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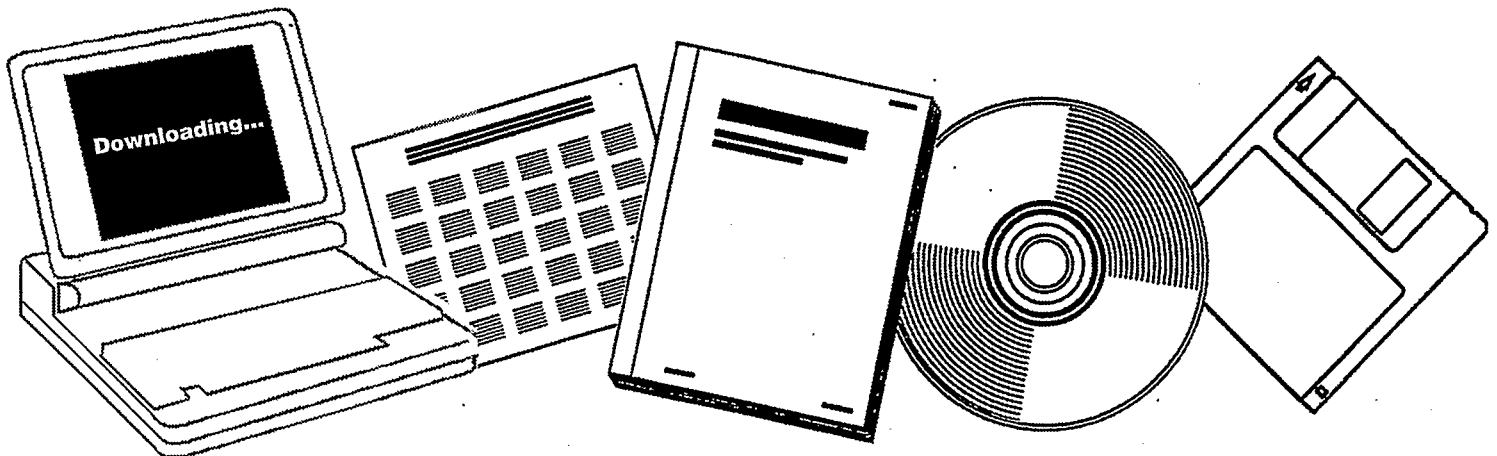
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**SYNTHESIS OF OCTANE ENHANCER DURING
SLURRY-PHASE FISCHER-TROPSCH. QUARTERLY
TECHNICAL PROGRESS REPORT NO. 4, JULY 1,
1991--SEPTEMBER 30, 1991**

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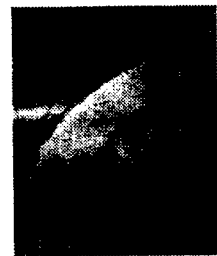
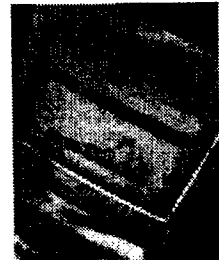
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QUARTERLY TECHNICAL PROGRESS REPORT No. 4

Covering the Period July 1, 1991 to September 30, 1991

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

Prepared for the U.S. Department of Energy Under
Contract No. AC-RA22-90PC90047.

December 15, 1991

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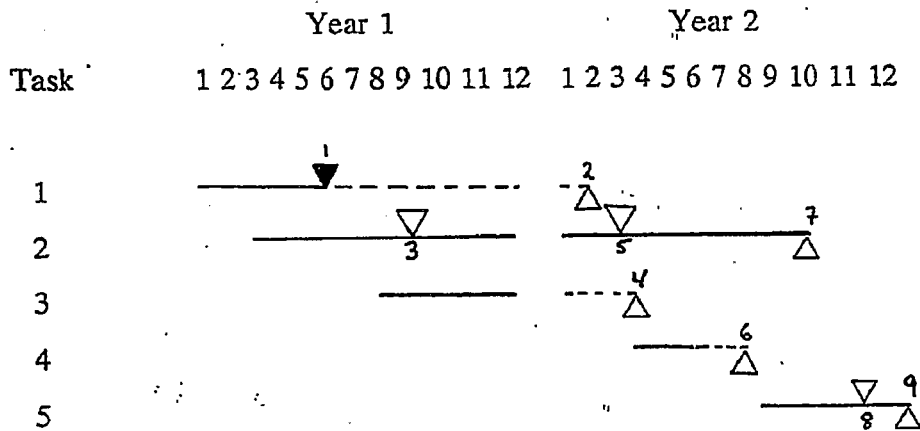
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TABLE OF CONTENTS

Planned Task and Milestone Schedule1
Objectives.....2
Work Accomplished This Quarter2
Fourth Quarter's Technical Report3
 Introduction3
 Experimental3
 Results and Discussion5
 Detection of MTBE and MIBE20
 Catalyst Selection23
Work Planned for Next Reporting Period23
References.....24

PLANNED TASK AND MILESTONE SCHEDULE



M = denotes milestone

List of Milestones

Milestone

<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

Work during the fourth quarter concentrated in the completion of the screening of the acid catalysts for the conversion of syngas-produced alcohols and isobutylene to MTBE (scheme 2). This subtask is now nearly complete and one catalyst has been selected for SBCR testing. Other tasks have been delayed due to equipment problem. The construction of the SBCR continues to be nearly complete, but full testing has not been finalized.

Tasks 3, 4, and 5 are awaiting completion of the SBCR system.

FOURTH QUARTER'S TECHNICAL REPORT

INTRODUCTION

Work this past quarter concentrated in comparing various acid catalysts, primarily zeolites, in terms of their catalytic properties for the gas phase synthesis of MTBE. This report presents the experimental data obtained with respect to their activity, selectivity, and lifetime, along with some preliminary conclusions relating their properties and a study of the effect of certain system parameters (e.g. space velocity) to the results obtained.

EXPERIMENTAL

A total of five solid acid catalysts have been evaluated this quarter for the gas-phase synthesis of MTBE. These consist of four H-Y zeolites with different Si/Al ratio and different acidities and one amorphous silica-alumina catalyst (Si-Al-O). The ion exchange resin Amberlyst-15 which is the commercially used MTBE-synthesis catalyst has also been studied previously and those results were reported in the Third Quarter's Technical Report.

The reaction was studied in the gas-phase using a fixed-bed reactor. Two important changes have been made to the experimental set-up since the last report. The first is the addition of a line pressure regulator for the isobutylene (IBu) in order to eliminate any fluctuations in the IBu pressure. The second change is the incorporation of a glass frit in the reactor onto which the catalyst bed is placed. Except for the experiment involving catalyst S(LZ12)8, all experiments were performed with this reactor type. In order to compensate for the increased flow resistance caused by the glass frit, the catalyst mass was reduced and the gas flow rates were adjusted to maintain a constant space velocity. A schematic of the fixed-bed reactor is shown in Figure 1.

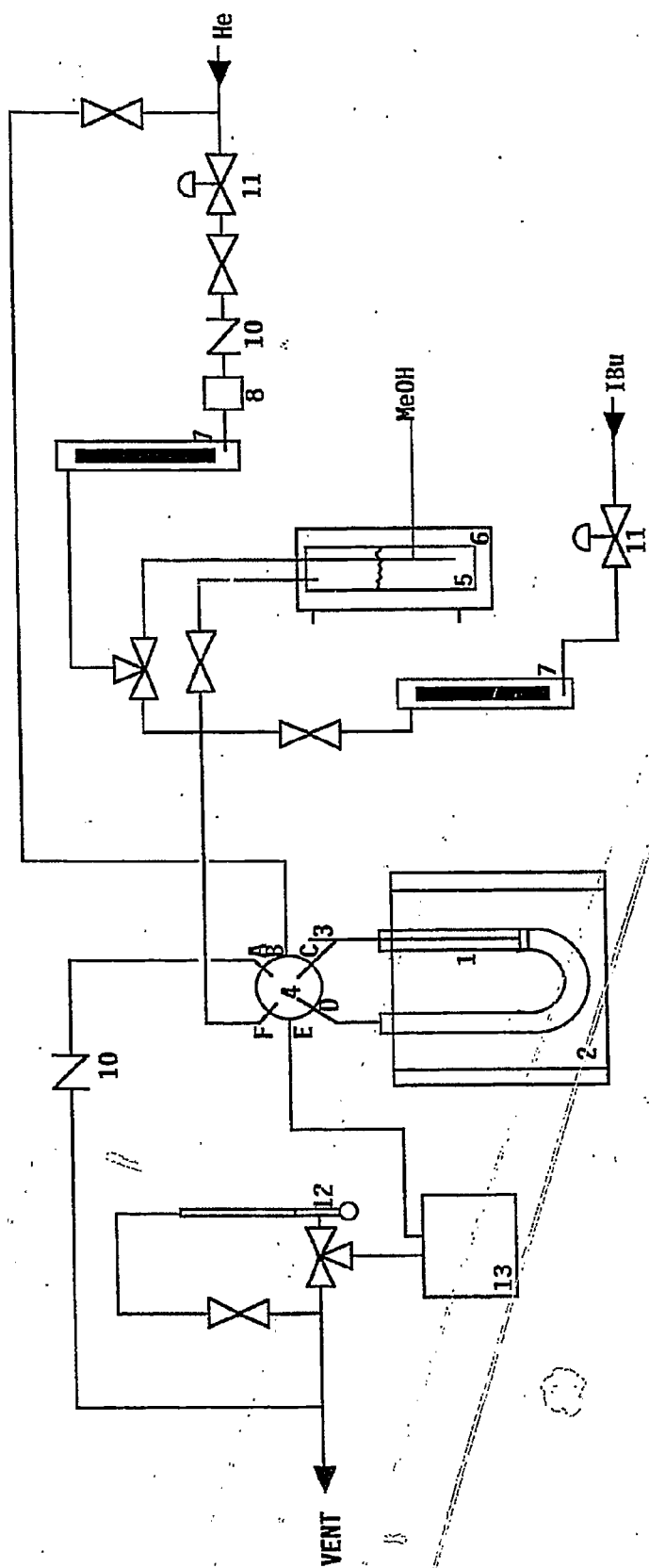


FIGURE 1. GAS PHASE MTBE SYNTHESIS SYSTEM

- | | | | |
|----|---------------|-----|--------------------------|
| 1. | Reactor. | 9. | Needle Valve. |
| 2. | Furnace. | 10. | Check Valve. |
| 3. | Thermocouple. | 11. | Line Pressure Regulator. |
| 4. | 6-port Valve. | 12. | Bubble Flowmeter |
| | | 5. | Saturator. |
| | | 6. | Heat Bath. |
| | | 7. | Rotometer. |
| | | 8. | Mass Flow Controller. |

Prior to the start of the reaction the catalysts were heated in-situ from room temperature to 400°C at 2°C/minute and held at the upper temperature for 12 hours in a 40 mL/min flow of helium. Each experiment typically consisted of measurements at 100°C, 175°C, 230°C, and 100°C, in that order. Product analyses were obtained at each temperature after 5 minutes, and approximately every hour thereafter for about four hours. In all cases a steady-state activity was reached very quickly and remained constant for the duration of the experiment. Other reaction conditions were as follows: IBu/MeOH = 2; WHSV = 4 - 15; P = 1 atmosphere (nominally). These conditions were chosen so as to obtain methanol conversions between 2 and 10%. The IBu/MeOH ratio is higher than used commercially. However, it is more representative of the relative concentrations that will be found in the proposed reaction schemes.

RESULTS AND DISCUSSION

Tables 1 through 5 summarize the catalytic behavior of the five catalysts at steady-state (i.e. more than two hours on-stream). In general all catalysts were highly active with the amorphous Si-Al-O being the least active. In the initial stages of the reaction, i.e. after five minutes, a wide variety of products were observed, including significant amounts of hydrocarbons formed presumably by cracking reactions. These hydrocarbon products disappeared quickly, however, and after 60 minutes on stream three major products were found, mainly MTBE, dimethyl ether (DME), and the C8 isobutylene dimer. These major products accounted for greater than 97% of all products at steady state. Table 6 compares the initial and steady-state product analyses for catalyst LZ210-12 at each of the temperatures studied.

Figures 2 through 6 shows how the overall conversion and MTBE yield varied with time on stream. The high methanol conversion observed at first for the zeolites may actually be an artifact due to the finite time of diffusion of the methanol into the pores of the zeolites. Also shown in the figures as a solid line, is the predicted equilibrium yield of MTBE based on the initial methanol to isobutylene ratio and assuming only gas phase reaction. It can be

Table 1. MTBE Synthesis over Zeolite S (LZ 12) 8

He Flow Rate : 15 cc/min.

IB Flow Rate : 7 cc/min.

IB : MeOH Ratio : 1.7

WHSV : 14 (gr/gr cat. *h)

Temp. (°C)	100	175	250	100
MeOH conv.%	10.1	3.0	4.1	1.25
MTBE prod.% of MeOH	99.85	42.7	3.25	100.
MTBE yield%	10.1	1.3	0.13	1.25

Product Analysis (mol%) :

Hydrocarbons :

C1	0.1	0	0	0
C2	0.1	0.2	0.4	0
C3	0	0.1	0.2	0
C5	0.1	0.5	0.3	0
C6	0.3	0	0	0
C7	0	0	0	0
C8	2.1	52.7	49.6	0

Oxygenates :

DME	0	18.6	43.2	0
t-BuOH	0.1	0	0	0
MTBE	97.2	27.9	3.0	100

Table 2. MTBE Synthesis over Zeolite Y62.

He Flow Rate : 12 cc/min.

IB Flow Rate : 4 cc/min.

IB : MeOH Ratio : 1.8

WHSV : 17 (gr/gr cat. *h)

Temp. (°C)	100	175	230	100
MeOH conv.%	12.4	2.0	2.3	0.9
MTBE prod.% of MeOH	99.05	36.5	7.25	97.5
MTBE yield%	12.3	0.7	0.16	0.9

Product Analysis (mol%) :

Hydrocarbons :

C1	0	0.2	0.6	0
C2	0	0.1	0.2	0
C3	0	0.2	0.1	0
C5	0	0.1	0	0
C6	0	0	0	0
C7	0	0	0	0
C8	3.7	49.7	50.8	0.6

Oxygenates :

DME	0	21.7	37.3	0
n-Propanol	0	1.1	4.8	0
t-BuOH	0.9	0.5	0	2.4
MTBE	95.4	26.4	6.2	97

Table 3. MTBE Synthesis over Zeolite LZ210-12

He Flow Rate : 11 cc/min.

IB Flow Rate : 4 cc/min.

IB : MeOH Ratio : 1.8

WHSV : 16 (gr/gr cat. *h)

Temp. (°C)	100	175	230	100
------------	-----	-----	-----	-----

MeOH conv.%	12.6	4.1	2.2	3.9
-------------	------	-----	-----	-----

MTBE prod.% of MeOH	98.65	17.0	4.5	97.3
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MTBE yield%	12.5	0.7	0.16	3.8
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Product Analysis (mol%) :

Hydrocarbons :

C1	0	0.2	0.5	0
C2	0	0.1	0.2	0
C3	0	0	0.1	0
C5	0	0.2	0.5	0
C6	0	0.1	0.1	0
C7	0	0	0	0
C8	2.5	59.1	65.1	0.8

Oxygenates :

DME	0	27.8	28.4	0
n-Propanol	0	0.6	2.8	0
t-BuOH	1.4	0.2	0	2.6
MTBE	96.1	11.7	2.3	96.6

Table 4. MTBE Synthesis over Zeolite Y82

He Flow Rate : 11 cc/min.

IB Flow Rate : 4 cc/min.

IB : MeOH Ratio : 1.8

WHSV : 16 (gr/gr cat. *h)

Temp. (°C)	100	175	230	100
------------	-----	-----	-----	-----

MeOH conv.%	7.9	3.7	3.7	1.3
MTBE prod.% of MeOH	99.05	18.0	2.9	98.6
MTBE yield%	7.95	0.7	0.1	1.3

Product Analysis (mol%) :

Hydrocarbons :

C1	0	0.1	0.5	0
C2	0	0.2	0.6	0
C3	0	0	0.3	0
C5	0	0.2	0	0
C6	0	0	0	0
C7	0	0	0	0
C8	1.4	40.5	39.6	0.9

Oxygenates :

DME	0	39.3	47.0	0
n-Propanol	0	1.5	8.8	0
t-BuOH	0.9	0.3	0	1.1
MTBE	97.7	17.9	3.29	98.0

Table 5. MTBE Synthesis over Silica-Alumina

He Flow Rate : 12 cc/min.

IB Flow Rate : 5 cc/min.

IB : MeOH Ratio : 1.8

WHSV : 18 (gr/gr cat. *h)

Temp. (°C)	100	175	230	100
MeOH conv. %	5.6	1.8	13.5	1.6
MTBE prod. % of MeOH	99.5	36.0	0.7	99.0
MTBE yield %	5.6	0.7	0.1	1.6

Product Analysis (mol%) :

Hydrocarbons :

C1	0	0	0	0
C2	0	0	0	0
C3	0	0	0	0
C5	0	0	0	0
C6	0	0	0.2	0
C7	0	0	0	0
C8	0.9	64.2	30.8	0.7

Oxygenates :

DME	0	15.0	58.8	0
n-Propanol	0	2.1	9.1	0
t-BuOH	0.4	0.3	0.1	1.2
MTBE	98.7	18.4	0.9	98.1

Table 6. Comparison between initial and steady-state product distribution for zeolite LZ210-12. Reaction conditions as in Table 3.

Temp. (°C)	100		175		230		100	
	In.	S.S.	In.	S.S.	In.	S.S.	In.	S.S.
<u>Hydrocarbons :</u>								
C1	0.	0.	0.	0.2	0.2	0.5	0.	0.
C2	0.	0.	0.6	0.1	1.3	0.2	0.	0.
C3	0.1	0.	0.7	0.	0.9	0.1	0.3	0.
Isobutene	0.	0.	0.	0.	1.9	0.	0.	0.
C5	0.6	0.	2.6	0.2	2.2	0.5	0.	0.
C6	0.2	0.	0.8	0.1	1.1	0.1	0.	0.
C7	0.	0.	0.	0.	0.	0.	0.	0.
C8	0.3	0.	4.7	2.1	14.3	5.8	0.	0.
DIB	8.8	2.5	64.6	57.0	44.5	59.3	1.1	0.8
<u>Oxygenates :</u>								
DME	0.	0.	21.9	27.8	32.5	28.4	0.	0.
iso-Propanol	0.	0.	0.1	0.	0.1	0.	0.	0.
n-Propanol	0.	0.	0.	0.6	0.	2.8	0.	0.
t-BuOH	0.5	1.4	0.3	0.2	0.1	0.	0.4	2.6
s-BuOH	0.	0.	0.	0.	0.1	0.	0.	0.
MTBE	89.5	96.1	3.4	11.7	0.8	2.3	98.2	96.6
n-BuOH	0.	0.	0.3	0.	0.	0.	0.	0.

FIGURE 2
 MTBE Synthesis over Zeolite S(LZ 12)8

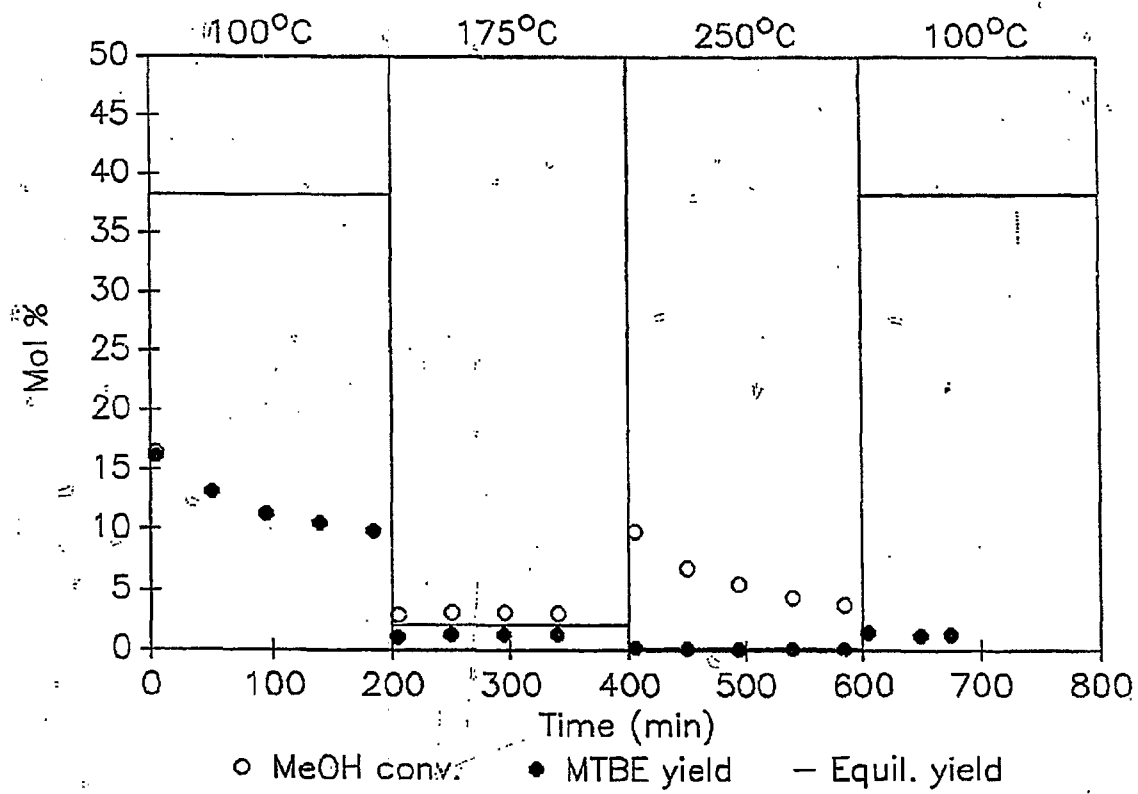


FIGURE 3
MTBE Synthesis over Zeolite Y62

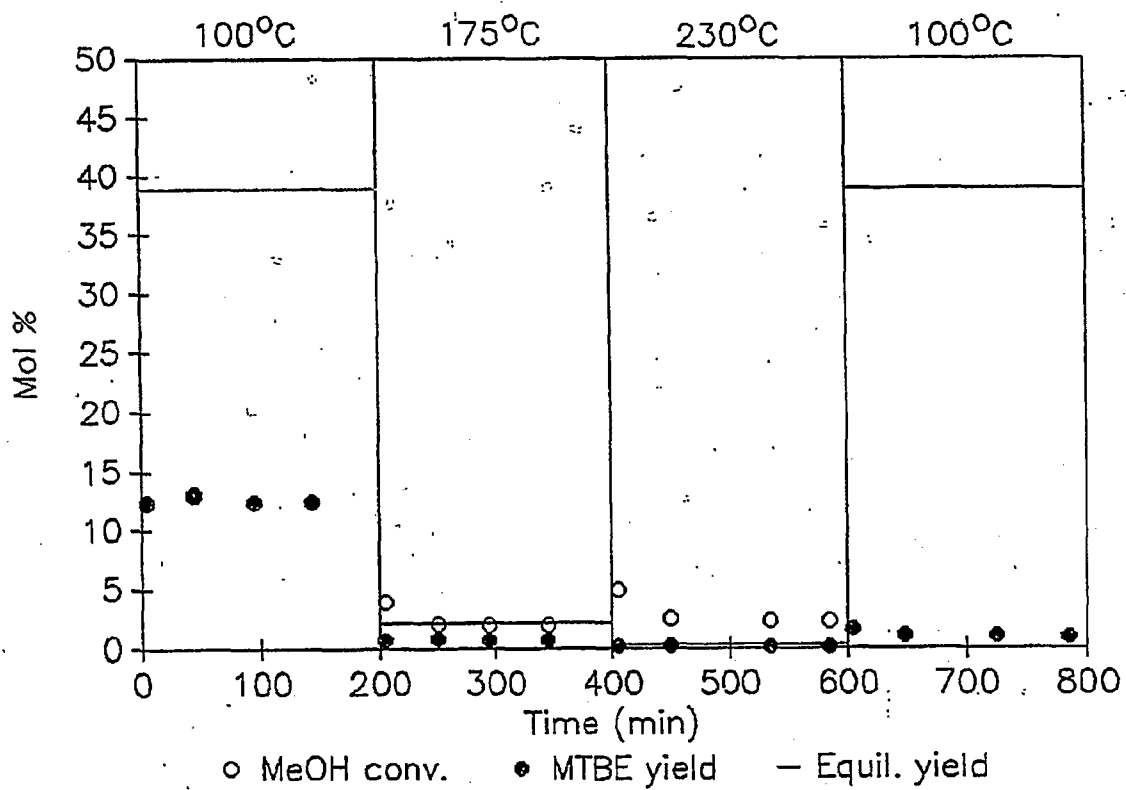


FIGURE 4
MTBE Synthesis over Zeolite LZ 210 12

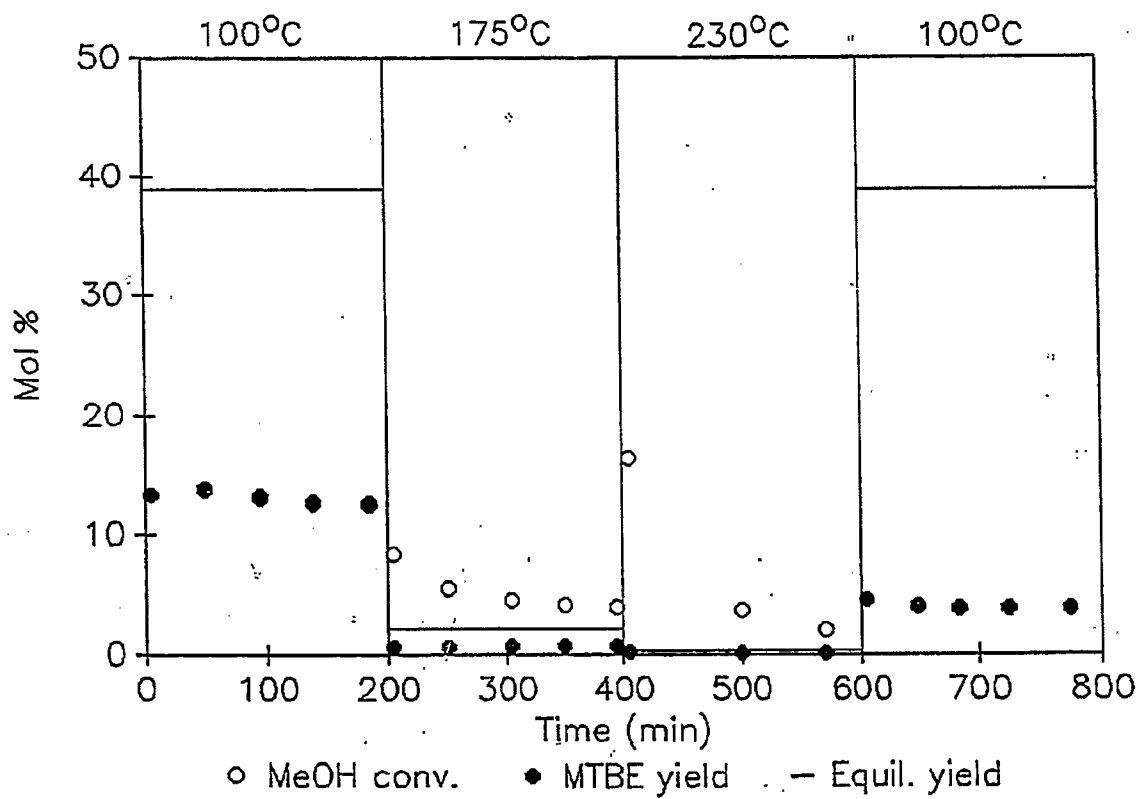


FIGURE 5
MTBE Synthesis over Zeolite Y82

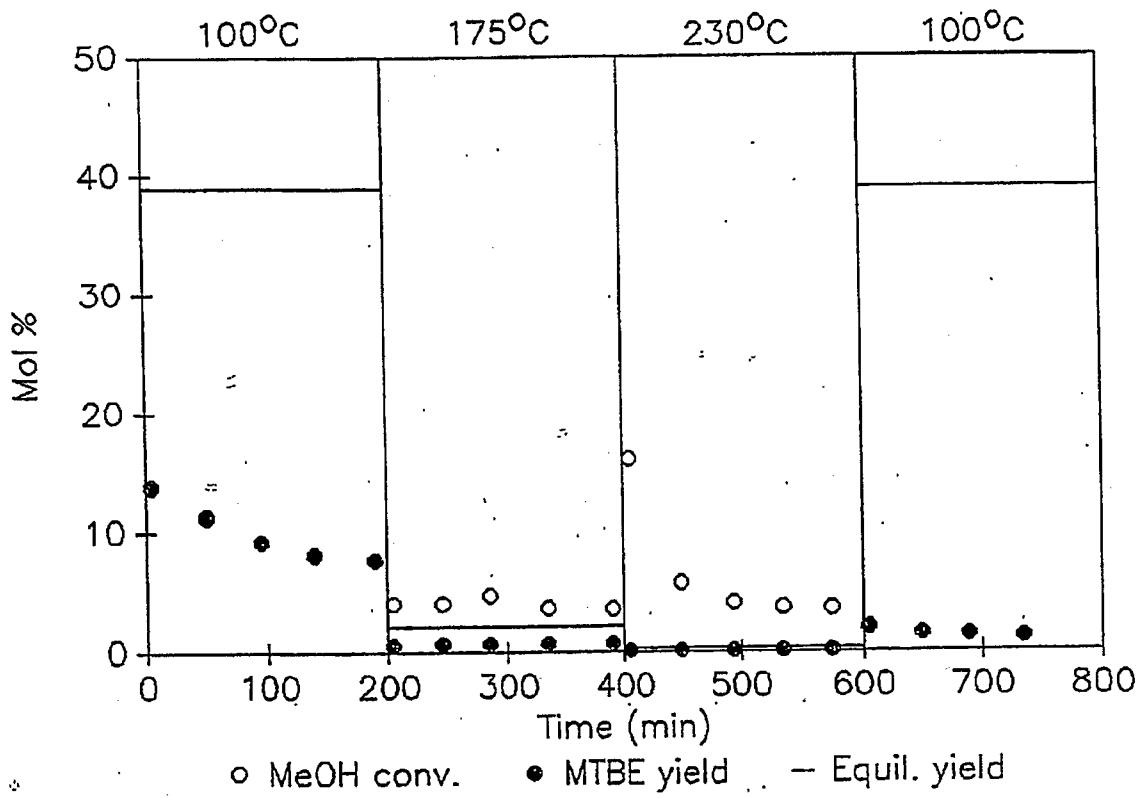
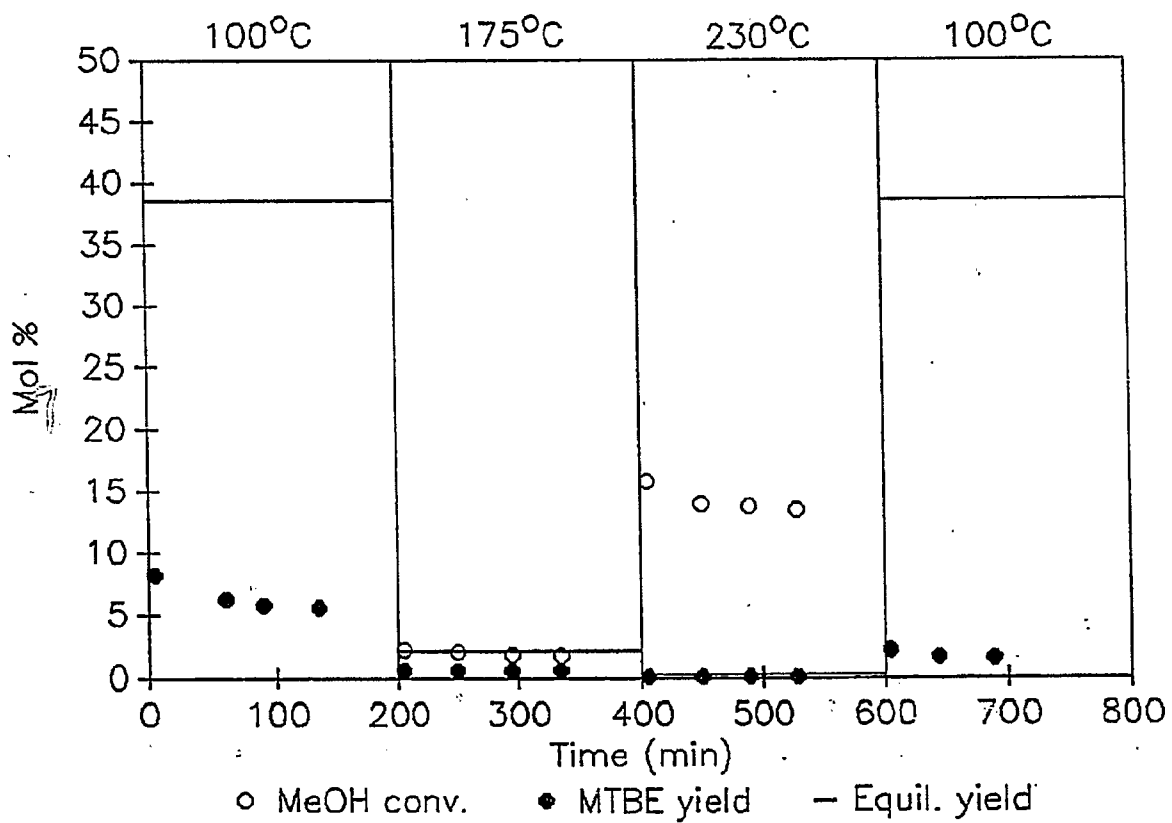


FIGURE 6
MTBE Synthesis over Silica-Alumina



seen that at these space velocities and at the higher temperatures, the observed MTBE yield is very nearly that predicted by the equilibrium calculation, indicating a predominant control of the reactions.

Table 7 summarizes the acid characteristics and the catalytic behavior of the zeolites. One important empirical parameter that is reported in this table is a deactivation coefficient which is defined as the difference in MeOH conversion at 100°C between the start and end of the experiment divided by the initial 100°C conversion value. Thus, the numbers obtained range between zero and one and represent the deactivation of each of the catalysts studied. The closer to unity the value of the coefficient is, the higher the deactivation of the catalyst.

It can be noted from Table 7, that zeolite LZ210-12 has the most desirable catalytic properties, showing high methanol conversion, high MTBE yield, and the lowest deactivation coefficient. The Si-Al-O material also exhibited low deactivation but conversion and MTBE yield were very small. Zeolites S(LZ12)8 and Y82 both show intermediate behavior, while zeolite Y62 appears to be the least desirable, showing both low methanol conversion and a high deactivation coefficient.

From the comparison of the results presented in Table 7 some generalizations can be made concerning the role of acidity to the reaction. Based only on the initial 100°C data, zeolites LZ210-12 and Y62 show the highest MTBE yields and Si-Al-O the lowest (the selectivities are all approximately the same). The low value for Si-Al might suggest that a low acid strength is not favorable for the reaction. However, Y62 also has a relatively low acid strength (although not as low as Si-Al-O) and it exhibited a high MTBE yield. Additionally, both Y-82 and S(LZ 12)8 which have the highest acid strengths exhibited lower yields. Thus, this study suggests that an intermediate acid strength is required for optimum MTBE synthesis. Unfortunately, similar comparisons cannot be made with the commercial Amberlyst-15 since it is structurally unstable above 100°C.

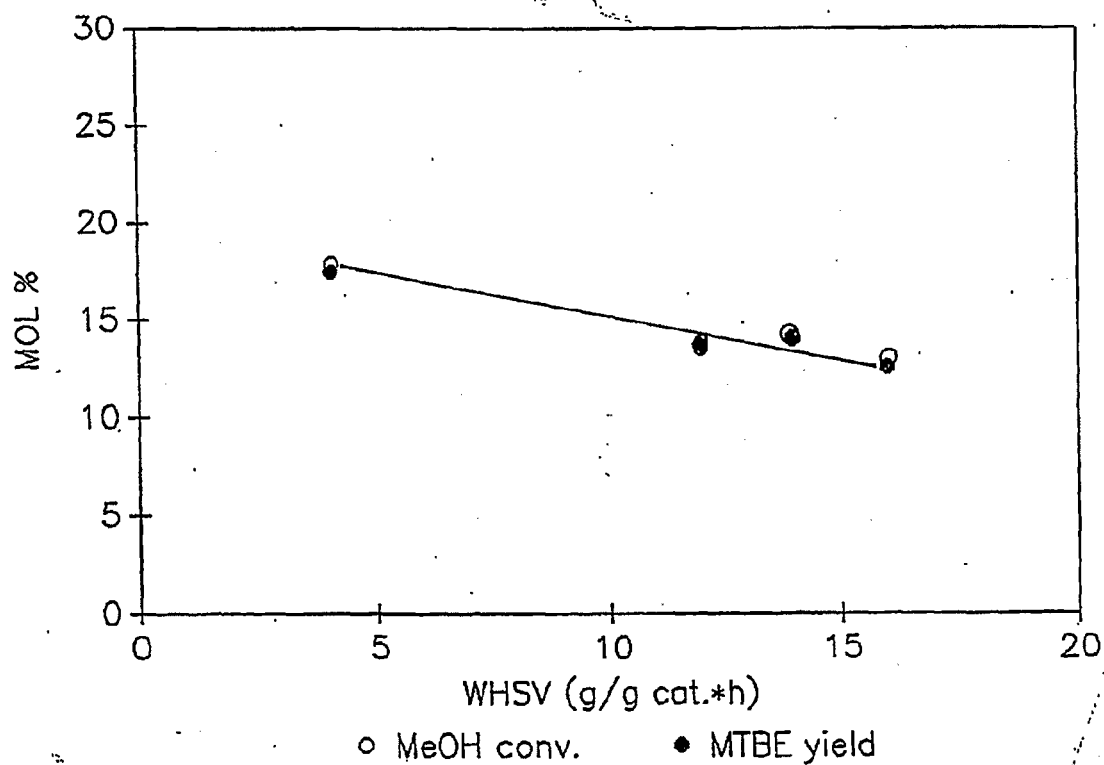
The effect of space velocity on the reaction was studied over catalyst LZ210-12 using fresh catalyst for each run and varying the space velocity between 4 and 16 hr⁻¹. Only data obtained at 100°C was used to minimize the effect of catalyst deactivation rate.

Table 7. Summary of acid properties and steady-state MTBE synthesis data over various acid catalysts

	Si-Al-O	Y62	Y82	S(LZ12)8	LZ210-12
Si/Al ratio	1.5	2.5	5.1	8.3	6.0
No. of acid sites ($\times 10^{20}/g$)	--	27	16	10	15
Acid strength	<1	1.3	8.0	11.5	5.2
<u>@ 100°C</u>					
MeOH conv.,%	5.6	12.4	7.9	10.1	12.6
MTBE yield, %	5.6	12.3	7.9	10.1	12.5
<u>@ 175°C</u>					
MeOH conv.,%	1.8	2.0	3.7	3.0	4.1
MTBE yield, %	0.7	0.7	0.7	1.3	0.7
Deactivation coefficient	0.71	0.93	0.84	0.88	0.69

FIGURE 7
Effect of Space Velocity on MeOH conversion
and MTBE yield.

Catalyst: LZ 210 12 R=1.8 T=100°C



The effect of space velocity on the steady state data for MeOH conversion and MTBE yield is shown in Figure 7. These results indicate an almost linear relationship between both the conversion and yield with the space velocity. Increasing the space velocity by 300% (from 4 to 16), resulted in a drop in the conversion and yield of about 30%. This decrease in conversion is far below what is expected for kinetically controlled reactions, i.e. the conversion should also have decreased by 300%. At present we have no definite explanation for this behavior except to suggest that the gas-phase reaction is affected by diffusion or by external mass transfer.

DETECTION OF MTBE AND MIBE

Gas chromatography-mass spectrometry (GC-MS) was used to verify the identity of the reaction products, particularly MTBE. It was also used to confirm the absence of methylisobutyl ether (MIBE), an octane reducer, in the MTBE signal which other investigators have reported as a major by-product in the reaction over strong acid sites (Klier, 1991).

The reaction products were analyzed using an Extrel GC-MS. The fragmentation pattern of the substance identified as MTBE by gas chromatography is shown in Figure 8. This pattern can be compared to those shown in Figure 9, corresponding to MTBE and MIBE obtained from the GC-MS library. Simple inspection shows a good match between the MTBE library spectrum and the product spectrum as well as the lack of a signal at $m/e=45$ corresponding to MIBE. It thus appears that these catalysts are not strong enough acid to catalyze the reaction to MIBE.

Scan at 1.8639

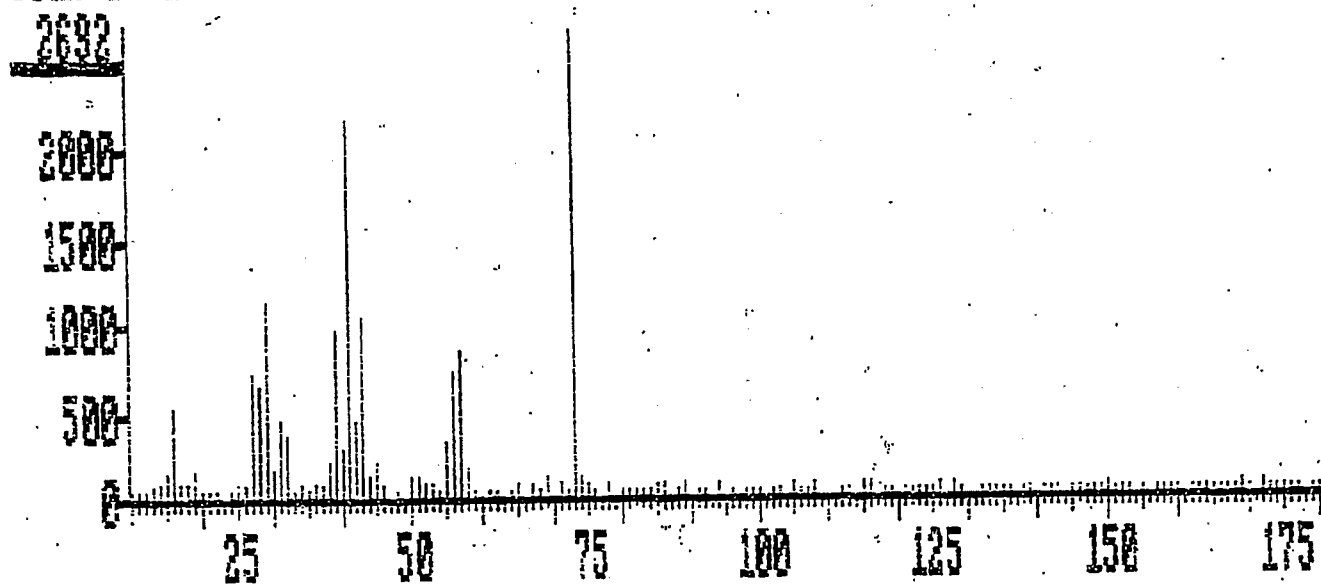
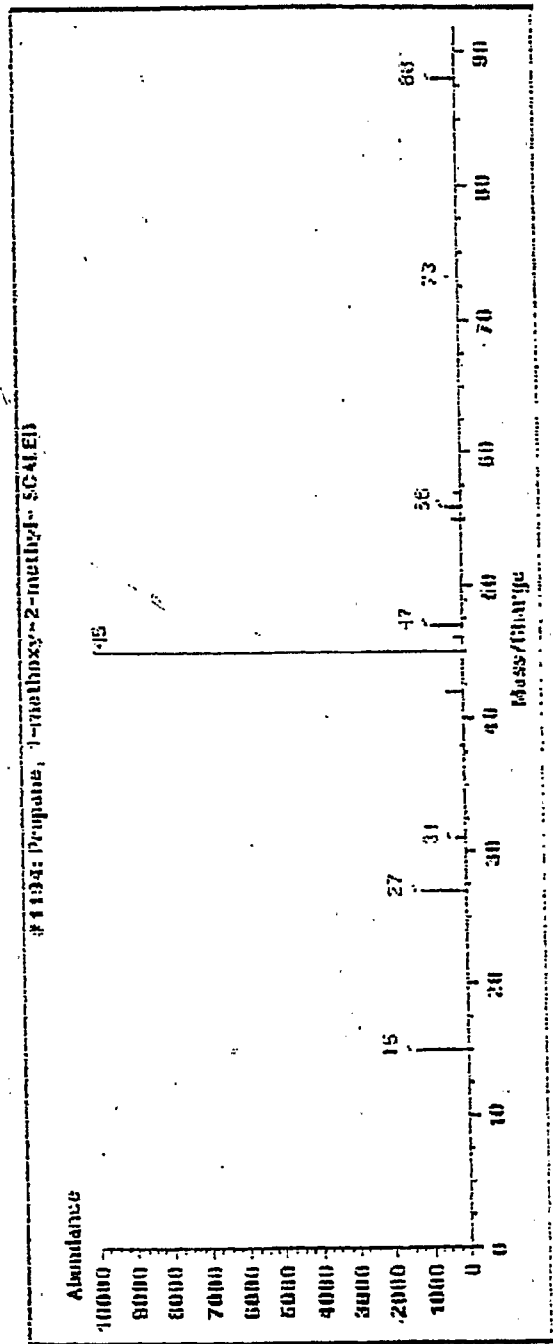
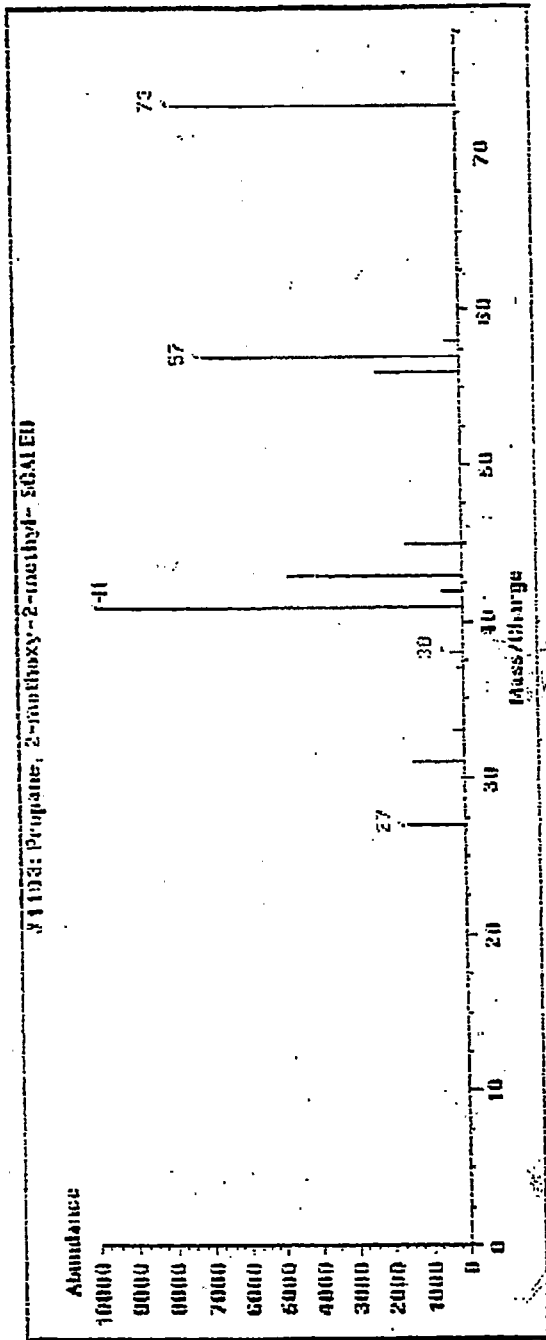


FIGURE 8. Mass spectral pattern of MTBE product from reaction stream.

FIGURE 9. Library mass spectra for MIBE (top) and MIBE (bottom).



CATALYST SELECTION

Based on the results to date and presented in this report, it is proposed to further evaluate catalyst LZ210-12 in the SBCR for the reaction of isobutylene with syngas-based alcohols. As was shown in Table 7, this particular catalyst represents a compromise between high methanol conversion activity and low deactivation during the gas-phase testing. All of the zeolites tested exhibited nearly 100% selectivity for MTBE from methanol at 175°C and 230°C.

WORK PLANNED FOR NEXT REPORTING PERIOD

During the fifth quarter of this work we plan to complete the study of the acid catalysts and resume the evaluation of catalysts for the incorporation of isobutylene during alcohol synthesis. We also plan to have the SBCR in operation.

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