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Thermodynamic and Kinetic Insights into MTBE and ETBE Production via Reactive Distillation.

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Abstract

Reactive distillation is increasingly recognized as a viable alternative to conventional separation techniques, particularly for systems involving azeotropic behavior. This study explores an advanced distillation methodology by emphasizing the application of reactive distillation in the synthesis of ETBE, MTBE, and methyl acetate, where complex multi-azeotropic systems are encountered. The research integrates theoretical analysis with essential experimental data to support future detailed experimentation and simulation-based process optimization.

Keywords: Reactive Distillation, Azeotropic Systems, ETBE, MTBE, Ion Exchange Resin.

Introduction

Reactive Distillation Columns:

Reactive distillation (R.D.) is a process that integrates chemical reaction and distillation within a single unit. This simultaneous execution of reaction and separation offers significant advantages over the conventional sequential approach. It is particularly beneficial for equilibrium-limited reactions such as esterification, etherification, and ester hydrolysis. In such systems, the continuous removal of products from the reactive zone shifts the equilibrium toward higher conversion, thereby achieving conversions beyond the conventional equilibrium limits (1). A typical reactive distillation column is illustrated in Figure 1.

Importance of Reactive Distillation Column:

The application of reactive distillation has increased significantly in recent years due to its potential to provide more economical and energy-efficient processes for various chemical syntheses. There is growing interest in the use of ethyl tert-butyl ether (ETBE) as a gasoline blending component, primarily as a substitute for methyl tert-butyl ether (MTBE), owing to the environmental concerns associated with MTBE (2).

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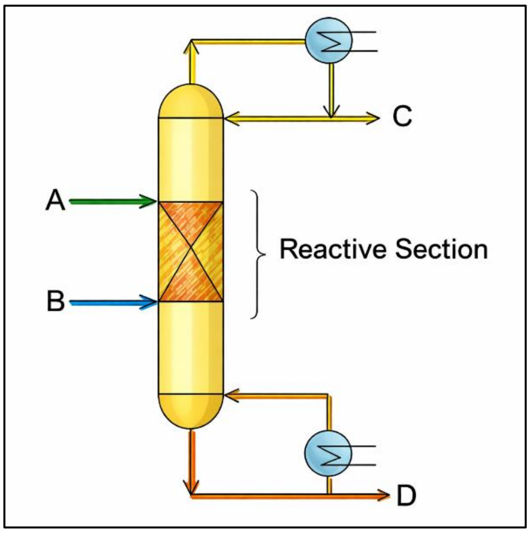

Figure-1: Typical Reactive Distillation Column.

In the proposed process, a reactive distillation column is typically divided into three distinct zones:

1. **Rectification zone** (non-reactive section)
2. **Reaction zone** (reactive section)
3. **Stripping zone** (non-reactive section)

The upper portion of the column is referred to as the **rectifying section**, while the lower portion is known as the **stripping section**.

Adaptation Technique of Reactive Distillation

Reactive distillation has been effectively applied to reactions with low equilibrium constants (K), enabling nearly complete conversion irrespective of the equilibrium limitations (3).

Two operational modes are commonly employed based on the relative volatility of the products compared to the reactants, as illustrated in Figure 2.

In **Operation Style I**, when one of the products (C) is the most volatile component, it is continuously removed from the reaction zone and withdrawn from the top of the column. This continuous removal shifts the equilibrium toward product formation, driving the reaction to near completion. Under these conditions, one of the reactants (B) is almost entirely consumed, particularly when the molar ratio of A/B is greater than one. The less volatile product (D), along with excess reactant (A), is collected from the bottom of the column.

In **Operation Style II**, when the reactant (A) is the most volatile component, it tends to reflux within the column and does not leave the system from the top. Instead, it is continuously

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recycled within the column. The reaction products (C and D), along with excess reactant (B), are withdrawn from the bottom section. In this case, component A is virtually absent in the bottom stream.

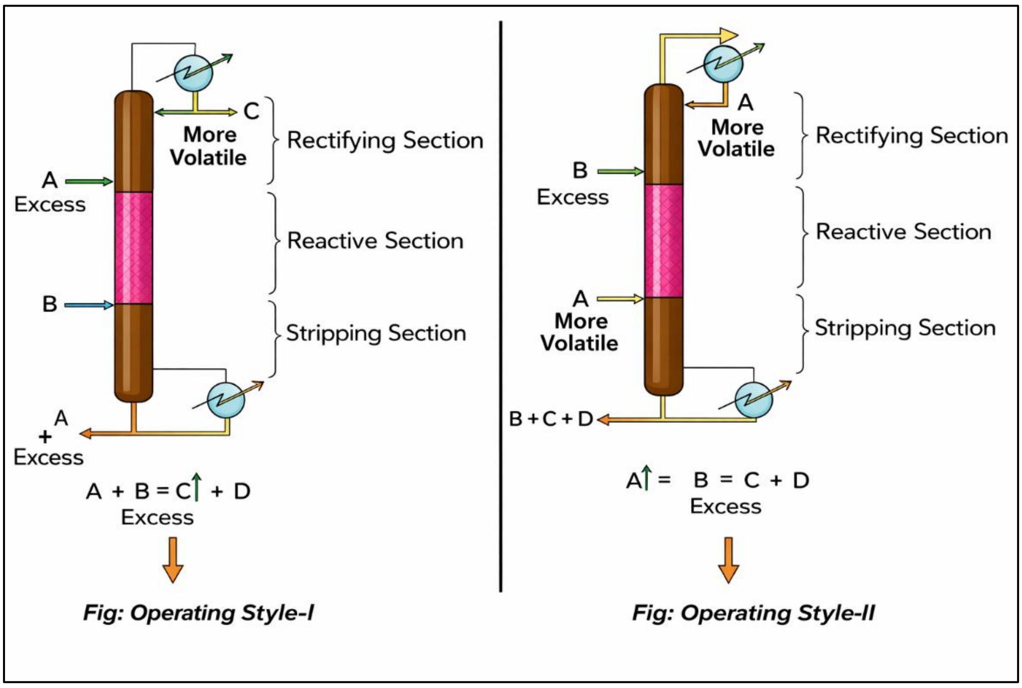

Figure-2: Operations Style of Reactive Distillation Column.

What are Oxygenates? (4)

Oxygenates are organic compounds that contain one or more oxygen atoms within their molecular structure. The most commonly used oxygenates include alcohols and ethers. Typical examples are fuel ethanol, methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), and tertiary amyl methyl ether (TAME). These compounds are widely used as fuel additives to improve combustion efficiency and reduce harmful emissions.

Methyl Tertiary Butyl Ether (MTBE) (4,5)

Methyl tertiary butyl ether (MTBE), with the molecular formula $C_5H_{12}O$ $(CH_3)_3COCH_3$, is a widely used oxygenated fuel additive. It is commonly referred to as MTBE and has been extensively utilized in gasoline blending to enhance octane rating and promote cleaner combustion.

Ethyl Tertiary Butyl Ether (ETBE) (6)

Ethyl tertiary butyl ether (ETBE), having the molecular formula $C_6H_{14}O$ $(CH_3)_3COCH_2CH_3$, is another important oxygenated compound used in fuel formulations. It is commonly known as ETBE and is considered a favorable alternative to MTBE due to its comparatively lower environmental impact.

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Use of Ethers in Gasoline Blending (5)

Ethers such as MTBE and ETBE are increasingly preferred over alcohols and butanes in gasoline blending due to their beneficial impact on fuel quality and emissions. Their use contributes to several environmental and performance advantages, including:

1. Reduction in carbon monoxide emissions
2. Decrease in aromatic content and associated toxic compounds
3. Lower olefin content in gasoline
4. Reduction in volatile organic compound (VOC) emissions
5. Decrease in carbon dioxide emissions

Table: Comparison of Oxygenates (MTBE and ETBE):

Property	MTBE	ETBE	Unit
Chemical Formula	$CH_3OC(CH_3)_3$	$CH_3CH_2OC(CH_3)_3$	—
Molecular Weight	88	102	$g \cdot mol^{-1}$
Boiling Point	55.2	73.1	°C
Oxygen Content	18.15	15.66	wt.%
Octane Number (R+M)/2	110	111	—
Blending Vapor Pressure (RVP)	8	4	psi
National Petrochemical Council, *U.S. Petroleum Refining: Meeting Requirements for Cleaner Fuels and Refineries*, Washington, DC, August 1993, Appendix L.			
R = Research Octane Number. M = Motor Octane Number.			

Amberlyst 15 Wet (7)

AMBERLYST 15 WET is a macroreticular, strongly acidic polymeric catalyst widely used in heterogeneous catalysis. Its continuous open-pore structure provides excellent accessibility to active sites, making it highly effective for a broad range of organic reactions. The polymeric matrix of AMBERLYST 15 WET exhibits high resistance to mechanical, thermal, and osmotic stresses, ensuring durability under varying process conditions. Additionally, it demonstrates superior resistance to oxidizing agents such as chlorides, oxygen, and chromates compared to many other polymeric catalysts.

AMBERLYST 15 WET can be directly utilized in aqueous systems or in organic media after suitable conditioning with a water-miscible solvent. It offers an optimal balance of surface area, acid capacity, and pore size distribution, making it particularly suitable for etherification reactions (such as MTBE, ETBE, and TAME synthesis), as well as esterification and hydration processes. Furthermore, it is employed in various chemical processing applications for the

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removal of impurities, including metal ions and basic organic compounds (e.g., amines), from both aqueous and non-aqueous systems, provided appropriate pretreatment is carried out.

Table: Physical Properties and Suggested Operating Conditions of Catalyst

Parameter	Specification	Unit
Physical Form	Opaque beads	—
Ionic Form (as shipped)	Hydrogen	—
Total Exchange Capacity	≥ 1.7	$eq \cdot L^{-1}$
Moisture Holding Capacity	52–57	%
Harmonic Mean Particle Size	600–850	µm
Average Pore Diameter	24	nm
Surface Area	45	$m^2 \cdot g^{-1}$
Shrinkage (Water → Methanol)	4.0	%
Shrinkage (Water → MTBE)	12	%
Maximum Operating Temperature	120	°C
Minimum Bed Depth	1000	mm
Operating Flow Rate	1–5	h^{-1} (LHSV)
Pressure Drop Limitation	≤ 1	bar

LHSV (Liquid Hourly Space Velocity) is defined as based on liquid density at 25 °C.

Experimental Procedure

Catalyst Treatment

A strong cation exchange resin, Amberlyst 15 in the H^+ form, was used as the catalyst. The average particle size selected was approximately 0.78 mm. The resin is a sulfonated styrene–divinylbenzene copolymer with a macroreticular structure.

The fresh catalyst was initially dried in a vacuum oven at 368 K overnight to remove any moisture content. The used catalyst was regenerated by thorough washing with distilled water, followed by soaking at room temperature overnight. Subsequently, it was dried again in a vacuum oven at 368 K for 24 hours before reuse. Preliminary experiments confirmed that the regenerated catalyst exhibited activity comparable to that of the fresh catalyst.

Procedure for MTBE Synthesis

Equimolar quantities of tert-butyl alcohol (TBA) and methanol (MeOH) were charged into a batch reactor. During the reaction, 7–8 samples were withdrawn at regular intervals and rapidly cooled to 277 K to quench further reaction. Experiments were conducted in the temperature range of 313 K to 323 K. The collected samples were analyzed using gas chromatography.

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Analysis for MTBE

The composition of reaction mixtures was determined using a gas chromatograph equipped with a 2.5 m column packed with Gaskuropack 54 (60–80 mesh). The column temperature was maintained at approximately 463 K (190°C), and helium was used as the carrier gas at a pressure of 0.12 MPa. Adequate separation of all components was achieved. n-Hexane was employed as an internal standard for quantitative analysis.

Procedure for ETBE Synthesis

Equimolar amounts of tert-butyl alcohol (TBA) and ethanol (EtOH) were introduced into the batch reactor. Similar to the MTBE procedure, 7–8 samples were collected during the reaction and rapidly cooled to 277 K to suppress further reaction. The experiments were carried out in the temperature range of 323 K to 338 K, and the samples were analyzed using gas chromatography.

Experimental Set Up:

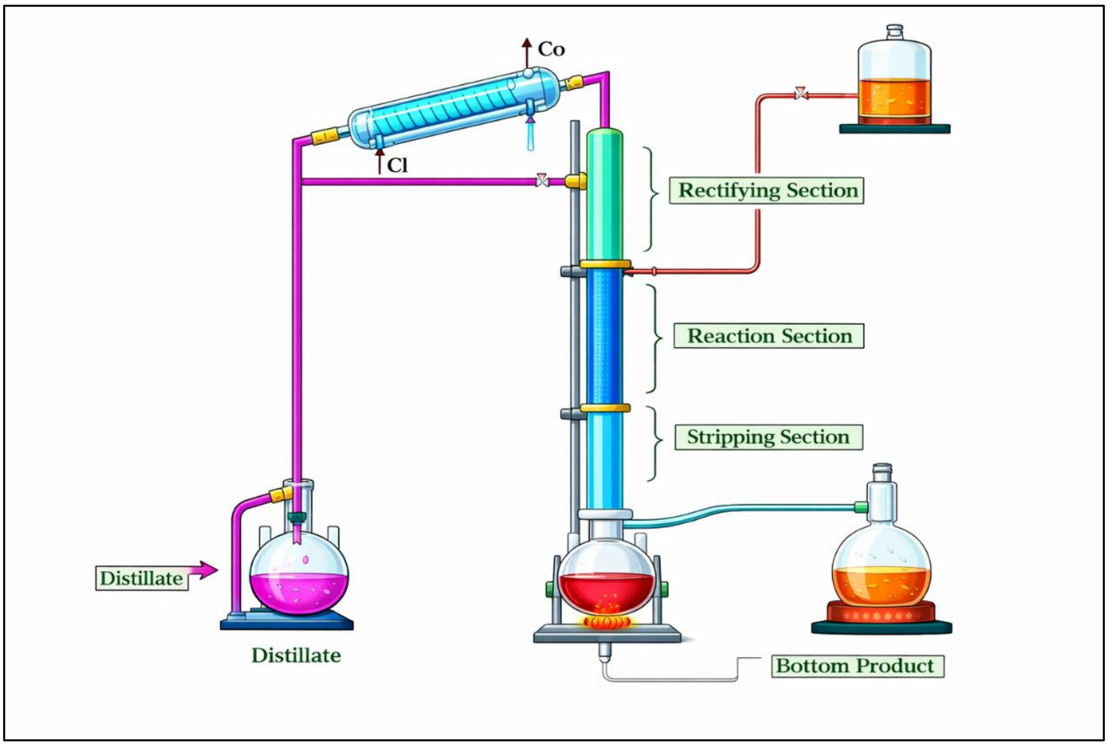

Figure-3: Experimental Set up.

Analysis for ETBE

The analysis of ETBE was performed using a **gas chromatograph** equipped with a **2.5 m column packed with Gaskuropack 54 (60–80 mesh)**. The column temperature was maintained at approximately **443 K (170°C)**, and **helium** was used as the carrier gas at a

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pressure of **0.12 MPa**. Effective separation of all components present in the reaction mixture was achieved under these operating conditions.

Advantages and Disadvantages of Reactive Distillation (1)

Advantages of Reactive Distillation

1. **Process simplification:** Integration of reaction and separation reduces or eliminates the need for separate units, resulting in significant capital cost savings.
2. **Higher conversion:** Reactant conversion can approach nearly 100%, thereby reducing the need for recycle streams and associated costs.
3. **Improved selectivity:** Continuous removal of products or control of reactant concentration minimizes side reactions, enhancing selectivity toward desired products.
4. **Lower catalyst requirement:** Reduced catalyst quantity is needed to achieve the same level of conversion compared to conventional processes.
5. **Azeotrope handling:** Reactive distillation is particularly effective for systems forming azeotropes, as it can shift equilibrium and facilitate separation.
6. **Reduced by-product formation:** Controlled reaction conditions help in minimizing unwanted side products.
7. **Energy efficiency (heat integration):** For exothermic reactions, the heat of reaction can be utilized for vaporization, thereby reducing reboiler duty and overall energy consumption.

Disadvantages of Reactive Distillation

1. **Volatility constraints:** Suitable relative volatility between reactants and products is essential to maintain effective separation and reaction within the column.
2. **Residence time limitations:** Reactions requiring long residence times may demand larger column sizes (in packed columns) or higher tray holdup (in tray columns), making the process less economical compared to conventional reactor–separator systems.
3. **Scale-up challenges:** Designing reactive distillation systems for very large flow rates is difficult due to issues such as liquid distribution in packed columns.
4. **Mismatch of operating conditions:** Optimal conditions for reaction (temperature and pressure) may differ from those required for distillation, which can limit process efficiency.

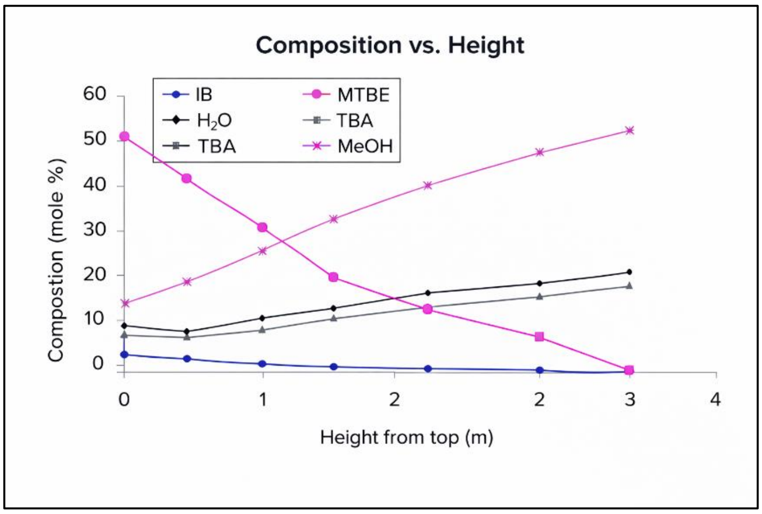

Figure-4: Composition V/s Height from Top. For MTBE system

Operating Parameters for Reactive Distillation

For MTBE System:

The experimental operating conditions for the MTBE system in the reactive distillation column are as follows:

1. **Column pressure:** 1 atm
2. **Flow rate of TBA:** 0.5 mol/h (equivalent to approximately 105 mL over 2 hours)
3. **Methanol feed (bottom):** 1 mol (≈ 43 mL)
4. **Feed molar ratio (TBA:MeOH):** 1 : 1
5. **Catalyst loading:** 50 g
6. **Reboiler temperature:** 341 K

For ETBE System:

The experimental operating conditions for the ETBE system in the reactive distillation column are as follows:

1. **Column pressure:** 1 atm
2. **Flow rate of TBA:** 0.5 mol/h (equivalent to approximately 105 mL over 2 hours)
3. **Ethanol feed (bottom):** 1 mol (≈ 60 mL)
4. **Feed molar ratio (TBA:EtOH):** 1 : 1
5. **Catalyst loading:** 50 g
6. **Reboiler temperature:** 355 K

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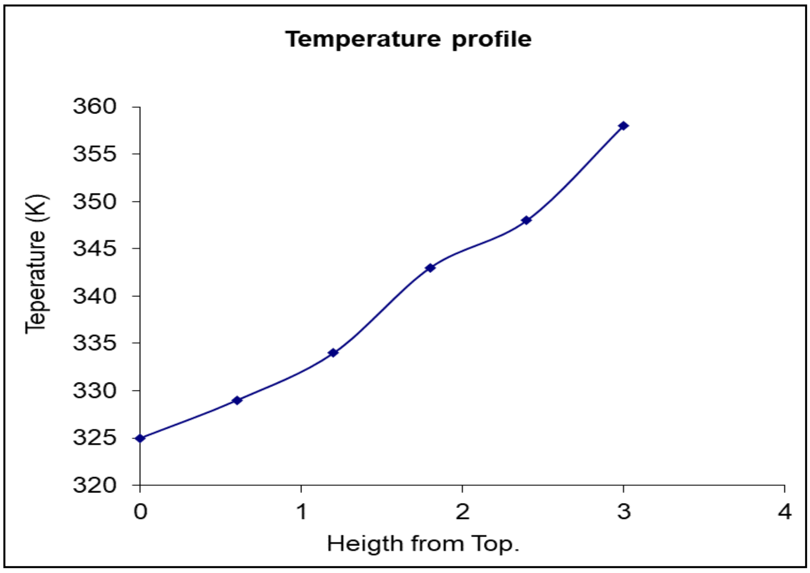

Figure-5: Temperature V/s Height from Top for MTBE system

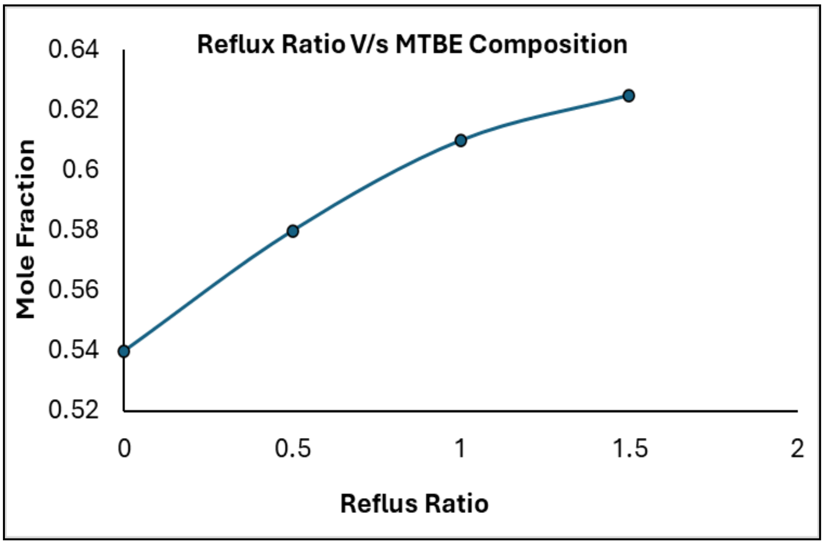

Figure-6: Reflux Ratio V/s Mole frication of for MTBE system

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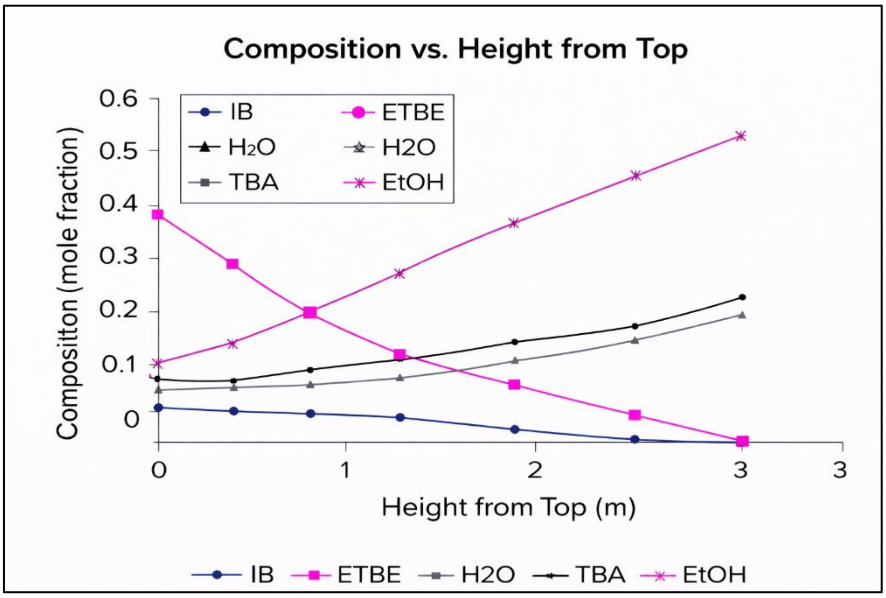

Figure-7: Composition V/s Height from Top For ETBE system

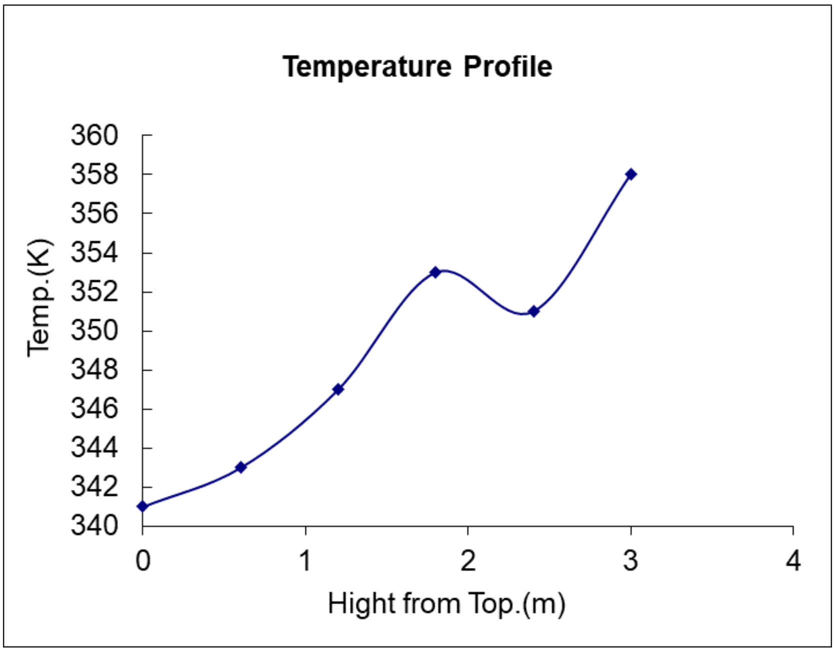

Figure-8: Temperature profile for ETBE system

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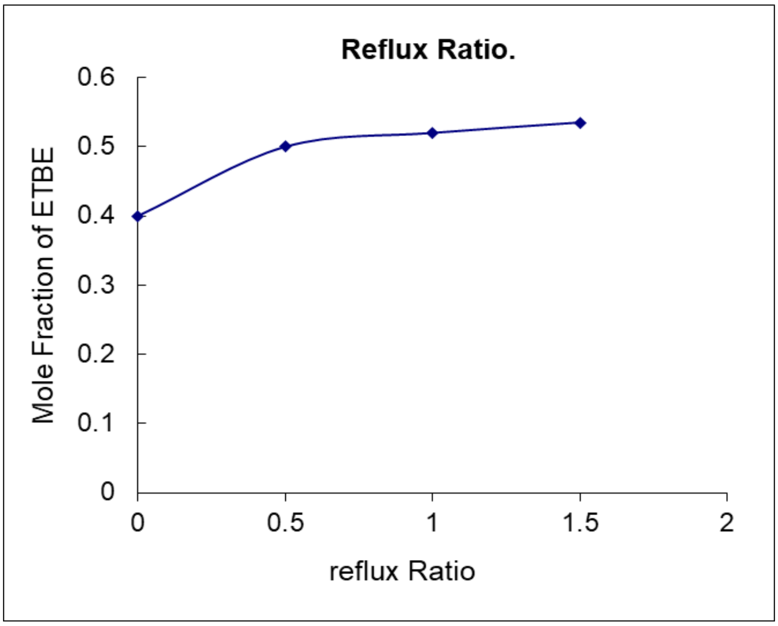

Figure-9: Reflux ratio V/s mole fraction, for ETBE system

Conclusion:

The direct synthesis of methyl tert-butyl ether (MTBE) from methanol (MeOH) and tert-butyl alcohol (TBA), as well as ethyl tert-butyl ether (ETBE) from ethanol (EtOH) and TBA, was investigated in the liquid phase using **Amberlyst 15 (H^+ form)** as a catalyst in a reactive distillation process under atmospheric pressure. The study indicates that the dehydration of TBA cannot be neglected, as multiple reactions occur simultaneously within the system.

Furthermore, the integration of reactive distillation with pervaporation appears to be a promising approach for the efficient production of MTBE and ETBE from MeOH, EtOH, and TBA, respectively, offering potential improvements in conversion and separation efficiency

Abbreviations

- k = Forward rate constant
- k′ = Backward rate constant
- r = Rate of reaction
- C = Concentration
- TBA = Tert-Butyl Alcohol
- IB = Iso-butene
- MeOH = Methanol
- EtOH = Ethanol
- MTBE = Methyl tert-Butyl Ether
- ETBE = Ethyl tert-Butyl Ether

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- Cc= Catalyst concentration
- Q = Ion exchange capacity
- W = Weight of catalyst
- V = Volume of reactant
- T = Temperature
- $C_{EtOH,0}$ = Initial concentration of ethanol
- A-15 = Amberlyst 15 WET catalyst
- E = Activation energy
- R = Universal gas constant

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