SYNTHESIS AND OPTIMIZATION OF SEPARATION
SECTION OF MTBE PROCESS

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ABSTRACT: Methyl tertiary butyl ether (MTBE) is known as a promising substitute for tetra ethyl lead (TEL) in order to increase the octane number of gasoline. MTBE process, as many other processes, has two distinguished sections, namely reaction section and separation section. In this paper we focus only on synthesis and optimization of separation section of this process. In order to achieve this objective, many possible flowsheets have been considered, among which, two alternatives are pointed out as optimum candidates. The second step involves determination of dominant design variables and their ranges of variation. Both selected flowsheets have been cost analyzed in their corresponding ranges of dominant design variables to determine plots of total annual cost (TAC). Knowing feed specifications at the entrance of separation section, the designer will be able to choose appropriate flowsheet and optimum conditions using the plots presented in this paper.


INTRODUCTION:

Lead and its derivatives are known as some of the worst air pollutants. TEL (tetra ethyl lead), the most common octane number enhancer of reformulated gasoline, is the main source of urban air pollutions. The existence of lead particulates in the air causes serious damage to the brain and the central nervous system [1]. Hence, a great deal of efforts have been exerted to find an appropriate substitute for TEL. Methyl tertiary ether butyl (MTBE)
has so far been considered as one of the best substitute ever known for TEL [2]. MTBE does not produce toxic gases in the combustion course. This advantage over TEL, one of the worst known air pollutants, has forced the industry to pay more attention towards its production. Hence the production of MTBE has been recognized in Iran as a program with high priority. Therefore a significant amount of work has been directed to the kinetics, synthesis and reactor design of this process. However, as far as the separation section of MTBE process is concerned, there has not been any considerable work reported in domestic literatures.

Since, there are two azeotropic pairs in the reactor effluent (separation section's feed) and also the excess methanol in the reactor feed is essential, the design of separation section of MTBE process is somewhat difficult.

In this paper we try to offer a suitable flowsheet along with optimum conditions for the separation section of MTBE process. Obviously the interactions between reaction and separation sections of the process have carefully been studied in order to find optimum conditions.

**Process Description**

MTBE can be produced from methanol and isobutene according to the following reaction:

\[
\text{CH}_3\text{OH} + (\text{CH}_3)\text{C}=\text{CH}_2 \rightarrow (\text{CH}_3)_2\text{COCH}_3
\]

Reaction temperature varies between 50 to 90°C and pressure should be kept between 1 to 1.5MPa in order to maintain the reaction in liquid phase [3]. Pure methanol is normally used as reactor feed. However, purity of isobutene feed depends on the C4 feedstock available from a nearby refinery or petro-chemical complex. Since the separation of isobutene from C4 cut is quite difficult and expensive, the crude C4 cut is usually fed to the reactor. Thus the reactor effluent will contain:

- C4: unconverted feed
- methanol: unconverted feed
- MTBE: desired product
- TBA; Di & Trimer of C4: byproducts

Purification of MTBE from these byproducts is not vital as they have high octane numbers themselves. It is only enough to keep their concentrations low at the reactor exit. This will limit the separation task to purification of MTBE from methanol and the C4 cut.

**Possible Alternatives for Separation**

Three possible alternatives* for separation are shown in Fig. 1. In alternative 1, C4 will be separated from the mixture by distillation. Then, a second distillation column will separate MTBE from MTBE.MeOH azeotrope as bottom product.

Separation of C4 from MeOH in the first column is difficult, and high pressure also should

*These alternatives are based on two most commonly used techniques of separation, namely distillation and liquid-liquid extraction [4].
be adapted in order to be able to use cooling water in the column condenser. These imply an expensive distillation. Furthermore, methanol recycle stream contains considerable amount of MTBE which will increase the reactor volume and its cost.

In alternative 2, MTBE is first separated from the mixture by distillation. Next, methanol would be extracted using water as solvent and finally methanol and water is to be separated in another distillation column. In this alternative, the pressure of the first distillation column depends on the percentage of methanol in the column feed. In fact, the minimum necessary pressure is equal to the azeotrope pressure of MeOH - C₄ to remove all methanol along with C₄ as the column overhead. This is a proper alternative which is adapted in most industrial plants [2].

In alternative 3, methanol is first extracted by water in the first column. Then two distillation columns separate MTBE from C₄ and methanol from water. The main difficulty of this alternative is the absorption of some water in MTBE in the extraction column. This will make MTBE unsuitable as an octane number enhancer of gasoline. To overcome this difficulty, an additional expensive unit (e.g. adsorber) is necessary [5,6]. However, some industrial plants have adapted this alternative.

In this work we have concentrated on the second alternative which is schematically shown in Fig. 2.

The second selected alternative shows the situation in which MTBE separation takes place in two stages. The advantage of this alternative is that the MTBE with higher purity can be produced. Moreover, as most of the methanol is removed from bottom of the first column, the cost of extraction will be significantly decreased. On the other hand, one has to bear the cost of an additional column. Furthermore, recycling of some MTBE with methanol increases the reactor cost.

In this paper both alternatives shown in Fig. 2 are examined as appropriate options. The following suggestion is also presented to reduce the cost of first alternative.

It is known that the pressure of the first column can be found by the following equation [7]:

\[
\frac{\text{MeOH}}{\text{MeOH} + C_4} \times 100 = 1 + \frac{P_1}{3}
\]

Fig. 2. Two selected alternatives for separation section.

Where \( P_1 \) is the pressure of the first column in (atm) and \( \text{MeOH} \) and \( C_4 \) are the amount of methanol and \( C_4 \) in the column feed. This equation shows that the column pressure can be reduced by increasing the amount of \( C_4 \) in the column feed. Therefore, it can be suggested that the \( C_4 \) from extraction column can be injected to the top tray of the first column. To avoid increasing the column diameter, the reflux ratio should be reduced [6]. This option will also be investigated in our study.

In alternative 1, the pressure of the first column and in alternative 2 the pressure of both
MTBE separation columns are taken as design variables. The amount of methanol in the main feed to the separation section is also considered as design variable for both alternatives. In fact, this is how the interaction between reaction and separation sections of the process has been taken into account. MTBE recovery in the second column plays also the same role.

**Procedure**

Our goal is to find the optimum pressure of the MTBE column in both alternatives on the basis of methanol percentage in the feed. Note that the pressure of extraction column has been fixed between 8 and 10 atm and the pressure of methanol recovery column is almost 3 atm. To accomplish this goal, design of first column in alternative 1 and first and second columns in alternative 2 are to be performed for different pressures and feed compositions.

The production rate of 100 ton of MTBE per annum, and C4 feedstock specification as shown in Table 1, is assumed [8].

**Table 1: C4 cut composition.**

<table>
<thead>
<tr>
<th>C4 component</th>
<th>Wt. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isobutane</td>
<td>16.631</td>
</tr>
<tr>
<td>Isobutene</td>
<td>1.556</td>
</tr>
<tr>
<td>1- Butene</td>
<td>47.706</td>
</tr>
<tr>
<td>1,3-Butadien</td>
<td>1.897</td>
</tr>
<tr>
<td>Butane</td>
<td>13.125</td>
</tr>
<tr>
<td>2-Butene Trans</td>
<td>11.014</td>
</tr>
<tr>
<td>2-Butene cis</td>
<td>8.07</td>
</tr>
</tbody>
</table>

This is a typical available C4 cut reported by some petrochemical complexes and refineries.

The feed ratio and pressure range, used for the optimization of first column in alternative 1 is presented in Table 2.

For higher feed ratios (more than 11%) the column pressure will exceed 30 atm which causes MTBE decomposition [5].

In the case of alternative 2, the same feed ratios shown in Table 2 and a feed with 20% methanol are assumed. Pressure of the first and the second column were changed as below:

First column pressure (atm): 6, 10, 14, 18, 22, 25.
Second column pressure (atm): 1, 5, 10, 15, 25.

**Table 2: Feed ratio and pressure range in the first column.**

<table>
<thead>
<tr>
<th>No.</th>
<th>( \frac{\text{MeOH}}{\text{MeOH} + C_4} \times 100 )</th>
<th>pressure (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>12</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>15</td>
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<tr>
<td>5</td>
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<tr>
<td>8</td>
<td>10</td>
<td>27</td>
</tr>
<tr>
<td>9</td>
<td>11</td>
<td>30</td>
</tr>
</tbody>
</table>

To reduce the tediousness of handling such a multidimensional optimization problem with wide ranges of continuous variables, usually short cut design methods are used. However, for distillation column designs, short cut methods are reliable only when the column feed is close to ideal solution conditions. Due to the nonideality of the column feed in this case rigorous design method was adapted. Design of all distillation columns have been performed by "PROCESS" simulator software. The cost of distillation and extraction columns have also been rigorously calculated [9, 10].

To realize the vastness of calculations needed for optimizing this problem, note that for alternative 1, 58 points are considered. With three columns in this alternative, 174 columns have been sized and costed. In alternative 2, 190 columns have been sized and costed. Column costing includes shell, internals and accessories.

**RESULTS AND DISCUSSION:**

Fig. 3 shows the total annual cost (TAC) of the separation section of MTBE process for different pressures in the first column. Fig (a)
shows the feeds with 4 to 6% of methanol. Note that for feed with 3% methanol, C₄ injection is not needed. Therefore, this case has not been shown. Fig. (b), (c) and (d) show the feeds with 7 to 9%, 10% and 11% methanol respectively. It can be seen that the curves with low methanol feeds do not pass through a minimum and in fact the last points in the curves are the optimum values. This means that in such situation, high pressure column without C₄ injection shows the lowest cost and pressure reduction due to the C₄ injection causes cost increase. As the methanol percentage in feed increases, pressure reduction due to the C₄ injection would be beneficial. Presence of minimum points in the curves with more than 8% methanol clearly confirms this conclusion. It is worthy to note that although C₄ injection causes pressure reduction in the first column, more C₄ in circulation increases the cost of extraction column. This economic trade off is the reason for existence of minimum values in the total annual costs. In the case of feeds with low methanol percentage, when there is no minimum values in the total annual cost curves, the cost increase due to the C₄ injection is higher than cost reduction due to the lower pressure operation. This vividly shows that C₄ injection in these cases is not beneficial at all.

Fig. 4 shows the optimum pressure curve of the first column in terms of methanol percentage in the feed. The tangent line indicates the

**Fig. 3:** TAC in alternative 1 as a function of methanol content of the feed and pressure of the first column.
column pressure with no C4 injection. It can be seen that for low methanol feeds, the optimum pressure curve coincides with the tangent line, while this curve diverges from the line as the methanol percentage increases.

![Graph](image)

*Fig. 4: Optimum pressure curve of the first column vs. methanol percentage.*

Fig. 5 presents the appropriate TAC curves of alternative 2 for separation section of the process vs. MTBE recovery and different pressures of the first column. The curves have been repeated for three different feeds with specific methanol percentages. Each point on the curves corresponds to a pressure of the first column (6, 10, 14, 18, 22, 26 atm).

As was mentioned before, in this alternative, perfect separation of MTBE from MeOH-MTBE azeotrope is not possible. Therefore, some MTBE will have to be recycled to the reactor along with methanol. For this reason, the curves of Fig. 5, show the TAC in terms of MTBE recovery. Obviously, one can not find the true optimum TAC values from these curves, unless the cost of reaction section of the process as a function of MTBE percentage recycled to the reactor be added to these TAC values.

Feeds with 4 to 9% methanol have not been included in Fig. 5, because in those cases, the cost of alternative 2 is higher than alternative 1 even without the cost of reaction section. The only advantage of alternative 2 in these situations (feeds with 4 to 9% methanol) is high purity of MTBE product.

Using Fig. 5, for any intended MTBE recovery, we can find the appropriate pressure for first and second column. For example, Fig. 5(b) shows that for 84% recovery of MTBE, the lowest cost occurs when the pressures of the first and second columns are 6 and 15 atm respectively (point a). However, if the point b is selected instead (pressure of 14 atm for first column and 10 atm for second column), the total annual cost (TAC) of the separation section will be much higher.

Another conclusion is that, for the feed with 10% methanol, the low pressure curves are located above the high pressure curves. This means that in this situation reduction of the second column pressure against the first column pressure increase, is not beneficial. Therefore, first column should operate at low pressure and second column at high pressure.

In the case of feed with 20% methanol, we face an opposite situation. It can be seen that the curve of 25 atm pressure is located above 15 atm. This means that, as the percentage of methanol in feed, entering the separation section increases, it is better to keep the pressure of first column high and second column low. Fig. 5(b) shows the intersection point of 25 and 15 atm curves for a feed with 11% methanol. Hence, this percentage of methanol in feed is the adverting point.

**CONCLUSIONS:**

Following conclusions can be drawn from this study:

1. If methanol percentage of the feed entering the separation section is less than 9%, alternative 1 is the only appropriate choice.
2. If methanol percentage of the feed is between 9 and 11%, alternative 2 can also be beneficial. The final selection in this situation can be made when the additional cost of reactor due to some MTBE recycle is considered. On the other hand, higher purity of MTBE product in alternative 2 can be an important factor for decision making.
3. If methanol percentage of the feed is more
than 11%, alternative 2 is the only appropriate choice. Because, if alternative 1 is selected, the pressure of the first column should be more than 30 atm which will cause the MTBE decomposition. However, in this situation alternative 1 with C4 injection to the first column can be comparable with alternative 2.

4- In alternative 1, C4 injection to the first column is only justifiable for feeds with more than 7% methanol.

5- Optimum pressure of the first column in alternative 1 can be found from Fig. 4.

6- Optimum pressure of the first and second columns in alternative 2 can only be found when the cost of reaction section of the process is added. However, using Fig. 5, these optimum pressures can be determined as a function of MTBE recovery.

Cost Data

The following cost data have been used to calculate TAC of the process in all cases:

Cooling water: $0.05/1000 gal.
Steam @ 150 psia and 366F: $3.4/1000 lb.
Working hours: 320 day/year
Capital Charge Factor (CCF): 1/3 [4].

Note that these values are used only for comparison between the possible alternatives. Evidently, when the location of the plant is decided, the cost of utilities should be corrected according to the local values.
Nomenclature

\[ M = \frac{\text{MeOH}}{\text{MeOH} + C_4} \text{ (wt\%)} \] entering the separation section.

MR : Percentage of MTBE recovery in the second column.

P_1 : First column pressure (atm).

P_2 : Second column pressure (atm).

TAC : Total annual cost ($/year).

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REFERENCES:


