



Study the etherification reaction from tert-butyl alcohol and ethanol catalyzed by Amberlyt – 15

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Abstract:

In this paper, the liquid phase reversible reaction of ethanol and tert-butyl alcohol catalyzed by Amberlyst - 15, ion exchange resin was carried out in a stirrer batch three neck round bottom glass reactor. The experiment was carried out in the temperature range of 323 K – 338K under atmosphere pressure. The data of the concentration of each component with time were recorded and studied the effect of water produced during the reaction on the synthesis of ethyl tert-butyl ether.

Key words: Distillation, Etherification, MTBE, ETBE, Ion exchange resin.

Introduction:

Ethyl ter-butyl ether (ETBE) can be produced by an exothermic reversible reaction between ethanol (EtOH) and isobutene (IB) using acid catalyst, Amberlyst - 15. However, IB sources are limited only to catalytic cracking and steam cracking processes. On the other hand, tert. butyl alcohol (TBA) as a co product of propylene oxide synthesis from iso-butane and propylene can be used as an alternative rout to produced ETBE.

There are two way to produced ETBE, that is, indirect and direct methods. In the indirect method, TBA is dehydrated to IB in the first reactor and then the produced IB is reacted with EtOH to produced ETBE in the second reactor. In the direct method, ETBE can be produced directly from TBA and EtOH in one reactor. This process is favorable not only because it shortens the process itself, but also because it would reduce demand to the purity of EtOH. Since the reaction itself will produced water, the content of water in EtOH will become unimportant.

However, the field of direct reaction of EtOH and TBA in the liquid phase to produced ETBE has still not been touched. Therefore, in this work, the rate of reaction, for synthesis of ETBE and the effect of water were studied in the direct method. The water produced during the reaction can inhibits the rate of reaction and can be removed by use of membrane and pervaporation technique.

Recently, the tertiary ethers such as methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), and tert-amyl methyl ether (TAME) have used the interest of refiners as nontoxic and nonpollution gasoline additives for their low blending Reid vapor pressure (bRvp), low vaporization latent heat, in the petroleum refining and distribution system. From viewpoint of environmental protection, ETBE has lower bRvp (4 psi) than MTBE (8-10 psi), which allows ETBE to be used successfully in obtaining gasoline.

The substitution of ethers (ETBE) for alcohols and butanes in gasoline blending would have a positive effect on emissions, in a number of specific areas:

1. Reduction of carbon monoxide.
2. Reduction of aromatic content of gasoline and resulting toxics.
3. Reduction of olefin content of gasoline.
4. Reduction of volatile organic compounds.
5. Reduction of carbon dioxide.

Mechanism and Kinetics

The accurate information about the reaction kinetics is most important for successful design of the reactive distillation processes. Information about the reaction kinetics for the synthesis of ETBE using the strongly acidic ion-exchange resin as a catalyst (Amberlyst-15).

The production of liquid phase ETBE by using tert-Butyl Alcohol and Ethanol by direct method under atmospheric pressure, from experimental results, the following three reversible reactions may take place in the presence of a strong acid catalyst such as ion-exchange resin Amberlyst-15 Wet.



According to the general rate expression for reversible reaction, the reaction rates can be represented by as simple kinetics according to the literature survey, Bolun Yang et. al (1995),

$$r_1 = k_1 \cdot C_{\text{TBA}} - k_1^* \cdot C_{\text{IB}} \cdot C_{\text{H}_2\text{O}} \quad \dots \{ \text{mol} / \text{s} \cdot \text{mol} \cdot \text{H}^+ \} \quad \text{--- 4}$$

$$r_2 = k_2 \cdot C_{\text{IB}} \cdot C_{\text{EtOH}} - k_2^* \cdot C_{\text{ETBE}} \quad \dots \{ \text{mol} / \text{s} \cdot \text{mol} \cdot \text{H}^+ \} \quad \text{--- 5}$$

$$r_3 = k_3 \cdot C_{\text{TBA}} \cdot C_{\text{EtOH}} - k_3^* \cdot C_{\text{ETBE}} \cdot C_{\text{H}_2\text{O}} \quad \dots \{ \text{mol} / \text{s} \cdot \text{mol} \cdot \text{H}^+ \} \quad \text{--- 6}$$

From mass balance,

$$dC_{\text{TBA}}/dt = Cc \cdot (-r_1 - r_3) \quad \text{--- 7}$$

$$dC_{\text{IB}}/dt = Cc \cdot (-r_2 + r_1) \quad \text{--- 8}$$

$$dC_{\text{EtOH}}/dt = Cc \cdot (-r_2 - r_3), \quad \text{--- 9}$$

$$C_{\text{ETBE}} = C_{\text{EtOH}, 0} - C_{\text{EtOH}}, \quad \text{--- 10}$$

$$C_{\text{H}_2\text{O}} = C_{\text{TBA}, 0} - C_{\text{TBA}}, \quad \text{--- 11}$$

Where the catalyst concentration is $Cc = Q \cdot W / V \dots \dots \dots [\text{mol} \cdot \text{H}^+ / \text{m}^3]$.

Initial concentrations of ETBE, IB, and H₂O are zero.

With, rate constant as,

$k_1 = \exp. (15.39 - 10270 / T)$	$\{m^3 / S. \text{mol- } H^+\}$	---12
$k_1^* = \exp. (1.22 - 7420 / T)$	$\{m^6 / \text{mol. S. mol- } H^+\}$	---13
$k_2 = \exp. (5.71 - 9556 / T)$	$\{m^6 / \text{mol. S. mol- } H^+\}$	---14
$k_2^* = \exp. (16.77 - 10860 / T)$	$\{m^3 / S. \text{mol- } H^+\}$	---15
$k_3 = \exp. (-3.38 - 6900 / T)$	$\{m^6 / \text{mol. S. mol- } H^+\}$	---16
$k_3^* = \exp. (11.19 - 11770 / T)$	$\{m^6 / \text{mol. S. mol- } H^+\}$	---17

Experimental Set Up:

A three necked round bottom flask having capacity 500 cm³ with a central opening were used for the experiment. A condenser was placed in one of the openings; a constant stirrer was placed in the central opening for suspending the resin. The glass reactor was kept in heating mental for obtaining the constant reaction temperature.

Material

The reactant of ethanol and Tert-Butyl Alcohol used was of A.R. grade (99.8%) and were obtain from research laboratory, Mumbai. Purity was determined by gas chromatography. The chemicals were used without further purification.

Table. 1. Properties of ETBE

Oxygenates	ETBE
Chemical Formula	CH ₃ CH ₂ OC(CH ₃) ₃
Molecular Weight	102
Boiling Point (°C)	73.1
Oxygen Content, (Percent by weight)	15.66
Octane Number, (R+ M) / 2*	111
Blending Reid Vapor pressure, bRvp (Pound per squire inch)	4
* R = Research Octane Number. M = Motor Octane Number	

Catalyst:

Amberlyst-15 (Wet) is a macro reticular, strongly acidic, polymeric catalyst. It is continuous open pore structure make it an excellent heterogenous acid catalyst for a wide variety of organic reactions. Amberlyst-15 catalyst polymeric structure is extremely resistance to breakdown by osmotic, mechanical & thermal shock. It also possesses greater resistance to oxidants such as chloride, oxygen and chromates than most other polymeric catalyst.

Amberlyst-15 can use directly in the aqueous system or in organic medium after conditioning with a water miscible solvent. Amberlyst-15 has the optimal balance of surface area, acid capacity & pore diameter, thus it makes a best choice for etherification (MTBE, ETBE, TAME) esterification and hydration reactions.

Amberlyst-15 can also be used for chemical process applications to remove the impurities (metal ions) and basic organic compounds (amines, etc) from aqueous and non aqueous environments (appropriate pretreatment required).

Properties:

1. Physical formsOpaque beads
2. Ionic form as shipped Hydrogen
3. Moisture holding capacity52 to 57 %
4. Average pore diameter24 nm
5. Surface area45 m²/gm

Suggested Operating Condition:

1. Maximum operating condition 120⁰C
2. Minimum bed depth1000mm
3. Pressure drop limitation 1 bar across the bed.

Catalyst Treatment:

A strong cation exchange resin, Amberlyst 15 in the H⁺ form, was used as the catalyst. The average sizes 0.78 mm were chosen. This ion exchange resin was a sulfonated styrene divinyl benzene copolymer with a macro-reticular structure. A new fresh catalyst was kept at 368 K in a vacuum oven, overnight to get rid of any moisture contents.

The used resin was washed with distilled water and then soaked over night at room temperature. Thereafter, it was kept at 368 K in a vacuum oven for 24 hr for reusing.

Procedure

The equimolar TBA and EtOH were taken in the batch reactor and 7-8 samples were taken and cooled rapidly to 277 K to avoid any further reaction. Measurements were preferred between the temperature 323 K to 338 K. The samples are analyzed by using the gas chromatography.

Results and Discussion

I) Study of Concentration profile

The samples from the batch reactor were taken for different temperature levels 323K, 333K and 338 K with different time intervals. The results are shown in fig.1 to 3.

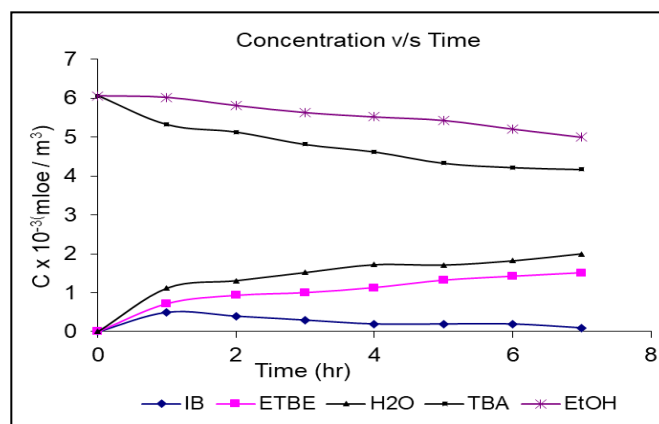


Fig.1. Concentration profiles (Equimolar ratio of EtOH/TBA, T =323K and W =10 gm.)

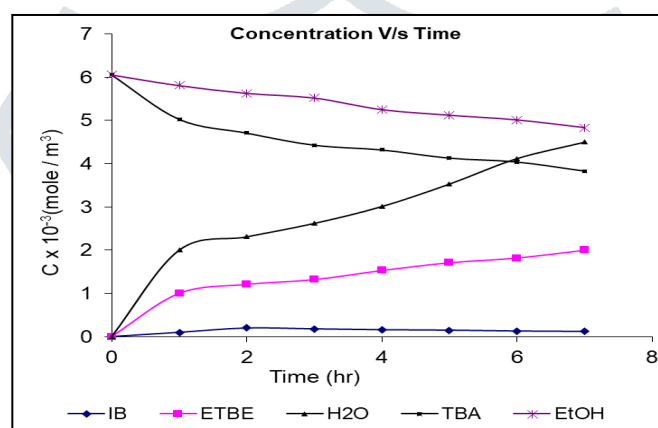


Fig. 2. Concentration profiles (Equimolar ratio of EtOH/TBA, T =333K and W =10 gm.)

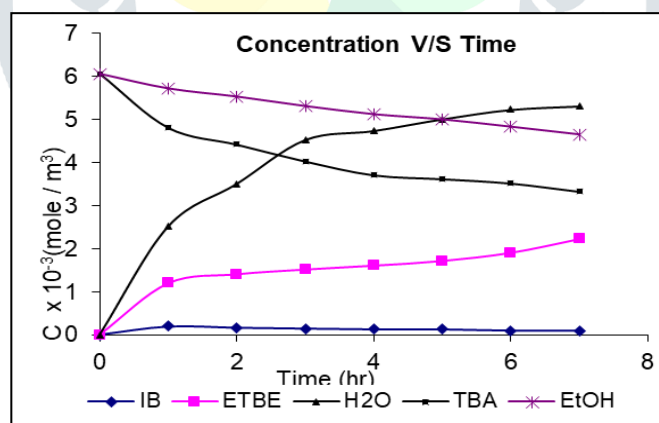


Fig. 3. Concentration profiles (Equimolar ratio of EtOH/TBA, T =338K and W =10 gm.)

Figures -1, 2, 3, show the results of concentration with time for synthesis of ETBE from TBA and EtOH catalyzed by Amberlyst -15. It was found from the figures that TBA is more rapidly consumed than EtOH, and H₂O is more rapidly produced than ETBE, and difference between them increases with increase in temperature. Dehydration of TBA to IB & water could not be neglected. The concentration of IB in the liquid phase was almost kept constant.

II) Concentration profile of ETBE and Ethanol

The concentration of the ETBE and EtOH were measured and recorded and shown in the fig. 4. at three different temperature level such as 323 K, 333 K and 338 K.

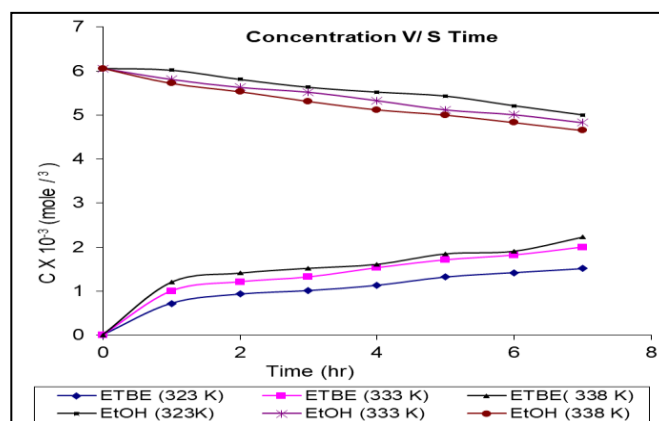


Fig. 4. Concentration profiles of ETBE and EtOH (Equimolar ratio of EtOH/TBA, W =10 gm.)

From figure -04, shows the result of concentration with time of ETBE synthesis increase with increase in time & temperature. Also the consumption rate of EtOH increase with increase in temperature & time.

III) The conversion profile of tert-butyl alcohol

The conversion of TBA were calculated at the temperature 323K with different time intervals and shown in the fig.5. The conversion of TBA increases with increase in time and after 6 hrs it is a level off.

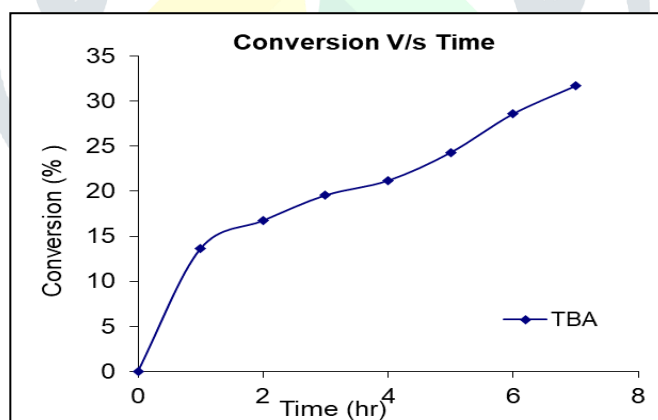


Fig. 5. Conversion Profile of TBA at 323K.

Conclusion

Direct synthesis of ETBE from EtOH and TBA in the liquid phase was studied by using Amberlyst -15 in a stirred batch reactor under atmosphere. The water is more rapidly produced than ETBE and the dehydration of TBA could not be neglected during the reaction. So, for the high productive capacity of ETBE, it is necessary to remove the water produced during the reaction.

Abbreviations

k = Forward rate constant. $\{m^3 / S. mol- H^+\}$

k^* = Backward Rate constant. $\{m^6 / mol. S. mol- H^+\}$

r = Rate of reaction. (mol/s m³)

C = concentration. (mol/ m³)

C_c = catalyst concentration. (mol H⁺/ m³)

W = Weight of catalyst. (gm)

V = volume of Reactant. (m³)

T = Temperature. (K)

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