Design Parameter for Reactive Distillation Column using etherification reaction with ion exchange resin

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Abstract- Nowadays Reactive Distillation is widely used as alternative for conventional distillation. In this work we have to suggest a new technique in Distillation technology rather than ordinary distillation process. Reactive Distillation technology sounds azeotrope system such as synthesis of ETBE, MTBE, and Methyl Acetate where more than one azeotropes are formed. In this work we have concentrate on all theoretical and basic experimental data which will be useful for some rigorous experimentation and process simulation work.

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

Introduction

Reactive Distillation Columns:

The combination of chemical reaction with distillation in only one unit is called Reactive Distillation (R. D). The performance of reaction with separation in one piece of equipment offers distinct advantages over the conventional, sequential approach. Especially for equilibrium limited reaction such as esterification, etherification and ester hydrolysis reaction, and conversion can be increased far beyond chemical equilibrium conversion due to continuous removal of reaction product from the reactive zone (1). Typical reactive distillation column is shown in the figure 1.

Important of Reactive Distillation Column:

The use of Reactive Distillation has grown in the recent years because it results in less expensive and more efficient processes for some chemical synthesis. There is increase interest in the use of ethyl tert-butyl ether (ETBE) for gasoline blending as a replacement for methyl tert – butyl ether (MTBE) because of the latter's environmental problems (2).

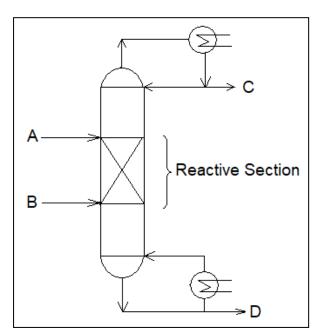


Figure-1: Typical Reactive Distillation Column.

In this new process, of Reactive Distillation Column consists of three zones: such as

- 1. Rectification zone (Non-reactive Section).
- 2. Reaction zone (Reactive Section).
- 3. Stripping zone (Non-Reactive section).

The top section is called as Rectifying Section.

The bottom section is called as Stripping section.

Adaptation Technique of Reactive Distillation:

Reactive Distillation has been successfully applied to reaction having a low equilibrium constant (K) to realize complete conversion independently the value of K (3)

There are two operations Style based on volatility of a product compared with starting material, as shown in figure 2. If one of the products, \mathbf{C} , is most volatile among the components. Operation style $-\mathbf{I}$ is adopted. The reaction proceeds completely since a reversible reaction can be driven away by continuously removing the product \mathbf{C} from the reaction zone and fractionating it away from the top of the column. Consequently, one of starting material, \mathbf{B} , essentially vanishes from the column (in the case of a mole ratio of $\mathbf{A} / \mathbf{B} > \mathbf{1}$.) The less volatile product \mathbf{D} and an excess of \mathbf{A} are realized together from the bottom of the column.

If starting material, \mathbf{A} is most volatile, operation style- \mathbf{H} is adopted. In this case component \mathbf{A} dose not vanishes but refluxes to the top of the column without release. The products of the reaction, $\mathbf{C} & \mathbf{D}$ are release from the bottom of the column along with the excess of \mathbf{B} . Component \mathbf{A} is essentially absent in the bottom flow.

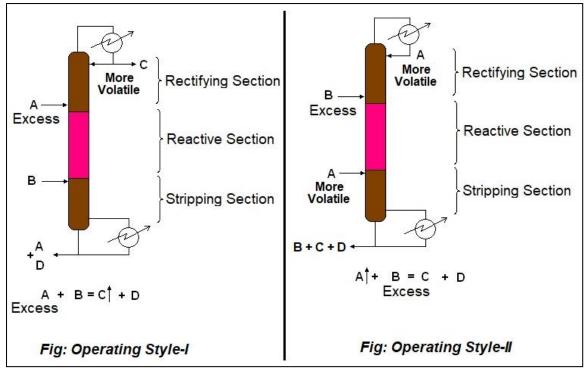


Figure-2: Operations Style of Reactive Distillation Column.

What are Oxygenates? (4)

Oxygenates are hydrocarbons that contain one or more oxygen atoms. The primary oxygenates are alcohols and ethers, for e.g. fuel ethanol, methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), and tertiary amyl methyl ether (TAME).

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

Molecular formula of Methyl tertiary-butyl ether: - C₅H₁₂O {(CH₃OC (CH₃)₃)}

Methyl tertiary-butyl ether is commonly referred to as MTBE.

Ethyl Tertiary Butyl Ether (ETBE),(6):

Molecular formula of Ethyl tertiary-butyl ether: - C₆H₁₄O (CH₃CH₂OC(CH₃)₃

Ethyl tertiary-butyl ether is commonly referred to as ETBE.

Ether is used in gasoline blending instead of alcohol and butanes (5):

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

- 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.

Comparative Properties of MTBE & ETBE:

Oxygenates	MTBE	ETBE
Chemical Formula	CH ₃ OC(CH ₃) ₃	CH ₃ CH ₂ OC(CH ₃) ₃
Molecular Weight	88	102
Boiling Point (⁰ C)	55.2	73.1
Oxygen Content, (Percent by weight)	18.15	15.66
Octane Number, (R+ M) / 2*	110	111
Blending Vapor pressure, RVP (Pound per square inch)	8	4

Source: 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 macro reticular, strongly acidic, polymeric catalyst. It is continuous open pore structure make it an excellent heterogeneous acid catalyst for a wide variety of organic reactions. AMBERLYST 15 WET 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 WET can use directly in the aqueous system or in organic medium after conditioning with a water miscible solvent. AMBERLYST 15 WET 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 WET 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:

Physical forms	Opaque beads
Ionic form as shipped	. Hydrogen
Total exchange capacity	$. \ge 1.7 \text{ eq} / \text{L}$
Moisture holding capacity	52 to 57 %
Particle size	
Harmonic mean size	600 to 850 μm.
Average pore diameter	24 nm
Surface area	$45 \text{ m}^2/\text{gm}$
Shrinkage	Water to methanol: 4.0%
-	Water to MTBE: 12 %.

Suggested Operating Condition:

Maximum operating condition	120^{0} C
Minimum bed depth	.1000mm
Operation flow rate	
Pressure drop limitation	1 bar across the bed.
* I UCV: Liquid Hourly Chang Valority for liqui	d density at 250C

^{*} LHSV: - Liquid Hourly Space Velocity for 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 sizes 0.78 mm were chosen. This ion exchange resin was a sulfonated styrene diviniyl 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 overnight at room temperature. Therefore, it was kept at 368 K in a vacuum oven for 24 h for reusing. It was confirmed from preliminary experiments that the regenerated resin had the same activity as the fresh resin.

Procedure for MTBE:

The equimolar TBA and MeOH 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 temperatures 313 K to 323 K. The samples are analyzed by using the gas chromatograph.

Analysis for MTBE:

Analysis was carried out in the gas chromatograph with 2.5 m column of Gaskuropack 54, 60, 80 mesh as packing material. The column temperature was set at 463°K=190°K and carrier gas was helium at 0.12 MPa. Good separations had been achieved for all components. Normal hexane was used as an internal standard for the analysis.

Procedure for ETBE:

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

Experimental Set Up:

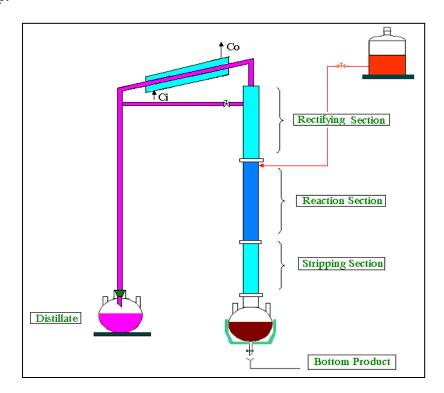


Figure-3: Experimental Set up.

Analysis ETBE:

Analysis was carried out in the gas chromatography with 2.5 m column of Gaskuropack 54, 60, 80 mesh as packing material. The column temperature was set at 443° K= 170° C and carrier gas was helium at 0.12 MPa. Separations had been achieved for all components.

Advantages and Disadvantages of Reactive Distillation (1): Advantages of Reactive Distillation:

- 1. Simplification or elimination of the separation process can lead to significant capital saving.
- 2. Improved conversion of reactant approaching 100%. This increase in conversion gives a benefit in reduced recycling cost.
- 3. Improved selectivity. Removing one of the products from the reaction mixture or maintaining a low concentration of one of the reagent can lead to reduction of the rates of side reactions and hence improved selectivity for the desired products.
- 4. Significantly reduced catalyst requirement for the same degree of conversion.
- 5. Avoidance of the azeotropes. RD is particularly advantageous when the reactor product is a mixture of species that can form several azeotropes with each other.
- 6. Reduced by- product formation.
- 7. Heat integration benefits. If the reaction is exothermic, the heat of reaction can be used to provide the heat of vaporization and reduced the reboiler duty.

Disadvantages of Reactive Distillation:

1. Volatility constraints. The reagent and product must have suitable volatility to maintain high concentration of reactant and low concentration of products in the reaction zone.

- 2. Residence time requirement. If the residence time for the reaction is long, a large column size (For packed column) and large tray hold ups (for tray column) will be needed, and it may be more economic to use a reactor separator arrangement.
- 3. Scales up to large flows. It is difficult to design RD processes for very large flow rates because of liquid distribution problems in packed Rd column.
- 4. Process conditions mismatch. In some processes the optimum conditions of temperature and pressure for distillation may be far from optimal for reaction and vice versa.

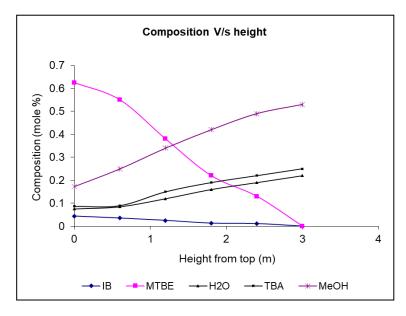


Figure-4: Composition V/s Height from Top. For MTBE system

Parameter condition for Reactive Distillation:

For MTBE System:

- 1. Column pressure:1 atm.
- 2. Flow rate TBA:0.5 mole/hr: 105 ml / 2 hr.
- 3. Feed to Bottom MeOH:1 mole = 43 ml
- 4. Feed molar Ratio: 1: 1
- 5. Catalyst loading: 50gm
- 6. Temperature of Reboiler: 341^oK

For ETBE System:

- 1. Column pressure: 1 atm.
- 2. Flow rate TBA:0.5 mole/hr = 105 ml / 2 hr.
- 3. Feed to Bottom EtOH:1 mole = 60 ml
- 4. Feed molar Ratio:1: 1
- 5. Catalyst loading: 50gm
- 6. Temperature of Reboiler:355^oK

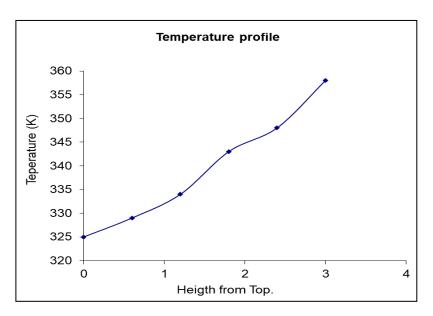


Figure-5: Temperature V/s Height from Top for MTBE system

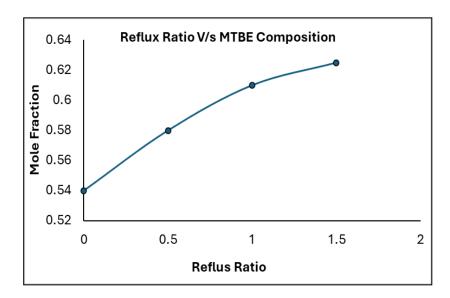


Figure-6: Reflux Ratio V/s Mole frication of for MTBE system

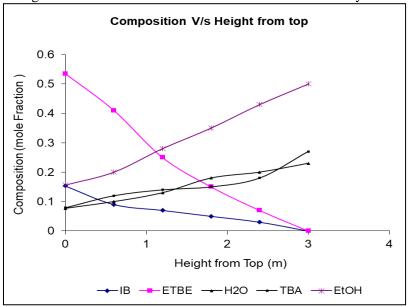


Figure-7: Composition V/s Height from Top For ETBE system

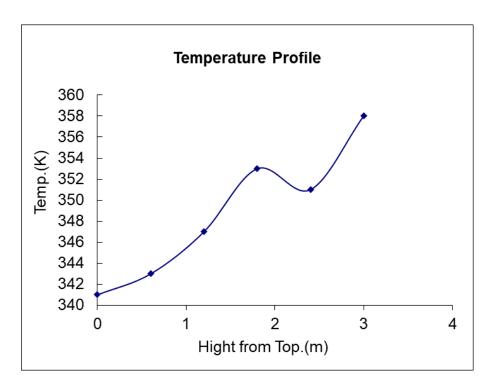


Figure-8: Temperature profile for ETBE system

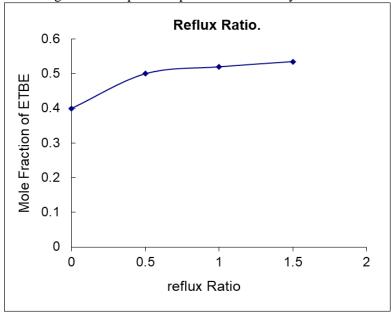


Figure-9: Reflux ratio V/s mole fraction, for ETBE system

Conclusion:

Direct synthesis of MTBE from MeOH and TBA and also ETBE from EtOH and TBA, in the liquid phase was studied by using Amberlyst 15 in the H+ form in Reactive distillation Process under atmospheric pressure. Dehydration of TBA not be neglected and three reactions took place simultaneously.

The reactive distillation combined with pervaporation would be suitable way for the direct production of MTBE & ETBE from MeOH, EtOH and TBA. respectively.

Abbreviations:

k = Forward rate constant.

k'= Backward Rate constant.

r = Rate of reaction.

C = concentration.

TBA = Tertiary Butyl Alcohol.

IB = Iso-Butene

MeOH = Methanol.

EtOH = Ethanol.

MTBE = Methyl tert. Butyl Ether.

ETBE = Ethyl tert. Butyl Ether.

Cc = catalyst concentration.

Q = Ion exchange capacity.

W = Weight of catalyst.

V = volume of Reactant.

T = Temperature.

C_{EtOH}, 0 = Initial Concentration of EtOH.

A-15 = Amberlyst - 15 WET catalyst.

E = Activation Energy

R = Gas constant.

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