## ENCLOSURE (B) 9

# STUDIES ON ETHYL ALCOHOL

(In Two Parts)

by

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# PART I

# PREPARATION OF ETHER FROM ETHYL ALCOHOL

by

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Research Period: 1944-1945

SUMMARY

Ethyl alcohol fuel is mixed with ether for good starting qualities; hence, large amounts of ether are necessary as blending fuel.

The sulfuric acid process for production of ether is used, but for mass production of ether, this is not satisfactory. Using activated acid clay, the solid catalytic process of preparing ether has been studied.

As the results of this study, the yield of ether to the alcohol consumed is shown to be 60.2% at 200°C and at 0.33 space velocity. This yield corresponds to 92.5% of the theoretical. (cf, Table II(B)9.) The life of the catalyst appears to be longer than 155 hours.

Date of the beginning Oct. 1944
Date of the finish Feb. 1945

## I. INTRODUCTION

K. KOBAYASHI observed that ether is produced from ethyl alcohol in the presence of acid clay at about 250°C, but the yield is low due to the formation of ethylene as a side reation, and the life of this catalyst is very short.

This study was projected to confirm these facts.

## II. DETAILED DESCRIPTION

The preparation of ether from ethyl alcohol was carried out in the apparatus shown in Figure 1(B)9.

Ethyl alcohol, contained in the calibrated glass cylinder, was run into the reaction tube at constant velocity by adjusting the stopcock. The silica reaction tube was 18mm i.d. and 1200mm long, and was placed in a tubular electric heater that was 1000mm long, and heated to reaction temperature (180°-230°C). The middle of the reaction tube was filled with the catalyst of active clay; and a Ni-Cr thermocouple, enclosed in a sheath of 5mm i.d. silica tubing, was imbedded in the center of the catalyst mass. Reaction products leaving the reaction tube were conducted through two condensers.

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The condensate was collected in the receivers and gas was collected in a gas bottle.

The composition of this condensate, mainly ether, unreacted alcohol, and water, was determined by distillation. The composition of gas (mainly ethylene) was determined by Hempel's gas analysis apparatus.

Samples: Concentrations of alcohol used in this study were 99.3% and 94.5%

Catalyst: Catalyst used in this study was activated acid clay obtained from Toyo Active Clay Co.

Experimental Result. The types of dehydration of ethyl alcohol may be represented as follows:

$$2\ C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O \quad \ldots\ldots\ldots (1)$$

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \quad \ldots\ldots\ldots (2)$$

Generally, reaction (1) occurs at temperatures below 300°C, and reaction (2) at temperatures above 300°C.

At first a study was carried out to clarify the effect of reation temperature and of space velocity. Results are shown in Table I(B)9.

It was found that lower yields of ether and higher gas formation were obtained at higher reaction temperatures. At the higher space velocity, the yield of both ether and ethylene was decreased. Concentrations of alcohol lower than 99.3% are not effective in this reaction. Consequently, it was found that the most effective reation conditions are 200°C and 0.33 space velocity.

The life of this catalyst was tested by the same method using 94.5% alcohol at 200°C and a space velocity of 0.33. Condensate was removed from the separator every two or three hours and tested by distillation.

Table II(B)9 tabulates typical data only, and the mean value in this table is the mean of the total data obtained throughout the experiment (155 hours).

These results show that during the first part of the reaction the catalyst activity is low, but the activity soon increases and remains constant during 155 hours of the experiment. Therefore, it appears that this catalyst is satisfactory for the preparation of ether from alcohol.

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Table I(B)9

PREPARATION OF ETHER BY THE DEHYDRATION OF ALCOHOL IN THE PRESENCE OF ACTIVE CLAY

| Expt. no. | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Alcohol Conc. (% by vol.) | 99.3 | 99.3 | 99.3 | 99.3 | 94.5 |
| Reaction Temp. ($^{o}$C) | 180 | 200 | 230 | 230 | 200 |
| Space Velocity* | 0.33 | 0.33 | 0.33 | 0.5 | 0.33 |
| Condensate Yield (% by vol.) | 95.2 | 92.8 | 82.8 | 88.0 | 92.8 |
| Condensate Comp. (% by vol.) | | | | | |
| Ether fraction,(%) | 37.0 | 57.0 | 59.0 | 46.8 | 57.3 |
| Alcohol fraction,(%) | 61.5 | 38.5 | 30.5 | 50.8 | 34.1 |
| Vol. ethylene gasified | | | | | |
| (lit/100cc of charge) | 1.69 | 2.07 | 6.14 | 3.84 | 0.81 |
| Yield of ether (Vol. % of charged | | | | | |
| alcohol) | 35.3 | 53.2 | 52.1 | 42.1 | 56.2 |
| or (Vol. % of reacted alcohol). | 88.6 | 90.5 | 70.8 | 82.2 | 92.0 |
| Material Balance | | | | | |
| Vol. of alcohol converted to | | | | | |
| ether, (%) | 39.6 | 59.6 | 53.5 | 46.6 | 63.2 |
| Vol. of alcohol converted to | | | | | |
| ethylene, (%) | 4.4 | 5.4 | 16.1 | 10.1 | 2.2 |
| Vol. of alcohol unreacted, (%) | 54.8 | 33.5 | 23.6 | 42.5 | 31.2 |
| Loss of alcohol (%) | 1.2 | 1.5 | 6.8 | 0.8 | 3.4 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

Notes: The material balance of this reaction was calculated by following explanation.

(1) Content of ethyl alcohol in the above fraction was analyzed to be 93%.

(2) Amount of ethylene gas is calculated on the basis of 0.38 of $C_2H_4$ from 1cc of ethyl alcohol.

(3) Ether is formed at rate of 89 per 100 of alcohol.

*Feed Vol./Cat. Vol./hr.

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Table II(B)9
LIFE TEST OF CATALYST

| Test Time, (hrs) | 3 | 39 | 155 | mean |
|---|---|---|---|---|
| Yield of condensate, (%) | 83.3 | 93.3 | 99.0 | 96.9 |
| Composition of condensate: | | | | |
| Ether fraction,(%) | 53.0 | 69.0 | 58.0 | 58.5 |
| Alcohol fraction,(%) | 28.9 | 20.2 | 27.7 | 28.1 |
| Yield of ether to used alc.,(%) | 46.5 | 68.0 | 61.7 | 60.2 |
| Yield of ether to theoretical(%) | 69.0 | 94.0 | 95.5 | 92.5 |

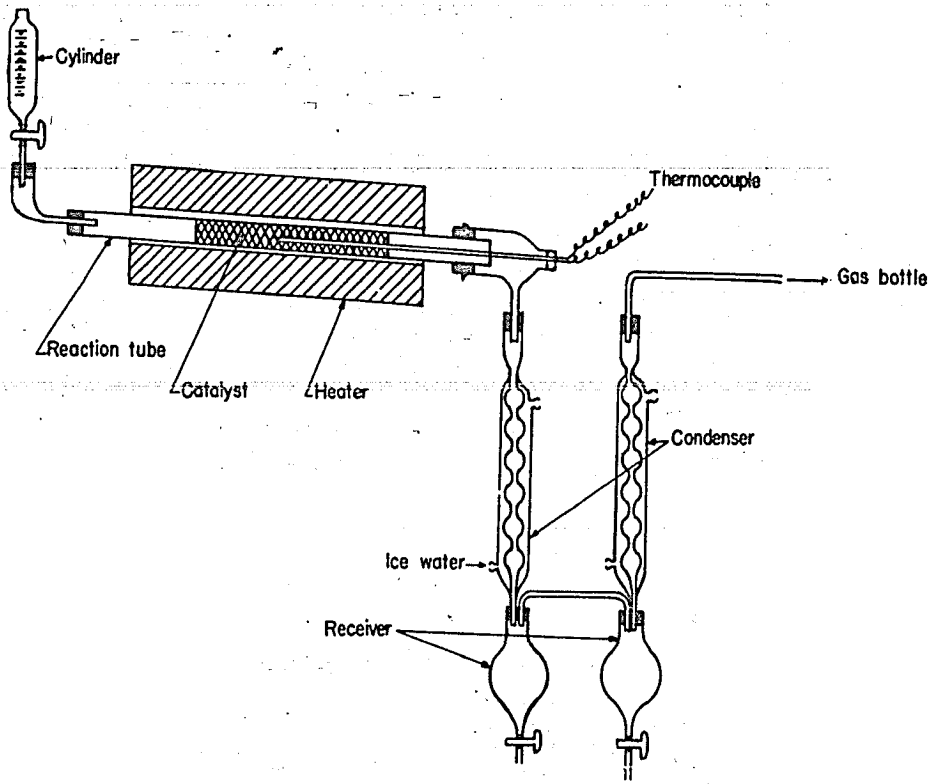


*Figure 1 (B)9*
*EXPERIMENTAL APPARATUS OF THE PREPARATION OF ETHER*

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# PART II

# PREPARATION OF ACETONE FROM ETHYL ALCOHOL

by

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Research Period: 1944-1945

SUMMARY

The object of our research is to produce acetone from ethyl alcohol catalytically, since acetone mixed with ethyl alcohol gives better results in combustion engines than ethyl alcohol alone.

This study was begun in April, 1945, and not finished. At present, it has been found that the yield of acetone from ethyl alcohol is 56%, using a mixed catalyst of Zn-Fe oxides at 430°C.

## I. INTRODUCTION

Demand of ethyl alcohol as an aviation fuel has increased with the scarcity of gasoline in Japan. Since acetone improves the quality of alcohol by blending, the demand of acetone has increased.

Acetone is at present prepared by the fermentation method and by the condensation of acetaldehyde.

There was a demand for other preparation methods such as the ethyl alcohol conversion to acetone by catalytic reation. This study was concerned with the most effective catalyst and most suitable reaction temperature for this reaction. Since the presence of water is necessary as indicated in the following equation,

$$2\ C_2H_5OH + H_2O = CH_3COCH_3 + CO_2 + 4H_2$$

The effect of water must be clarified.

## II. DETAILED DESCRIPTION

Experimental apparatus of the preparation of acetone is shown in Fig. 1(B)9. This apparatus and experimental method is the same as was used in preparing ether from alcohol.

Samples: Samples used for this study were prepared by mixing water and ethyl alcohol in the following proportions: 5:5, 8:2, and 84:16 (by volume ratio).

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Catalyst: Catalysts used in this study were ZnO and $Fe_2O_3$ and their mixtures, prepared by precipitation from corresponding metallic nitrate solutions with sodium carbonate and subsequent ignition to the oxides. The weight ratios of ZnO to $Fe_2O_3$ used were: 1:9, 3:7, and 5:5.

Results: The experimental results are shown in Tables III(B)9, IV(B)9, and V(B)9.

## III. CONCLUSIONS

Increasing concentration of charged alcohol resulted in increasing formation of gaseous products such as $CO_2$, $H_2$, aldehydes, etc. Consequently, it appears that the most suitable concentration of alcohol for use in this reaction is under 16 per cent.

Catalytic action of a mixture of Zn-Fe oxide is superior to that of either by itself. The desirable mixing ratios of ZnO to $Fe_2O_3$ appears to be from 3:7 to 5:5.

The lower the reaction temperature, the less the decomposition or alcohol, and the more the quantity of unreacted alcohol. The yield of acetone decreases with the decreasing reaction temperature.

On the contrary, at higher temperatures, the greater is the decomposition and loss of alcohol. Consequently, it appears that the suitable reaction temperature in the presence of this mixed catalyst is about 430°C.

No study was made of the effect of varying space velocity on the yield of acetone, since the investigation was not completed. It was also intended to investigate further the use of other catalysts in this reaction.

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Table III(B)9
PREPARATION OF ACETONE IN PRESENCE OF ZnO

| | Experiment No. | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| Alcohol Concentration (% by vol.) | 50 | 20 | 16 | 16 |
| Reaction Temperature (°C) | 450 | 450 | 450 | 430 |
| Space Velocity* | 0.5 | 0.5 | 0.5 | 0.5 |
| Condensate Yield (% by vol.) | 67 | 72 | 84 | 88 |
| Condensate Composition (% by vol.) Acetone Content | 8.4 | 8.8 | 8.3 | 6.6 |
| Condensate Composition (% by vol.) Alcohol Content | 38.0 | 5.8 | 1.6 | 2.6 |
| Yield of Acetone to used Alcohol (% by vol.) | 11.2 | 31.7 | 43.5 | 36.5 |
| Unreacted Alcohol; (% by vol.) | 50.8 | 19.2 | 8.6 | 23.7 |
| Loss of Alcohol; (% by vol.) | 31.4 | 30.6 | 22.2 | 18.3 |

* Feed vol/cat.vol/hr

Table IV(B)9
ACETONE PREPARATION IN PRESENCE OF $Fe_2O_3$

| | Experiment No. | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| Alcohol Concentration (% by vol.) | 50 | 20 | 16 | 16 |
| Reaction Temperature (°C) | 450 | 450 | 450 | 430 |
| Space Velocity | 0.5 | 0.5 | 0.5 | 0.5 |
| Condensate Yield (% by vol.) | 64.5 | 75.0 | 82.5 | 86.0 |
| Condensate Composition (% by vol.) Acetone Content | 7.5 | 8.7 | 8.1 | 6.5 |
| Condensate Composition (% by vol.) Alcohol Content | 42.1 | 5.7 | 2.1 | 4.6 |
| Yield of Acetone to used Alcohol (% by vol.) | 9.7 | 32.4 | 41.7 | 35.0 |
| Unreacted Alcohol; (% by vol.) | 54.0 | 21.3 | 10.8 | 24.7 |
| Loss of Alcohol; (% by vol.) | 30.3 | 27.1 | 22.9 | 19.6 |

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Table V(B)9

PREPARATION OF ACETONE IN PRESENCE OF MIXTURES OF ZnO & $Fe_2O_3$

| | Experiment No. | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Alcohol Concentration (% by vol.) | 16 | 16 | 16 | 20 | 50 | 16 | 16 |
| Ratio of ZnO to $Fe_2O_3$ (by wt) | 5:5 | 5:5 | 5:5 | 5:5 | 5:5 | 3:7 | 1:9 |
| Reaction Temperature (°C) | 450 | 430 | 400 | 430 | 430 | 430 | 430 |
| Space Velocity | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Condensate Yield (% by vol.) | 85.0 | 90.0 | 93.0 | 76.0 | 70.0 | 86.8 | 84.6 |
| Condensate Acetone Content | 9.4 | 9.9 | 8.0 | 10.8 | 9.7 | 8.5 | 1.0 |
| Composition (% by vol.) Alcohol Content | | 7.0 | 3.5 | 2.0 | 33.7 | 2.3 | 4.2 |
| Yield of Acetone to used Alcohol (% by vol.) | 50.0 | 55.7 | 46.5 | 41.0 | 13.6 | 46.0 | 37.0 |
| Unreacted Alcohol (% of used Alcohol) | | 5.6 | 20.3 | 7.6 | 47.2 | 12.5 | 22.2 |
| Loss of Alcohol (% of used Alcohol) | 20.4 | 5.8 | 5.7 | 27.2 | 31.2 | 14.3 | 19.2 |