

Short communication

# Application of a fluidized reaction–distillation column for hydrolysis of methyl acetate

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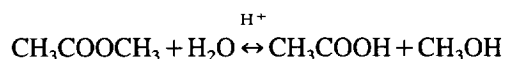
## Abstract

A new method for the hydrolysis of methyl acetate, which consists of a prereactor and a reactive distillation column, has been proposed. The operating variables, including the feed rate, feed ratio of water to MeOAc and reflux ratio, are investigated. It has been found that the conversion of MeOAc increases with increasing reflux ratio, but decreases with increasing feed rate. The feed ratio of water to MeOAc has a considerable effect on the conversion of MeOAc, and an optimum feed ratio has been obtained for the present process. © 1997 Elsevier Science S.A.

*Keywords:* Reactive distillation; Hydrolysis of MeOAc

## 1. Introduction

Polyvinyl alcohol (PVA) is an important material for producing synthetic fiber, film, etc. In the process of PVA synthesis, methyl acetate (MeOAc) is produced as a by-product with a high yield. MeOAc is usually hydrolysed to methyl alcohol (MeOH) and acetic acid (HOAc) for recycling to methanolysis of PVA. The reaction is



The degree of conversion of MeOAc is low in the hydrolysis reaction, because of the small equilibrium constant of the reaction ( $K=0.14$ ). In most industrial PVA plants, the process for the hydrolysis of MeOAc uses a fixed-bed reactor packed with ion-exchange resin, followed by a series of distillation columns for separation of each of the components. As a result of the low conversion of MeOAc, the traditional process is very energy consuming.

To improve the conversion of MeOAc, the coupling of hydrolysis with other unit operations of chemical engineering is required to enhance the hydrolysis reaction. Fuchigami [1] has applied a new process of reaction–distillation coupling for the hydrolysis of MeOAc. It was reported that the conversion of MeOAc can reach a high value by means of a reactive distillation column packed with specially shaped ion-exchange resin, in which the heat requirement is estimated to be lower than that of the traditional process. Because industrial-scale production of the catalysts for this process is rela-

tively difficult and a novel layout of distillation column is required, it is very expensive to use this process.

In the present study, a new method for the hydrolysis of MeOAc and modified sieve-type distillation trays are proposed. Compared with the traditional process, the conversion of MeOAc is greatly improved in the present process.

## 2. Structure of reactive distillation column

In the reactive distillation process, to enhance the catalytic reaction and the vapor–liquid mass transfer efficiency, it is very important to provide efficient vapor–liquid–particulate catalyst contact. Moreover, to keep the operating condition stable, it is also important to retain particulate catalysts in the reactive distillation column.

It has been proposed that the particulate catalysts are retained by a series of contiguous screens above each tray, in such a way that the bed may expand or fluidize in response to the passage of distillation vapor through the tray. A horizontal bottom containment screen is located at the tray deck to retain catalysts during times when there is no vapor flow through the tray. Vapor–liquid–solid three-phase contact is provided on the tray [2]. As a result of the intensive agitation within the screen that occurs on introducing vapor, there exist some disadvantages with this process, such as blocking of the screen mesh by particulate catalysts and high pressure drops across beds.

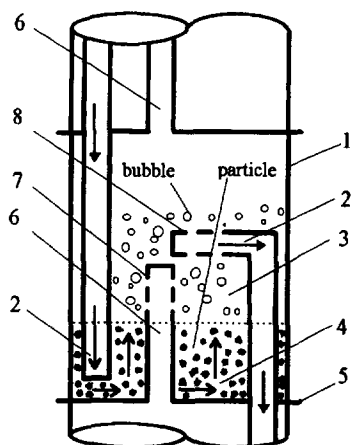


Fig. 1. Structure of reactive distillation column: 1, column; 2, downcomer; 3, vapor-liquid separation zone; 4, liquid-solid reaction zone; 5, tray; 6, vapor tube; 7, vapor inlet; 8, liquid outlet.

In this paper, a modified sieve-type distillation tray is proposed. The structure of the reactive distillation column is shown in Fig. 1. On the tray, there exist a liquid-solid catalytic reaction zone and a vapor-liquid separation zone. The reactive distillation column includes a vessel and five vertically spaced trays, so that the particulate catalyst is carried from one tray to another. The trays are interconnected by a number of downcomers, on the horizontal part of which a few holes are drilled, for conducting liquid downward from tray to tray. A number of vapor tubes are located on the tray. In the upper part of the vapor tubes, a few holes are drilled for the passage of the vapor stream. Vapor inlet and liquid outlet sections are wound around by mesh screens to avoid leakage of the particulate catalysts.

### 3. Experimental procedure

A schematic diagram of the experimental apparatus is shown in Fig. 2. The present process mainly consists of a fixed-bed pre reactor and a reactive distillation column, which are made from stainless steel. The reactive distillation column includes three zones, i.e., reactive distillation, rectifying and stripping zones.

The pre reactor consists of a column that is 400 mm high with an inner diameter of 90 mm, which is packed with strong acid ion-exchange resins as catalysts, and wound around by electric heating wire to control the reaction temperature in the region of  $50 \pm 1$  °C. The weight of the ion-exchange resins in the pre reactor is about 1.9 kg.

In the reactive distillation zone, the column (inner diameter, 90 mm; height, 550 mm) is composed of five modified sieve-type trays, the structure of which is as mentioned above. The operating temperature in the reactive distillation zone is about  $61 \pm 1$  °C. The weight of ion-exchange resin in each tray is about 0.33 kg.

In the rectifying zone, the column is of inner diameter 32 mm and 1200 mm in height, and is packed with Raschig rings. In the stripping zone, the column is of inner diameter

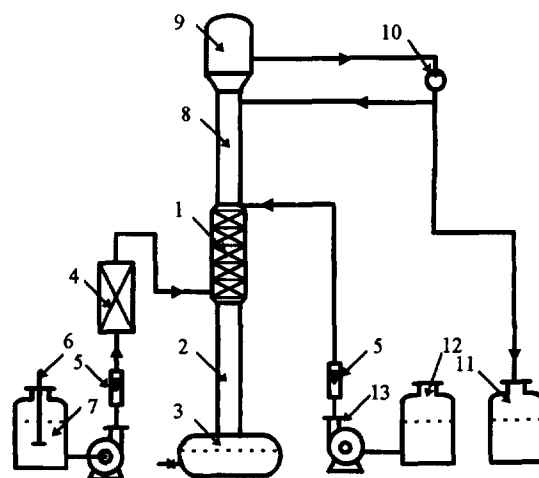


Fig. 2. Schematic diagram of experimental set-up: 1, reactive distillation zone; 2, stripping zone; 3, reboiler; 4, pre reactor; 5, flow meter; 6, agitator; 7, feedstock tank; 8, rectifying zone; 9, vapor condenser; 10, viewer; 11, overhead product tank; 12, water tank; 13, pump.

Table 1  
Parameter index of ion-exchange resin

Item		Unit	Standard
Density		kg m <sup>-3</sup>	1400
Size	- 16 mesh	%	< 2
	16-28 mesh	%	> 60
	28-42 mesh	%	36
	+ 42 mesh	%	< 2

32 mm and 800 mm in height, and is also packed with the same packing materials as those in the rectifying zone. The rectifying and stripping columns are wound around by electrical heating wires to control the operating temperature. The operating temperature at top of the column is in the region of  $54 \pm 1$  °C. The reboiler is heated by an electrical furnace, and the operating temperature is about  $104 \pm 1$  °C.

For the present process, the total molar feed ratio of water to MeOAc is maintained at 1:1. According to the molar feed ratio  $m$  ( $0 < m < 1$ ), a mixture of MeOAc and water is fed to the pre reactor. Additional water is fed to the top of the reactive distillation column. The product of the pre reactor is fed to the reactive distillation zone. The overhead vapor is condensed by cooling water and a portion of the condensed vapor is returned to the rectifying zone as reflux.

The product components are analyzed by gas chromatography. Once all the operating variables and the analyzed results become steady, the conversion of MeOAc is calculated.

The standard ion-exchange resin results for the experiment are summarized in Table 1.

### 4. Results and discussion

In the process, the total conversion of MeOAc consists of two parts—one in the pre reactor and the other in the reactive distillation zone.

The effect of the (hourly) feed rate  $F$  on the conversion of MeOAc is shown in Fig. 3. It can be seen that the total conversion of MeOAc decreases with increasing feed rate, but the conversion in the reactive distillation zone remains nearly constant. The residence time of reactants in the pre-reactor decreases with increasing feed rate, so it can be expected that the conversion of MeOAc in the pre-reactor decreases with increasing feed rate, as also shown in Fig. 3. Figs. 4 and 5 show that, with the increase in the feed rate, the concentration of MeOAc decreases in the overhead product, but increases in the bottom product. It is demonstrated that the increase in the feed rate will result in a decrease in the separating capacity of the reactive distillation column.

The effect of the reflux ratio  $r$  (mol/mol) on the conversion of MeOAc is illustrated in Fig. 6. It can be expected that the increase in the reflux ratio will lead to an increase in the conversion of MeOAc. However, a higher reflux ratio causes higher energy consumption.

An increase in  $m$  will result in a decrease in the residence time of the reactants in the pre-reactor, but will increase the water content in the mixture of water and MeOAc. The decrease in the residence time of the reactants in the pre-reactor reduces the conversion of MeOAc, while the increase in the water content in the mixture of water and MeOAc

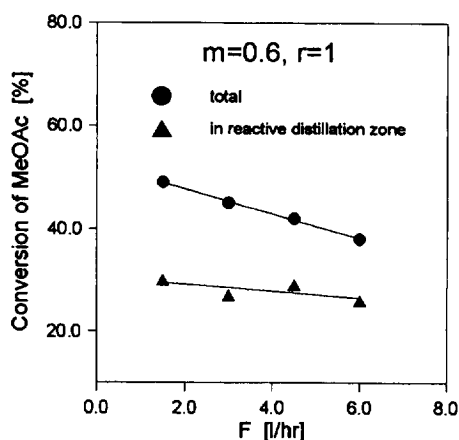


Fig. 3. Effect of feed rate on conversion of MeOAc: ●, total; ▲, in reactive distillation zone;  $m=0.6$ ;  $r=1$ .

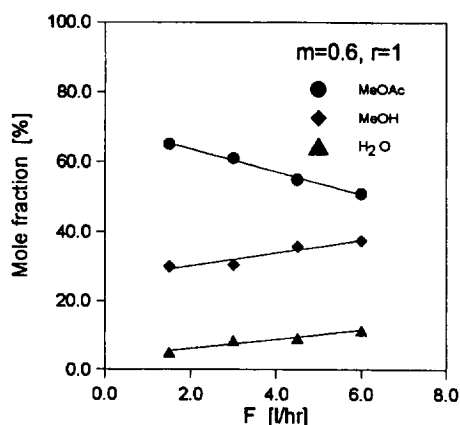


Fig. 4. Effect of feed rate on mole fraction at overhead product: ●, MeOAc; ◆, MeOH; ▲, H<sub>2</sub>O;  $m=0.6$ ;  $r=1$ .

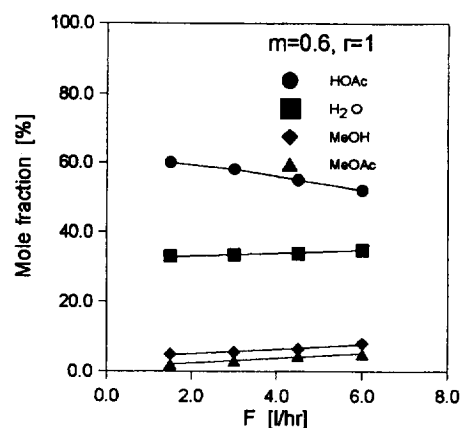


Fig. 5. Effect of feed rate on mole fraction at bottom product: ●, HOAc; ■, H<sub>2</sub>O; ◆, MeOH; ▲, MeOAc;  $m=0.6$ ;  $r=1$ .

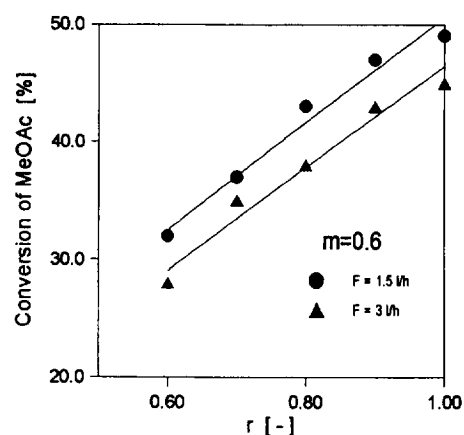


Fig. 6. Effect of reflux ratio on conversion of MeOAc: ●,  $F=1.5 \text{ h}^{-1}$ ; ▲,  $F=3 \text{ h}^{-1}$ ;  $m=0.6$ .

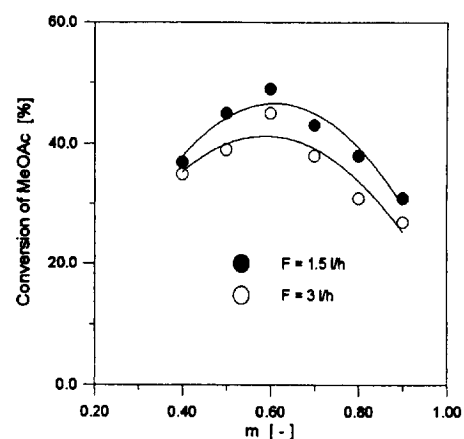


Fig. 7. Effect of  $m$  on conversion of MeOAc: ●,  $F=1.5 \text{ h}^{-1}$ ; ○,  $F=3 \text{ h}^{-1}$ ;  $r=1$ .

enhances the conversion of MeOAc. It is demonstrated in Fig. 7 that the conversion of MeOAc in the pre-reactor increases with increasing  $m$ . Fig. 7 also indicates that  $m$  has a marked effect on the total conversion of MeOAc, and there exists an optimum value of  $m$  (about 0.6).

In the present process, the main operating variables are the feed rate, the feed ratio of water to MeOAc and the reflux ratio. From the above discussion, there exists an optimum

operating condition for higher conversion of MeOAc and relatively lower energy consumption.

In the traditional process, the conversion of MeOAc reaches about 20%. From Fig. 7, it can be seen that the total conversion of MeOAc can reach about 50% in the present process. Compared with the traditional process, the process described here requires no more energy consumption. Little reconstruction of traditional distillation columns is required in the present process. Therefore, it can be concluded that the present process is promising for the hydrolysis of MeOAc.

## 5. Conclusions

A new method for the hydrolysis of MeOAc has been proposed. Compared with traditional processing, the process

described here can improve the conversion of MeOAc and requires no more energy consumption. An optimum feed ratio of water to MeOAc has been obtained.

## Acknowledgements

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## References

- [1] Y. Fuchigami, *J. Chem. Eng. Jpn.*, 23 (1990) 354.
- [2] *US Patent 4471154*.