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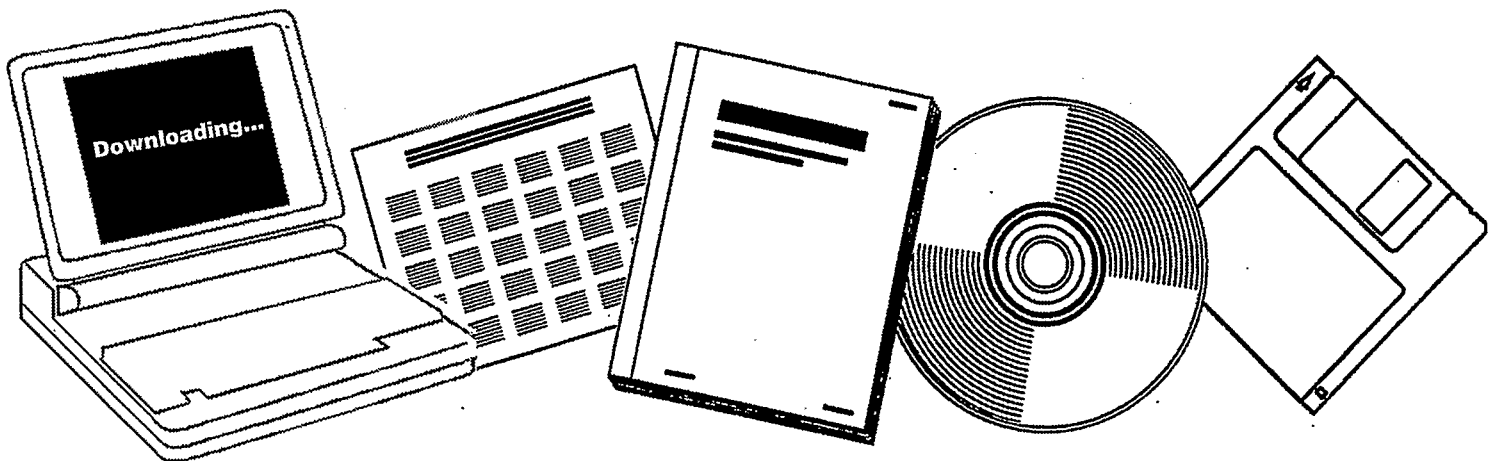
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**SYNTHESIS OF OCTANE ENHANCERS DURING
SLURRY-PHASE FISCHER TROPSCH. QUARTERLY
TECHNICAL PROGRESS REPORT NO. 2, JANUARY
1-MARCH 31, 1991**

**ALTAMIRA INSTRUMENTS, INC.
PITTSBURGH, PA**

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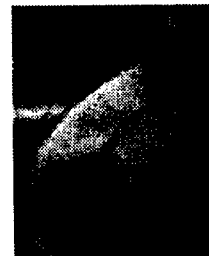
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QUARTERLY TECHNICAL PROGRESS REPORT No. 2

Covering the Period January 1 to March 31, 1991

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

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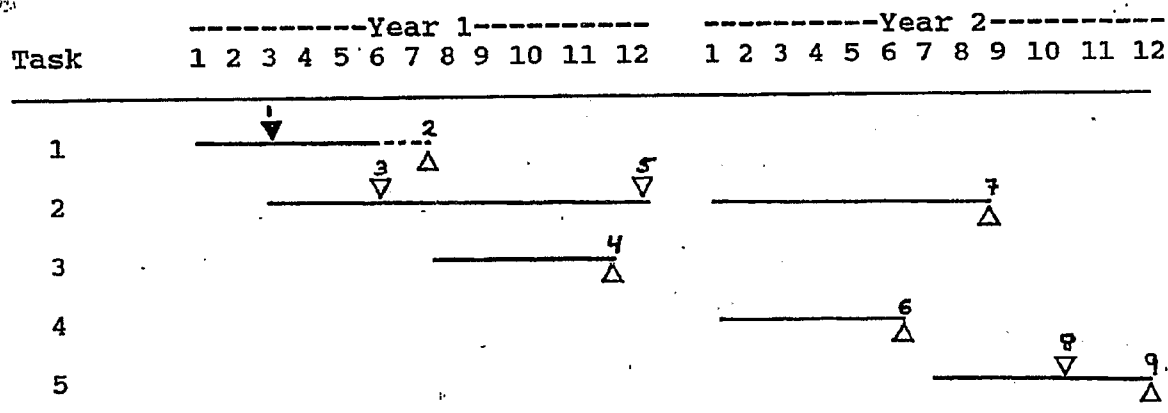
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PLANNED TASK AND MILESTONE SCHEDULE



M = denotes milestone

List of Milestones

<u>Milestone Number</u>	<u>Description</u>
M1	Finalize design of slurry bubble column reactor (SBCR).
M2	Finalize construction and successful testing of SBCR. Topical report prepared.
M3	Completion of catalyst screenings for study on 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 on 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-phase study 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 (FT) reaction. The three reaction schemes to be investigated are:

Scheme 1

- * Addition of isobutylene during the formation of methanol and/or higher alcohols directly from CO and H₂ during slurry-phase Fischer-Tropsch.

Scheme 2

- * Addition of isobutylene to FT liquid products including alcohols in a slurry-phase reactor containing an MTBE or other acid catalyst.

Scheme 3

- * Addition of methanol to slurry phase FT synthesis making iso-olefins.

WORK ACCOMPLISHED THIS QUARTER

Work conducted during the second quarter has concentrated in two specific areas: (1) the construction of a laboratory-scale bubble column slurry reactor (BCSR) for use in the study of each of the three routes defined above, and (2) initial selection, characterization and screening of catalysts for schemes 1 and 2 above. The design of the reactor was completed in the last quarter and its design described in Quarterly Report No.1. We had hoped to have completed the construction of the BCSR in this quarter, but long delivery and machining times have delayed its completion. This task is approximately one month behind schedule. Work on Task 2 is proceeding slightly ahead of schedule, as various catalysts suitable for reaction schemes 1 and 2 have been identified.

SECOND QUARTER'S TECHNICAL WORK

CATALYSTS SUITABLE FOR THE 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-96 (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

A series of four H-Y zeolites having different Si/Al ratio were obtained. Three of these were commercial zeolites obtained from Linde Co. having Si/Al of 2.5, 3, and 6, respectively, and will be referred to by their commercial names (LZY-62, LZ210-6, and LZ210-12, respectively). The fourth 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 deaminated to their proton form ($\text{NH}_4^+ \rightarrow \text{NH}_3 + \text{H}^+$) by heating the zeolite in a 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.

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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
LZ210-6	3	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 dealumi- nated 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 on the 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 $5^\circ/\text{min}$ 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 $20^\circ\text{C}/\text{min}$ to 500°C 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 are controlled by needle valves and measured with calibrated rotometers. The helium passes 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=:	1.0
Total flow rate:	35 cc/min
Catalyst weight:	250 mg

The reactants were analyzed before and after a reaction run. The reaction products were sampled after 5 minutes, 30 minutes, and one hour of reaction. In general, although there was some variation in the individual analyses, no significant deactivation was noted. All data reported correspond to analysis taken after one hour at a particular set of conditions. The reaction was performed under integral conditions, i.e. conversion greater than 10%, in order to approach thermodynamic equilibrium. 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 will be associated with a charge-compensation 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 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.

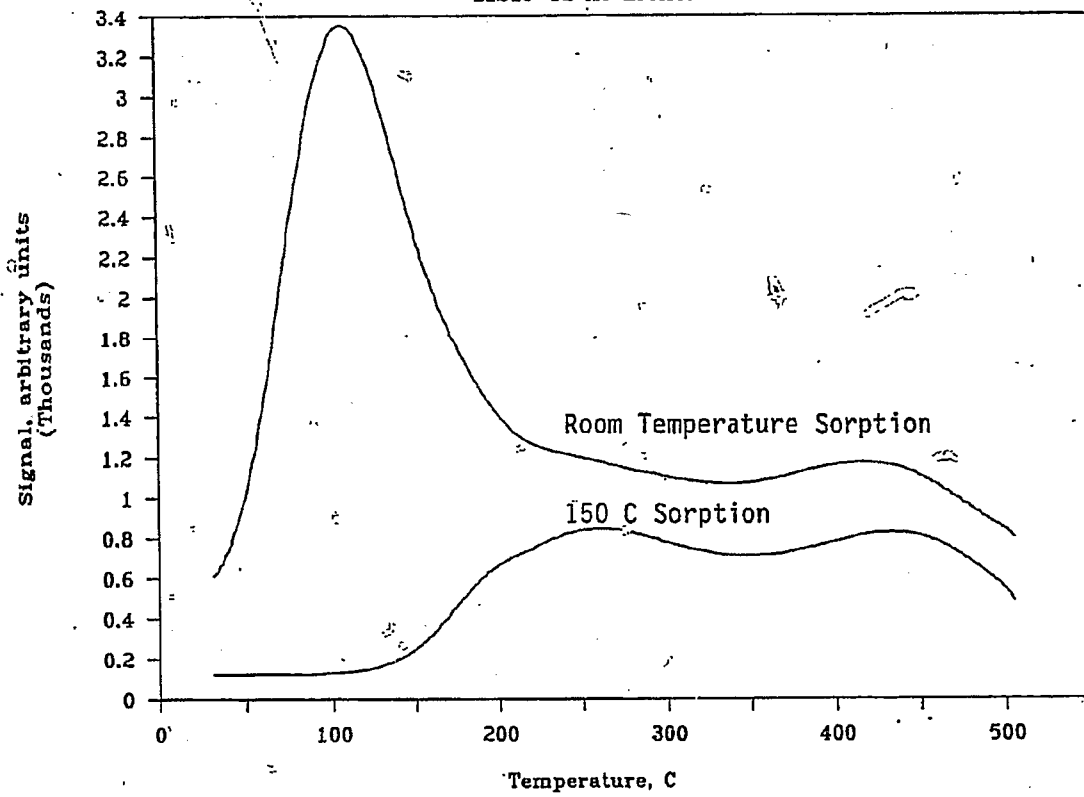
Typical ammonia TPD spectra for one of the catalysts is shown in Figure 1. Spectrum 1A corresponds to the TPD spectrum after ammonia sorption at room temperature. It shows three clear desorption signals at approximately 120, 280, and 430°C. The first of these (lowest temperature) correspond simply to weakly held ammonia, perhaps physisorbed, on various surfaces including the reactor walls. The two higher temperature signals correspond to ammonia sorbed on acid sites. Figure 1B shows a similar spectrum in which the ammonia was sorbed at 150°C, thereby eliminating the physisorption. Similar spectra were obtained for all the zeolites. The temperature at which the ammonia desorbs is

Table 2
Summary of structural characteristics of zeolites

Zeolite	Si/Al	Lattice Al, $10^{20}/g$			Extralattice
		XRD	$^{29}\text{Si-NMR}$	$^{27}\text{Al-NMR}$	Al, $10^{20}/g^1$
LZY-62	2.5	28	29	26	3
LZ210-6	3	22	23	24	0
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 $+ 1 \times 10^{20}$ Al/g.

Figure 1
Ammonia TPD
LZ210-12 HY zeolite



indicative of the heat of sorption and can be taken as a 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 TOFs are also summarized in Table 3.

Comparison of the acid properties of the zeolites show an increase in cracking TOF, hence acidity, by approximately one order of magnitude as the lattice aluminum content decreases. In particular, catalyst SLZ12-8 exhibited the highest acid TOF and thus can be considered to be significantly more acidic than the others. The value obtained for TOF agreed, at least qualitatively, with the ammonia TPD results. Thus, this series of four zeolites represent a range of both acid sites and acid strength and as such they will serve to probe the acid requirement of a catalyst to selectively carry out the desired MTBE synthesis reaction.

MTBE Synthesis

To date, only one of the zeolites has been examined for activity towards the MTBE synthesis. The results for LZ210-12 are shown in Table 4. The reaction showed significant conversion at the temperatures examined (100 to 250°C) and at the lower temperatures showed good selectivity for MTBE (ca. 75%). Indeed, even at 250°C a selectivity for MTBE of 15% was observed, with the major by-product being dimethyl ether. Other significant products of the reaction were methane and, at higher temperatures, the disproportionation products such as C5 hydrocarbons. It should be emphasized however that these results are preliminary.

Table 3
Summary of acid properties of zeolites

Zeolite	Si/Al	NH ₃ sorption(°C) ¹		n-pentane cracking 10 ⁵ xTOF ²
		LT signal	HT signal	
LZY-62	2.5	287	402	1.3
LZ210-6	3	296	425	3.7
LZ210-12	6	273	436	5.2
SLZ12-8	8	267	442	11.5

¹ Data represents the temperature maxima of the desorption signal.

² TOF reported are for 400°C using other conditions as outlined in the text.

TABLE 4
 MTBE synthesis over Zeolite H-Y LZ210-12

Temperature, °C	100	175	250	100
Methanol Conversion, %	79	58	40	78
SELECTIVITIES				
Methane	16.7	9.5	19	16
C2	3.2	1.9	5.2	1.8
C3	0.9	0.8	1.8	0.3
C5	4	2.8	10.8	4.4
Dimethylether	0	70	49	0
t-Butanol	0.6	0.3	0.1	0
MTBE	74.6	14.7	15.0	77.5

CATALYSTS SUITABLE FOR THE LOW TEMPERATURE SYNTHESIS OF ALCOHOLS

Commercial methanol catalysts operate at high temperatures, i.e. above 250°C. Since at high temperatures the formation of MTBE is unfavorable, one of the initial goals of this program has been to identify catalysts which can selectively form methanol or higher alcohols at lower temperatures. Prior work at the University of Pittsburgh (Chuang 85) and various reports in the literature suggested the use of promoted, supported Rh or Pd catalysts as suitable candidates. Several of these materials have been prepared and are currently being tested for the desired activity and selectivity.

EXPERIMENTAL

Catalysts

Initial work has concentrated on supported rhodium catalysts. Rhodium catalysts supported on silica and alumina were obtained from Strem Chemicals. Rhodium catalysts promoted with molybdenum were prepared in-house by incipient-wetness impregnation. These consisted 1.5 wt% Rh, promoted with an equimolar amount of Mo and supported on silica and alumina, respectively. After preparation the catalysts were calcined in air for 16 hours at 400°C.

CO Hydrogenation

The CO hydrogenation reaction was studied using a small fixed-bed reactor operated in a differential mode, i.e. CO conversion was kept below 3%. Prior to reaction the catalysts were reduced overnight at 300°C. The conditions used for this phase of the study were:

Temperature:	180 - 250°C
Pressure:	1 to 10 atm
H ₂ /CO:	1.0
Syngas flow rate:	100 cc/min
Catalyst weight:	0.5 g

The reactant by-pass and the reaction products were sampled periodically into an in-line gas chromatograph. All data reported corresponds to analysis taken after three hours at a particular set of conditions. Selectivity is expressed on a molar basis.

RESULTS

Table 5 shows the reaction results obtained with the unpromoted Rh/Al₂O₃ at 8 atm. At temperatures between 200 and 240°C, the selectivity for oxygenates ranged between ca. 38 and 53% and was primarily distributed among methanol, ethanol, and acetaldehyde. Table 6 shows the results of a similar study using the Rh-Mo/SiO₂ catalyst. Overall activity was higher by about a factor of 3 and selectivity for oxygenates increased somewhat. The most noticeable change is the increase in selectivity for methanol which was over 90% at temperatures below 200°C. Table 7 shows the results for the same catalyst but at one atmosphere pressure. As expected, at the lower pressure both rate and total oxygenate selectivity decreased. In all three cases the major hydrocarbon product formed was methane.

TABLE 5
 Reaction of syngas over 5% Rh/Al₂O₃
 H₂/CO=1.0, 8 Atm.

Temperature, °C	200	220	240
CO Conversion, %	0.16	0.39	0.79
Rate, mol g ⁻¹ h ⁻¹	0.009	0.022	0.044
SELECTIVITIES			
Hydrocarbons	48.3	47.1	61.9
Oxygenates	51.7	52.9	38.1
OXYGENATES			
Methanol	54.5	40.1	26
Ethanol	19.8	36.3	49.6
Acetaldehyde	25.7	23.5	24.4

TABLE 6
 Reaction of syngas over 1.5% Rh-Mo/SiO₂
 H₂/CO=1.0, 8 Atm.

Temperature, °C	180	200	230	250
CO Conversion, %	0.35	0.53	2.25	2.75
Rate, mol g ⁻¹ h ⁻¹	0.02	0.029	0.098	0.15
SELECTIVITIES				
Hydrocarbons	29	26.1	44.1	55.0
Oxygenates	71	73.9	55.9	45.0
OXYGENATES				
Methanol	95.1	91.8	89.4	82.8
Ethanol	4.9	8.2	10.6	15.5
Acetaldehyde	0	0	0	1.6

TABLE 7
 Reaction of syngas over 1.5% Rh-Mo/SiO₂
 H₂/CO=1.0, 1 Atm.

Temperature, °C	180	200	230	250
CO Conversion, %	0.11	0.26	0.61	0.75
Rate, mol g ⁻¹ h ⁻¹	0.006	0.015	0.034	0.042
SELECTIVITIES				
Hydrocarbons	23.2	47.6	70.6	86.9
Oxygenates	76.8	52.4	29.4	13.1
OXYGENATES				
Methanol	81.9	84.5	81.1	68.0
Ethanol	4.0	9.8	12.5	25.4
Acetaldehyde	14.2	5.6	6.4	6.6

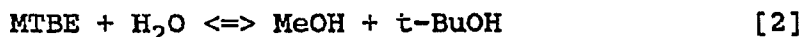
THERMODYNAMIC ANALYSIS OF THE GAS PHASE MTBE SYNTHESIS REACTION AND
MTBE HYDROLYSIS REACTION

Two of the major obstacles to the production of MTBE are the fact that the reaction conversion from methanol and isobutylene is equilibrium limited at high temperatures and the possible side reaction of hydrolysis of MTBE to form t-butanol and methanol. This portion of the reports details the results of a thermodynamic analysis of the MTBE synthesis reaction, from methanol and isobutylene, and of the hydrolysis of MTBE into methanol and t-butanol. The analysis is based on the calculations of the equilibrium constants of the above reactions as functions of temperature and pressure. The calculations have been performed based on thermodynamic data found in the literature. This analysis gives an indication of the conditions that maximize the production of MTBE. The kinetics of the reactions has not been taken into account.

There are 2 reactions involved in the system of interest. The first, is the synthesis of MTBE from isobutylene (IB) and methanol (MeOH):



The second reaction (which is undesirable), is the hydrolysis of MTBE to form methanol and t-butanol:



For each of the 2 reactions the effect of temperature, pressure, and initial reactant ratio has been examined in order to maximize the production of MTBE. The range of the values used for these parameters, is the one that corresponds to the experimental application of interest.

Table 8 shows the thermodynamic properties of the various components of interest. From these data the equilibrium constant as a function of temperature can be calculated for the above reactions and consequently, the equilibrium conversion at a given pressure and initial ratio of reactants.

Table 8. Temperature and Pressure Dependence of the Equilibrium Conversion X_e for the MTBE Synthesis Reaction.

T (°C)	K_y	%Xe (1:1)	%Xe (10:1)	
140	0.065	3.10	5.58	P = .5 atm.
160	0.0275	1.35	2.44	
180	0.0125	0.62	1.12	
200	0.00625	0.31	0.56	
220	0.00330	0.16	0.30	
240	0.00185	0.09	0.17	
140	0.130	5.93	10.56	P = 1. atm.
160	0.055	2.64	4.76	
180	0.025	1.23	2.22	
200	0.0125	0.62	1.12	
220	0.0066	0.33	0.60	
240	0.0037	0.18	0.34	
140	0.26	10.91	19.09	P = 2. atm.
160	0.11	5.08	9.08	
180	0.05	2.41	4.35	
200	0.025	1.23	2.22	
220	0.0132	0.65	1.19	
240	0.0074	0.37	0.67	
140	0.65	22.15	37.06	P = 5. atm.
160	0.275	11.44	19.97	
180	0.125	5.72	10.20	
200	0.0625	2.99	5.37	
220	0.0330	1.61	2.91	
240	0.0185	0.91	1.65	
140	1.3	34.06	54.04	P = 10. atm.
160	0.55	19.68	33.26	
180	0.25	10.56	18.49	
200	0.125	5.72	10.20	
220	0.066	3.15	5.66	
240	0.037	1.80	3.25	

Table 9. Thermodynamic Properties of the MTBE Reacting System.

Standard state: Ideal gas, $p=1$ atm., $T=25^{\circ}\text{C}$.

	MeOH	IB	MTBE	H ₂ O	t-BuOH
M.W.	32.04	56.10	88.15	18.0	74.12
TB ($^{\circ}\text{C}$)	64.8	-6.7	55.5	100.0	82.9
ΔH°_f (kcal/mol)	-48.08	-4.04	-67.75	-57.80	-74.68
ΔG°_f (kcal/mol)	-38.84	13.88	-28.04	-54.635	-42.45

c_p coefficients ($c_p = a + b T + c T^2 + d T^3$ cal/mol $^{\circ}\text{K}$)

a	5.052	3.834	-0.5498	8.22	11.54
b	0.01694	0.06698	0.1302	15×10^{-5}	0.0522
c	$.6179 \times 10^{-5}$	-2.61×10^{-5}	-7.162×10^{-5}	134×10^{-8}	
d	$-.6811 \times 10^{-8}$	$.2173 \times 10^{-8}$	5.530×10^{-8}		

References: Perry and Green, Chemical Engineer's Handbook
 Handbook of Chemistry and Physics
 Tejero 88

From the thermodynamic properties of Table 8, corresponding thermodynamic properties for the MTBE gas phase synthesis reaction can be calculated (Tejero 88):

$$\begin{aligned}\Delta H^{\circ} &: & -15.63 \text{ (kcal/mol)} \\ \Delta G^{\circ} &: & -3.08 \text{ (kcal/mol)}\end{aligned}$$

The c_p coefficients for the reaction are:

$$\Delta a = -9.4358$$

$$\Delta b = 0.4628 \times 10^{-1}$$

$$\Delta c = -5.1729 \times 10^{-5}$$

$$\Delta d = 5.9938 \times 10^{-8}$$

Using the relations:

$$\Delta G^{\circ} = -RT \ln K_a$$

$$d(\ln K_a)/dT = \Delta H^{\circ}/RT^2$$

$$\partial(\Delta H^{\circ})/\partial T|_p = \sum i c_{p,i} = \Delta c_{p,i} \quad (\text{Kirchoff})$$

gives the following expression for the equilibrium constant, K_a , as a function of temperature:

$$\begin{aligned}\ln K_a &= 7315/T - 4.749 \ln T + 1.169 \times 10^{-2} T \\ &\quad - 4.339 \times 10^{-6} T^2 + 2.514 \times 10^{-9} T^3 + 4.58\end{aligned}$$

The equilibrium constant is pressure dependent since there is a net loss of one mole in the formation of MTBE. Thus:

$$K_y = K_a \quad p(-\sum v_i) = K_a \quad p$$

since in this case $v_a = -1$.

Using this equilibrium expression, the maximum conversion of the limiting reactant to MTBE can be readily calculated. Table 9 summarizes the equilibrium constant as well as the % conversion of the limiting reactant to MTBE for the temperature range of 140°-240° C (413-513 K) and pressure range between 0.5-10.0 atm. These results are presented for two initial reactant ratios, 1:1 and 10:1. The analysis is not affected by which of the two reactants, MeOH or IB, is limiting. The same information can be more clearly seen in Figures 2 and 3. Clearly MTBE formation is favored by operating in a low temperature, high pressure regime.

A similar procedure can be used for examining the hydrolysis reaction (eq. 2). There are two important differences, though, from the previous case of the formation of MTBE. The first difference is, that the hydrolysis reaction has 2 reacting molecules (MTBE and H₂O) and 2 products (MeOH and t-BuOH). Consequently, there is no influence of the pressure on the equilibrium constant K_y and on the % conversion for various temperatures. The other important difference is that, in our reaction system, the water is not added but rather it is produced by the FT reaction. Thus, one only needs to consider the solubility of water in the slurry medium.

There is information in the literature concerning the maximum solubility of H₂O in FT liquids [8]. Mainly:

$$\text{at } T = 400 \text{ K (127 } ^\circ\text{C)} \quad X_w = 0.14$$

$$\text{at } T = 500 \text{ K (227 } ^\circ\text{C)} \quad X_w = 0.34$$

where X_w is the mole fraction of water in the liquid phase.

Since the relationship between the mole fraction X_w and T is shown to be almost linear (Morsi 88), a good approximation for X_w as a function of T in the region of interest is:

$$X_w(T) = X_w(400 \text{ K}) + 0.2 \times 10^{-2} \Delta T \quad (400-500 \text{ K})$$

Fig 2. MTBE Synthesis Reaction Data

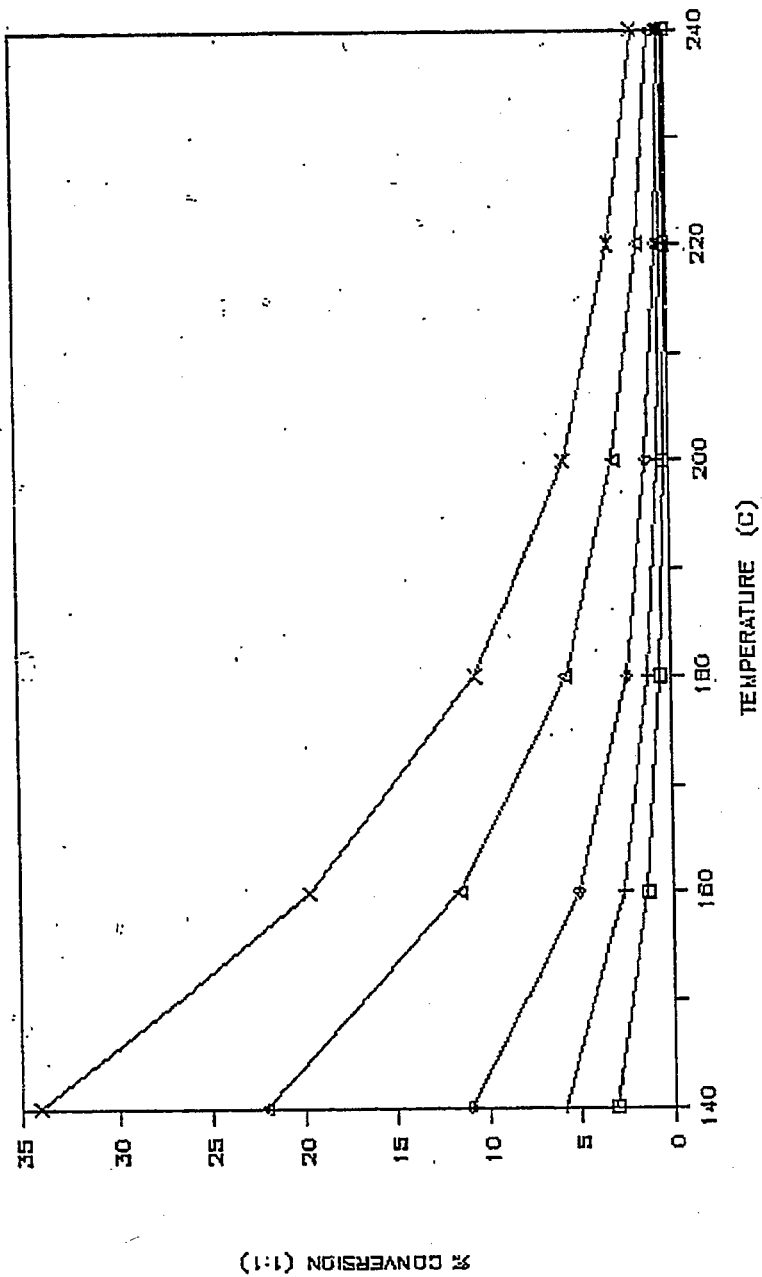
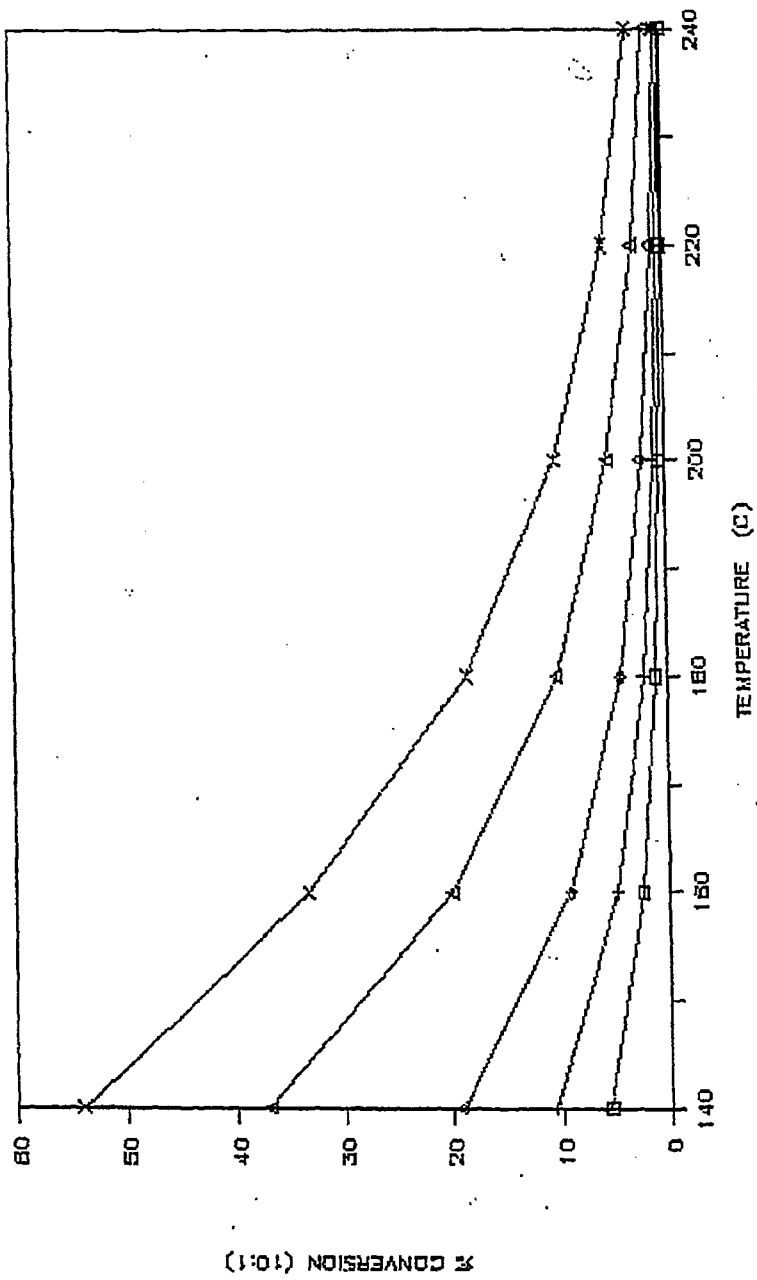


Fig. 3. MTBE Synthesis Reaction Data



From this expression and the previous analysis for the equilibrium production of MTBE, a "theoretical" ratio of H₂O to MTBE can be calculated as a function of temperature. The assumptions made are that only H₂O, MTBE, MeOH, and IB are present (the latter in an initial ratio of 1:1) and the pressure is p = 10 atm. (the effect of pressure is not analyzed because data for the solubility of MTBE in FT liquids are not available in the literature). These results are presented in Table 10.

It should be stressed that these results give only a very rough estimate of the actual ratio.

From the thermodynamic properties given in Table 8 and the relations used previously, the equilibrium constant K_a, as a function of temperature can be calculated and it is given by the following expression:

$$\ln K_a = -1103.95/T + 4.49 \ln T - 0.015 T + 6.42 \times 10^{-6} T^2 - 20.25$$

Since there is no effect of pressure:

$$K_a = K_y$$

In Table 11, the calculated equilibrium constant, K_a, and the % equilibrium conversion, X_e, for the hydrolysis of MTBE formed from MeOH and IB are presented as a function of temperature. The same data are also presented in Figure 4.

From the information and results for the MTBE synthesis reaction, as presented in Sec.3 above, we can draw some important conclusions about the production of MTBE and the conditions that optimize it. The MTBE synthesis reaction is shown to be exothermic (H = -15.63 kcal/mol) and is therefore favored at low temperatures for all pressures and initial reactant ratios. From Table 8 we can see that a 100°C increase in temperature (from 140° to 240°C) results in a 35-fold drop in the equilibrium conversion X_e, at p=0.5 atm. and with an initial reactant ratio of R=1:1; and a 17-fold drop at p=10.0 atm. and R=10:1. It can also be noted that increased pressure enhances the MTBE synthesis. For a 20-fold increase of pressure

Table 10. Temperature Dependence of the Theoretical Ratio
of Water to MTBE in an FT Reacting System.

Data for $p = 10.0$ atm.

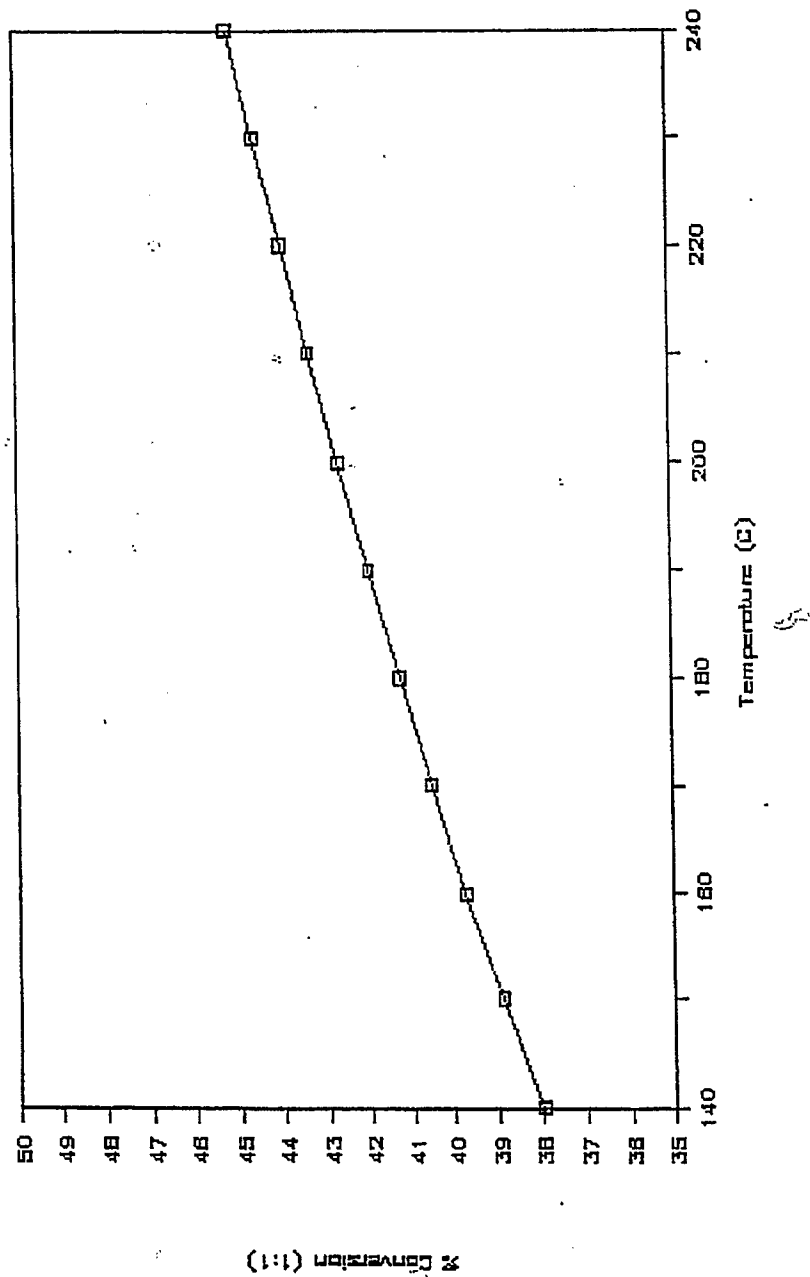
T(°C)	%X _e (1:1)*	X _w	X _{MeOH} =X _{IB}	X _{MTBE}	Ratio (W/MTBE)
140	34.06	0.16	0.42	0.14	1.14
160	19.68	0.20	0.40	0.08	2.5
180	10.56	0.24	0.38	0.04	6.0
200	5.72	0.28	0.36	0.02	14.0
220	3.15	0.32	0.34	0.01	32.0
240	1.80	0.36	0.32	0.006	60.0

* Equilibrium conversion for the MTBE synthesis reaction.

Table 11. Temperature Dependence of the Equilibrium Conversion X_e for the MTBE Hydrolysis Reaction.

T (°C)	K_a	% X_e (1:1)
140	0.376	38.02
150	0.405	38.90
160	0.435	39.73
170	0.464	40.53
180	0.495	41.29
190	0.525	42.01
200	0.555	42.70
210	0.586	43.36
220	0.616	43.98
230	0.647	44.58
240	0.678	45.16

Fig. 4. MTBE Hydrolysis Reaction Data



(from 0.5 to 10.0 atm.), there is a 10-fold increase in the % equilibrium conversion at T=140°C and a 20-fold increase at T=240°C. An increase of the initial reactant ratio results in an increase of the conversion to MTBE.

From the above analysis we can conclude that the synthesis of MTBE is favored at low temperatures, high pressures, and using an excess of one reactant. The MTBE hydrolysis reaction is slightly endothermic ($\Delta H=2.82$ kcal/mol) and as such it is favored at high temperatures. However the effect of temperature is of much less significance for this conversion. Pressure does not influence the hydrolysis conversion directly but can indirectly affect it by changing the relative solubilities of MTBE and H₂O in the liquid phase medium.

WORK PLANNED FOR NEXT REPORTING PERIOD

We expect to complete the construction and testing of the SBCR. The evaluation of the zeolite catalysts should be complete by the end of the next quarter and some preliminary runs in which isobutylene is added during alcohols synthesis will be complete.

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