

DOE/PC/90047-47

DOE/PC/90047--T5

DE92 019718

QUARTERLY TECHNICAL PROGRESS REPORT No. 6

Covering the Period January 1, 1992 to March 31, 1992

**SYNTHESIS OF OCTANE ENHANCERS DURING
SLURRY-PHASE FISCHER-TROPSCH**

Prepared for the U.S. Department of Energy Under
Contract No. DE-AC22-90PC90047

June 24, 1992

Prepared by: George Marcellin, President
Altamira Instruments, Inc.
2090 William Pitt Way
Pittsburgh, PA 15238

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

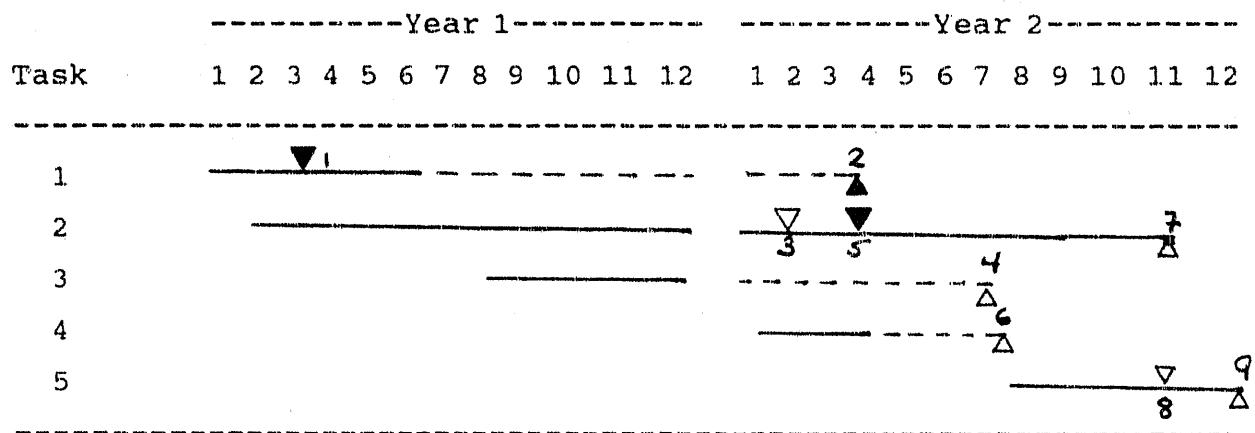
TABLE OF CONTENTS

| | |
|---|----|
| Planned Task and Milestone Schedule | 1 |
| Objectives | 2 |
| Work Accomplished This Quarter | 2 |
| Sixth Quarter's Technical Report | 3 |
| 1. Construction of SBCR | 3 |
| 2. Gas-Phase Synthesis of MTBE | 6 |
| Introduction | 6 |
| Experimental | 6 |
| Results and Discussion | 7 |
| Study of MTBE Synthesis at High Temperature . | 7 |
| Study of Adsorption Behavior | 8 |
| References | 19 |
| 3. Work Planned for Next Quarter | 23 |

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PLANNED TASK AND MILESTONE SCHEDULE



M = denotes milestone

List of Milestones

| <u>Number</u> | <u>Description</u> |
|---------------|---|
| M1 | Finalize design of slurry bubble column reactor (SBCR). |
| M2 | Finalize construction and testing of SBCR. Topical report prepared. |
| M3 | Completion of catalyst screenings for study of isobutylene addition during formation of alcohols. Decision made on catalysts to be studied in SBCR. |
| M4 | Completion of slurry reaction of isobutylene addition during formation of alcohols. |
| M5 | Completion of catalyst screenings for study of isobutylene addition to FT liquid products using acid catalysts. Decision made on catalysts to be studied in SBCR. |
| M6 | Completion of slurry reaction of isobutylene addition to FT liquid products using acid catalysts. |
| M7 | Completion of catalyst screenings. |
| M8 | Completion of slurry reaction of alcohol addition during iso-olefin synthesis. |
| M9 | Final report issued. |

OBJECTIVES

The objective of this project is to investigate three possible routes to the formation of ethers, in particular methyl tert-butyl ether (MTBE), during slurry phase Fischer-Tropsch reaction. The three reaction schemes to be investigated are:

- * Addition of isobutylene during the formation of methanol and/or higher alcohols directly from CO and H₂ during slurry-phase Fischer-Tropsch.
- * Addition of isobutylene to FT liquid products including alcohols in a slurry-phase reactor containing an MTBE or other acid catalyst.
- * Addition of methanol to slurry phase FT synthesis making iso-olefins.

WORK ACCOMPLISHED THIS QUARTER

During the sixth quarter we completed the construction of the SBCR, conducted initial shake-down experiments in a cold-flow mode, and finalized the selection process of the acid catalysts for conversion of syngas-produced alcohols and isobutylene to MTBE (scheme 2). Tasks 3, 4, and 5 are awaiting complete implementation of the SBCR system.

SIXTH QUARTER'S TECHNICAL REPORT

1. Construction of Slurry Bubble-Column Reactor

The slurry bubble column reactor is completed. The criteria for the design was described in detail in the First Quarterly Technical Report.

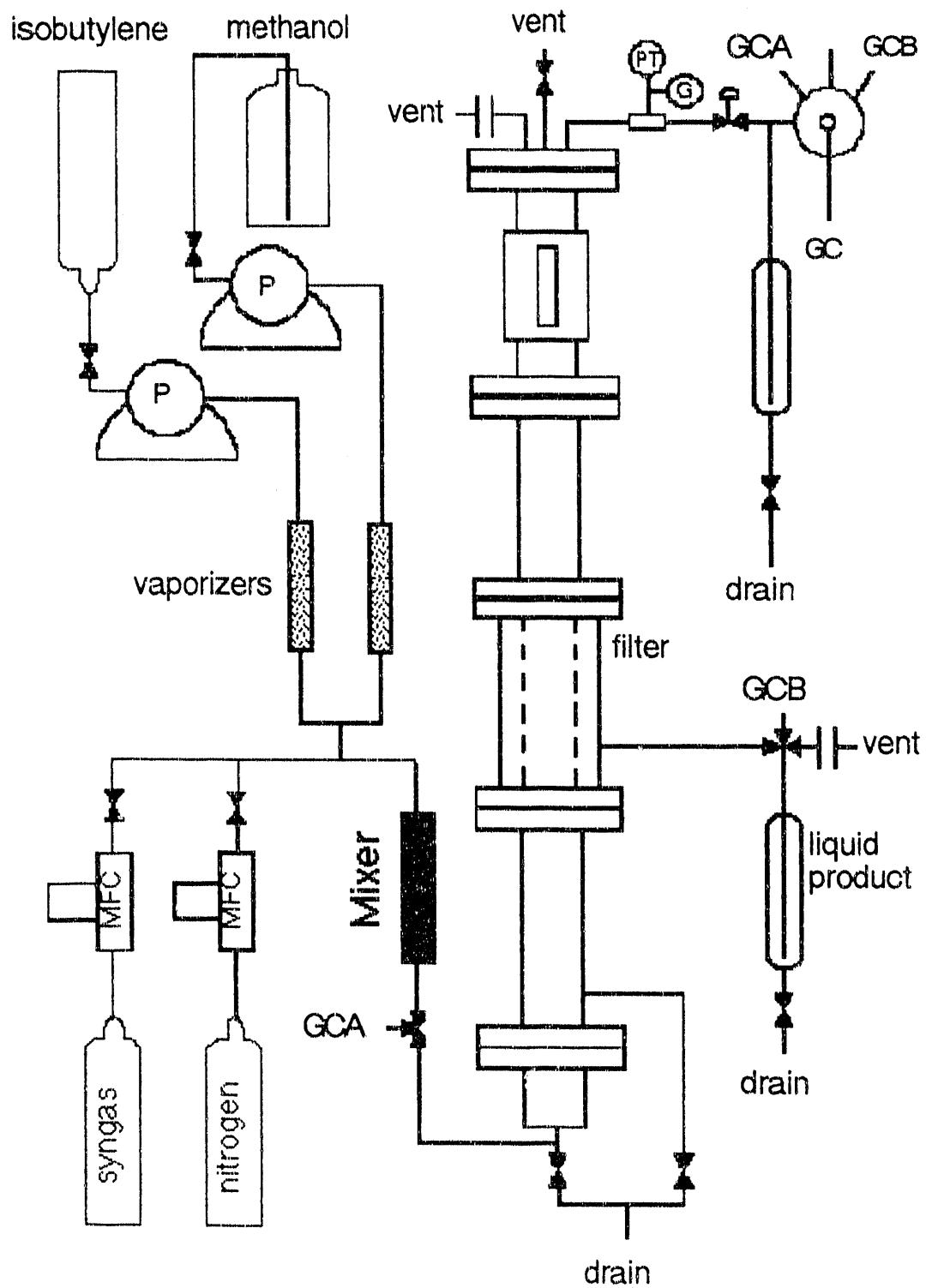
The final reactor is schematically depicted in Figure 1 and a photograph of the system, prior to final insulation, is shown in Figure 2. It consists of a one-inch internal diameter tube of 36" working length and a 2-inch i.d., 12" long disengaging zone with built-in sight glass. A concentric filter arrangement in the middle of the reaction zone is used for filtering the liquid. The gas distributor consists of a plate with three 1-mm holes equally spaced. The reactor is built in flanged sections.

The system is capable of handling two gas feeds and two liquid feeds. Current plans call for using pre-mixed synthesis gas as one of the liquid feeds and an inert diluent as the other. The effluent passes through a gas-liquid separator and the gas is directed to a gas chromatograph for analysis. Liquid products will be taken periodically and analyzed off-line.

Due to cost restrictions, a number of desirable automation features which we identified in the initial design were not included in the final system. Thus, liquid withdrawal and gas sampling into the GC will be performed manually. We also did not include a differential pressure cell for measuring level.

Initial shake-down runs were performed in a cold mode by filling the reactor with hexane to the disengaging zone and starting a nitrogen gas flow corresponding to a linear velocity of 2.5 cm/sec. Approximately 20 g. of alumina powder which had been crushed and sized to 30-80 μm were then introduced into the reactor. The reactor was operated in this mode for about thirty minutes with periodic small withdrawals of liquid. The system performed as expected during this period with no disruptions.

Figure 1: Slurry Bubble Column Reactor



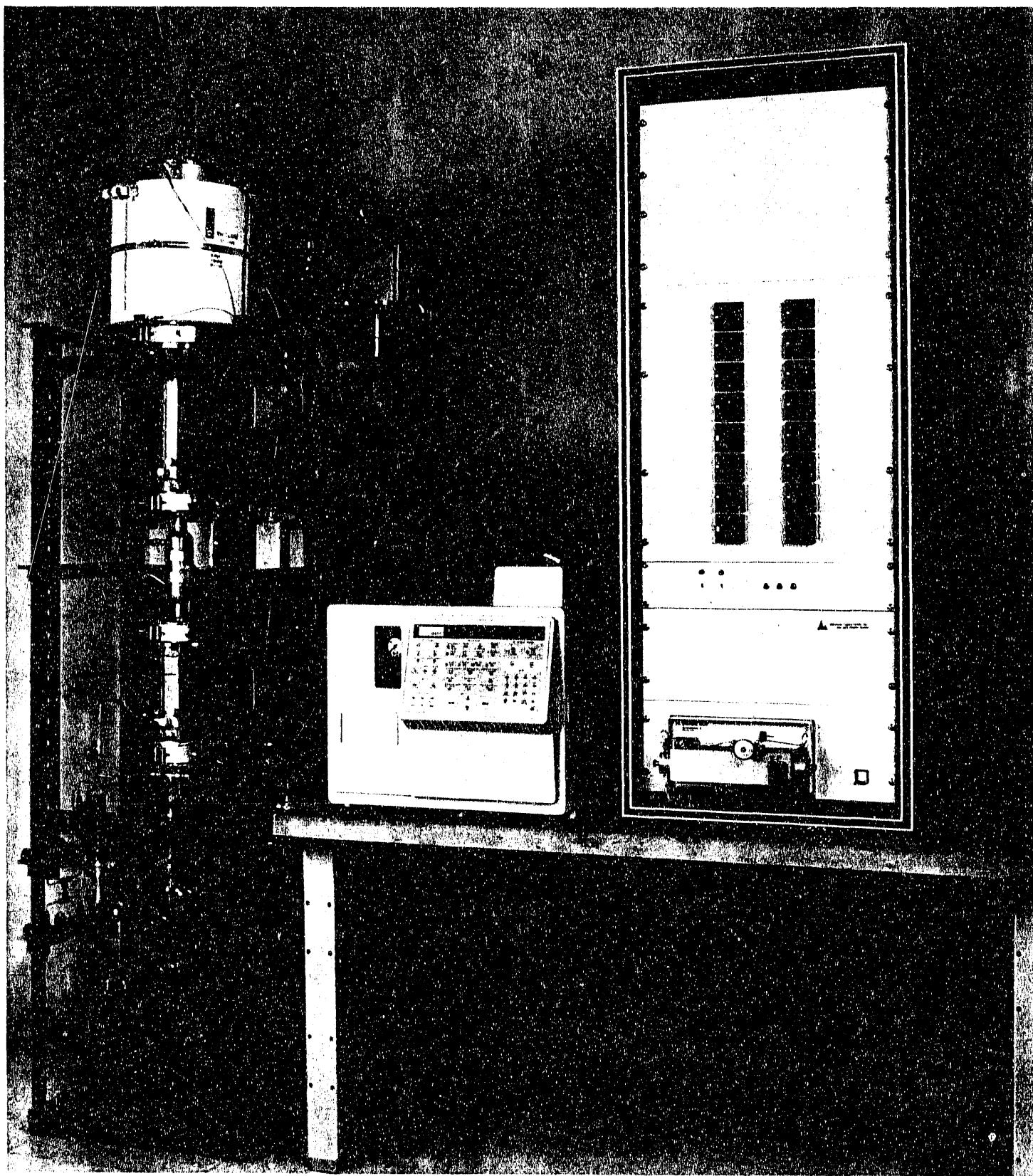


Figure 2.
Photograph of one-inch slurry bubble column reactor.

During a hot shake-down runs some heaters failed. Replacements have been ordered.

2. Gas-Phase Synthesis of MTBE Using Acid Catalysts

INTRODUCTION

In the Fourth and Fifth Quarterly Technical Reports, a screening study of various catalysts for the gas phase MTBE synthesis reaction was presented. These catalysts included a series of HY zeolites with different acidic properties, a silica-alumina catalyst, and the commercially used Amberlyst-15 resin. Based on those results, two catalysts were selected for further evaluation, including runs in the SBCR.

In this report, we conclude the studies on the acid catalysts by further evaluating the deactivation behavior of the selected catalysts during the MTBE synthesis reaction at elevated temperature and by examining the adsorption behavior of methanol (MeOH) and iso-butylene (IB) on the catalysts under conditions similar to those encountered in the reaction. Experiments included adsorption at a given temperature followed by temperature programmed desorption (TPD), along with analysis of the desorption signals obtained. The purpose of the adsorption study was to get a better understanding of the conditions in the vicinity of the reaction sites and to gain a better understanding about the mechanism of the reaction under such conditions.

EXPERIMENTAL

The zeolites studied were the ZSM-5 zeolite, obtained from Air Products, with Si/Al ratio of 15, and an HY zeolite, LZ210-12, obtained from UOP and having a Si/Al ratio of 6. The characteristics of these zeolites were summarized in the Fifth Quarterly Technical Report.

The experimental set-up for the gas phase MTBE synthesis reaction and the procedure followed have been presented in

previous reports. The MTBE synthesis reaction was carried out at 175°C with periodic analysis of the reactor effluent until it reached steady-state. Steady-state was reached typically in three to five hours.

The adsorption of methanol and iso-butylene in the zeolite catalysts were measured at 100°C using the same experimental set-up as in the reaction studies. A mixture of methanol or iso-butylene in helium was passed through the catalyst bed at approximately the same partial pressure and total flow as used during reaction. The adsorption curves at a given temperature were obtained by sampling the gas stream into the GC. The sampling was continued until the effluent concentration remained constant.

The dead-time response of the system was calibrated by performing similar adsorption experiments using methane and iso-butane. These were chosen as they are presumably non-adsorbing on the catalyst surface yet have approximately the same kinetic diameter as methanol and iso-butylene, respectively.

After completion of the adsorption experiment, the system was flushed in 30 ml/min He at 100°C for 30 min. Temperature programmed desorption was then performed by heating up the reactor at a ramp rate of 5°C/min under He flow while continuously monitoring the effluent using the gas chromatograph's FID. Gas samples were taken and analyzed off-line.

RESULTS AND DISCUSSION

Study of MTBE Synthesis at High Temperatures.

In this study, MTBE synthesis was carried out at 175°C in order to observe the deactivation behavior at constant temperature. Since one of the criteria for the selection of catalysts to be used in the SBCR work was the rate of the deactivation, it was deemed desirable to measure the deactivation

of these materials at a temperature comparable to that which will be used in the SBCR runs.

The initial and steady-state results obtained for zeolite LZ210-12 are presented in Table 1. Also presented are similar results obtained in a two-step experiment where the catalyst was first used for two hours at 100°C prior to the measurements at 175°C. The latter results have been presented before in the Fourth Quarterly Technical Report. As can be seen, the two sets of results are very similar, within the limits of experimental error. The minor differences in the selectivity towards some compounds that were observed are most probably due to slight variations in the flow rates of the 2 reactants.

The results for ZSM-5 are presented in Table 2. Similar observations are valid in this case indicating no major influence of the reaction at 100°C on the catalytic behavior of the zeolites at the higher temperatures.

Study of Adsorption Behavior of MeOH and IB over Acid Catalysts.

A typical response curve for the elution of MeOH from zeolite LZ210-12 is shown in Figure 3. The x-axis represents the time from the introduction of methanol; the y-axis is the effluent concentration normalized to the steady-state concentration. A similar response curve for isobutylene is given in Figure 4. Ideally, these curves should be step functions. The deviation observed is caused by two factors: the time response of the system, i.e. the time required for MeOH to travel from the catalyst to the detector and be measured; and the adsorption of MeOH on the catalyst. In both cases, steady-state was reached in approximately 6 minutes. It should be noted that the graphs are not superimposable due to the different steady-state concentration values in the two cases. The difference between these curves and the ideal step function area can be expressed in a molar basis after the time response of the system is taken into account.

Table 1
MTBE Synthesis over Zeolite LZ210-12
Comparison between 1 and 2 step experiments at 175°C

$m = 30-50$ mg. $p = 1$ atm. $T = 175^\circ\text{C}$.

He Flow Rate : 6.5-9.2 cc/min.

IB Flow Rate : 2.9-3.2 cc/min.

IB : MeOH Ratio : 1.8

WHSV : 15-16 h^{-1}

| | 1-step | | 2-step | |
|---------------------------------|--------|----------|--------|----------|
| | Init. | St.State | Init. | St.State |
| MeOH conv. (%) | 8.2 | 4.3 | 8.3 | 4.1 |
| MeOH selectivity to MTBE (%) | 6.3 | 14.2 | 7.1 | 17.7 |
| MTBE yield% | 0.5 | 0.6 | 0.6 | 0.7 |

Product Analysis (mol%) :

Hydrocarbons :

| | | | | |
|-------|------|------|------|------|
| C1-C7 | 8.0 | 0.4 | 4.7 | 0.6 |
| C8 | 57.0 | 37.4 | 69.3 | 59.1 |

Oxygenates :

| | | | | |
|--------|------|------|------|------|
| DME | 29.2 | 45.6 | 21.9 | 27.8 |
| n-PrOH | 0.3 | 0.9 | 0.1 | 0.6 |
| t-BuOH | 0.3 | 0.3 | 0.3 | 0.2 |
| MTBE | 4.0 | 15.4 | 3.4 | 11.7 |
| n-BuOH | 1.2 | 0. | 0.3 | 0. |

Table 2
MTBE Synthesis over Zeolite ZSM-5
Comparison between 1 and 2 step experiments at 175°C

$m = 40$ mg. $p = 1$ atm. $T = 175^\circ\text{C}$.

He Flow Rate : 7.5 cc/min.

IB Flow Rate : 3.2 cc/min.

IB : MeOH Ratio : 1.8

WHSV : 16 h^{-1}

| | 1-step | | 2-step | |
|---------------------------------|--------|----------|--------|----------|
| | Init. | St.State | Init. | St.State |
| MeOH conv. (%) | 14.1 | 2.7 | 18.7 | 3.5 |
| MeOH selectivity to MTBE (%) | 3.4 | 21.3 | 2.7 | 17.2 |
| MTBE yield% | 0.5 | 0.6 | 0.5 | 0.6 |

Product Analysis (mol%) :

Hydrocarbons :

| | | | | |
|-------|------|------|------|------|
| C1-C7 | 2.5 | 0.5 | 2.2 | 1.1 |
| C8 | 51.5 | 61.0 | 41.9 | 51.5 |

Oxygenates :

| | | | | |
|--------|------|------|------|------|
| DME | 41.5 | 23.0 | 51.3 | 31.2 |
| n-PrOH | 1.3 | 2.2 | 1.5 | 2.6 |
| t-BuOH | 0.2 | 0. | 0.3 | 0. |
| MTBE | 3.0 | 13.3 | 2.8 | 13.6 |
| n-BuOH | 0. | 0. | 0. | 0. |

Figure 3.
Response Curve for Methanol
over LZ210-12 at $T = 100^\circ\text{C}$

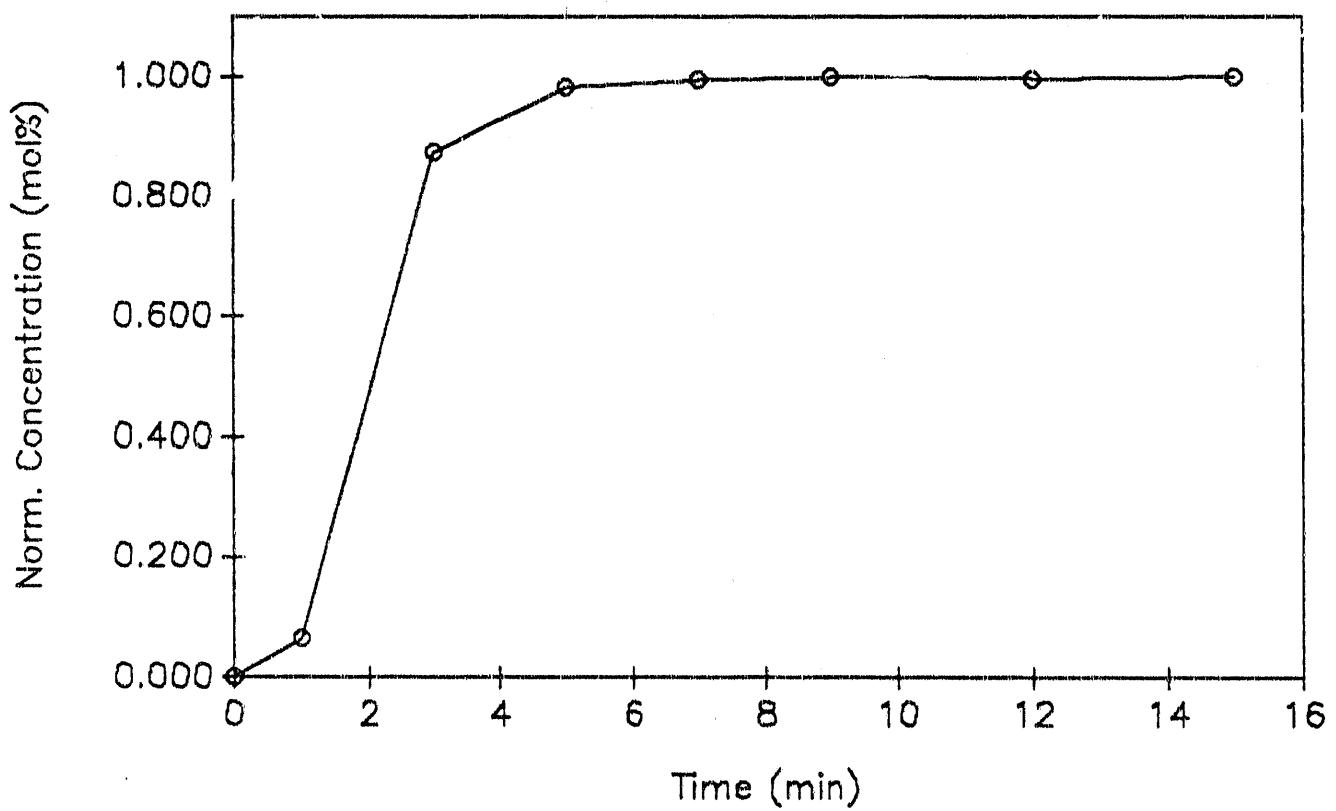
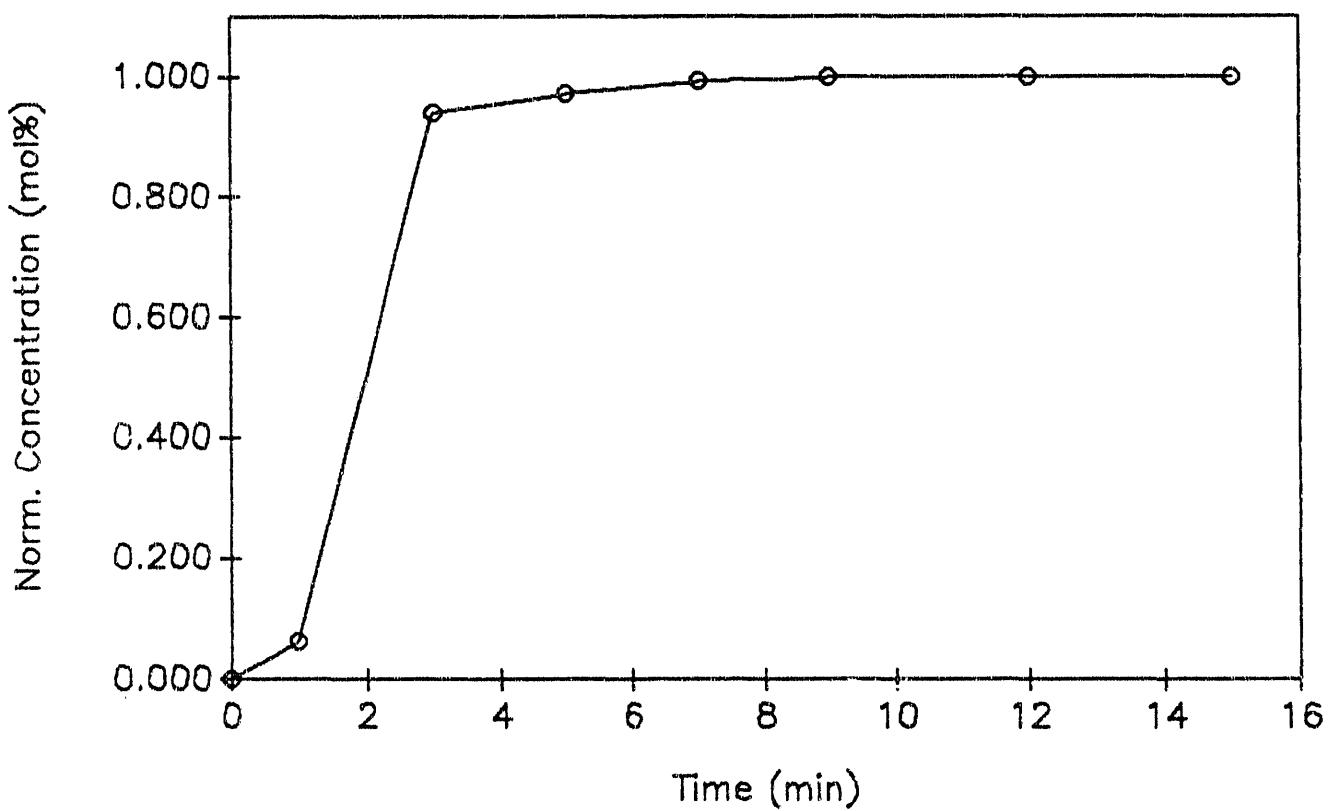


Figure 4.

Response Curve for Isobutylene
over LZ210-12 at $T = 100^\circ\text{C}$



The system time response was measured by carrying out the same experiment using non-adsorbing gases. Methane was used for methanol and iso-butane for iso-butylene in order to simulate the diffusion behavior through the pores. The normalized response curve for methane is shown in Figure 5. Figure 6 shows the absolute response curves for methanol and methane over zeolite LZ210-12. As can be seen, a significant amount of methanol is retained in the catalyst as compared with methane.

Figure 7 shows a similar comparison between i-butylene and i-butane. In this case, the absolute amounts measured were similar, 210 and 190 μmol , respectively, suggesting that there is little or no iso-butylene adsorbed under the conditions studied.

MeOH adsorption experiments were also performed on Amberlyst-15 resin and zeolite ZSM-5 having a Si/Al ratio of 12. The response curve for MeOH over zeolite ZSM-5 is given in Figure 8.

From the amount of MeOH adsorbed, an equivalent liquid volume was calculated. Comparison with the pore volume of 0.33 cc/gr reported for these materials, indicates that there is a 75% saturation of the catalyst pore volume. These results are summarized in Table 3.

By dividing the number of molecules adsorbed by the number of acid sites, which was reported in the Fifth Quarterly Report, a molecular density of adsorption can be calculated. For Amberlyst this corresponds to one MeOH molecule per site, whereas for ZSM-5(12) there are four molecules per site and for LZ210-12 there are two molecules per site if one considers all sites or three if only the accessible sites (as determined by pyridine TPD) are considered. The multiple methanol molecules in the pores of the zeolites suggests that, under reaction conditions, methanol exists as a liquid within the pores.

Similar results have been reported in the literature for alcohols in ZSM-5 zeolites (1,2). Gorte and co-workers found 70%

Figure 5.
Response Curve for Methane
over LZ210-12 at $T = 100^\circ\text{C}$

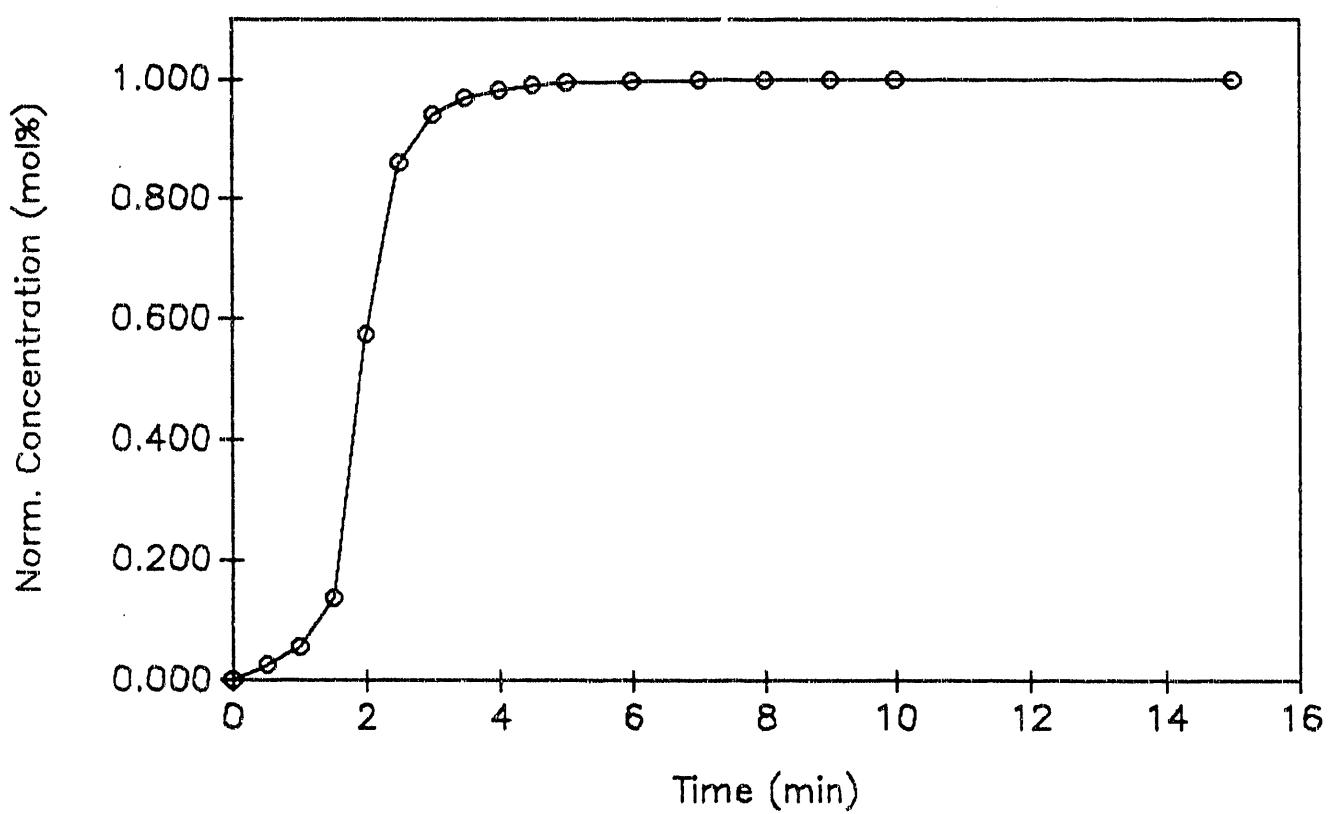


Figure 6.
Response Curve for Methanol & Methane over LZ210-12

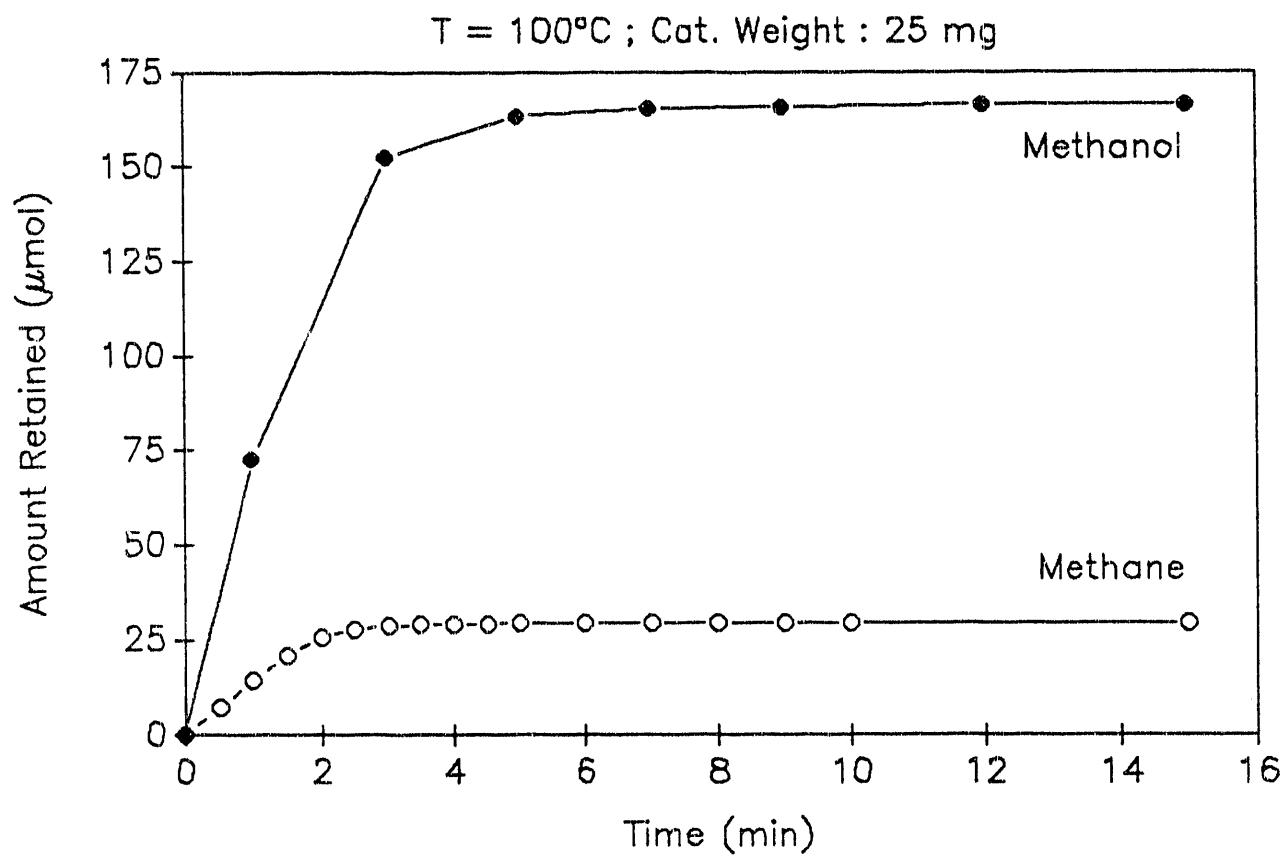


Figure 7.
Response Curve for i-butene & i-butane over LZ210-12

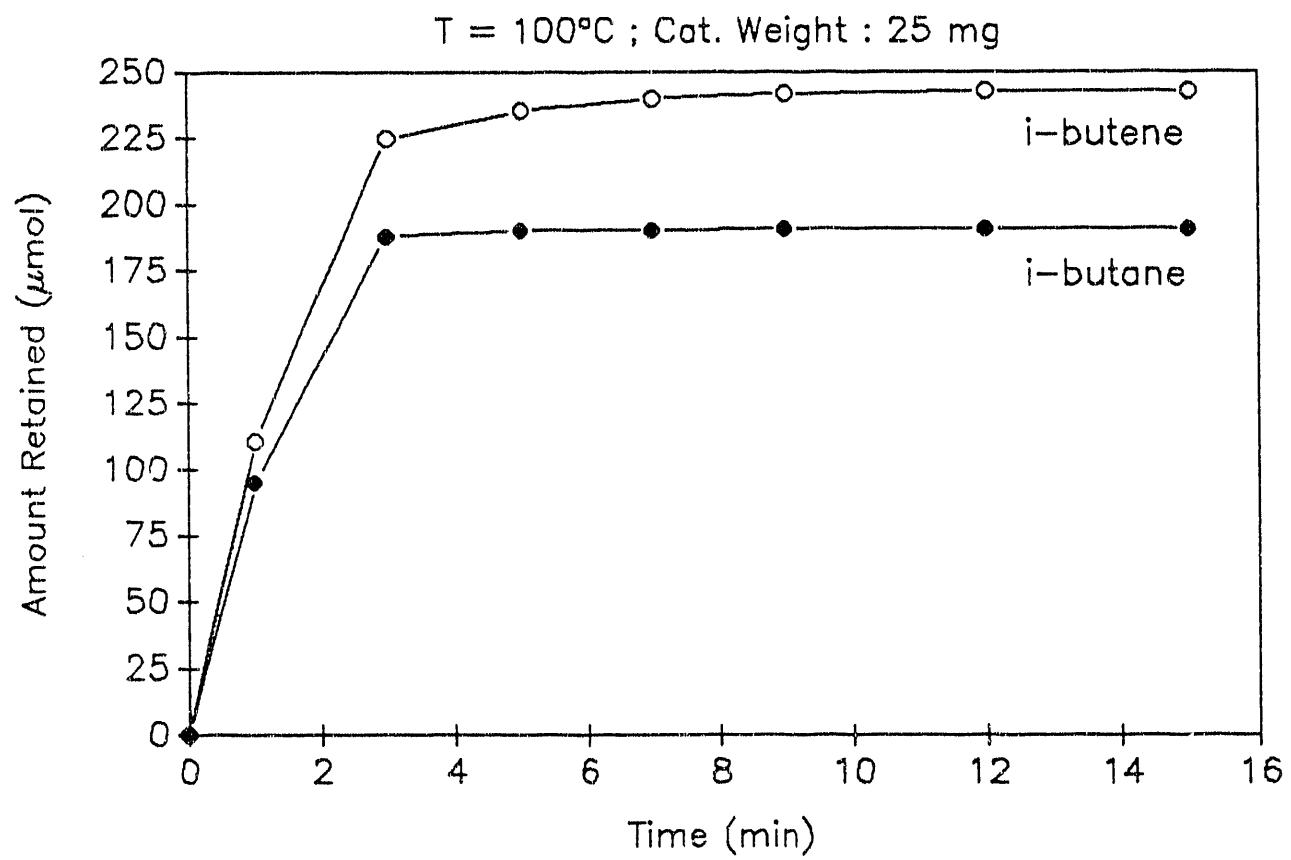


Figure 8.
Response Curve for Methanol & Methane over ZSM-5(12)
 $T = 100^{\circ}\text{C}$; Cat. Weight : 25 mg

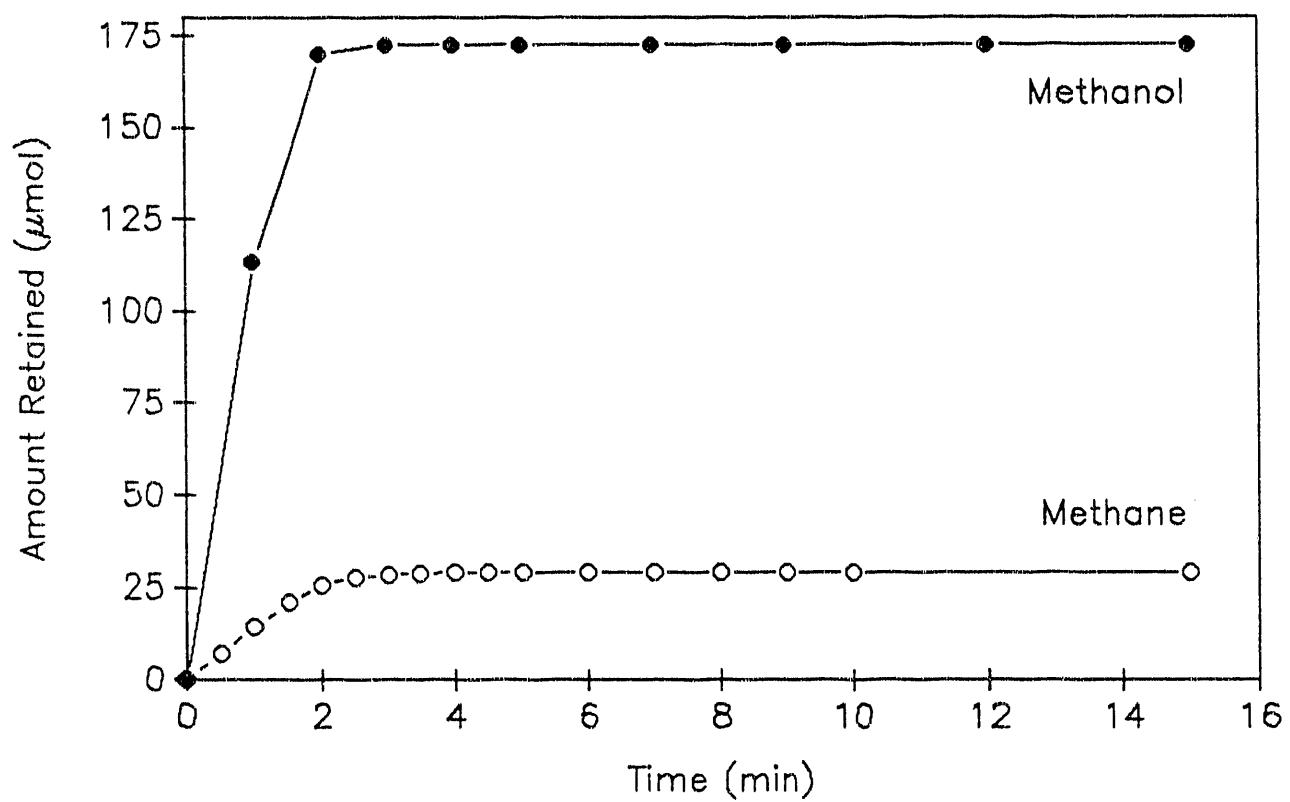


Table 3.
Adsorption of Methanol at 100°C
over various catalysts.

| | Amount ads. (mmol/gr) ^a | Vads. liq. (ml/gr) ^b | MeOH molec. per site ^c | MeOH molec. per Pyr. site ^d |
|-----------|---------------------------------------|------------------------------------|--------------------------------------|---|
| LZ210-12 | 5.2 | 0.24 | 2.1 | 3.1 |
| Amberlyst | 5.2 | 0.24 | 1.1 | -- |
| ZSM-5 | 5.6 | 0.26 | 4.4 | -- |

- a. Amount of MeOH adsorbed, based on the difference of response curves of MeOH and methane.
- b. Equivalent liquid volume of amount adsorbed. Catalyst pore volume : 0.33 cc/gr.
- c. Number of MeOH molecules adsorbed per acid site (based on Si/Al ratio).
- d. Number of MeOH molecules adsorbed per acid site (based on Pyridine TPD data).

saturation of the pores with MeOH at room temperature and a partial pressure of 10 torr.

The desorption behavior of the catalysts was examined using TPD of the adsorbed methanol. The TPD curves for LZ210-12 and ZSM-5(12) are shown in Figures 9 and 10, respectively. For LZ210-12, three desorption peaks were observed, at 180, 240 and 275°C. Analyses of the effluent was performed at approximately the peak maxima and are listed in Table 4. The low temperature peak was composed solely of MeOH and DME, whereas both the second and the third peaks contained significant amounts of olefins (mainly C2, C3 and C4). The peak at ca. 240°C was very sharp. This temperature corresponds to the critical temperature of MeOH and suggests that a strongly adsorbed species desorbs at this temperature.

The TPD of MeOH over ZSM-5(12) did not exhibit a desorption peak at 180°C, but gave a very sharp peak at 240°C with a shoulder at about 250°C. The amount of MeOH desorbing at 240°C is larger than in the case of the LZ210-12 zeolite, probably because it includes the MeOH that did not desorb at lower temperatures. The absence of the lower temperature signal may be attributed to the different acid strength of the sites between the two zeolites, their different pore structure, or a combination of these factors.

These results seem to suggest that there might be at least 2 types of sites for MeOH adsorption in the case of LZ210-12, a weaker one forming preferentially DME and a strong one forming olefins. However, for ZSM-5(12), the sites seem to be of uniform strength.

REFERENCES

1. A. Ison, R. J. Gorte, The Adsorption of Methanol and Water on H-ZSM-5, *J. Catal.*, 89, (1984) 150.

Figure 9.

Temperature Programmed Desorption of Methanol
over zeolite LZ210-12 ; Ramp rate : 5°C/min

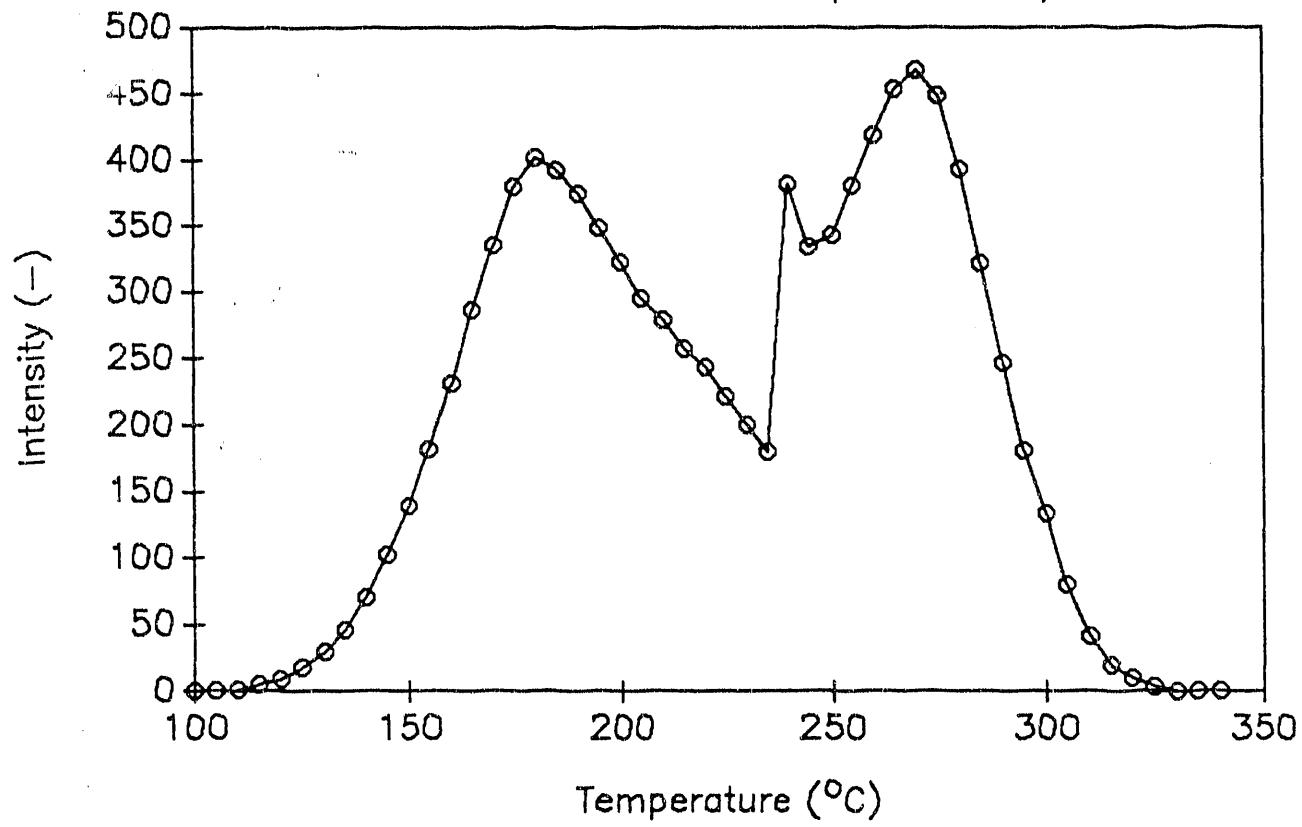


Figure 10.
Temperature Programmed Desorption of Methanol
over zeolite ZSM-5(12) ; Ramp Rate : 5°C/min

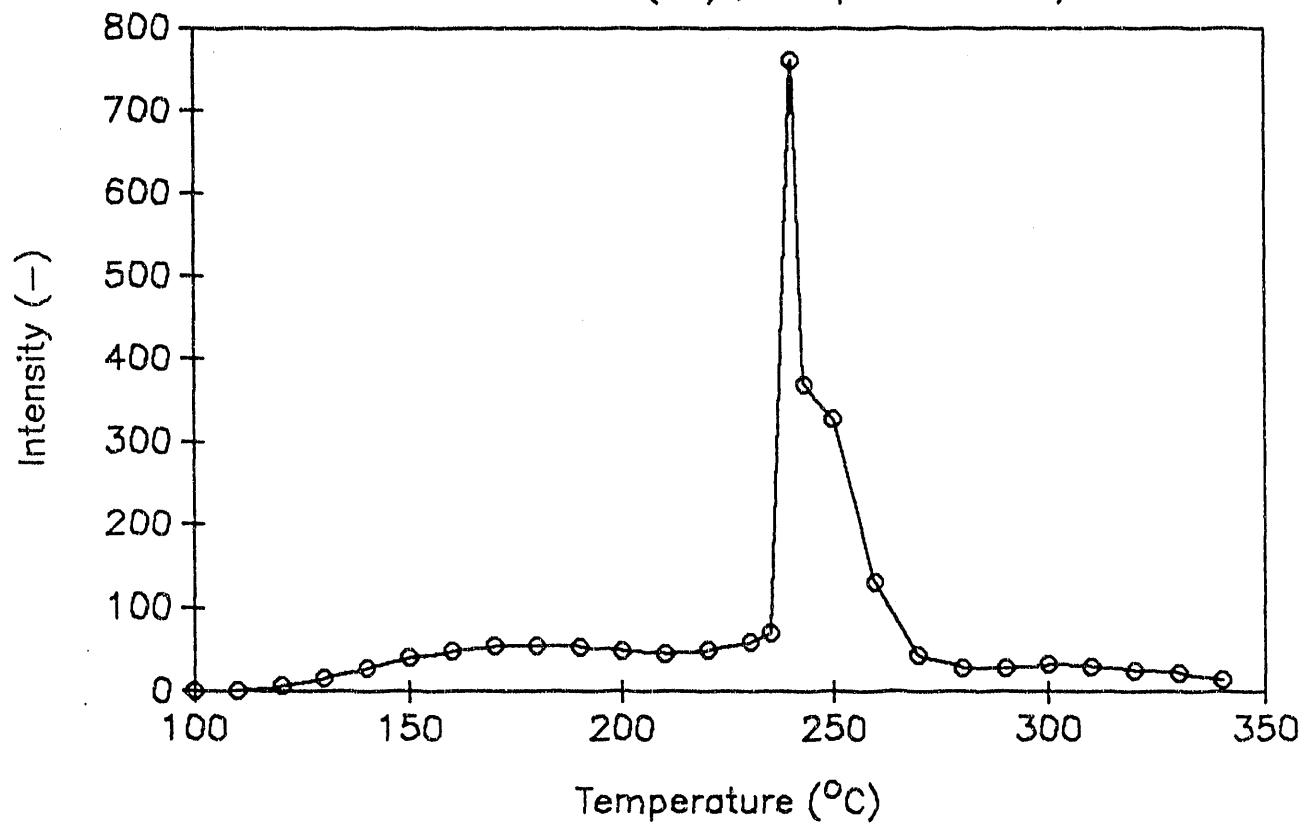


Table 4
Effluent Analysis During TPD Experiments

| Temperature: | -----LZ210-12----- | | | ZSM-5 |
|-----------------------------|--------------------|-----|-----|-------|
| | 190 | 240 | 275 | 250 |
| <u>Product Analysis (%)</u> | | | | |
| Methanol | 81 | 50 | 46 | 13 |
| Dimethyl ether | 19 | 30 | 6 | 38 |
| Paraffins (C1-C5) | 0 | 4 | 3 | 4 |
| Olefins (C2-C5) | 0 | 16 | 45 | 45 |

2. M. T. Aronson, R. J. Gorte, W. E. Farneth, The Influence of Oxonium Ion and Carbenium Ion Stabilities on the Alcohol/H-ZSM-5 Interaction, *J. Catal.*, 98, (1986) 434.

3. Work Planned for Next Quarter

Work for next quarter will concentrate in the SBCR runs for the synthesis of MTBE from iso-butylene and methanol, and the continuation of studies involving the addition of isobutylene during the synthesis of alcohols.

END

DATE
FILMED
10/20/92