparent mass transfer limitation was observed during the September, 1994 methanol synthesis run, the hollow agitator shaft was thoroughly cleaned, and all possible measures were taken to ensure that the shaft remained open during reactor assembly and pressure testing. An open agitator shaft should enhance gas circulation from the reactor headspace through the catalyst slurry, thereby decreasing the gas/liquid mass transfer resistance. Also, the tachometer on the agitator shaft was verified using a photoelectric tachometer.

As shown in Figure 1, the catalyst productivity values at 750 psig, for both 5000 and 10000 gas hourly space velocity (GHSV), show a strong dependence on stirrer speed. The data for 5000 GHSV are consistent with similar data from the September, 1994 synthesis run, as shown in Figure 2. The correspondence of these two sets of data suggests that either: 1) a plugged agitator shaft was not the cause of the mass transfer limitation observed in September, 1994; 2) the shaft was plugged during the present run, or, 3) it does not matter whether the shaft is plugged. Upon shutdown, the shaft was inspected and was found to be open and free of catalyst. Apparently, an open agitator shaft does not have a major influence on the rate of gas/liquid mass transfer in this reactor configuration, at these operating conditions.

The methanol productivities at 16500 GHSV and 2500 psig showed essentially no dependence on stirrer speed, as shown in Figure 3. However, this data is scattered, probably due to intermittent methanol condensation in the overhead system. The methanol concentrations in the reactor exit gas stream exceeded 15 mole% and approached the equilibrium value of 20.5 mole%. This necessitated operating the overhead system at around 160°C in order to prevent methanol condensation. However, the mineral oil loss rate from the reactor was significantly increased at this temperature. Based on this, future high pressure methanol synthesis runs using the Cu/ZnO catalyst should utilize a higher boiling mineral oil, such as Drakeol 34, to compensate for the higher overhead system operating temperature.

The only possible cause for the mass transfer limitations that is consistent with the results from both the September and October methanol synthesis runs is the location of the gas inlet feed dip tube. In both the September and October runs, the tube discharged about 1 cm above the agitator impeller blades. Air Products and Chemicals' gas inlet dip tube discharges below the impeller blades, essentially at the bottom of the reactor. This design has two advantages:

- The gas discharges in the mixing zone where the liquid circulation draws the gas toward the impeller, and
- The gas actually passes through the impeller mixing zone, increasing gas dispersion into the catalyst slurry with smaller bubble size.

2. Second Methanol Synthesis Run - Stirrer Speed Experiments

A second methanol synthesis run using the BASF S3-86 catalyst was conducted during December, 1994. The effect of feeding gas at two different locations in the stirred autoclave was evaluated. The gas feed locations were: 1) through the dip tube, which terminated above the reactor agitator impeller, and; 2) into the reactor "headspace", the gas area above the slurry. The dip tube extended to exactly the same position that it did during the October, 1994 tests. With the headspace feed location, the action of the "gas-inducing" agitator is the only mechanism for mixing and dispersion of the gas feed into the reactor slurry. This is the configuration that is recommended by the autoclave manufacturer, Autoclave Engineers, Inc.

All experiments were conducted at 5000 GHSV, 750 psig, 250°C, Drakeol® 10 slurry liquid, 20 weight percent catalyst, and with Texaco synthesis gas as described above. A set of tests at stirrer speeds ranging from 1100 to 2500 rpm was conducted for each gas feed location. The results in Figure 4, show a dependency of catalyst performance, as measured by methanol productivity, on stirrer speed, for both feed locations. However, feeding into the headspace caused a greater decrease in methanol productivity, possibly resulting from "by-passing", since the reactor outlet is also located in the reactor headspace.

A third gas feed configuration, i.e., feeding through a dip tube extending below the reactor agitator, will be evaluated during the next quarter.

Figure 1
Effect of Stirrer Speed on Methanol Productivity
October 1994 Synthesis Run
750 psig and 250 C Reactor Conditions

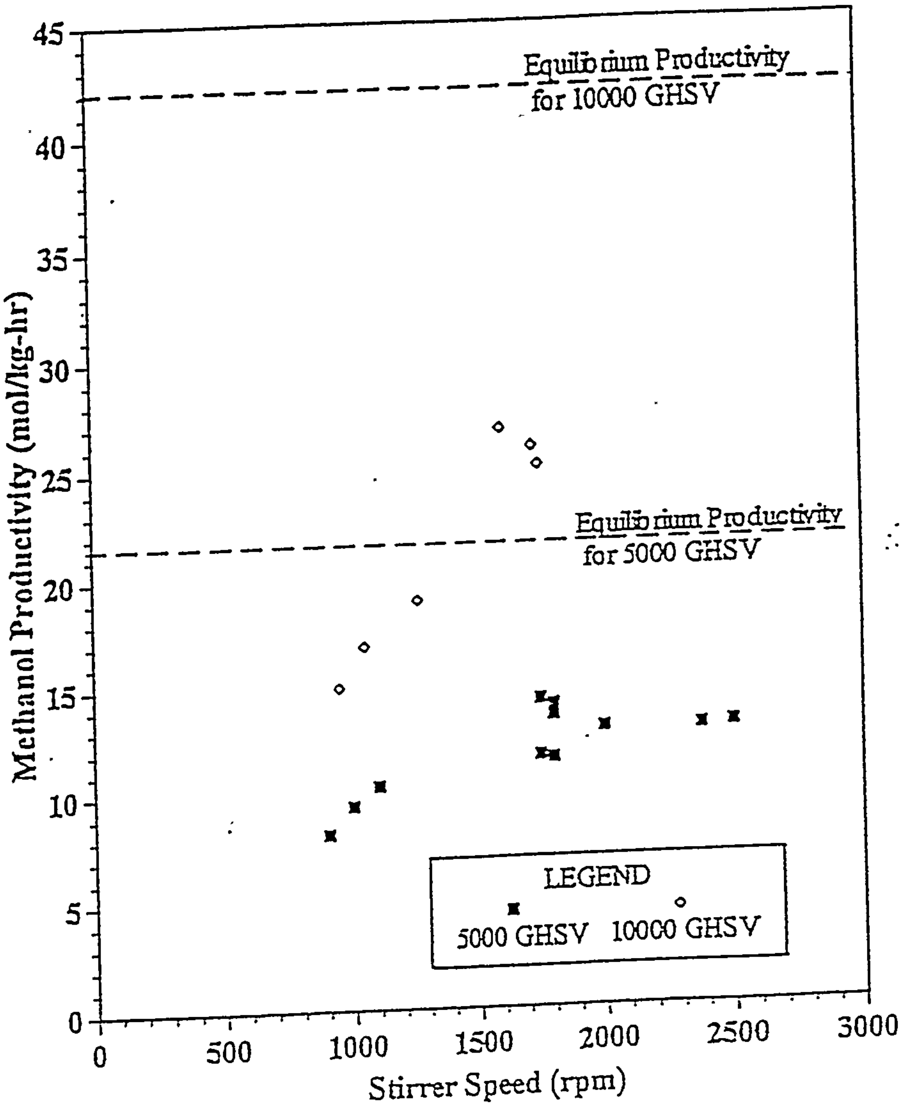


Figure 2

Comparison of September and October Methanol Producitivies
5000 GHSV, 750 psig, 250 C Reactor Conditions

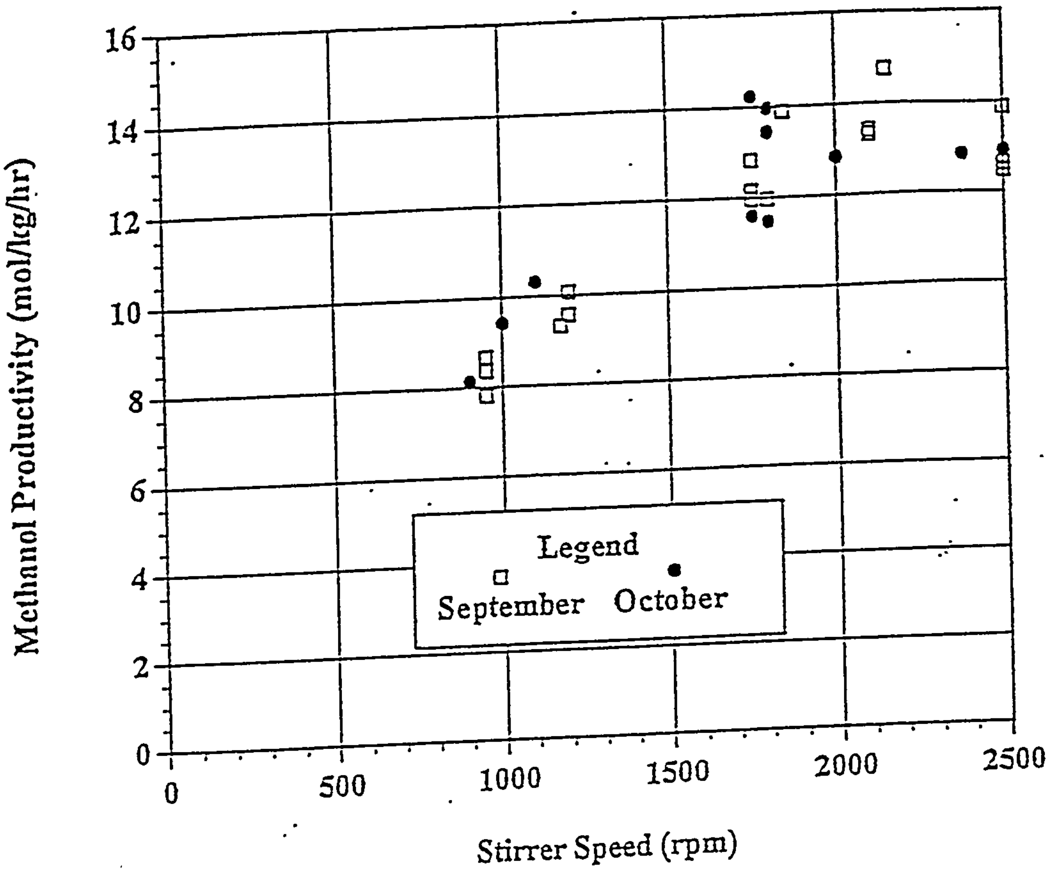


Figure 3

Effect of Stirrer Speed on Methanol Productivity
October 1994 Synthesis Run
16500 GHSV, 2500 psig, 250 C Reactor Conditions

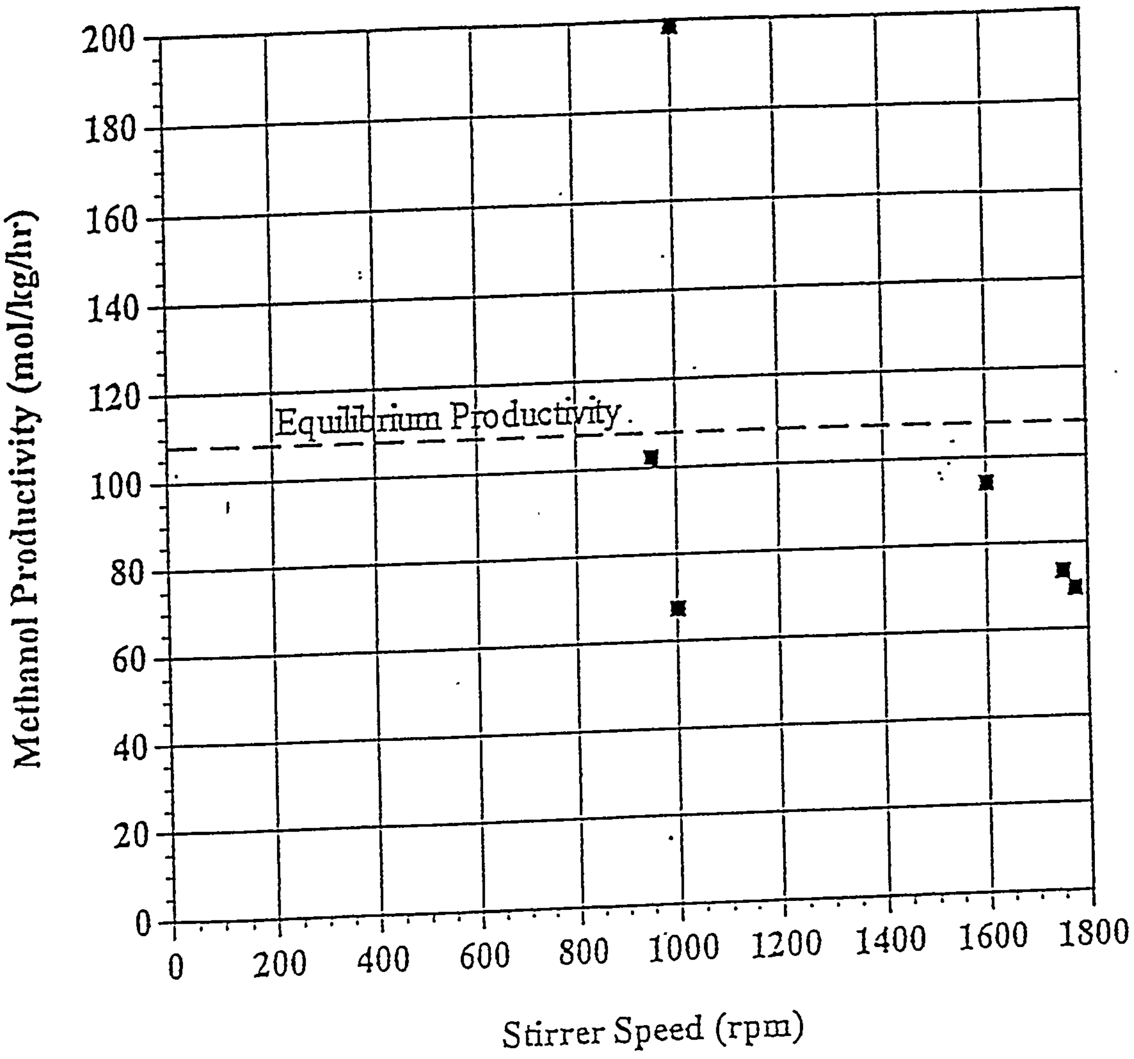
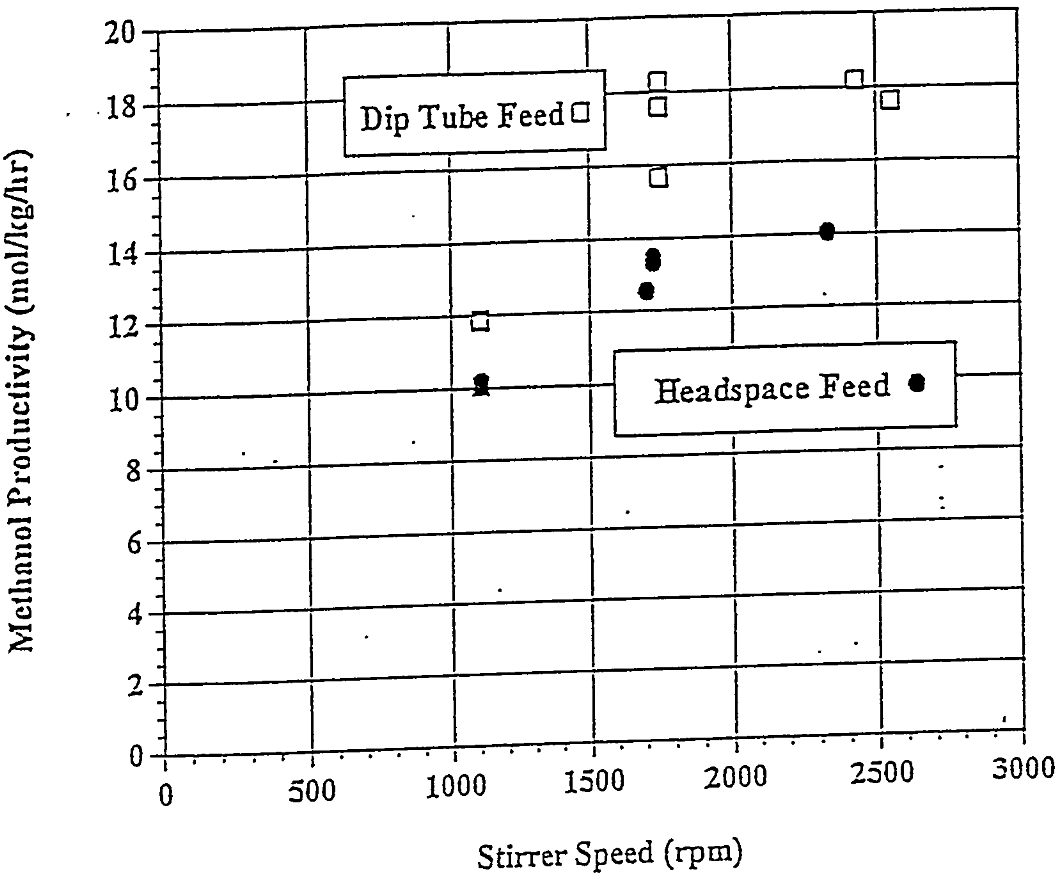


Figure 4

Evaluation of Reactor Gas Feed Configurations
5000 GHSV, 750 psig, 250 C Reactor Conditions



B. High Temperature Blank Run with Decahydronaphthalene

A "blank" run was conducted during November, 1994 using decahydronaphthalene ($C_{10}H_{18}$, tradenamed Decalin®), the fully hydrogenated form of naphthalene ($C_{10}H_8$). Decahydronaphthalene (DHN), like perhydrofluorene (PHF, $C_{13}H_{22}$), has a naphthenic structure with no alkyl groups. The purpose of this "blank" run was to provide another test of the hypothesis that a non-alkylated naphthenic structure is inherently more stable thermally than a paraffinic structure. However, the primary motivation for testing DHN is that it costs substantially less than PHF.

The reactor was charged with 133 grams of DHN with a purity of 99^{+}%, and was operated at 850 psig, 375°C and an inlet gas flow of 3780 sccm hydrogen with no catalyst in the reactor. After running for 73 hours, 98 grams of DHN remained in the reactor, a loss of 35 grams. A majority of this loss can be attributed to vapor losses during pre-run pressure testing. The pre-run pressure tests usually last only 24 hours, but the test for this run lasted over 72 hours.

Gas chromatographic analyses of the reactor exit gas showed an initial loss rate of about 0.1 grams/hour, about the same as the final loss rate during a similar test with perhydroflourene (PHF), conducted in August, 1994. The DHN loss rate decreased rapidly to <0.01 grams/hour after 6 hours. The differences in loss rates between DHN and PHF can be attributed partially to differences in impurity concentrations. DHN is

99+% pure, while the PHF used for the August, 1994 test was only about 97% pure.

As with perhydrofluorene, the performance of decahydronaphthalene was very good at the reactor conditions tested, and far superior to conventional mineral oil. This test further illustrates the excellent thermal stability of non-alkylated naphthenic structures, as compared to their paraffinic counterparts.

C. Runs with Zinc Chromite Catalyst

1. November, 1994

Two stirred autoclave runs using "zinc chromite", the high temperature methanol synthesis catalyst, were carried out in November, 1994. Both runs ended abruptly after the catalyst reduction procedure, due to failure of the liquid return pump from the gas/liquid separator. The reactor was charged with about 34 g of unreduced "zinc chromite" catalyst obtained from Englehard Corporation. After the reduction and subsequent shutdown, the catalyst had changed from the original bright yellow color to a dull gray-green, consistent with the color of a commercial sample of reduced and stabilized "zinc chromite" catalyst from the same manufacturer. The initial charge of slurry liquid was 131 grams in both runs.

The reactor liquid, decahydronaphthalene (Decalin®) (DHN) appeared very stable during the brief runs. Reactor gas outlet samples did not reveal any significant levels of light hydrocarbons, which are normally associated with liquid decomposition. The reactor temperature was 375°C for a few hours, so any liquid interaction with the catalyst should have been evident. After shutdown, the liquid was clear after removal from the reactor in both runs. The lack of gas formation and the clear appearance of the liquid are potentially significant, since the "blank" runs that showed DHN to be stable were conducted without catalyst, whereas catalyst was present during these short runs.

2. December, 1994

Another stirred autoclave run using Engelhard "zinc chromite" catalyst ended abruptly, after the catalyst reduction procedure, again due to failure of the liquid return pump from the gas/liquid separator. The reactor was charged with about 34 g of unreduced "zinc chromite" catalyst obtained from Engelhard. After the reduction and subsequent shutdown, the catalyst had once again changed from the original bright yellow color to a dull gray-green, consistent with a commercial sample of reduced and stabilized "zinc chromite" catalyst. The initial liquid charge was 131 grams.

The reactor liquid medium, decahydronaphthalene (Decalin®), appeared very stable during the brief run. Reactor gas outlet samples did not reveal any significant levels of light hydrocarbons, which are normally associated with liquid decomposition. The reactor temperature was 375°C for a few hours, so any liquid interaction with the catalyst should have been evident. After shutdown, the liquid was clear after removal from the reactor.