STUDIES ON CATALYTIC PRODUCTION OF DIETHYL ETHER FROM ALCOHOL[1]

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The efficiency of a specially prepared catalyst from potash alum and aluminium sulphate has been investigated for the maximum conversion of alcohol into diethyl ether. With the catalyst mesh size 20-40, temperature of reaction 220-250°C., feed rate of alcohol 0.55 g./h./g. catalyst at atmospheric pressure, the yield of ether is as high as 76%. The catalyst can convert sixty times of its weight of alcohol into ether.

Introduction

Diethyl ether, simply called as ether, is an important basic material which finds numerous applications in chemical, industrial, pharmaceutical and research fields.[2] At present the total demand of ether in the country is entirely being met through imports. This obviously costs considerably in foreign exchange and it is necessary, therefore, that the chemical should be locally produced, particularly when all the wherewithals for its production are easily and economically available in the country.*

Many processes are in use for the manufacture of ether and the one which is most conventional and extensively employed after some modifications and standardization is that of Barbet.[3,4] The process involves the action of sulphuric acid on alcohol in a special lead-lined stainless steel vessel. However, the bulk of ether used in industry today is manufactured by absorbing ethylene, produced by the cracking of petroleum hydrocarbons, in concentrated sulphuric acid at fairly high pressure and under controlled conditions to make mixed ethyl hydrogen sulphate and diethyl sulphate.[5,6]

Ether is also produced by passing alcohol vapours over different dehydrating solid catalysts as kaolin, activated clay and potash alum with yields of 60.2, 60.2 and 75%, respectively.[7-11]

Because of the conditions presently existent in the country when the petrochemical industrial complex has yet to come into being and when there is plenty of alcohol produced through fermentation of surplus molasses and also, because of technical or economical questions, the last mentioned method, i.e., the one involving catalytic dehydration of alcohol vapours has been selected for the present investigations.

In these studies authors have examined a combined catalyst consisting of potash alum and aluminium sulphate. When this combined catalyst is used the quality of ether produced improves considerably; the formation of side products such as aldehydes and acids is the most minimum, whereas when potash alum is used the ether is highly contaminated with these side-products. Consequently although the yield of ether is just about the same, the refining losses are heavy. The present report deals with the application of this catalyst in the production of ether from alcohol (rectified 95% purity).

Equipment.—All experiments, to determine optimum conditions such as the temperature of dehydration, the effect of the particle size of the catalyst, the concentration of alcohol, the feed rate of alcohol and the temperature of ingoing vapours which have pronounced effect on ether yield, were carried out in a laboratory-scale plant designed in these laboratories. The essential features of the apparatus are described below:-
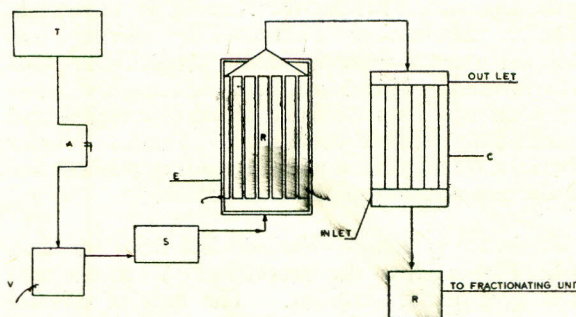
T, Alcohol feed tank; A, Feed control valve; V, Alcohol vapouriser; S, Electrically heated preheater; F, Temperature-controlled electric furnace; R, Ether reactor; C, Condenser; R, Receiver.

Experimental

Selection of the Catalyst.—Various catalysts were prepared from indigenous materials and were tried for the maximum conversion of alcohol into

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* While this paper was being sent for publication, it was learnt that the Wah Industries Ltd., would set up an ether plant.

ether. A list of the catalysts used with respective ether yields is presented in Table 1.

TABLE 1.—THE DIFFERENT CATALYSTS TRIED IN THE CONVERSION OF ALCOHOL TO ETHER.

Catalyst used			Temperature range °C.	Yield %
Silica gel	..	..	.. 200–350	0
Kaolin (acid treated)..	..		.. 200–350	7
Clays (K.D. clay acid treated)	..		.. 200–350	10
Feldspar (activated)	..		.. 200–350	15
Natural aluminium sulphate (dried)			.. 200–300	35
Commercial aluminium sulphate (Special prepared catalyst)	..		.. 200–300	61
Commercial Potash alum (Special prepared catalyst)	..		.. 200–300	71
Potash alum and aluminium sulphate (prepared catalyst)	..		.. 200–300	73

Particle size of the catalyst, 10–20 mesh.

Preparation of the Catalyst.—1.5 kg. of potash alum and 0.5 kg. of aluminium sulphate, both crushed to small pieces, were mixed together and the mixture transferred to a melting vessel. The mixture was heated 250–275° long enough to remove all the water of crystallization. The resultant dry mass was cooled and then powdered to 100 mesh.

Fresh batches of potash alum and aluminium sulphate in above proportion were again heated at the above temperatures and the powder prepared already was regularly mixed in the melted mass in small instalments, stirring it vigorously with a mechanical stirrer. The stirring was stopped when a uniform, dense ceramic-like mass was formed. This mass, after heating for three hours at 250°, was allowed to cool, crushed and graded into different mesh sizes. The fine powder obtained during crushing and grading was re-used in the preparation of the next batch.

Production of Ether.—The alcohol from the feed tank (T) was fed to the vapourizer (V) at the rate of 0.55 g./hr./g. catalyst. The flow of alcohol was controlled at this uniform rate by means of control valve (A). The vapours of alcohol obtained at atmospheric pressure were further heated to 180–200° in a pre-heater (S). The hot vapours were then intimately brought in contact with the catalyst in the reactor (R) heated by an electric furnace maintained at 220–250°. From the reactor the products were passed through a condenser cooled at 16–20°. The condensate was received in an ice cooled receiver (R') from where it was transferred to a fractionating unit and the fraction distilling between 34–38° was collected.

Purification of Ether.—The fraction as obtained contained water, alcohol, acidic and carbonyl compounds. To get pure material, the fraction was treated with sodium hydroxide; 35 lb. of ether required 1 lb. of sodium hydroxide for complete purification. The fraction was refractionated and purified ether distilling at 34–36° was collected.

The purified ether was comparable with E. Merck pure ether as shown by infra-red spectroscopic analysis which was conducted with double beam Beckmann spectrophotometer, Model IR 5A.

Discussion and Conclusions

The catalyst selected is superior to all the catalysts used (Table 1) because not only it gives an improved yield of ether but also the quality of the product is comparatively better. The ether is less contaminated with side products such as acidic and carbonylic compounds.

Alcohol vapours were continuously passed over this catalyst and no appreciable decrease in its efficiency was noticed until as much as ten times of alcohol had not passed over it. At this stage the catalyst was regenerated by passing hot air over it at 250° for one hour. Again, the same amount of alcohol as above could be passed and the catalyst regenerated. The catalyst could stand six such regenerations after which the ether yield would not rise more than 56%. In this way, therefore, the catalyst, under continuous use, can convert sixty times of its weight of alcohol. The spent catalyst was, however, reclaimed and used in the preparation of the next batch of the catalyst.

The best yield is obtained between the temperature range of 220–250°; below this range the catalyst is easily hydrated and at higher temperatures the proportion of gaseous products begins to increase (Table 2).

TABLE 2.—EFFECT OF THE CATALYST—TEMPERATURE ON ETHER YIELD.

Temperature range °C.	Yield %
175–200	No reaction yielding ether
200–220	55
220–250	76
250–280	75
280–300	56

Size of the catalyst=20–40 mesh; Feed rate of alcohol= 0.55 g./hr./g. catalyst.

Variation in feed rates of alcohol shows that upto the feed rate of 0.55 g. alcohol/hr./g. catalyst, the yield remains almost constant. With higher rates it begins to fall gradually (Table 3).

TABLE 3.—THE EFFECT OF THE VARIATION IN FEED RATES OF ALCOHOL.

Flow rate of alcohol		Yield %
0.4 g. alcohol/hr./g. catalyst ..	..	76.4
0.55 g. alcohol/hr./g. catalyst ..	..	76.00
0.70 g. alcohol/hr./g. catalyst ..	..	73.00
0.90 g. alcohol/hr./g. catalyst ..	..	69.00
1.00 g. alcohol/hr./g. catalyst ..	..	68.5

Size of the catalyst=20-40 mesh; Temperature=220-250°.

The particle size of the catalyst with which a maximum yield of ether is obtained and which easily allows the passage of vapours at atmospheric pressure is 20-40 mesh. With higher mesh, i.e., with the particle size being smaller, resistance to the vapour flow increases which necessitates the application of pressure for the passage of vapours through the catalyst bed, although the yield does not register any increase at all (Table 4).

TABLE 4.—PARTICLE SIZE DISTRIBUTION OF THE CATALYST.

Particle size of the catalyst	Yield %
10-20 mesh B.S.S.	73
20-40 mesh B.S.S.	76
40-60 mesh B.S.S.	76 (Vapours pass with difficulty).
60-80 mesh B.S.S.	——Vapours do not pass altogether

Temperature=220°-250°; Feed rate alcohol=0.55 g./h. g./catalyst.

Rectified alcohol (95%) is found to be the most suitable concentration of alcohol to obtain the maximum yield (Table 5).

TABLE 5.—DIFFERENT CONCENTRATIONS OF ALCOHOL AND THEIR EFFECT ON ETHER YIELD.

Concentration of alcohol%		Yield%
75	.. ..	57
80	.. ..	61
85	.. ..	67
90	.. ..	72
95	.. ..	76

Catalyst size=20-40 mesh; Temperature=220-250°; Feed rate alcohol=0.55 g./hr./g. catalyst.

Temperature of ingoing vapours must be above 180°. Below this temperature the catalyst is rapidly cooled and hydrated as more and more alcohol is passed and finally the reaction stops altogether (Table 6).

TABLE 6.—EFFECT OF THE TEMPERATURE OF INGOING VAPOURS OF ALCOHOL.

Temperature of preheater °C.		Yield%
0	.. ..	55
100—120	.. ..	60
120—150	.. ..	64
150-180	.. ..	72
180—210	.. ..	75
210—250	.. ..	75

Catalyst size=20-40 mesh; Temperature=220-250°; Feed rate alcohol—0.55 g./hr./g. Catalyst.

The process is remarkably simple; it neither requires special attention when once started, nor special materials for the fabrication of the plant. The product obtained possesses a high degree of purity which is comparable to that of the foreign product.

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