

Preparation of Ethylene Glycol Monoethyl Ether Acetate Using a Tubular Reactor

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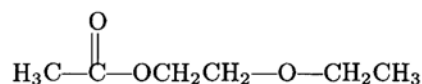
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Abstract Ethylene glycol monoethyl ether acetate (EGEA), an excellent solvent, is prepared with ethylene oxide (EO) and ethyl acetate (EA) in a tubular reactor under suitable reaction condition. The single circulation yield can reach 81%. This technology is not only safe but also makes it possible to continuously produce EGEA in industry, with low content of high boiling point by-products.

Keywords ethylene glycol monoethyl ether acetate, ethyl acetate, tubular reactor

1 INTRODUCTION

Ethylene glycol monoalkyl ether carboxylic acids, a series of compounds used as important solvents, were exploited and developed in early 1970s, which not only have better capability than common solvents such as benzene, acetone and EA, but also have better solvent properties than ethylene glycol ether. Among them, EGEA was the first to reach a yield of ten thousand tons per year^[1]. Its chemical structure can be expressed as



There are ether, carbonyl and alkyl structure in the molecule, including non-polarity part and polarity fragment, as contribute much to the good solubility of EGEA, which can dissolve not only low molecular organic substance, but macro-molecular materials as well, such as cellulose and high polymer. Furthermore, it can be well dissolved in water. EGEA is a highly effective solvent.

In the recent several decades, large-scale manufacture equipment has been set up over the world to exploit and synthesize a variety of relevant products, for instance ethylene glycol methyl ether acetate and ethylene glycol butyl ether acetate. However, the security of the traditional tank reactor could not be assured in the presence of EO, moreover, lots of by-products come out at the same time. In this study we industrialize the synthesis of EGEA by exploiting a new process and adopting a tubular reactor.

2 EXPERIMENTAL

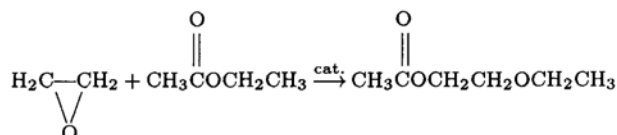
2.1 Synthesis

It is known that EGEA can't be produced by a one-step reaction with EO and EA, which is gener-

ally prepared through a two-step reaction in the presence of a strongly acidic cationic exchange resin as a catalyst^[2]. However, for this two-step process it needs a long time to complete the reaction, furthermore, water and alcohol are produced as by-products, which form azeotrope with the reactants and products and it is very difficult to separate the mixture to obtain the pure product.

In recent years, one-step reaction was widely researched and exploited, in which EO directly reacts with EA to produce EGEA in a tank reactor in the presence of catalyst^[3]. This technology has been applied extensively in industry owing to the advantage that no water and alcohol are produced during the reaction, so it is convenient to refine the react mixture. However, the disadvantage is that it will bring about lots of by-products of diethylene glycol, triethylene glycol and diethylene glycol monoethyl ether acetate (DGEA), together with relevant ramifications.

After several years' research work and experiments, we found that one-step reaction process could be well promoted using a tubular reactor, in which almost no by-product is formed during the whole reaction. In this paper, we propose a new process to synthesize EGEA by carrying out the one-step reaction in a tubular reactor. The reaction formula of EO and EA is as follows:



2.2 The reaction process

A simple flow chart for the reaction is shown in Fig. 1.

The pre-mix unit whose structure and measure are shown in Table 1 together with those of the tubular

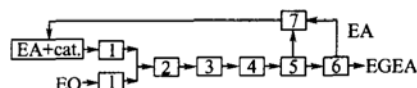


Figure 1 A simple process chart

1—metering pump; 2—pre-mix unit; 3—tubular reactor;
4—buffer tank; 5—flash evaporator; 6—rectification tower;
7—middle tank

Table 1 The structure and dimension of tubular reactor and pre-mix unit(mm)

	Tubular reactor	Pre-mix unit
tube diameter	$\phi 10 \times 1.5$	$\phi 15 \times 2$
tube length	40000	400

reactor, is charged with raw materials (EA and EO) and catalysts in a certain proportion, the amount of which can be measured and controlled by metering pump. After mixed sufficiently, the mixtures are fed into a tubular reactor, at $10\text{--}20\text{ g}\cdot\text{min}^{-1}$ afflux, then increase the temperature by 0.5°C per min. The reaction temperature is well controlled by an oil bath, and the pressure is dominated by a reducing valve. The buffer tank is used to increase the retention time of the reactants and to prevent the remanent EO from entering the separating system. There is a fixed apparatus at the back of the reactor, which is used to pick up sample for analyzing the content of the remaining EO, in order to accordingly control the reaction temperature and the retention time. After fully reacting, mixtures are pumped into the flash evaporator to recover a part of unreacted EA. Remanent EA is separated by distillation under atmospheric pressure, then re-circulated to a middle tank after being condensed and liquefied, and sent back to EA tank to join the next reaction. Finally the mixture is distilled in the rectification tower under vacuum to obtain pure EGEA.

2.3 Experimental results

The results are shown in Table 2, in which DGEA is the main by-product and the yield of EGEA is calculated only based on a single circulation.

In this technology, anhydrous aluminium trichloride is selected as catalyst, and triethyl amine as co-catalyst. Hence, water should be excluded from the whole reacting system, no matter in raw materials or in catalyst, or in the tubular reactor. Generally, no water exists in industrial EO, so it is necessary to ensure that mass content of water in EA is less than 0.1%. As shown in Table 2, the yield of EGEA would be very low if the water content exceeds 0.1%.

The amount of the catalyst used can range from 6% to 8% based on the reactant EO by mass in accordance with related patent^[4] and based on many experiments. The most preferable molar ratio of aluminium trichloride to triethyl amine is about (2—4):1.

In the process the reaction is at a temperature about $150\text{--}200^\circ\text{C}$. At temperature above 200°C , the reaction is too fast to control and by-products will ascend. At temperature below 150°C , reaction rate is low and satisfactory results can not be obtained.

Pressure should be high enough for the reaction to proceed at the indicated temperature. However, the reaction pressure is desired to be as high as possible to ensure the minimum pressure to proceed reaction in the liquid phase, to assure high reaction rate. In general, the pressure between 1.0 MPa and 1.5 MPa is more appropriate.

The tubular reactor should be long enough to assure the retention time not less than 2 h, so that EO is completely reacted^[5]. As shown in Table 2, the longer the retention time is, the higher the yield of EGEA and the less the by-product DGEA.

Table 2 Results of the experiments

Exp. No.	Ratio of EA to EO (by mole)	Water content in EO % (by mass)	Ratio of cat. to EO % (by mass)	Ratio of AlCl_3 to triethyl amine % (by mass)	Temp. $^\circ\text{C}$	Pressure MPa	Retention time min	Yield of EGEA %	Yield of by-product DGEA %
1	3	0.45	6	2.3	160	1.5	120	19.2	0.5
2	3	0.45	7	2.3	160	1.5	120	21.4	0.6
3	3	0.08	6	2.3	160	1.5	120	49.1	15.2
4	3	0.08	7	2.3	160	1.5	120	54.9	10.5
5	4	0.08	7	2.3	160	1.5	120	61.8	9.8
6	6	0.08	7	2.3	160	1.5	120	70.7	8.4
7	8	0.08	7	2.3	160	1.5	120	71.6	7.8
8	10	0.08	7	2.3	160	1.5	120	73.2	6.4
9	6	0.08	7	2.3	160	1.5	154	80.3	5.2
10	6	0.08	8	2.3	160	1.5	154	81.4	7.1
11	6	0.08	7	2.3	160	1.5	154	81.6	7.0
12	6	0.08	7	2.3	160	1.5	154	74.9	7.1
13	6	0.08	7	2.3	160	1.5	154	81.0	7.0
14	6	0.08	7	2.3	160	1.5	176	81.4	5.7
15	6	0.08	7	2.3	170	1.6	176	80.7	6.6

The amount of EA should be in excess of that of EO to avoid the repeating reaction of product and superfluous EO. According to Fig. 2, the yield of EGEA increases when the ratio of EA to EO increases, while the yield of DGEA falls. When the ratio exceeds 8, the variation becomes unobvious. The preferable ratio of EA to EO is in the range of 6:1 to 8:1.

We controlled the reaction at temperature 160°C and pressure 1.5 MPa, and adjusted the mass ratio of catalysts to EO at 7. The mass ratio of aluminium trichloride to triethyl amine is 2.3, and the ratio of EA to EO is varied gradually, as shown in Fig. 2.

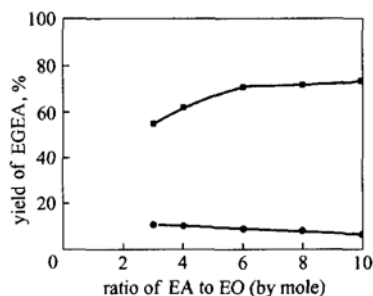


Figure 2 Effect of mole ratio of reactants on the yield of EGEA and DGEA

■— yield of EGEA; ●— yield of DGEA

3 DISCUSSION

(1) The content of high boiling point by-products can be greatly decreased with tubular reactor. The higher the molar ratio of EA to EO, the less by-products. According to related literature^[6], the content of high boiling point by-products will rise by 20% using traditional tank reactor under the same reacting condition. Owing to the restriction of pressure in a tank reactor, EO must be fed to the tank reactor at a time. When reactants are heated and agitated, though EO can be dispersed sufficiently in the surrounding of EA, EGEA is apt to re-react with EO to produce DGEA, a high boiling point by-product. Whereas, in a tubular reactor raw materials flow forward and react each other after fully pre-mixing, so

that EO is uniformly dispersed in the superfluous EA and the probability of EGEA to re-react with EO is greatly reduced. The content of by-products is much lower than that in a tank reactor.

During the whole reaction, EA and EO are fully dispersed and move forward along the tube. It is impossible for EO to gather together, which also avoids the danger of explosion and makes it practical to react in liquid environment with high temperature and high pressure.

This technology has been well applied in industrial synthesis of ethanolamine (the reaction of EO and NH_3). As we predicted, it should be also suitable for large-scale production of EGEA.

(2) Water contained in the raw materials and catalysts greatly affects the yield of EGEA. First, aluminium trichloride is prone to hydrolyze in the presence of water, which not only reduces the content of effective catalyst, but also jams valves and pumps owing to the hydrolyzing deposits; secondly, EO also reacts with water to produce ethylene glycol, so the raw materials and catalysts should be treated in dry nitrogen gas before being fed in a dried tubular reactor.

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