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NOVEL APPROACHES TO THE PRODUCTION OF HIGHER ALCOHOLS FROM SYNTHESIS GAS

Quarterly Technical Progress Report No. 18

For The Period January 1, 1995 to March 31, 1995

Contractor

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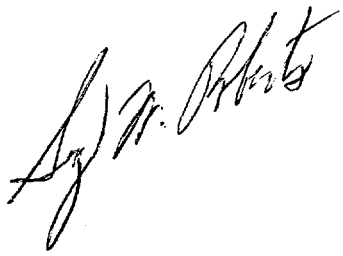

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NOVEL APPROACHES TO THE PRODUCTION OF HIGHER ALCOHOLS FROM SYNTHESIS GAS

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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

A set of stirrer speed experiments using the Cu/ZnO methanol synthesis catalyst showed that introducing the gas feed into the reactor through an extended dip tube eliminated the dependency of catalyst performance on stirrer speed. The methanol productivity data from the reactor gas feed configuration tests conducted in December, 1994 and January, 1995, were correlated with stirrer speed. The influence of mass transfer on catalyst performance was clearly illustrated for each gas feed location.

The "high pressure, high temperature" zinc chromite methanol synthesis catalyst showed surprising activity at temperatures as low as 300°C during the first successful stirred autoclave run with this catalyst. No C_2+ alcohols were detected, but significant levels of C_2 - C_4 olefins and dimethyl ether (DME) were produced. The presence of olefins suggests that higher alcohols might have formed and subsequently dehydrated. The slurry liquid, decahydronaphthalene, showed no evidence of decomposition during 15 days of continuous operation.

TECHNICAL DETAILS

A. Reactor Gas Feed Location Tests with Cu/ZnO Catalyst

1. Experimental Evaluation - "Extended" Dip Tube

In December, 1994, the effects of feeding gas at two different locations in the stirred autoclave reactor were evaluated, using the BASF S3-86 Cu/ZnO methanol synthesis catalyst. The gas feed locations were: 1) into the reactor headspace, and; 2) through a dip tube that terminated just above the agitator. For both locations, the methanol production rate depended on the rate of agitation.

The most recent set of reactor runs included one additional gas feed location. The gas feed dip tube was extended below the reactor agitator, so that the feed gas had to pass through the impeller zone before leaving the reactor. This feed location was compared with the headspace feed location by switching the feed between these two locations during a single continuous run with the same catalyst.

All experiments were carried out with the Cu/ZnO methanol synthesis catalyst at 5000 GHSV, 750 psig, 250°C, and with Texaco (CO rich) synthesis gas (35%H_2, 51% CO, 14% CO_2). A set of tests at stirrer speeds ranging from 1100 to 2500 rpm was conducted for each reactor gas feed configuration. Figure 1 illustrates the relationship between reactor gas feed location, stirrer speed and catalyst performance (methanol productivity). Clearly, the extended dip tube eliminates the dependency of catalyst performance on stirrer speed. The headspace feed shows a definite influence of stirrer speed, consistent with the December, 1994 results. The productivity values for the present runs were lower than those obtained for the runs made in December, 1994, possibly because of differences in catalyst reduction. Despite the difference, the overall result remains that an extended dip tube appears to be necessary in order to eliminate the influence of stirrer speed on catalyst performance for this system. All future runs will use the extended dip tube configuration.

2. Simple Mass Transfer Model

A simple mass transfer model, utilizing a correlation developed by Yagi and Yoshida between stirrer speed and the overall gas/liquid mass transfer coefficient, k_La, has been applied to the data from all of the previous reactor gas feed configuration tests. The mass transfer correlation by Yagi and Yoshida shows a general relationship:

$$k_La \propto AN^{2.22} \qquad (1)$$

The variable N represents the stirrer speed in revolutions per hour, and A is a proportionality constant including several physical parameters such as density, viscosity, and impeller diameter.

In a slurry reactor, the catalyst performance depends upon the mass transfer rate of reactants at the gas/liquid and liquid/solid interfaces, plus the intrinsic kinetics at the catalyst surface. The Cu/ZnO methanol synthesis catalyst particles are very small, usually <10 μm, so liquid/solid and intraparticle mass transfer resistances probably can be neglected. The overall rate of mass transfer from the gas bubbles to the catalyst can then be expressed as:

$$R_m = k_La\ (P_i - P_b) \qquad (2)$$

where P_i = partial pressure of reactant at the gas/liquid interface, determined by Henry's Law, and:

P_b = bulk concentration of reactant in the slurry
R_m = methanol productivity (mol/kg catalyst - hr)

To simplify the overall model, a simple, first-order kinetic expression was assumed:

$$R_m = kP_{H2} \qquad (3)$$

where k = intrinsic rate constant

P_{H2} = partial pressure of hydrogen in the bulk slurry

If Equations 1-3 are combined, the following relationship between the catalyst activity, as measured by methanol productivity, and the stirrer speed results:

$$R_m = \frac{kP_{H_2}}{1+\frac{k}{AN^{2.22}}} \qquad (4)$$

This equation can be rearranged into a linear form:

$$\frac{P_{H_2}}{R_m} = \frac{1}{k} + \frac{1}{AN^{2.22}}$$

The ratios of the hydrogen partial pressure in the reactor exit gas and the methanol productivity for the December, 1994 and January, 1995 Cu/ZnO catalyst runs were plotted versus $1/N^{2.22}$. Figure 2 shows the resulting data for the four runs, each corresponding to a different reactor feed configuration. The plot clearly illustrates that the extended dip tube essentially eliminates any influence of mass transfer on methanol productivity, i.e. catalyst performance. However, the "short" dip tube and the headspace gas feeds show strong relationships with stirrer speed, indicating a definite influence of mass transfer on overall catalyst performance. The linear curve fits are fairly good for all the data sets, suggesting that the mass transfer correlation is reasonable.

References

Yagi, H. and Yoshida, F. "Gas Absorption by Newtonian and Non-Newtonian Fluids in Sparged Agitated Vessels", *Ind. Eng. Chem.*, Process Des. Dev., **14**, 488 (1975).

Figure 1

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

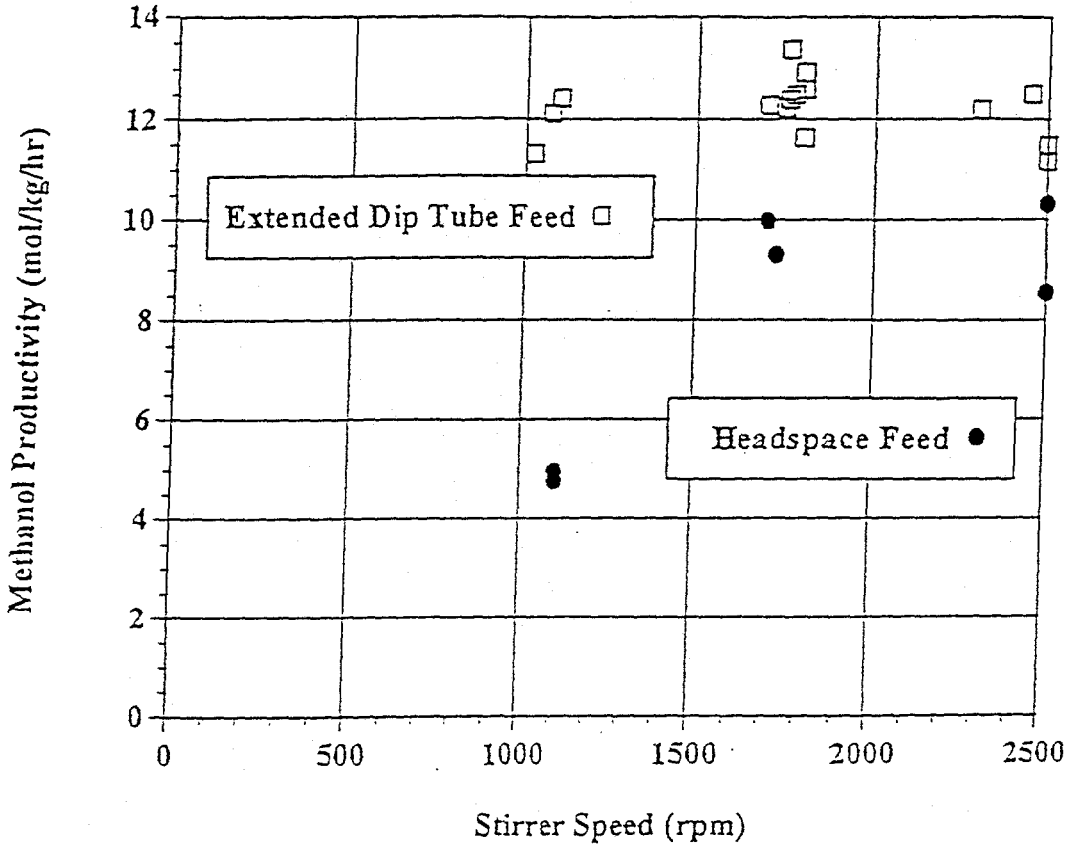
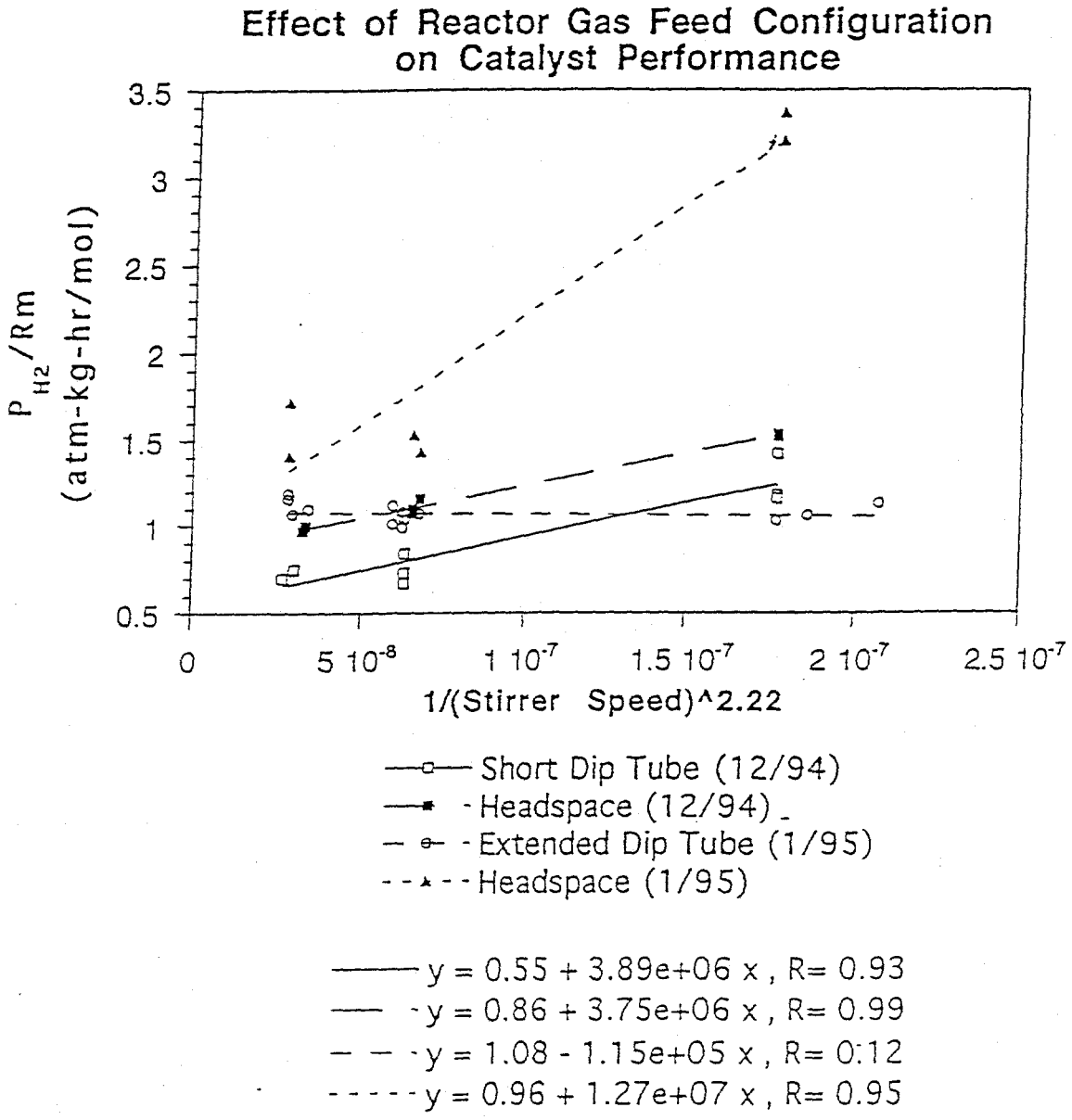


Figure 2


Effect of Reactor Gas Feed Configuration
on Catalyst Performance
P H2 /Rm
(atm-kg-hr/mol)
3.5
3
2.5
2
1.5
1
0.5
0
5 10-8
1 10-7
1.5 10-7
2 10-7
2.5 10-7
1/(Stirrer Speed)^2.22
Short Dip Tube (12/94)
Headspace (12/94)
Extended Dip Tube (1/95)
Headspace (1/95)
y = 0.55 + 3.89e+06 x , R= 0.93
y = 0.86 + 3.75e+06 x , R= 0.99
y = 1.08 - 1.15e+05 x , R= 0.12
y = 0.96 + 1.27e+07 x , R= 0.95

B. Zinc Chromite Catalyst Run

A stirred autoclave run to evaluate the performance of a commercial "high pressure, high temperature" zinc chromite methanol synthesis catalyst was successfully completed. A summary of the reactor process conditions tested during the run is listed below in Table 1.

Table 1
Zinc Chromite Catalyst Evaluation Run
Reactor Pressure at 1000 psig
20 Weight % Catalyst Loading

Reactor Condition Set #	H_2/CO Ratio	Temperature (°C)	GHSV (sl/kg-hr)	Stirrer Speed (rpm)
1A	1	375	5000	1750
1B	1	375	5000	1075
1C	1	375	5000	2325
2	1	375	1500	1750
3	1	375	3000	1750
4	0.5	375	5000	1750
5	0.5	350	5000	1750
6	0.5	325	5000	1750
7	0.5	300	5000	1750
8	2	300	5000	1750
9	2	300	10000	1750
10	0.5	300	10000	1750

The catalyst (Zn-0312 T1/8) was obtained from Engelhard Corporation in a reduced and stabilized form. It contained 60 wt. % Zn and 15 Wt. % Cr, with ZnO and $ZnCr_2O_4$ detectable by x-ray diffraction. The as-received BET surface area was 145 m^2/g. The catalyst was ground and sieved to -120 mesh prior to use. This run was made with Decalin as the slurry medium. The catalyst was activated in-situ by: pressurizing the reactor to 69 atma with N_2 and heating it to 130°C while sparging N_2 through the slurry; heating from 130 to 300°C at about 40°C/hr with a sparge gas consisting of 5% H_2 in N_2; heating to 375°C at 25°C/hr while progressively increasing the H_2 mole fraction in the sparge gas from 0.05 to 1, and; holding at

375°C with a pure H_2 sparge until no water was present in the gas leaving the reactor.

The stirrer speed experiments (Reactor Condition Sets 1A through 1C) showed no significant change in catalyst activity or product distribution, suggesting no influence of mass transfer. The dip tube through which gas was fed terminated below the agitator, i.e., the "extended" dip tube referred to in Section A above. However, the major product under these conditions, methanol, was close to thermodynamic equilibrium. Its production rate probably would not be affected significantly by changes in stirrer speed. Another series of stirrer speed experiments is needed under conditions where methanol is not at equilibrium to conclusively demonstrate that no influence of gas/liquid mass transfer is present.

Additional results of this initial catalyst evaluation are summarized as follows:

1) Methanol and dimethyl ether were the only significant oxygenated products under all conditions tested.

2) The methanol synthesis reaction was close to equilibrium for reactor condition sets 1 through 6, i.e., when the reactor temperature exceeded about 325°C.

3) The formation of dimethyl ether by the dehydration of methanol was not at equilibrium under any of the conditions tested.

4) The primary paraffinic product was methane, with considerably smaller amounts of ethane and propane.

5) C_2-C_4 olefins were detected in small quantities. Since butene was detected, but butane was not, this suggests that at least butene could have been formed by the dehydration of a C_4 alcohol.

6) Increasing reactor temperature increased the selectivity to hydrocarbons, increased the relative formation of dimethyl ether, and caused the methanol synthesis reaction to approach equilibrium.

7) The high quantity of CO_2 detected and the absence of water suggests that the water-gas-shift reaction was close to equilibrium.

8) Run 9 yielded a methanol productivity of 4.7 moles/kg catalyst/hour, which is surprising for this catalyst at only 300°C reactor temperature. The literature reports that significantly higher pressures and temperatures were required for similar activity in packed bed reactors. The superior performance could be related to the small particle size of the catalyst in the slurry reactor, possibly increasing the effectiveness factor.

9) The decahydronaphthalene used for the reactor slurry did not appear substantially degraded upon visual inspection at run completion. After filtering to remove the catalyst, the liquid was clear with a light green color and had about the same viscosity as it had originally. Nuclear magnetic resonance (NMR) and molecular weight analyses will be conducted on samples of the spent liquid to determine the extent of decomposition.