SYNTHESIS OF OCTANE ENHANCERS DURING SLURRY-PHASE FISCHER-TROPSCH

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DOE CONTRACT NUMBER: DE-RA-90PC90047

PERIOD OF PERFORMANCE: Sept. 26, 1990 to Sept. 25, 1992

INTRODUCTION

The production of quality fuels either from traditional petroleum sources or synthetically from coal requires the addition of octane enhancers. This requirement was fulfilled for many years by the addition of small amounts of tetraethyl lead to the gasoline until its use was forbidden because of environmental concerns. Oxygenates in general are finding wide use as gasoline additives due to their octane enhancing properties and their low polluting properties. In particular, methyl-tert-butyl ether (MTBE) has gained wide acceptance as a clean, non-polluting octane enhancer for gasoline. Commercially, MTBE is made by the acid-catalyzed reaction of methanol and isobutylene using an ion-exchange resin catalyst. The reaction is typically carried out in the liquid phase below 90°C.

The large coal reserves of the U.S are capable of supplying this country's energy needs for the next several centuries via direct combustion and liquefaction to produce transportation fuels. The synthesis of gasoline, however, will also necessitate the addition of octane enhancers in order to fully utilize the gasoline range fraction. Ideally these octane enhancers should also be synthesized for syngas or from products of CO hydrogenation

reactions. This program is aimed at examining some possible routes for the synthesis of ethers, particularly MTBE, during slurry phase syngas reactions. Three routes are to be investigated:

* Addition of isobutylene during the formation of methanol and/or higher alcohols directly from CO and H_2 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.

The project is divided into five main tasks, i.e., (1) the design and construction of a laboratory-scale bubble column reactor; (2) the identification and characterization of suitable catalysts for the above reaction schemes; and (3) to (5) the evaluation of each of the above reaction schemes, respectively, in a slurry medium.

Work to date has concentrated in tasks (1) and (2).

DESIGN AND CONSTRUCTION OF A BENCH-SCALE BUBBLE COLUMN REACTOR

The bench-scale bubble column reactor was designed to have a nominal column diameter of one inch (2.54 cm) and a height not to exceed 1.2 m. This diameter is imposed primarily due to the cost of gases required to maintain proper bubble column conditions. It will also be operating at about six times the critical gas velocity. Under these conditions it can be assumed that there will be uniform catalyst dispersion throughout the reactor. Hence the mathematical model of Deckwer et al. (1981) can be used to predict conversions.

For this model the final design equation is:

$$-St = (1 + \alpha') \ln (1 - x_w^*) + \alpha' X^*$$

where:

α' is the modified contraction factor

$$= \alpha (1 + U)/(1 + I);$$

α is the contraction factor, defined as:

$$\frac{V_{g(X=1)} - V_{g(X=0)}}{V_{g(X=0)}} \quad ;$$

V_g = volumetric gas flow rate;
U = usage ratio $\Delta N_{CO}/\Delta N_{H_2}$;
N = molar flow rate;
I = CO and H_2 concentration ratio in the inlet gas;
X = fractional conversion of synthesis gas;
St = Stanton number, defined as:

$$k_o \, RTL/U_g^{\,i} \, m_H'' \quad ; \quad \text{and}$$

L = reactor length;
$U_g^{\,i}$ = gas velocity at the reactor inlet;
m_H'' = Henry's law constant for H_2;
k_o = overall rate constant, defined as:

$$1/k_o = (1/ak_{L,H}) + (1/k_c \, \epsilon_l).$$

In the above equation:

a = gas-liquid interfacial area;
$k_{L,H}$ = mass transfer coefficient;
k_c = rate constant for H_2 consumption;
ϵ_l = liquid holdup.

The first and second terms on the right side of the above relation represent the mass and kinetic resistances, respectively.

The kinetic data of Schlesinger et al. (1954) was used to determine the reaction rate constants.

SUMMARY OF DESIGN ASSUMPTIONS AND CALCULATIONS

Physical Parameters

Column i.d.	= 1" (2.54 cm)
Reactor length	= 4' (1.2 m)
Operating temp.	= 220°C
Operating pressure	= 15 atm
Catalyst size	= 44μm
H_2/CO ratio	= 0.7
Catalyst bulk density	= 3.25 g/ml
Catalyst loading	= 20 wt%

Assumed Parameters

Contraction ratio, α	= -0.5 (Deckwer 1982)
Usage ratio, U	= 1 (Deckwer 1981)

Other Design Parameters

Density of liquid medium	= 0.69 g/cm
Mass fraction of catalyst	= 0.167
Volume fraction of catalyst	= 0.0407
Density of slurry	= 0.792 g/cm
Viscosity of liquid medium	= 0.039 g/cm-sec
Viscosity of slurry	= 0.046 g/cm-sec
Mass transfer coefficient	= 0.0137 cm/sec
Henry's law coeff. for H_2	= 2.15×10^5 atm ml/g-mole
Modified contraction factor	= -0.413
Particle terminal velocity	= 0.069 cm/sec
Critical gas velocity, U_c	= 0.14 to 0.27 cm/sec

Gas Consumption

Maintenance of a 1.5 cm/sec superficial gas velocity at the inlet will require a gas flow rate at STP = 4.5 l/min, with corresponding flow rates for H_2 and CO of 1.85 and 2.65 l/min, respectively.

Hydrogen Conversion

Estimates of hydrogen conversion are naturally dependent on the catalyst considered and exact temperature and pressure used. For purpose of reactor design, the above operating conditions were used in terms of the model of Deckwer et al. (1981) and using the kinetic data of Schlesinger et al. (1954). These data refer to an Fe catalyst for producing hydrocarbons from syngas. The predicted hydrogen conversion for such a system is ca. 11%.

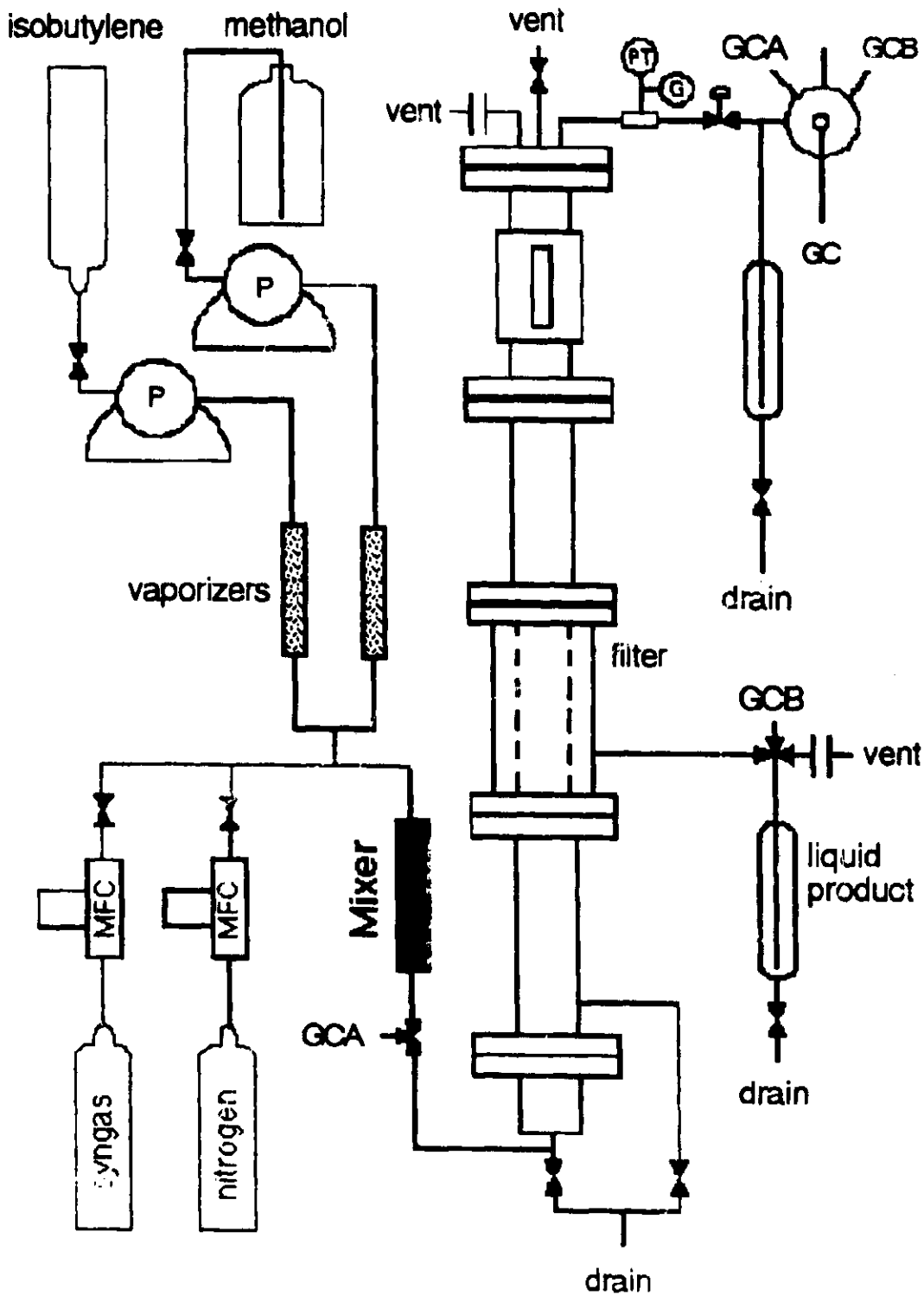
SCHEMATIC DIAGRAM OF LABORATORY SCALE BCSR

A schematic diagram of the laboratory BCSR system showing the reactor as well as all necessary ancillary equipment is shown in Figure 1. The reactor itself is constructed of one-inch stainless-steel pipe in four flanged sections for easy assembly and modification. Syngas and inert gas feeds are controlled via electronic mass flow controllers capable of operating to 1500 psig at a flow of 0 to 5 Std.L/min. Liquid feed pumps are used for delivery of isobutylene and other liquid feeds when necessary. An additional section of the reactor, consisting of a 2-inch diameter sight glass serves as a disengaging zone for the solids and will allow the direct observation of the liquid medium. In addition, provisions for the incorporation of a differential pressure cell for measurement of the liquid level inside the reactor are included in the design. A thermowell located in the internal periphery of the reactor serves for temperature measurement via a movable thermocouple.

A filter section is located approximately half-way along the slurry reaction zone of the reactor. This filter consists of a double wall six-inch length of stainless steel tube with the inner wall consisting of a 2 μm porous stainless steel one-inch internal diameter pipe. The outer wall is piped through a liquid drain valve to a liquid collection vessel.

Figure 1

Slurry Bubble Column Reactor



Gaseous product will be analyzed gas chromatographically in-line. Liquid product will be collected and analyzed ex-situ. Reactor by-pass lines are also available for direct analyses of the reaction mixtures.

REACTION OF ISOBUTYLENE WITH FT ALCOHOL PRODUCTS

The commercial process for making MTBE consists of reacting methanol with isobutylene over a sulfonic acid ion-exchange resin, typically Amberlyst-15 (Rohm & Haas Co.). Due to the instability of this resin at temperatures above 90°, it cannot be used for the proposed syngas schemes, as alcohol production from syngas requires temperatures in excess of 200°C. Thus, we have been investigating the use of acid zeolites which are stable to ca. 400°C.

EXPERIMENTAL

Catalysts

Amberlyst-15 was obtained from Rohm and Haas and used as received. Three H-Y zeolites having different Si/Al ratio and different acid properties have been investigated. Two of these were commercial zeolites obtained form Linde Co. having Si/Al of 2.5 and 6, respectively, and will be referred to by their commercial names (LZY-62 and LZ210-12, respectively). A third zeolite (referred to as SLZ12-8) was obtained by mild steam dealumination at 200°C for four hours of LZ210-12. Steam dealumination results in zeolites with enhanced acid properties. All zeolites were originally in their sodium form and were converted to the ammonia form by ion-exchanging in a solution of ammonium nitrate at 70°C for one hour. This exchange was repeated three times. Measurement of residual sodium by AA indicated that > 95% of the sodium had been exchanged. In the case of SLZ12-8 the ion-exchange procedure was repeated after the steaming treatment. Prior to reaction, the ammonium zeolites were deamminated to their proton form (NH_4^+ ---> NH_3 + H^+) by heating the zeolite in an helium

stream at <5°C/min to 400°C and holding this maximum temperature for sixteen hours. A summary of the zeolite catalysts and their preparation is given in Table 1.

Table 1
Summary of zeolite catalysts studied

Zeolite	Si/Al	Source	Treatment
LZY-62	2.5	commercial from Linde	ammonium exchange followed by deamination at 400°C
LZ210-12	6	commercial from Linde	ammonium exchange followed by deamination at 400°C
SLZ12-8	8	steam dealuminated LZ-210	ammonium exchange followed by steaming, ammonium exchange, deamination at 400°C

Structural Characterization

The total aluminum content of the zeolites was obtained by atomic absorption spectroscopy. Magic angle spinning NMR, MAS-NMR, was performed using a Bruker MSL-300 spectrometer. ^{29}Si and ^{27}Al spectra were obtained on the samples of interest. ^{29}Si spectra were obtained on the fully hydrated samples at 59.627 Mhz using a spinning rate of 4 KHz, a 90° pulse length of 6 microseconds, and a repetition time of 10 seconds. Depending of Si/Al ratio, between 200 and 10,000 scans were necessary to obtain a satisfactory signal-to-noise ratio. The ^{27}Al spectra were obtained at 78.205 MHz using a similar sample in a zirconia rotor. In this study a 10° flip angle was used to minimize quadrupolar

line broadening effects. Typically 1000 scans were collected with a repetition rate of 1 second. Aluminum phosphate was used as a quantitative standard.

Ammonia temperature programmed desorption was conducted using an Altamira Instruments AMI-1 system. The sample was deaminated in situ by heating to 400°C at 5°/min and maintaining this temperature for 12 hours. Ammonia was chemisorbed to saturation at either room temperature or 150°C. The sample was cooled to room temperature, flushed for 1 hour in helium, and then programmed at 20°C/min to 500 while recording the desorption spectra.

The total acidity of the catalysts was measured in terms of the cracking activity of n-pentane, which was studied in a fixed-bed reactor. After pretreatment to 400°C , nitrogen was bubbled through liquid pentane in a saturator maintained at 25°C and flowed over the catalyst. The reaction was carried out at 400°C. On-line analyses of the product was carried out using a dual TCD-FID gas chromatography system.

MTBE Synthesis

The synthesis of MTBE was studied using a lab scale fixed-bed reaction system operating at atmospheric pressures. The flows of isobutylene and helium were controlled by needle valves and measured with calibrated rotometers. The helium passed through a saturator containing methanol at 30°C, thus becoming saturated with the methanol at its vapor pressure (ca. 200 torr). Prior to reaction the catalysts were heated from room temperature to 400°C at 5°C/min and held at the upper temperature overnight. In this way the ammonium form of the zeolite was converted to the proton (acid) form. Conditions used for this study were:

Temperature:	100 - 250°C
Pressure:	1 atm
MeOH/i-Bu=:	ca. 2.0

The reactants were analyzed before and after a reaction run. The reaction products were sampled after 5 minutes and approximately

every hour thereafter. The reaction was performed under integral conditions, i.e. conversion greater than 10%, in order to determine the effect of thermodynamic equilibrium on the overall activity/selectivity behavior. Selectivity is expressed in a molar basis.

Product analyses was calibrated using known mixtures of gases and/or pure liquid components. For compounds for which standards were not available, response factors were obtained from the literature (Dietz 67). Conversion was calculated from the concentration of the products obtained. The selectivities are reported on a molar basis.

RESULTS

Characterization of zeolite catalysts

The amount of lattice aluminum gives a direct measure of the Bronsted site density in each of the zeolites. Each aluminum is associated with a a charge-compensating cation, in this case a proton. Thus, a measure of the aluminum atom concentration is also a measure of the Bronsted proton concentration.

The amount of lattice aluminum in the zeolites was determined independently using XRD lattice parameter measurements, ^{29}Si MAS-NMR, and ^{27}Al MAS-NMR. A comparison of the values of lattice aluminum obtained by the three methods is summarized in Table 2. In general there was fairly good agreement between them.

Table 2 also shows the amount of extralattice aluminum in each zeolite determined by subtracting the total aluminum, as determined by AA spectroscopy, from the average value of lattice aluminum determined by the three independent methods. In two cases, there was a significant amount of extralattice aluminum present in the sample. Specifically, it can be seen that the steaming treatment resulted in the formation of extralattice aluminum.

Although the amount of lattice aluminum can be directly related to the the number of acid sites, it does not serve as a measure of the strength of these sites. The strength of the acid

sites of the zeolites was determined by two methods, temperature programmed desorption (TPD) of adsorbed ammonia and n-pentane cracking.

Ammonia TPD of the zeolites showed three clear desorption signals at approximately 120, 280, and 430°C. The first of these (lowest temperature) was determined to be due to weakly held

Table 2
Summary of structural characteristics of zeolites

Zeolite	Si/Al	Lattice Al, 10^{20}/g XRD	^{29}Si-NMR	^{27}Al-NMR	Extralattice Al, 10^{20}/g[1]
LZY-62	2.5	28	29	26	3
LZ210-12	6	14	14	16	0
SLZ12-8	8	11	11	9	3

[1] Obtained by subtraction of total Al (by AA) from average value of lattice Al. Value is estimated accurate to $\pm$ 1 x 10^{20} Al/g.

ammonia, perhaps physisorbed, on various surfaces including the reactor walls. The two higher temperature signals corresponded to ammonia sorbed on acid sites. The temperature at which the ammonia desorbs is indicative of the heat of sorption and thus can be taken as a qualitative measure of the average acid strength of the sites. For our purposes we considered the temperature of the highest temperature peak to be related to the strength of the sites. These

data are summarized in Table 3 and indicate that the acid strength of the catalysts increased as the amount of lattice aluminum was decreased.

The overall activity of these catalysts towards an acid catalyzed reaction can also be considered a measure of the total acidity. We can also express the average acid strength of an individual average site by calculating a turnover frequency (TOF), that is, the rate of reaction per site per second. This has been done for all these catalysts for the cracking of n-pentane using the measured reaction rate and the lattice aluminum content. The TOF are also summarized in Table 3.

Table 3

Summary of acid properties of catalysts

	Si/Al	Acid sites, $x10^{20}$	NH_3 sorption(^oC)[1] LT signal	HT signal	n-pentane cracking 10^5xTOF[2]
LZY-62	2.5	28	287	402	1.3
LZ210-12	6	15	273	436	5.2
SLZ12-8	8	8.3	267	442	11.5
Amberlyst	--	30	--	--	>1 (est.)

[1] Data represents the temperature maxima of the desorption signal.

[2] TOF reported are for 400^{o}C using other conditions as outlined in the text.

Comparison of the acid properties of the zeolites show an increase in cracking TOF and hence acidity by approximately one order of magnitude as the lattice aluminum content decreases form 27 to 10. In particular, catalyst SLZ12-8 exhibited the highest acid TOF and thus can be considered to be significantly more acidic that the others. The value obtained for TOF agreed, at least qualitatively, with the ammonia TPD results. Similar values for Amberlyst-15 are also shown.

MTBE Synthesis

Table 4 shows a comparison of two of the zeolite catalysts and Amberlyst-15 resin for the synthesis of MTBE at 100°C. Although the individual runs were conducted at slightly different conditions they are sufficiently similar for comparison. The activities of the catalysts in terms of methanol conversion were approximately equal for the three catalysts. Selectivities, however, were significantly different, with zeolites favoring the formation of MTBE while the Amberlyst-15 resin favored formation of dimethyl ether (DME) and the C8 isobutylene dimer.

A comparison of the three zeolites at steady-state at 175°C is given in Table 5. It should be noted that because of experimental difficulties a significantly different space velocity was used with zeolite S(LZ12)8 than with the other two. In general, all three catalysts were highly active. They appeared to initially deactivate and quickly reach a steady-state. Figures 2, 3, and 4 show the conversion and MTBE yield as a function of time-on-stream. The high methanol conversion observed at first 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 iso-butylene to methanol ratio and assuming only gas-phase reaction. In some cases, i.e. for catalyst LZ210-12 and Y62 at high temperatures, the observed MTBE yield exceeded the predicted

Table 4

MTBE Synthesis over Acid Catalysts at 100°C
Comparison of Ion-Exchange Resin and Zeolites

	Amberlyst 15	LZ210-12	S(LZ12)8
Wt. of catalyst, g:	0.25	0.25	0.10
i-Bu/MeOH:	2.0	3.0	2.0
WHSV, hr^{-1}:	9	7.7	13.2
MeOH conv., %:	19.0	24.5	17.8
MeOH to MTBE, %:	27.0	41.8	70.2
Product Analysis (mol %)			
Hydrocarbons			
C1	0.2	0.2	0.9
C2	0.1	0.1	0.5
C3	–	tr.	0.1
C5	3.4	2.5	1.5
C6	0.9	0.2	0.5
C7	–	–	0.8
C8	61.1	13.7	24.4
Oxygenates			
DME	20.3	--	0.3
t-BuOH	0.4	--	0.4
Pentanols	3.4	12.6	1.3
MTBE	10.6	70.9	69.1

Table 5

MTBE Synthesis over zeolites at 175°C

	LZ210-12	S(LZ12)8	Y62
Wt. of catalyst, g:	0.10	0.10	0.10
i-Bu/MeOH:	1.8	1.7	1.6
WHSV, hr^{-1}:	4	14	6
MeOH conv., %:	31.3	3.7	12.3
MeOH to MTBE, %:	22.8	34.5	16.1
Product Analysis (mol %)			
Hydrocarbons			
C1	0.1	--	0.4
C2	0.1	0.1	0.3
C3	0.1	0.1	0.3
C5	0.5	0.5	1.3
C6	0.1	--	0.8
C7	--	--	--
C8	42.3	50.9	36.4
Oxygenates			
DME	22.8	18.2	27.2
t-BuOH	2.2	0.2	1.2
Pentanols	2.0	3.3	1.7
MTBE	29.8	26.8	30.4

Figure 2

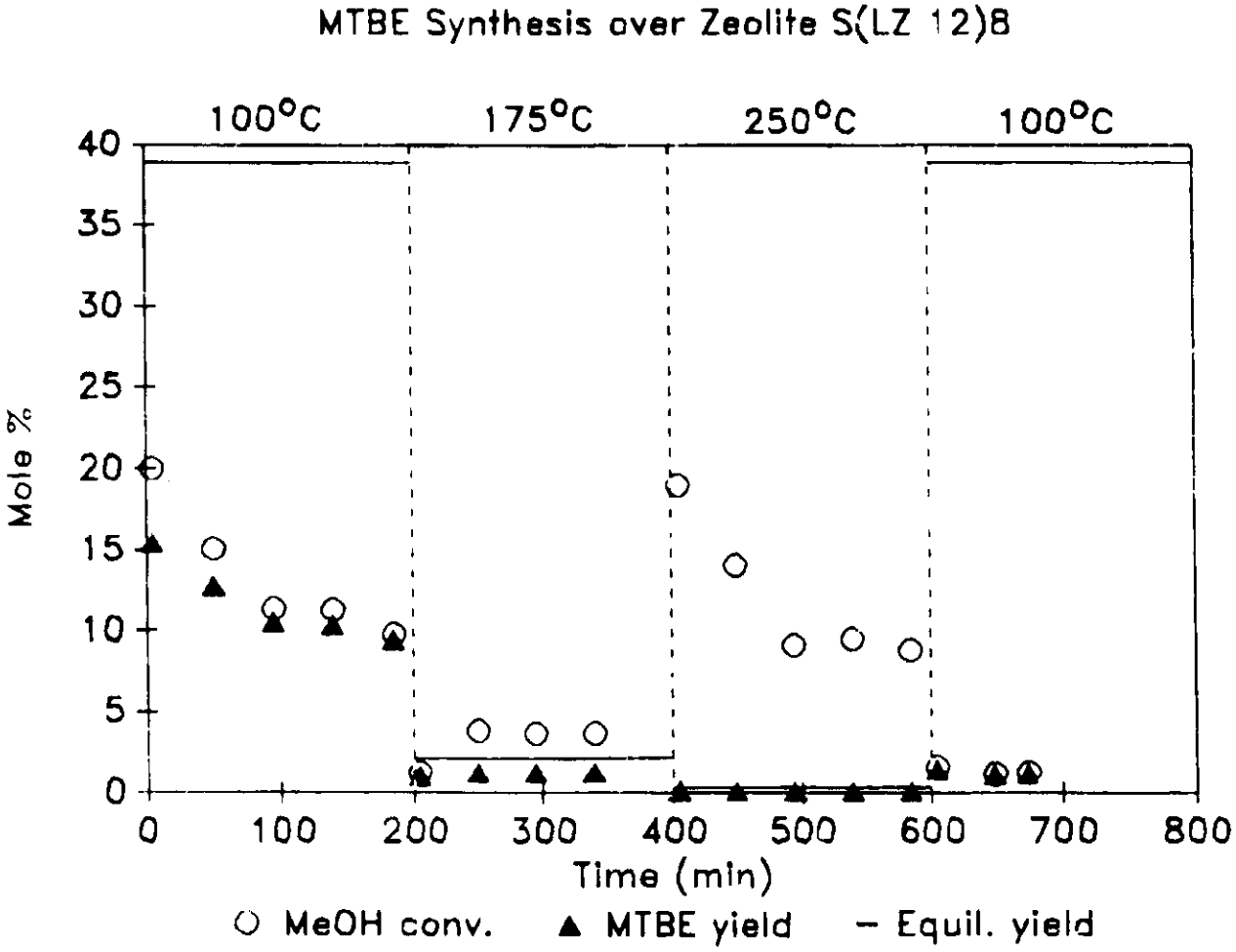

MTBE Synthesis over Zeolite S(LZ 12)8
100°C
175°C
250°C
100°C
40
35
30
25
20
15
10
5
0
Mole %
0
100
200
300
400
500
600
700
800
Time (min)
○ MeOH conv.
▲ MTBE yield
– Equil. yield

Figure 3

MTBE Synthesis over Zeolite LZ 210 12

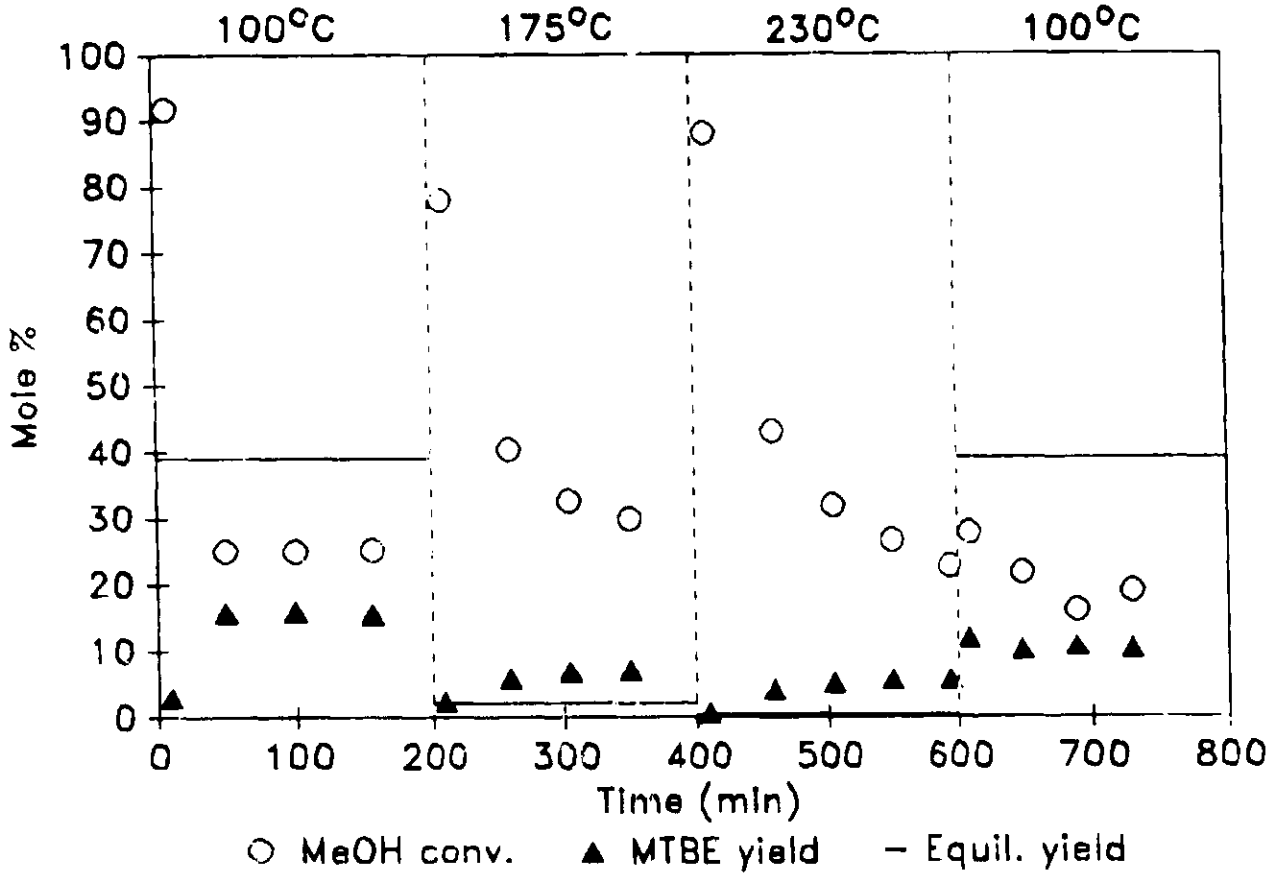
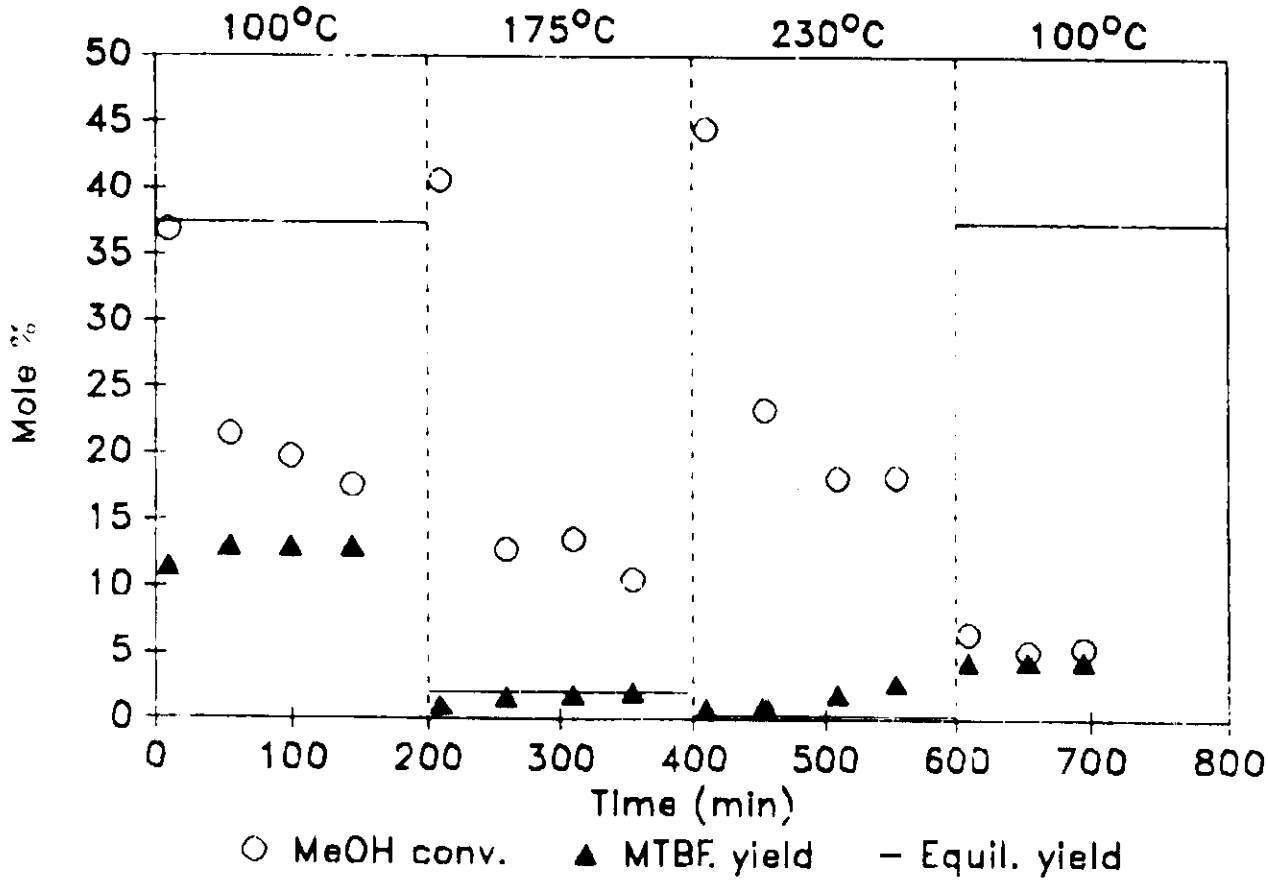


Figure 4

MTBE Synthesis over Zeolite Y62



equilibrium. This excess yield may be due to the preferential diffusion of the smaller methanol into the pore resulting in a smaller iso-butylene to methanol ratio than used in the calculations.

SUMMARY

The initial work on the synthesis of MTBE shows that zeolite catalysts exhibit a higher selectivity to MTBE at 100°C than the commercially used Amberlyst-15 ion-exchange resin. In all cases the zeolites were initially very active and yielded a large number of products. Particularly at higher temperature, however, they quickly deactivated and reached a steady-state. At this point the reaction products consisted primarily of MTBE, DME, and the C8 dimer of iso-butylene. This latter product can be greatly reduced by changing to a feed with excess methanol as will be done during the slurry reactor runs.

It was noted that over the zeolites MTBE was produced in excess of equilibrium concentrations. This phenomenon is likely due to diffusion effects leading to a different isobutylene to methanol ratio in the pores than that used for the calculation. This idea will be further examined by conducting the reaction over zeolite ZSM-5 which has smaller pores that Y-zeolites.

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