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# SYNTHESIS OF OCTANE ENHANCERS DURING SLURRY-PHASE FISCHER-TROPSCH. QUARTERLY TECHNICAL PROGRESS REPORT NO. 3, APRIL 1, 1991--JUNE 30, 1991

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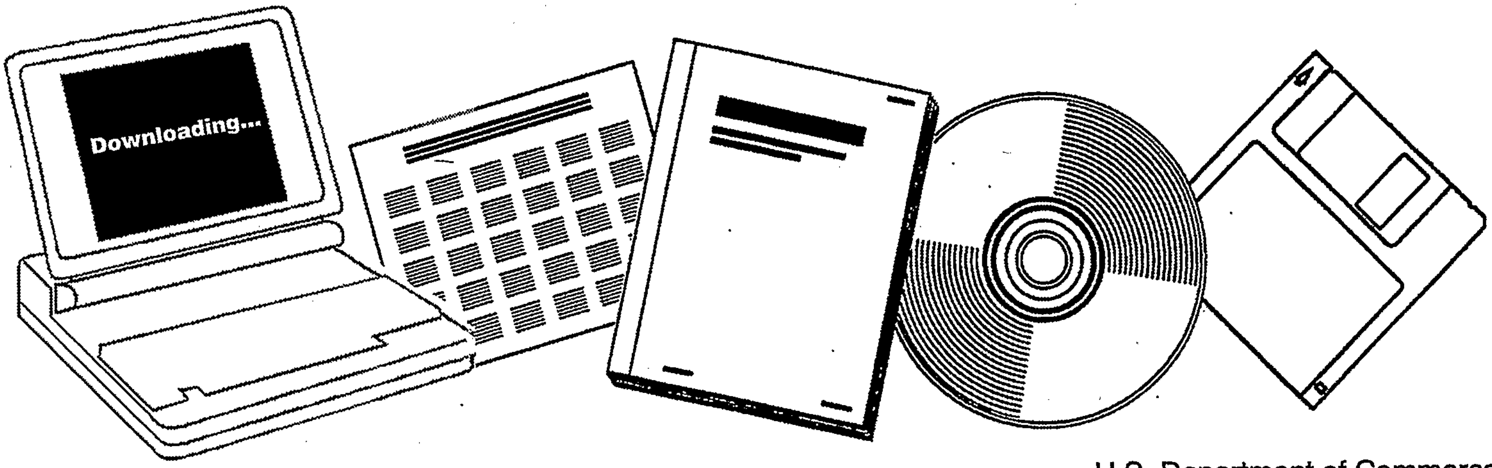

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## QUARTERLY TECHNICAL PROGRESS REPORT No. 3

Covering the Period April 1, 1991 to June 30, 1991

# SYNTHESIS OF OCTANE ENHANCERS DURING SLURRY-PHASE FISCHER TROPSCH

Prepared for the U.S. Department of Energy Under
Contract No. DE-~~RA~~ac22-90PC90047
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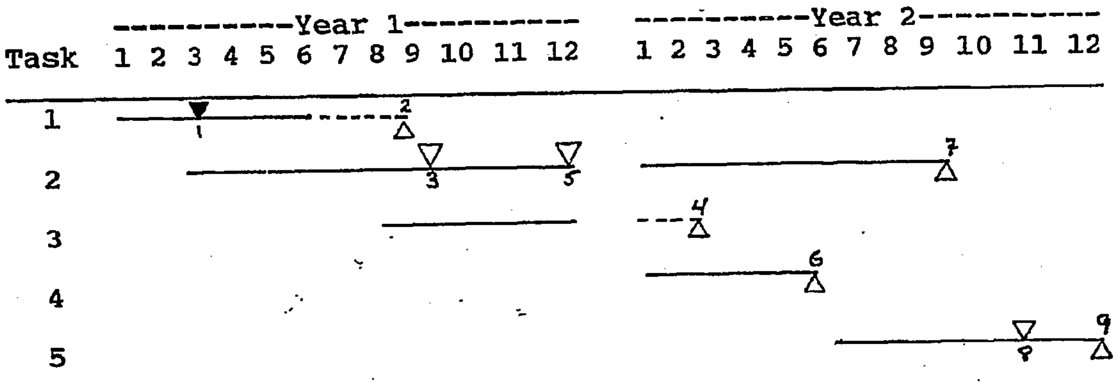
## PLANNED TASK AND MILESTONE SCHEDULE



M = denotes milestone

List of Milestones

| Milestone Number | Description |
|---|---|
| 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:

Scheme 1

- * Addition of isobutylene during the formation of methanol and/or higher alcohols directly from CO and $H_2$ durring 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 during the third quarter continues to concentrate in finalizing the construction of a laboratory scale bubble column reactor and in identifying and screening catalysts suitable for reaction schemes (1) and (2).

The construction of the reactor (Task 1) has been delayed by the late delivery of a critical component, i.e. a high pressure sight-glass. This component is now in-house and properly fitted to the reactor. The construction task is approximately 4 months behind the original schedule. Work on task 2 is proceeding on schedule. Other tasks are running behind schedule only because they require completion of Task 1 in order to proceed.

# THIRD QUARTER'S TECHNICAL REPORT

## GAS PHASE MTBE SYNTHESIS OVER ACID CATALYSTS

### Introduction

Preliminary experiments have been conducted on the synthesis of MTBE over three acid catalysts, the commercially utilized microreticular ion exchange resin (Amberlyst-15) and two HY zeolites of different acidity. Since the Amberlyst resin decomposes at about 100°C, this comparison was conducted at low temperature in order to evaluate the performance of all these catalyst at the same conditions. The main purpose of the experiments on the resin was to provide a baseline comparison between the commercial state-of-the-art catalyst and the zeolites.

### Experimental

The experimental set-up was described in last quarter's Technical Report. Some modifications were necessary in order to improve the reproducibility of the experiments. The major system modification was the inclusion of an on-line gas chromatograph for the analysis. The problems encountered and their solutions are described later.

The catalysts evaluated included two H-Y zeolites with different Si/Al ratio, labelled LZ210-12 and S(LZ12)8. The physical and acid characteristics of these two materials was described last quarter. It should be noted that the latter was considerably more acidic than the former. Also studied, for comparison, was a sample of Amberlyst-15 (Rohm & Haas, Co.), which is the catalyst used in the commercial production of MTBE.

The reaction conditions used were:

| | |
|---|---|
| Temperature: | 100°C |
| Pressure: | 1 atm. |
| He flow rate: | 15-25 cc/min |
| MeOH flow rate: | 2-4 ml/min |
| IBu flow rate: | 6-12 ml/min |
| IBu/MeOH ratio: | 1-3 |
| Catalyst weight: | 100-250 mg |

## Problems Encountered

A number of experimental difficulties were encountered during the start-up of these experiments. These difficulties related to flow fluctuations and analysis reproducibility. It should be mentioned that a significant number of experiments have been conducted but because of these difficulties many experiments did not give reliable data and have thus been disregarded.

One particular problem was the fluctuation in the flow of the reactants, specifically the isobutylene. IBu is used in the form of a liquefied gas having a vapor pressure of about 2 atmospheres at room temperature. The IBu is introduced by controlling the flow out of the cylinder with a needle valve. It was observed that at high flow rates significant fluctuations in the blank analysis occurred. This is perhaps due to cooling of the liquefied IBu upon expansion accompanied by a lowering in vapor pressure. The limit for steady flow of IBu was determined experimentally to be about 10 cc/min. All subsequent experiments were conducted below that value.

An additional potential difficulty involves that product analysis and separation. Some expected products elute very close to each other in the column currently being used giving a potential error in the selectivities reported. We will be switching to a capillary column to resolve this matter.

## Results and Discussion

The results for the title reaction over LZ210-12, S(LZ12)8, and two separate experiments for Amberlyst-15 are given in Tables I-IV, respectively. All the data reported refers to steady-state conditions which was achieved after about 1-2 hours and was stable for a long period of time (>4 hours). Although the conditions were not identical for the various experiments, Tables I and IV and Tables II and III are sufficiently similar to make general comparisons.

All catalyst exhibited significant conversion of methanol and sufficiently high selectivity to MTBE for accurate measurement. In addition to MTBE, dimethyl ether (DME), some higher alcohols, and hydrocarbons were also observed. In all cases the isobutylene dimer ($C_8$ hydrocarbon) was the most significant byproduct. In one case (Table IV) it was the principal product. Surprisingly, MTBE selectivity was significantly lower for the Amberlyst-15 catalyst showing a clear advantage to using H-Y zeolites in the reaction. Dimethyl ether was only found to be a significant side product in the reaction over Amberlyst-15. There also appears to be a small difference in the total methanol conversion, again favoring the zeolites, however due to the differences in conditions a definite conclusion is not possible.

It is impossible at this point to make any conclusions relating the acid strength of the zeolites to the reaction, as we do not have sufficient data. The zeolites appear to be very stable at this temperature (100°C) and exhibit higher selectivity to MTBE than the Amberlyst-15 resin. In future work we plan to compare various HY zeolites with different acidities at the same conditions in order to evaluate the effects of acidity in selectivity and deactivation. We also plan to include other zeolites, such as ZSM-5, in the screening process.

## TABLE I

MTBE Synthesis over Zeolite LZ 210 12

m = 250 mg  T = 100 C
He Flow Rate : 15 cc/min
MeOH Flow Rate : 3 cc/min
IB Flow Rate : 10 cc/min
IB : MeOH Ratio : 3.0
WHSV : 7.7 (gr/gr cat.*h)

Total MeOH Conversion : 24.5%
MeOH Conversion to MTBE : 41.8% of total

Product Analysis (mol%):

| | |
|---|---|
| Hydrocarbons : | |
| C1 | 0.23 |
| C2 | 0.1 |
| C3 | 0.05 |
| C5 | 2.46 |
| C6 | 0.16 |
| C7 | -- |
| Dimer | 13.72 |
| Oxygenates : | |
| DME | -- |
| t-BuOH | -- |
| Pentanols | 12.58 |
| MTBE | 70.9 |

## TABLE II

MTBE Synthesis over Zeolite S(LZ 12)8

m = 100 mg   T = 100 C
He Flow Rate : 15 cc/min
MeOH Flow Rate : 3 cc/min
IB Flow Rate : 6 cc/min
IB : MeOH Ratio : 2.0
WHSV : 13.2 (gr/gr cat.*h)

Total MeOH Conversion : 17.8%
MeOH Conversion to MTBE : 70.2% of total

Product Analysis (mol%):

| | |
|---|---|
| Hydrocarbons : | |
| C1 | 0.87 |
| C2 | 0.51 |
| C3 | 0.18 |
| C5 | 1.54 |
| C6 | 0.54 |
| C7 | -- |
| C8 | 0.77 |
| Dimer | 24.41 |
| Oxygenates : | |
| DME | 0.34 |
| t-BuOH | 0.43 |
| Pentanols | 1.31 |
| MTBE | 69.1 |

## TABLE III

MTBE Synthesis over Amberlyst 15 Resin

m = 100 mg T = 100 C
He Flow Rate : 24 cc/min
MeOH Flow Rate : 4 cc/min
IB Flow Rate : 9 cc/min
IB : MeOH Ratio : 1.0
WHSV : 19.5 (gr/gr cat.*h)

Total MeOH Conversion : 6.9%
MeOH Conversion to MTBE : 62.3% of total

Product Analysis (mol%):

| | |
|---|---|
| Hydrocarbons : | |
| C1 | 0.24 |
| C2 | 0.13 |
| C3 | -- |
| C5 | 0.71 |
| C6 | 0.48 |
| C7 | -- |
| C8 | 4.65 |
| Dimer | 34.66 |
| Oxygenates : | |
| DME | 17.13 |
| t-BuOH | 0.26 |
| Pentanols | 0.42 |
| MTBE | 41.32 |

## TABLE IV

MTBE Synthesis over Amberlyst 15 Resin

m = 250 mg   T = 100 C
He Flow Rate : 30 cc/min
MeOH Flow Rate : 5 cc/min
IB Flow Rate : 10 cc/min
IB : MeOH Ratio : 2.0
WHSV : 9 (gr/gr cat.*h)

Total MeOH Conversion : 19.2%
MeOH Conversion to MTBE : 27.0% of total

Product Analysis (mol%):

| | |
|---|---|
| **Hydrocarbons :** | |
| C1 | 0.2 |
| C2 | 0.1 |
| C3 | -- |
| C5 | 3.4 |
| C6 | 0.9 |
| C7 | -- |
| C8 | 61.1 |
| **Oxygenates :** | |
| DME | 20.3 |
| t-BuOH | 0.4 |
| Pentanols | 3.4 |
| MTBE | 10.6 |

## SYNTHESIS OF MTBE BY INCORPORATION OF ISOBUTYLENE DURING ALCOHOL SYNTHESIS

### Introduction

One of the schemes proposed for the direct synthesis of MTBE from syngas involves the incorporation of isobutylene during methanol synthesis from syngas. Because the reation of methanol and isobutylene to MTBE is thermodynamically limited at high temperatures, we have concentrated our work in low temperature methanol synthesis catalysts. Last quarter's Technical Report described the synthesis of methanol at 180-250°C with high selectivity using a catalyst consisting of 1.5 wt% Rh, an equimolar concentration of Mo, and a silica support.

These same Rh-Mo/$SiO_2$ catalysts have been studied for their ability to incorporate isobutylene, and thus form MTBE, during CO hydrogenation. The use of this catalyst coupled with an acidic zeolite catalyst to provide the traditional MTBE-synthesis acid sites was also studied.

### Experimental

The preparation of the Rh-Mo/$SiO_2$ catalysts and the LZ-210-12 zeolite were described in our Second Quarter's Technical Report. The general operating conditions for methanol synthesis were also detailed in that report.

For the isobutylene addition experiments, a high pressure saturator was added to the reactor system to provide a means of delivering a constant concentration of isobutylene. Before filling the saturator with isobutylene it was first purged with helium and then evacuated. The isobutylene tank was inverted and liquid isobutylene was transferred directly into the saturator. The isobutylene was added to the reacting mixture by flowing a constant amount of helium through the saturator and then passing this gas stream through a de-mister in order to avoid liquid carry-over. The saturator was maintained at room temperature resulting in a nominal isobutylene partial pressure of 2.6 atm. and a $H_2$:CO:i-Butylene ratio of 1:1:0.8. A number of problems were discovered in the course of these experiments and these will be detailed later.

Results

In last quarter's Technical Report the hydrogenation of CO over Rh-Mo/$SiO_2$ catalysts was detailed. The reaction was carried out at temperatures ranging from 180 to 250°C and pressures of 1 and 8 atm. In all cases selectivity towards alcohols, particularly methanol, were found to be quite high, i.e. between 70 and 90% of the oxygenates. Tables V and VI summarize the results of these reactions which have already been reported. Note that in all these experiments NO MTBE WAS FORMED.

Since the reaction of isobutylene and methanol to form MTBE requires initiation by acid sites, a composite catalyst bed was also studied. The dual bed consisted of 0.5 g of the Rh-Mo/$SiO_2$ catalysts and an equal amount of of the H-Y zeolite LZ-210-12 described in last quarter's Technical Report. Prior to reaction the zeolite catalyst was converted from the ammonium form to the proton form by heating in flowing hydrogen at 2°C/min to 300°C and maintaining it at that temperature for approximately 16 hours. This pretreatment also accomplished the reduction of the Rh catalyst. The product distribution for the 8 atm. run is presented in Table VII. The product distribution is significantly different over this catalyst formulation than over the Rh-Mo/$SiO_2$, particularly with respect to the increased selectivity for oxygenates and the higher yield of methanol at 200°C. It should be noted that the overall CO conversion rate is not markedly changed by addition of the zeolite. Also, note that NO MTBE was detected.

## TABLE V

Reaction of syngas over 1.5% Rh-Mo/$SiO_2$

$H_2$/CO=1.0, 1 atm.

| Temperature, °C | 200 | 230 | 250 |
|---|---|---|---|
| CO Conversion, % | 0.26 | 0.61 | 0.75 |
| Rate, mol/g h | 0.015 | 0.034 | 0.042 |
| SELECTIVITIES | | | |
| Hydrocarbons | 47.6 | 70.6 | 86.9 |
| Oxygenates | 52.4 | 29.4 | 13.1 |
| OXYGENATES | | | |
| Methanol | 84.5 | 81.1 | 68.0 |
| Ethanol | 4.0 | 9.8 | 25.4 |
| Acetaldehyde | 14.2 | 5.6 | 6.6 |

## TABLE VI

### Reaction of syngas over 1.5% Rh-Mo/$SiO_2$

### $H_2/CO=1.0$, 8 atm.

| Temperature, °C | 200 | 230 | 250 |
|---|---|---|---|
| CO Conversion, % | 0.53 | 2.25 | 2.75 |
| Rate, mol/g h | 0.029 | 0.098 | 0.15 |
| **SELECTIVITIES** | | | |
| Hydrocarbons | 26.1 | 44.1 | 55.0 |
| Oxygenates | 73.9 | 55.9 | 45.0 |
| **OXYGENATES** | | | |
| Methanol | 91.8 | 89.4 | 82.8 |
| Ethanol | 8.2 | 10.6 | 15.5 |
| Acetaldehyde | 0 | 0 | 1.6 |

## TABLE VII

## Reaction of syngas over 1.5% Rh-Mo/$SiO_2$ + H-Y zeolite
$H_2/CO=1.0$, 8 atm.

| Temperature, °C | 200 | 220 |
|---|---|---|
| CO Conversion, % | 0.49 | 1.84 |
| Rate, mol/g h | 0.032 | 0.103 |
| **SELECTIVITIES** | | |
| Hydrocarbons | 11 | 35.5 |
| Oxygenates | 89 | 64.5 |
| **OXYGENATES** | | |
| Methanol | 99.4 | 72.7 |
| Ethanol | 0.6 | 20.8 |
| Acetaldehyde | 0 | 6.5 |

Isobutylene was added to the syngas over the Rh-Mo/$SiO_2$ catalysts at 1 and 8 atm. and temperatures between 180 and 250°C. In no case was MTBE observed in the products. In contrast, when isobutylene was added to the reaction mixture using the combination catalyst consisting of Rh-Mo/$SiO_2$ and H-Y zeolite, AN APPRECIABLE AMOUNT OF MTBE WAS PRODUCED. Unfortunately, there were a number of experimental difficulties which led to fluctuations in the exact amount of isobutylene which was mixed with the syngas. This made reproducibility nearly impossible and affected the conversion and selectivity calculations. For this reason these numbers are not reported at this time. However, even these preliminary experiments resulted in a number of definite observations which can be reported:

* The product distribution for the composite catalyst was quite different than that for the Rh-Mo/$SiO_2$ catalyst alone. The former being much more selective for oxygenates, particularly methanol.

* Addition of isobutylene during methanol synthesis over the Rh-Mo catalyst alone did not result in the formation of measurable amounts of MTBE.

* Addition of isobutylene during methanol synthesis over the composite catalyst bed resulted in the formation of appreciable amounts of MTBE. In addition, significant amounts of C8 hydrocarbons and other yet unidentified heavy products were also formed.

Problems encountered

There have been a number of experimental problems encountered mainly related to the introduction of isobutylene. Isobutylene tended to condense in dead spaces within the reactor lines even when these lines were heated. This resulted in a continuous background containing isobutylene even for experiments in which no isobutylene was desired. This problem has now been solved by relocating the isobutylene injection point and changing the location of the pressure transducer and the pressure relief valve.

## WORK PLANNED FOR NEXT REPORTING PERIOD

We expect to complete the gas-phase evaluation of the acid catalysts as well as have identified several candidates for the SBCR work. The SBCR should be operational.

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