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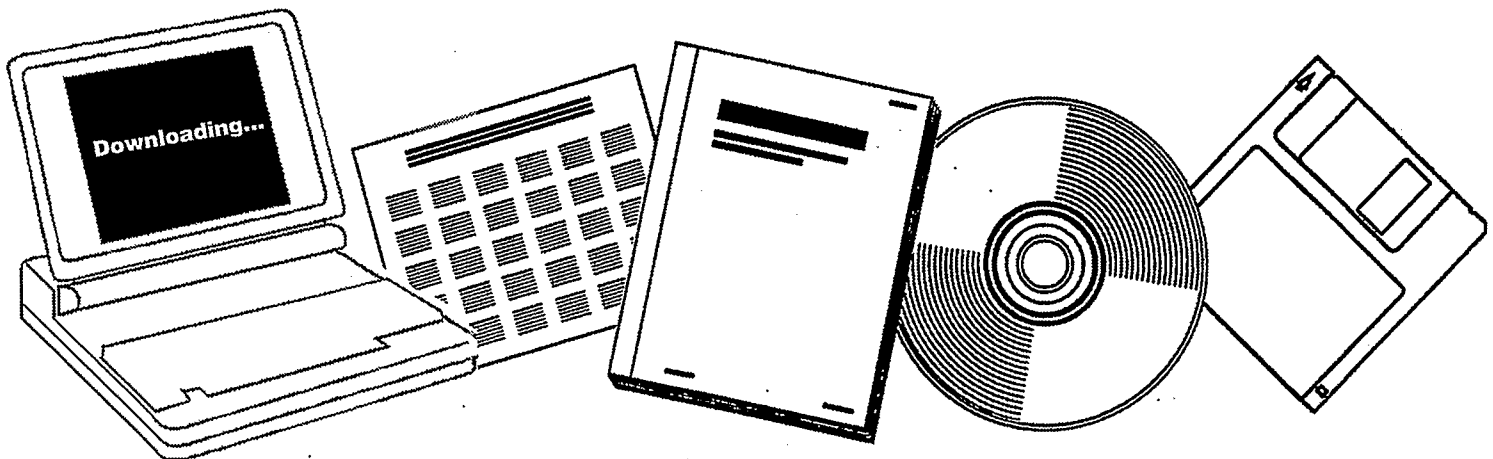
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**SYNTHESIS OF OCTANE ENHANCERS DURING  
SLURRY-PHASE FISCHER-TROPSCH. QUARTERLY  
TECHNICAL PROGRESS REPORT NO. 9, OCTOBER  
1, 1992--DECEMBER 31, 1992**

ALTAMIRA INSTRUMENTS, INC.  
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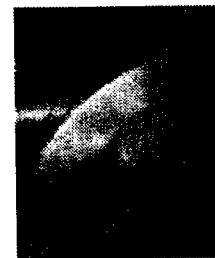
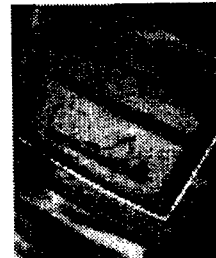
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**QUARTERLY TECHNICAL PROGRESS REPORT No. 9**

Covering the Period October 1, 1992 to December 31, 1992

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

Prepared for the U.S. Department of Energy Under  
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June 30, 1993

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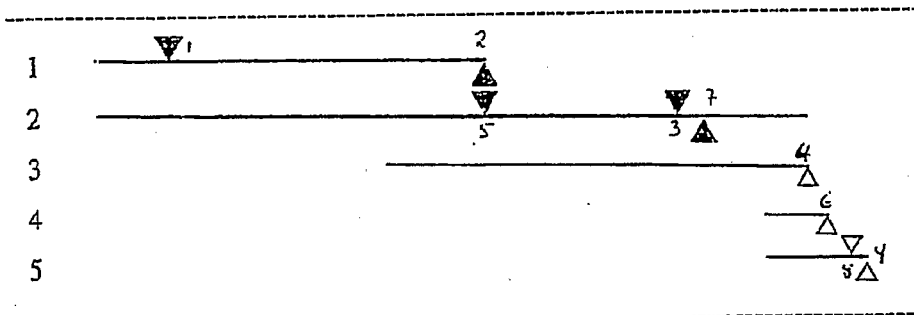
## TABLE OF CONTENTS

Planned Task and Milestone Schedule .....	1
Objectives .....	2
Work Accomplished This Quarter .....	2
Ninth Quarter's Technical Report .....	3
1. Ether Synthesis During FT Reaction .....	3
1.1. Introduction .....	3
1.2. Experimental .....	3
1.2.1. Catalysts .....	3
1.2.2. Reaction Studies .....	5
1.3. Results and Discussion .....	5
1.3.1 CO Hydrogenation .....	5
2. Slurry-Phase MTBE Synthesis .....	7
2.1 Introduction .....	7
2.2 Experimental .....	13
2.3 Results and Discussion .....	13
3. Work Planned for Next Quarter .....	19

## PLANNED TASK AND MILESTONE SCHEDULE

-----Year 1-----      -----Year 2-----      ---Year 3---

Task    Qt1    Qt2    Qt3    Qt4    1 2 3 4 5 6 7 8 9 10 11 12    1 2 3 4 5 6



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 i-butylene addition during formation of alcohols. Decision made on catalysts to be studied in SBCR.
M4	Completion of slurry reaction of i-butylene addition during formation of alcohols.
M5	Completion of catalyst screenings for study of i-butylene addition to FT liquid products using acid catalysts. Decision made on catalysts to be studied in SBCR.
M6	Completion of slurry reaction of i-butylene 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 i-butylene during the formation of methanol and/or higher alcohols directly from CO and H<sub>2</sub> during slurry-phase Fischer-Tropsch.
- Addition of i-butylene 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 ninth quarter we completed all the catalyst characterization and screening experiments related to the three reaction schemes outlined above. We also have completed two runs related to the slurry-phase synthesis of MTBE from methanol and i-butylene in a slurry bubble column reactor.

## NINTH QUARTER'S TECHNICAL REPORT

### 1. ETHER SYNTHESIS DURING FT REACTION

#### 1.1 INTRODUCTION

One of proposed schemes for the direct synthesis of MTBE from syngas involves the incorporation of i-butylene during methanol synthesis from syngas. This incorporation can take place in one of the following two ways:

1. By interception of a methanol reaction intermediate by i-butylene at a methanol synthesis site.
2. By secondary reaction of methanol produced from syngas and i-butylene on an acid site.

Detailed data for these two schemes over various catalysts have been presented in previous technical reports. This report summarizes the work done in this project to test each of these approaches for the synthesis of MTBE and to identify suitable catalysts for the conversion.

#### 1.2 EXPERIMENTAL

The catalyst preparation, reaction system, and conditions used in this portion of the work was described in detail in the Seventh and Eighth Technical Reports. The only change made to the experimental setup was the installation of an automatic sampling system for online GC analysis. This has resulted in significant improvement in the reproducibility of data collection.

##### 1.2.1 Catalysts

A series of unpromoted and lithium-promoted silica-supported palladium catalysts were used as the bases of this portion of the work. A Pd-exchanged Y-zeolite was also studied. The composition of these catalysts as determined by ICP spectroscopy are summarized in Table 1.

The silica supported catalysts were used by themselves or in a composite with either of two zeolites, an HY (UOP LZ210-12) or ZSM-5 (Mobil).

Table 1  
Metal Loadings from Elemental Analysis

Catalyst Name	Description	Pd (wt%)	Li (wt%)	Li/Pd Atomic
Pd/S1	Pd/SiO <sub>2</sub>	4.36	-	-
Li5.8/Pd/S1	Li-Pd/SiO <sub>2</sub>	"	1.66	5.85
Li4/Pd/S1	Li-Pd/SiO <sub>2</sub>	"	1.17	4.1
Pd/S2	Pd/SiO <sub>2</sub>	5.01	-	-
Li1/Pd/S2	Li-Pd/SiO <sub>2</sub>	"	0.26	0.8
Li4/Pd/S2	Li-Pd/SiO <sub>2</sub>	"	1.14	3.6
PdNaY		6.21	-	-



### 1.2.2 Reaction studies

Since the formation of MTBE from methanol and i-butylene is thermodynamically limited at high temperatures, the reactions were carried out in the temperature range of 175-200°C. At these low temperatures the total CO conversion was typically less than 2%, and the low concentration of products made their analysis very difficult. Even at the higher temperature of 200°C, total conversion never approached the equilibrium limit.

## 1.3 RESULTS AND DISCUSSION

### 1.3.1 CO hydrogenation

#### 1.3.2.1 Synthesis of MeOH during CO hydrogenation

Activity for CO hydrogenation was evaluated for all the Pd/SiO<sub>2</sub> and Li-promoted Pd/SiO<sub>2</sub> catalysts described in Table 1. These catalysts were all found to be active for methanol synthesis. Preliminary results for most these catalysts were described in the Seventh and Eighth Quarterly Technical Reports.

#### 1.3.2.2 Addition of i-Butylene During CO Hydrogenation

The incorporation of i-butylene during CO hydrogenation was studied over the following four catalysts systems:

- i. FTS catalysts active for MeOH synthesis;
- ii. Bi-functional catalysts active for MeOH synthesis and having acid sites;
- iii. Composite catalysts, i.e., physical mixtures of (i) and an zeolite; and
- iv. Dual bed arrangements of (i) and an acid zeolite.

It was determined that, in the absence of acid sites, i-butylene could not be incorporated into the reaction products during CO hydrogenation. However, when acid sites were included in the catalyst in the form of a zeolite, measurable production of MTBE could be observed. Table 2 compares the rates of MTBE formation and MeOH elution over the Li5.8/Pd/S1 catalyst by itself and composited, either in a physical mixture or in a dual-bed arrangement, with the two different zeolites. Figures 1, 2 and

Table 2

Rate of MeOH Elution and MTBE Formation During CO Hydrogenation Over Composite Catalysts : Li5.85/Pd/S1 + Zeolite

T = 175° C , P = 7 atm, H<sub>2</sub>/CO = 1

Zeolite	Configuration	Rate <sub>MTBE</sub> <sup>1</sup> μ mol/g.hr	Rate <sub>MeOH</sub> <sup>2</sup> μ mol/g.hr
-	single cat	0	60
LZ-210-12	dual bed	0.53 <sup>@</sup>	6.5
LZ-210-12	physical mix	0.22	3.5
ZSM-5	dual bed	0.44	5.5
ZSM-5	physical mix	1.8	8.25

1 Average MTBE formation rate 4-7 hrs after IB addition.

2 Average MeOH elution rate 4-5 hrs before IB addition.

@ 2 hrs after IB addition after which rate dropped to zero.

3 shows typical rates of formation, conversions, and selectivities to various products for a Li-Pd catalyst composited with a zeolite (Li4/Pd/S2 and ZSM-5). Prior to the addition of i-butylene at 20 hours, the main products of the reaction were C<sub>1</sub> to C<sub>3</sub> hydrocarbons and methanol. Upon addition of i-butylene the rate of MeOH formation dropped to near zero and i-butylene was converted to C<sub>3</sub> to C<sub>7</sub> hydrocarbons. With time-on-stream the selectivity for the C<sub>8</sub> i-butylene dimer increased.

Table 3 summarizes the rates of MeOH and MTBE formation over various catalysts systems. Table 4 shows the conversion of i-butylene to other various products for the same experiments.

This portion of the study has clearly shown the inability of Pd metal sites (and in previous studies, Rh) to incorporate i-butylene into the reaction intermediates during methanol synthesis. Likewise, they show that MTBE can be synthesized from syngas and i-butylene over bifunctional catalysts having both methanol synthesis sites and acid sites. Such a bifunctional catalyst may consist of a physical mixture of Li-Pd/SiO<sub>2</sub> with an acid zeolite, such as ZSM-5. This combination will be further studied under slurry-phase conditions for the reaction.

## 2. SLURRY-PHASE MTBE SYNTHESIS

### 2.1 INTRODUCTION

The reaction of methanol with i-butylene has been demonstrated in the gas-phase over inorganic acid catalysts, i.e., zeolites, at temperatures as high as 175°C. These results have been reported in the Second through Sixth Quarterly Technical Reports. One primary objective of this project is to evaluate this reaction using methanol produced during FT synthesis, that is, having a significant amount of hydrocarbons in the mix.

We are currently evaluating this process using a laboratory-scale slurry bubble column reactor (SBCR) and using as the slurry medium a mixture of C<sub>30</sub> to C<sub>50</sub> paraffinic hydrocarbons.

Figure 1. Rate of hydrocarbon formation for a 10:1 composite of catalyst Li4/Pd/S2 and ZSM-5. Syngas only: 0 to 20 hours; syngas and i-butylene: after 20 hours.

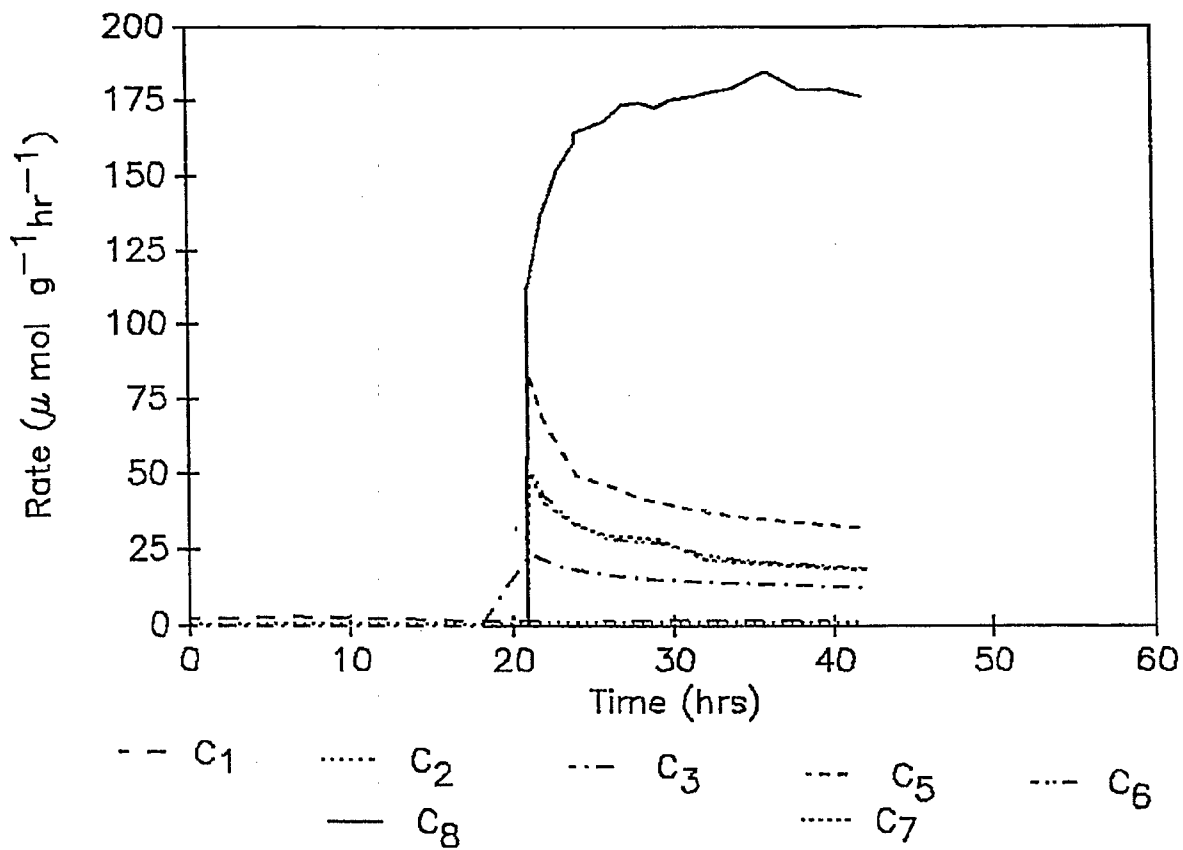


Figure 2. Rate of MTBE (○) and methanol (Δ) formation for a 10:1 composite of catalyst Li4/Pd/S2 and ZSM-5. Syngas only: 0 to 20 hours; syngas and i-butylene: after 20 hours.

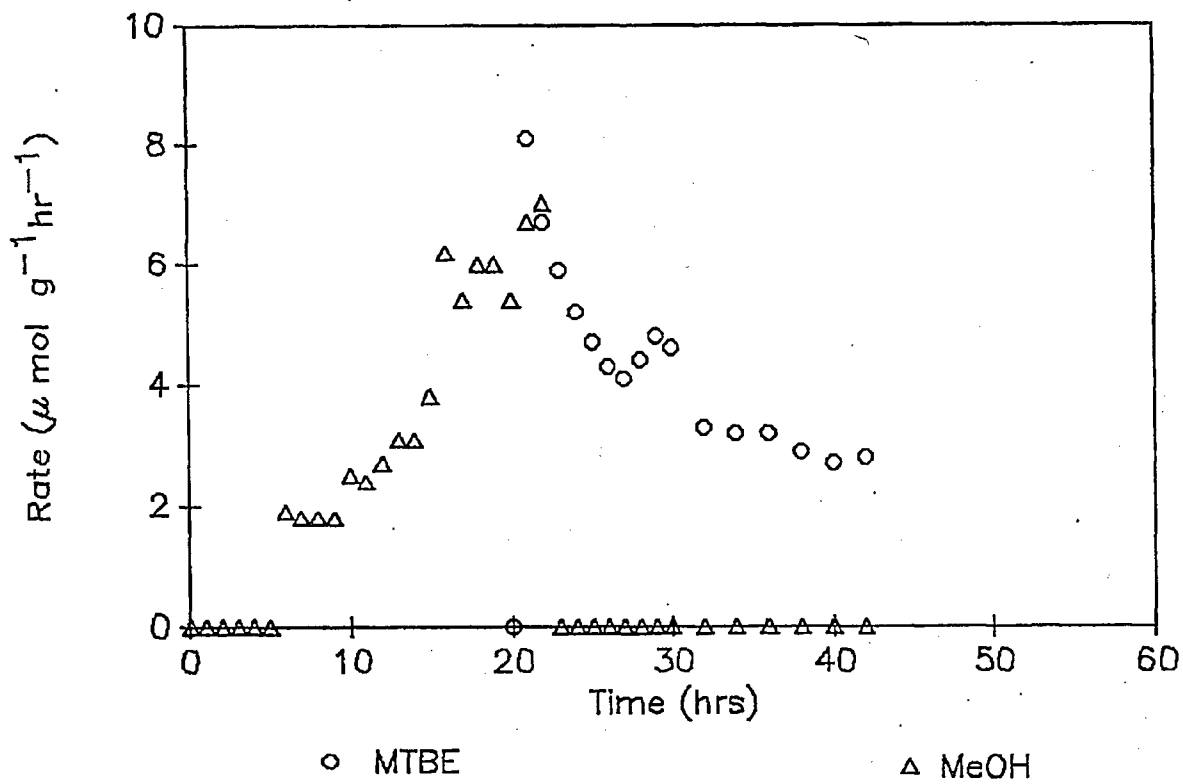


Figure 3. Conversion of i-butylene and selectivities to major products during co-feeding of syngas and i-butylene over a 10:1 composite of catalyst Li4/Pd/S2 and ZSM-5.

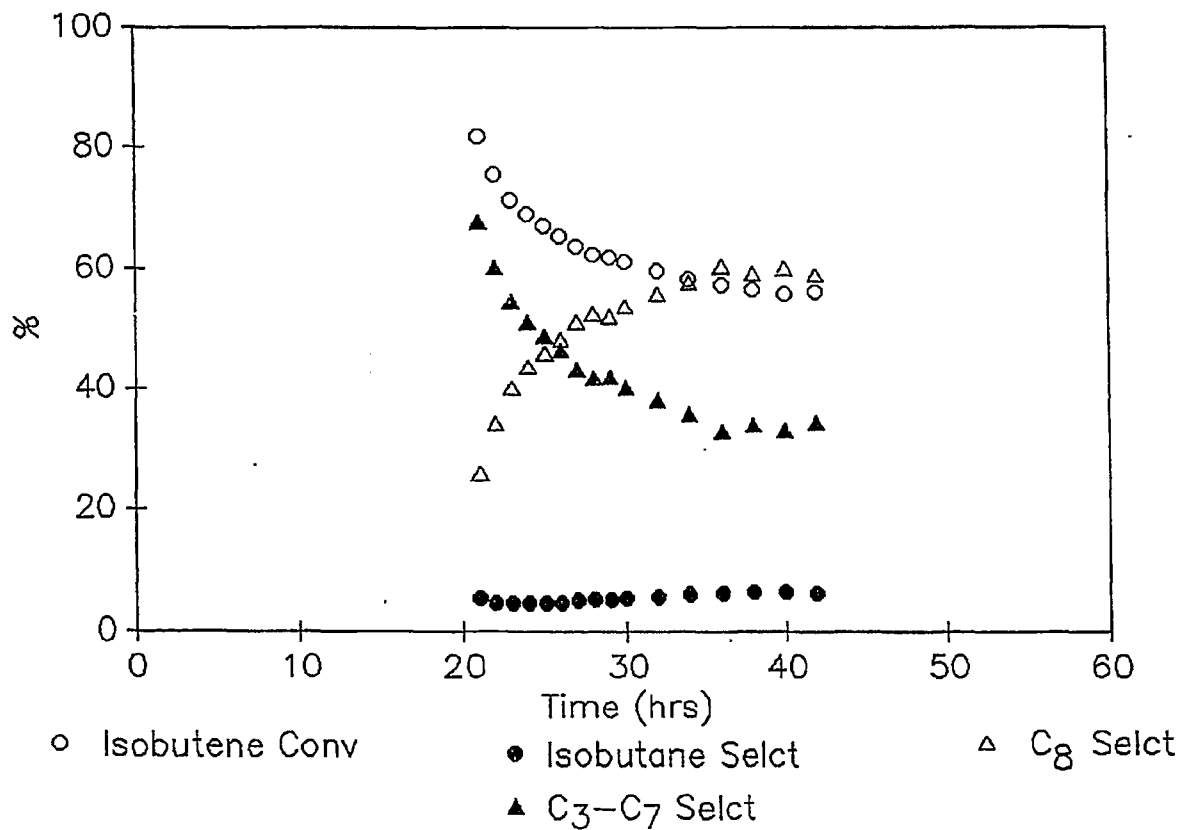


Table 3

Rates of MeOH Elution and MTBE Formation During CO Hydrogenation

Catalysts	Exp. No.	Rate <sub>MeOH</sub> μ mol/g.h			Rate <sub>MTBE</sub> μmol/g h	
		12 hrs.	22 hrs. <sup>1</sup>	42 hrs. <sup>2</sup>	22 hrs. <sup>1</sup>	42 hrs. <sup>2</sup>
Pd/S2	23	275	200	*	0	0
Li1/Pd/S2	17	550	*	325	0	0
Li1/Pd/S2 + ZSM-5 <sup>@</sup>	18	330	104 <sup>#</sup>	*	0.8 <sup>#</sup>	*
Li4/Pd/S2	26	49	40.8	26.5	0	0
Li4/Pd/S2 + ZSM-5 <sup>@</sup>	24	2.8	7.0	0	3.6	3.8
Li4/Pd/S2 + LZ210-12 <sup>@</sup>	27	11.5	12.3	2.1	4.2	0
PdNaY	25	375.8	330	34.2	3.6	3.8
PdNaY + ZSM-5 <sup>@</sup>	28	288.1	199.7	1.2	2.4	1.3

- 1 2 hrs. after the addition of IB started.  
2 22 hrs. after the addition of IB started.  
\* Data not available.  
# Reaction time 38 hrs.  
@ Physical mixture

Table 4  
 Selectivity and Conversion of Iso-butylene Added During CO Hydrogenation<sup>1,2</sup>  
 ( After 2 and 22 hrs of IB addition )

Catalyst	Exp NO.	IB Conv %		IB-ane Select %		C8		Select %	C3-C7		Select t%
		2 hrs	22 hrs	2 hrs	22 hrs	2 hrs	22 hrs		2 hrs	22 hrs	
Pd/S2	23	100	100	100	100	0	0	0	0	0	0
Li1/Pd/S2	17	100	100	100	100	0	0	0	0	0	0
Li1/Pd/S2 + ZSM-5 <sup>a</sup>	18	100	100 <sup>#</sup>	34.5	75.7 <sup>#</sup>	7.9	14.9	57.5	9.3 <sup>#</sup>		
Li4/Pd/S2	26	7.7	7.6	88.9	97.8	6.7	2.0	0	0		
Li4/Pd/S2 + ZSM-5 <sup>a</sup>	24	75.6	56.1	4.8	6.3	34.2	58.9	60.2	34.4		
Li4/Pd/S2 + LZ210-12 <sup>a</sup>	27	51.5	12.0	17.7	47.8	13.3	59.8	68.4	-		
PdNaY	25	90.4	93.4	72.9	74.6	0	1.8	26.7	10.5		
PdNaY + ZSM-5 <sup>a</sup>	28	90.9	91.7	52.7	63.4	4.7	9.9	42.3	26.5		

1 T = 200° C, P = 7 atm., H<sub>2</sub>/CO = 1  
 2 20 hrs total reaction time before IB addition.  
 # 16 hrs after IB addition.  
 @ Physical Mixture.



## 2.2 EXPERIMENTAL

The SBCR has been fully described in the Sixth Quarterly Technical Report. The dispersing medium consisted of Chevron Synfluid PAO 4, a hydrogenated poly- $\alpha$ -olefin having a molecular weight of ca. 600.

The start-up procedure was as follows:

- 1) The reactor was brought to operating temperature overnight. The SBCR and transfer lines were maintained at 100°C and 150°C, respectively. A flow of nitrogen was started to flush the reactor column (about 2 hours).
- 2) Meanwhile, the Synfluid was heated to operating temperature in a separate in-line vessel prior to introduction into the SBCR. It was introduced into the reactor using nitrogen pressure.
- 3) After the temperatures stabilized (about 2.5 hours) the catalyst was loaded and the methanol and i-butylene feeds were started.

The catalyst used was an H-Y zeolite (UOP LZ210-12) which had been crushed and sieved to 30-100  $\mu$ m. A 20% catalyst loading (weight of catalyst/weight of liquid) was used. The following feed flow rates were used:

Nitrogen:	1.13 SL/min
5% i-butylene in He:	90 Scc/min
methanol:	0.11 mL/min

This corresponded to a methanol/i-butylene=6.0 and a linear gas velocity of 2.1 cm/sec. The effluent was analyzed periodically during the run by on-line gas chromatography.

## 2.3 RESULTS AND DISCUSSION

Two similar runs were conducted. Results from Run #2 are summarized in Figures 4 through 7 in which various parameters are summarized as a function of time. Figures 4, 5 and 6 are each divided into four time periods. Period I represents analyses taken prior to the introduction of the catalyst. Period II represents analyses taken after introduction of the catalyst. In Period III the i-butylene was cut-off. The i-butylene was restored in Period IV.

Figure 4. Relative molar concentrations of methanol and i-butylene feeds in SBCR. Experimental conditions and meaning of regions I, II, III, and IV is explained in text.

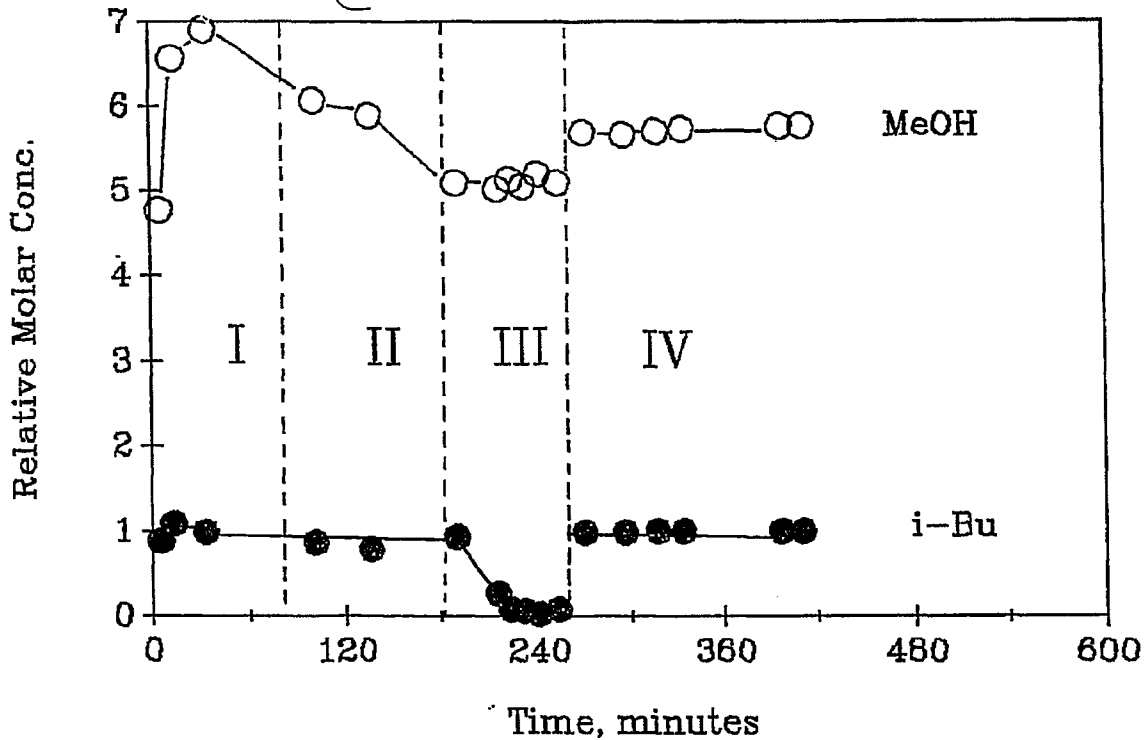


Figure 5. Iso-butylene conversion during reaction of methanol and i-butylene in SBCR. Experimental conditions and meaning of regions I, II, III, and IV is explained in text.

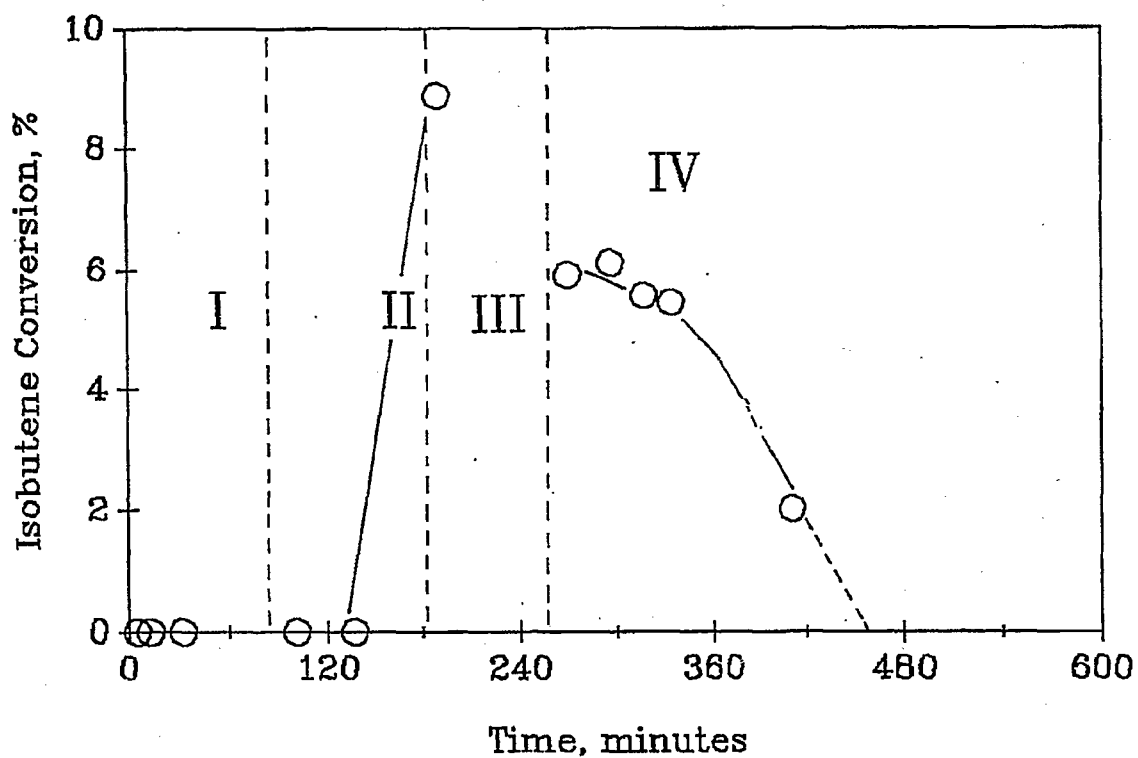


Figure 6. Selectivities to major products during reaction of methanol and i-butylene in SBCR. Experimental conditions and meaning of regions I, II, III, and IV is explained in text.

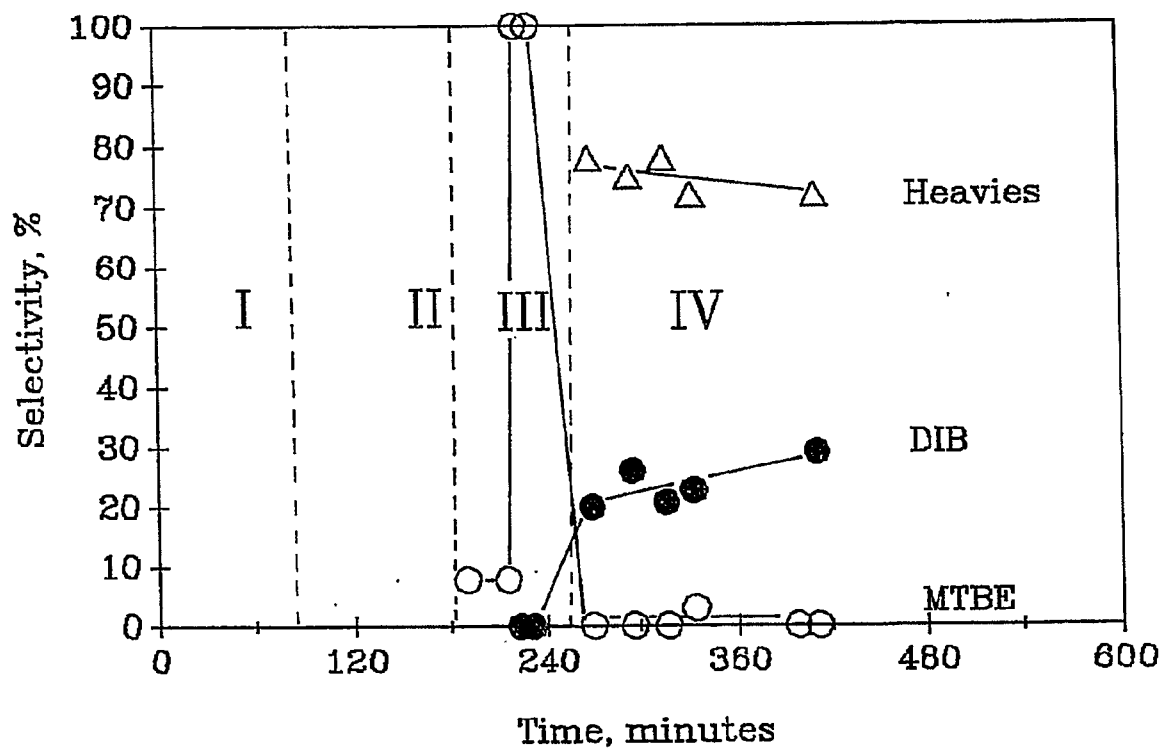


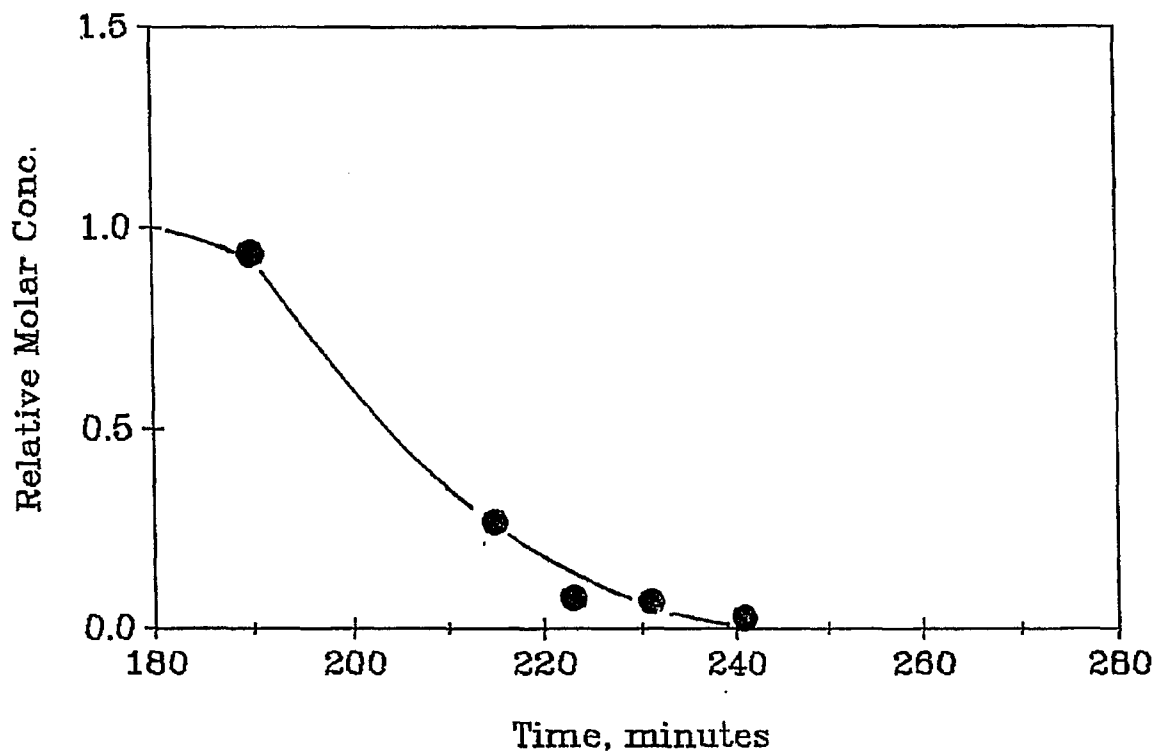
Figure 4 shows the stability of the feed as a function of time. After approximately one hour, the methanol/i-butylene ratio stabilized and remained fairly constant at 6 except for Period III when the i-butylene was shut-off. Figure 5 shows the i-butylene conversion as a function of time. An induction period of over one hour was noted before measurable conversion was obtained. It can also be noted that the reaction rate decreased rapidly, reaching negligible conversion after only 7 hours on-stream. The main products observed in the reaction were MTBE, the i-butylene dimer, and a broad GC peak at long elution times which corresponds to i-butylene oligomers, possibly a C<sub>12</sub> hydrocarbon. We have observed these heavies during gas-phase reaction at low methanol/i-butylene ratios.

Figure 7 summarizes the carbon selectivities observed towards the main products. During Period IV, the main products observed were the heavy hydrocarbons, with selectivity for MTBE being less than 3-5%. The only time that high MTBE selectivity was noted was during period III, when the i-butylene feed was shut-off.

The large amounts of heavy products and the low selectivity to MTBE were surprising in view of our previous experiments in the gas phase and the high methanol-to-i-butylene ratio used in these runs. In the gas-phase and with methanol/i-butylene = 0.5, over 95% selectivity to MTBE was observed with this catalyst at this temperature. The higher level of methanol used here would be expected to further improve the MTBE selectivity.

Perhaps one reason for the poor MTBE selectivity relates to the relative solubilities of the reactants in the Synfluid changing the effective methanol/i-butylene ratio. Figure 8 shows the relative molar concentration of i-butylene during Period III. At 180 minutes, the gas supply of that reactant was shut-off, yet the analyses show that i-butylene continued to elute from the reactor for at least an additional 2 hours. It seems reasonable that the i-butylene is highly soluble in the Synfluid since they are both non-polar hydrocarbons. Likewise, one would expect the methanol to not be quite as soluble and thus the methanol/i-butylene ratio in the liquid medium may be very low, favoring the oligomerization of i-butylene. Indeed, the only time that MTBE selectivity was high was after the i-butylene supply was shut-off. We intend to quantify these solubilities in future experiments.

Figure 7. Relative concentration of i-butylene in SBCR effluent after feed shut-off during reaction.



3. WORK PLANNED FOR NEXT QUARTER

Next quarter will concentrate in the SBCR runs. We expect to complete all experimental runs in the next quarter.

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