HYDROLYSIS OF METHYL ACETATE IN DISTILLATION COLUMN PACKED WITH REACTIVE PACKING OF ION EXCHANGE RESIN

YOSHIO FUCHIGAMI
Central Research Laboratory, Kuraray Co., Ltd.
Kurarashiki 710

Key Words: Reactive Distillation, Ion Exchange Resin, Hydrolysis of Methyl Acetate

Introduction

Polyvinyl alcohol (PVA) is a useful polymer which is converted into synthetic fiber, film, an adhesive agent, a sizing agent for paper and fiber manufacturing, and other products. In 1988 about 320,000 metric tons of PVA was produced worldwide. PVA is synthesized industrially by polymerization of vinyl acetate (VAc), followed by methanolysis of the resultant polymer (PVAc) to PVA and methyl acetate (MeOAc) at a ratio of 1.68 tons of MeOAc per ton of PVA. Unfortunately, MeOAc has few industrial uses as a solvent, so it is necessary for the PVA industry to convert MeOAc to a more valuable compound.

In industrial PVA plants, MeOAc is usually hydrolysed to methyl alcohol (MeOH) and acetic acid (HOAc) for recycle to methanolysis of PVAc and VAc synthesis. Conversion of MeOAc in the hydrolysis reaction is low because of the small equilibrium constant of the reaction \( K = 0.14 \). Moreover, MeOAc forms azeotropic mixtures with MeOH and water. Then the conventional process for recovery of MeOH and HOAc from the reaction mixture of MeOAc hydrolysis has a fixed-bed reactor packed with ion exchange resin (IER) followed by a complicated combination of several distillation columns for separation of each of the components. In the process a large portion of the MeOAc is recycled because of the low conversion. As a result the MeOAc hydrolysis process requires relatively large-scale equipment and is very energy-consuming. One of the most important targets for engineers concerning PVA plants is therefore the improvement of the MeOAc hydrolysis process. In this paper, the application of reactive distillation to the conventional MeOAc hydrolysis process is proposed.

The key technology for the new process is preparation of the reactive column-packing (catalyst), consisting of IER. Only a few patents for this purpose can be found. Among them the patent of Chem. Res. & License Co. has been successfully applied to MTBE (Methyl t-butyl ether) production from isobutylene and MeOH since 1981 in Houston, USA. But in the process IER beads are packed in a plurality of closed fiberglass cloth pockets imbedded with the regular type of stainless-steel wire mesh column packing, hence the reactive distillation zone is only a mixture of the reaction parts and the distillation parts. In the strict sense this case is not true reactive distillation because the column packing itself is not reactive.

Recently Toray Co. has developed cloth or felt type IER fiber (IONEX), which has as large an exchanging capacity as Amberlite IR-120. Ion exchange cloth or felt seems to be the most suitable material for use in the reactive column packing because of its large contacting surface area with liquid reactant and its flexibility, making it an effective regular-type column...
packing. It is expected to be supplied at almost the same price for the same packing volume as IER beads.

1. Adaptation of Reactive Distillation

Reactive distillation has been successfully applied to reactions having a low equilibrium constant ($K$) to realize complete conversion independently of the value of $K$. There are two operation styles based on the volatility of a product compared with the starting materials, as shown in Fig. 1. If one of the products, C, is the most volatile among the components, operation style-I is adopted. The reaction proceeds completely since a reversible reaction can be driven away by continuously removing product C from the reaction zone and fractionating it away from the top of the column. Consequently, one of the starting materials, B, essentially vanishes from the column (in the case of a mole ratio of $A/B > 1$). The less-volatile product D and an excess of A are released together from the bottom of the column. If starting material A is the most volatile, operation style-II is adopted. In this case component A does not vanish but refluxes to the top of the column without release. The products of the reaction, C and D, are released from the bottom of the column along with the excess of B. Component A is essentially absent in the bottom flow.

In the conventional reactive distillation a liquid catalyst such as sulfuric acid is used in the reaction zone as shown in Fig. 1. So a flash drum must be provided at the bottom of the reaction zone in order to separate the catalyst from the reaction mixture.

In a new process, solid catalyst is packed in the reaction zone of the column. This avoids the need for the flash drum for catalyst separation and the use of an expensive anti-corrosive material for the column.

For the hydrolysis of MeOAc, operation style-II should be applied, because the azeotropic mixture of MeOAc and water is the most volatile of the related components. The way in which the reactive distillation can be incorporated into the MeOAc hydrolysis process is shown in Fig. 2, compared with a conventional process. It is a fusion of two towers, combining the functions of a hydrolysis reactor and a water-wash extractive distillation column for separation of the azeotropic mixture of MeOAc and MeOH. In the reactive distillation column, water acts simultaneously as a reactant in the hydrolysis reaction and an extractive solvent for separation of MeOAc from MeOH.

One of the advantages of the new process is the elimination of two towers: the water-wash tower for separation of MeOAc from MeOH, and the MeOH-enriching tower for recovery of MeOH from the water-diluted MeOH. Another advantage is a reduction of the heat requirement for the total process.

In this paper the operation variables of reactive distillation for the hydrolysis reaction of MeOAc is determined experimentally, in order to estimate the economical advantage of the application of reactive distillation to the MeOAc hydrolysis process in PVA production.
2. Experimental

2.1 Preparation of reactive column packing

Eighty-five parts of dry and H-type IER (Amberlist-15, Japan Organo Co., Ltd.) and 15 parts of 100-mesh polyethylene powder (Hizex 2100 GP, Mitsui Toatsu Co., Inc.) were well mixed by a V-type rotating mixer. The mixture was packed tightly in each hole (7 mm-diameter and 7 mm-thick) of a Teflon-coated perforated plate and molded at 140°C in an electric furnace for 1 hour. After keeping it in saturated moisture at 40°C for 24 hours the molding pellet was successively dipped in MeOH, a 50%-aqueous solution of MeOH and water for 1 hour each.

The resulting wet pellet was comprised of 350 g/l of IER on a dry basis and its exchanging capacity was 1.28 g-eq/l (fresh Amberlist-15 had a capacity of 1.65 g-eq/l on a wet basis).

2.2 Apparatus and procedure

A schematic diagram of the experimental apparatus is shown in Fig. 3. A Pyrex glass tube of 36 mm ID and 800 mm height was employed as the reaction zone and an Oldershaw column of 32 mm ID and 30 plates was employed as the distillation zone. Each apparatus was located in an electric furnace so that heat loss from the surface of the tube was eliminated. A 200-ml flask equipped with a thermometer and a pressure gauge was fitted at the bottom of the column as a still. It was heated by a mantle-heater. The reactive column packing described above was packed into the Pyrex glass tube.

A mixture of MeOAc and MeOH in the ratio of 75:25 by weight (a near-azeotropic composition, 0.89 g/ml at 25°C) was fed to the bottom of the reaction zone. Water was fed to the top of the reaction zone. The top vapour was condensed by a Liebig condenser and led to a 10-ml buret. All the condensed liquid was recycled to the top of the reaction zone. The reaction mixture containing the resulting products was pumped out from the bottom flask. Each flow was set to a given rate by respective metering pumps (Sanyo Rikagaku T-63 K). Throughout vapour was controlled by adjusting the heating rate of the mantle-heater so as to keep the liquid level in both the bottom flask and the 10 ml-buret constant. When the flow rate of the product from the bottom still was equal to the rate based on the material balance of a run, the reaction mixture was analysed by gas chromatograph (PEG 20M on Celite 545 AW, 5 m, at 100°C), using methylal as internal standard for quantitative analysis. After all the operating variables and the analysed values were kept constant, conversion of MeOAc was calculated.

3. Experimental Results and Discussion

Operating variables of the process are a) LHSV = (feed rate of MeOAc–MeOH and Water)/(volume of the packed catalyst) [m³/h/m³], b) Feed ratio of water/MeOAc (= m [mol/mol]) and c) Ratio of top vapour/feed MeOAc (= r [Kg/Kg]).

The experimental results are summarised in Table 1. As shown in Fig. 4, the most important operating variable is the feed ratio of water/MeOAc (= m). A high value of the ratio m leads to high conversion of MeOAc even at a low value of the ratio of reflux/feed (= r). But a higher value of m results in a more dilute bottom flow, which requires a lot of energy for recovery of the components (MeOH and HOAc). A high value of r as well as a low value of LHSV are also necessary to obtain a high conversion of MeOAc. But the high value of r requires higher energy consumption in the reactive distillation column, and the low value of LHSV requires a catalyst zone of large volume. The volume can be reduced by using a catalyst which has larger ion-exchanging capacity.

The rate constant of the reverse reaction catalysed
Table 1. Experimental results\(^1\) of MeOAc hydrolysis by reactive distillation

<table>
<thead>
<tr>
<th>Run</th>
<th>Cat.(^2)</th>
<th>(m)(^3)</th>
<th>LHSV(^4)</th>
<th>(r)(^5)</th>
<th>Temp.</th>
<th>Top</th>
<th>Bott.</th>
<th>(H_2O)</th>
<th>MeOH</th>
<th>HOAc</th>
<th>MA</th>
<th>Conv.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[ml]</td>
<td>[h(^{-1})]</td>
<td>[---]</td>
<td>[---]</td>
<td>[°C]</td>
<td>[°C]</td>
<td>[wt%]</td>
<td>[wt%]</td>
<td>[wt%]</td>
<td>[wt%]</td>
<td>[%]</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>350</td>
<td>4.1</td>
<td>0.446</td>
<td>4.35</td>
<td>55.6</td>
<td>55.6</td>
<td>81.1</td>
<td>3.20</td>
<td>3.08</td>
<td>27.79</td>
<td>6.51</td>
<td>84.9</td>
</tr>
<tr>
<td>2</td>
<td>8.10</td>
<td>55.6</td>
<td>83.3</td>
<td>3.37</td>
<td>4.92</td>
<td>30.34</td>
<td>3.77</td>
<td>91.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>8.2</td>
<td>0.636</td>
<td>0.80</td>
<td>56.0</td>
<td>84.6</td>
<td>4.53</td>
<td>0.554</td>
<td>21.10</td>
<td>3.27</td>
<td>89.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1.60</td>
<td>56.1</td>
<td>87.3</td>
<td>4.40</td>
<td>0.410</td>
<td>22.73</td>
<td>0.771</td>
<td>97.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2.16</td>
<td>56.2</td>
<td>88.0</td>
<td>3.99</td>
<td>0.270</td>
<td>23.47</td>
<td>0.496</td>
<td>98.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>700</td>
<td>4.1</td>
<td>0.223</td>
<td>2.16</td>
<td>55.9</td>
<td>78.5</td>
<td>4.01</td>
<td>3.14</td>
<td>27.12</td>
<td>8.49</td>
<td>80.2</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>4.28</td>
<td>55.8</td>
<td>81.5</td>
<td>4.15</td>
<td>4.51</td>
<td>31.08</td>
<td>4.15</td>
<td>90.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>8.10</td>
<td>55.7</td>
<td>84.5</td>
<td>3.85</td>
<td>5.87</td>
<td>33.50</td>
<td>0.832</td>
<td>98.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>8.2</td>
<td>0.318</td>
<td>0.54</td>
<td>55.5</td>
<td>85.2</td>
<td>3.81</td>
<td>1.97</td>
<td>21.48</td>
<td>2.59</td>
<td>91.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.80</td>
<td>55.7</td>
<td>86.5</td>
<td>3.63</td>
<td>1.47</td>
<td>22.72</td>
<td>1.25</td>
<td>95.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>1.62</td>
<td>55.9</td>
<td>87.6</td>
<td>3.70</td>
<td>1.91</td>
<td>23.55</td>
<td>0.541</td>
<td>98.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>700</td>
<td>4.1</td>
<td>0.112</td>
<td>1.90</td>
<td>55.6</td>
<td>81.2</td>
<td>3.22</td>
<td>3.10</td>
<td>29.23</td>
<td>6.56</td>
<td>84.7</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>3.80</td>
<td>55.7</td>
<td>84.4</td>
<td>3.83</td>
<td>4.00</td>
<td>33.73</td>
<td>1.19</td>
<td>97.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1) Feed composition: MeOAc/MeOH = 75/25 [Kg/Kg]; Feed rate: 100 ml/h (89.0 g/h) for Runs 1–11 and 50 ml/h for Runs 12, 13. Bottom pressure: 400–450 mm-aqueous; Volume of bottom flask: 200 ml for Runs 1–11 and 100 ml for Runs 12, 13.
2) Ion-exchanging capacity = 1.28 eq./l (wet base).
3) \(m\) = Feed ratio of water/MeOAc [mol/mol].
4) LHSV = Feed (MeOAc + MeOH + \(H_2O\))/(Cat. vol.) [m\(^3\)/h/m\(^3\)].
5) \(r\) = Ratio of top vapour/ feed MeOAc [Kg/Kg].

Fig. 4. Influence of LHSV and feed ratio of water to methyl acetate \((=m)\) on the relationship between conversion of methyl acetate and ratio of reflux to methyl acetate in a feed \((=r)\)

by generated HOAc in the bottom still was found to be 1/25 of that of the hydrolysis reaction in the reaction zone. This is the reason why we could not obtain a conversion above 99% in Table 1. So the volume of the still must be made as small as possible for practical equipment. Actually, we succeeded in obtaining a conversion of 99.5% when a 100-ml flask was used for the still in the place of the 200-ml flask in run 11.

Material flow (mol/h) of the process is shown in Fig. 5. Among the components of the liquid which descends to the enriching column from the reaction zone, MeOAc accompanied by azeotropic water (MeOAc/water = 1.0/0.217 by mol) is boiled up through the reaction zone to the reflux condenser and recycled totally after being condensed. If a large enough volume of the catalyst is packed, an equilibrium should be set up between each component of the liquid which leaves the reaction zone to the enriching zone. So we
can get the following equation.

\[ K = \frac{1}{1 \cdot (R \times (m - 1 + 0.217R))} = 0.14 \]  \hspace{1cm} (1)

where \( R \) is molar ratio of MeOAc in the top vapor to MeOAc in feed. The value of \( R \) from this equation must be the minimum value for the complete conversion of MeOAc in the process.

From Eq. (1) \( R \) [mol/mol] is calculated to be 3.31 and 1.67 in the case of \( m = 4.1 \) and 8.2, respectively. These values are converted to \( r \) [Kg/Kg] = 3.48 and 1.75 respectively. A comparison of our experimental results with the calculated minimum value of \( r \) is summarized in Table 2.

From this Table Run 11 turned out to be performed almost at the minimum value of \( r \), and hence a lower LHSV than 0.318 is not necessary. In Run 13 the value of \( r \) should have dropped to 3.48 from 3.80 had we adopted a lower LHSV than 0.112.

The heat requirement of each column in Fig. 2b is estimated by using the minimum value of \( r \) as a function of \( m \) in the reactive distillation column. Figure 6 shows the result of the estimation study. The minimum value of the heat requirement of the total process is obtained with \( m = 1 \); that is, the feed rate of water is stoichiometric for hydrolysis of MeOAc. The minimum value is estimated to be about 40\% of the total heat requirement of the conventional process shown in Fig. 2(a). But this is only the limiting case, and when considered with the data of Fig. 4, this case must require almost infinite volume of catalyst or an almost infinite activity (exchanging capacity) of the catalyst. Practically, Run 13 in Table 2 seems to be the optimum case and the heat requirement of the total process is estimated to be about half that of the conventional hydrolysis process. But in this case the volume of the reaction zone is about 2 or 3 times that of the fixed-bed reactor packed with IER beads in the conventional process, and consequently a more active column packing is desired.

**Conclusion**

A reactive distillation technique was applied to the hydrolysis reaction of methyl acetate by using reactive column-packing of ion exchange resin molded with polyethylene powder in a furnace. The influence of operating variables on the conversion of methyl acetate was investigated. A optimum operation condition was recommended from an estimation study of heat requirement of the total process. The total heat requirement of the optimum process was estimated to be about half that of the conventional hydrolysis process.

**Nomenclature**

- \( K \) = equilibrium constant of reaction \([-]\)
- \( R \) = molar ratio of methyl acetate in top vapour to that in feed \([\text{mol/mol}]\)
- \( m \) = feed ratio of water to methyl acetate \([\text{mol/mol}]\)
- \( r \) = ratio of top vapour to methyl acetate in feed \([\text{Kg/Kg}]\)

**Literature Cited**