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# Synthesis of Ethyl Acetate by the Esterification Process: Process Optimization

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## Abstract

Ethyl acetate was efficiently synthesized by the esterification process, using concentrated sulfuric acid as a catalyst. Systematic studies showed that the molarity ratio of ethanol to acetic acid, dosage of catalyst, reaction temperature, feeding rate of reactants, and washing times played a key role in controlling the productivity and purity of the products. The purity of synthesized ethyl acetate was characterized by the capillary gas chromatograph. It found that with only 5mL of concentrated sulfuric acid the productivity of ethyl acetate reached up to 71.05%. It also revealed that the rate of the addition of the mixture was controlled as 1-3s per drop in order to get high theoretical conversion rates. The optimal temperature of the esterification reaction is 80-85℃. It demonstrated that to reduce the ethanol of the crude product, it is necessary to wash the crude product with saturated calcium chloride at least 2 times to obtain high purity ethyl acetate product. In the paper, the usage of a catalyst of concentrated sulfuric acid was much less than in the other relevant studies.

## Keywords

Ethyl acetate, synthesis, esterification, process optimization

## 1. Introduction

Ethyl acetate (EAC) is an important chemical raw material, often used in medicine, paint, rubber, paint, cellulose, ink, dye, organic acid, and artificial flavor production [1]. Today, the synthesis methods of ethyl acetate mainly include esterification reaction [2], acetaldehyde condensation reaction, addition reaction method, ethanol dehydrogenation reaction, and biotechnological production [3]. To the best of our knowledge, the esterification reaction is still the classical method of the synthesis of ethyl acetate. However, it is typically energy energy-intensive and environmentally unfriendly process.

In the paper, we optimized the technology of the synthetic process of ethyl acetate in order to minimize the losses of raw materials and the consumption of auxiliaries. This will both improve the economy of the process and reduce pollutant emissions. The rate of the addition of the mixture of acetic acid (HAc) and ethanol (EA) is approximately equal to the rate of evaporation of distillate of ethyl acetate, which obviously increases the yield of the products.

## 2. Experimental Procedure

### 2.1 Reagents and apparatus

Acetic acid, ethanol, concentrated sulfuric acid, sodium carbonate, sodium chloride, calcium chloride, ethyl acetate standard substance, and n-propyl acetate standard substance were purchased from Sinopharm Chemical Reagent Company. All reagents were of analytical grade and used without further purification. The electric heating sleeve was purchased from Hebei Fissford Instrument Company. The synthesized samples were analyzed by the Gas Chromatograph (GC) system of the Fuli GC9720 Plus series from Zhejiang Fuli Analytical Instruments Company.

## 2.2 Synthesis of ethyl acetate

Reactions were conducted by mixing a certain amount of ethanol and concentrated sulfuric acid in a three-mouth flask with a magneton. An appropriate amount of ethanol and 15g of acetic acid were added into the drip funnel and made them mix evenly. Then a portion of the mixture was poured into the three-mouth flask, and next, it was heated to a suitable temperature on the electric heating sleeve. A certain amount of the mixture was added into a three-mouth flask rapidly and kept the reaction at a suitable temperature for 20 minutes. Next, the mixture was slowly added into the three-mouth flask, and the drip rate was adjusted to make the drip rate roughly equal to the rate of evaporation of distillate of ethyl acetate. Until no substance was distilled from the flask, the heating was stopped. The overall reaction and side reaction can be depicted in equations 1-3.

$$CH_3COOH + HOCH_2CH_3 \rightleftharpoons CH_3COOCH_2CH_3 + H_2O \quad (T<140°C) \tag{1}$$

$$CH_3CH_2OH + HOCH_2CH_3 \rightleftharpoons CH_3CH_2OCH_2CH_3 + H_2O \quad (T\geq140°C) \tag{2}$$

$$CH_3CH_2OH \rightleftharpoons CH_2{=}CH_2 + H_2O \quad (T\geq170°C) \tag{3}$$

## 2.3 Refining of ethyl acetate

In order to refine the crude product of the synthesized ethyl acetate, 5ml saturated sodium carbonate solution was added to the crude product until the ester layer turned neutral. Next, move the mixture into the separatory funnel. After making them mix evenly by shaking them fully, stand for stratification, and separate the water layer from the organic facies in the separatory funnel. Then 7ml saturated sodium chloride solution was added into the separatory funnel, and the water layer from the organic facies again. At last, 15ml saturated calcium chloride solution was added into the separatory funnel, and the water layer from the organic facies and performed twice.

The ester layer containing the refined ethyl acetate was transferred from the separatory funnel into the grinding conical bottle, and 2g of anhydrous magnesium sulfate was added to it. After shaking it fully, stand for 15 minutes in order to remove the water from the ethyl acetate.

The dried ethyl acetate was filtered through the absorbent cotton into the dry distillation flask, with a magneton added to it. Set up the distillation device, and next heated the distillation flask. The ethyl acetate was obtained by collecting the distillate at 72°C-80°C. Record the output of the product.

## 2.4 Quantitative and qualitative analysis

Accurately weighed a certain mass of the synthetic product of ethyl acetate into the sample bottle, and then added a certain mass of internal standard (n-propyl acetate) in it to prepare the sample solution. It was analyzed by the Gas Chromatograph (GC) system of the Fuli GC9720 Plus series, which was equipped with a polar RB-5 PEG Restek Capillary Column (30m × 250um × 0.25um, Fuli, China) and a Flame Ionization Detector (FID). 0.5uL liquid sample was injected and vaporized at the temperature of 200°C. It will be separated with the nitrogen as carrier gas at 0.5 mL/min with the split ratio of 50: 1 at 140°C in the column and identified by FID with hydrogen: air = 30: 300 at 200°C. Calculated the contents of ethyl acetate and various impurities according to the corresponding peak area by the gas chromatograph. All the analyses were performed in triplicate and the data were expressed as mean values with standard deviations (±SD) [4].

The relative mass correction factor of the internal standard ($f_{i/s}$) was calculated in accordance with equation 4 given as follows:

$$f_{i/s}=(A_s*m_i)/(A_i*m_s) \tag{4}$$

where $A_i$ is the peak area of the ethyl acetate standard substance, $m_i$ is the quality of the ethyl acetate standard substance, $A_s$ is the peak area of the n-propyl acetate standard substance, $m_s$ is the quality of the n-propyl acetate standard substance. The final result as mean values of 3 parallel experiments was computed by equation 4. The content of the ethyl acetate in the sample solution ($W_i$) was calculated in accordance with equation 5 given as follows:

$$W_i=(A_i*m_s)/(A_s*m)* f_{i/s}*100\% \tag{5}$$

where $A_i$ is the peak area of the ethyl acetate in the sample solution, m is the quality of the refined ethyl acetate in the sample solution, $A_s$ is the peak area of the n-propyl acetate standard substance, $m_s$ is the quality of the n-propyl acetate standard substance. The final result was expressed as mean values of 3 parallel experiments as exhibited in Table 2. The refined yield of the ethyl acetate was calculated in accordance with equation 6 given as follows:

$$Y_i =(m_{EAC} * M_{HAc})/(m_{HAc} *M_{EAC})* W_i \tag{6}$$

where $m_{EAC}$ is the quality of the refined ethyl acetate, $M_{EAC}$ is the relative molecular mass of ethyl acetate with 88.11g/mol, $m_{HAc}$ is the quality of the acetic acid added in the esterification reaction, $M_{HAc}$ is the relative molecular mass of acetic acid with 60.05g/mol.

## 3. Results and discussion

### 3.1 Effect of the Mass Ratio of Ethanol to Acetic Acid

15g acetic acid and 5mL concentrated sulfuric acid reacted at 85℃ with the mixture in the drip funnel added in 1-3 seconds per drop, and a drop was about 0.03mL. When the amount of ethanol added in the three-mouth flask was changed as calculated in equation 7, the experimental results were shown in Table 1. The yield of ethyl acetate increased with the increasing molarity ratio of ethanol to acetic acid [5]. When the molarity ratio of ethanol to acetic acid was 1.5:1, the yield was the highest. In the other related paper, the mass ratio was even 3:1. In our experiment, the yield of ethyl acetate was no longer significantly changed by increasing the molarity proportion over 1.5:1.

$$m_{EA}=(m_{HAc}*M_{EA}/M_{HAc})*k_1 \tag{7}$$

where $m_{EA}$ is the quality of the ethanol, $M_{EA}$ is the relative molecular mass of ethanol with 46.07g/mol, $m_{HAc}$ is the quality of the acetic acid, $M_{HAc}$ is the relative molecular mass of acetic acid with 60.05g/mol, $k_1$ is the mass ratio of ethanol to acetic acid.

**Table 1. Effect of the molarity ratio of ethanol to acetic acid on the synthesis of ethyl acetate**

| $k_1 = n_{EA} : n_{HAc}$ | $m_{EA}$ | $m_{EAC}$ | $W_i$(purity) | $Y_i$(yield) |
|---|---|---|---|---|
| 1.0: 1 | 11.50g | 3.28g | 96.41% | 14.37% |
| 1.1: 1 | 12.65g | 6.69g | 95.12% | 28.91% |
| 1.2: 1 | 13.80g | 8.88g | 95.59% | 38.57% |
| 1.3: 1 | 14.95g | 13.62g | 91.49% | 56.62% |
| 1.4: 1 | 16.10g | 16.64g | 87.90% | 66.46% |
| 1.5: 1 | 17.25g | 17.82g | 87.75% | 71.05% |
| 2.0: 1 | 23.00g | 17.98g | 85.23% | 69.63% |
| 2.5: 1 | 28.75g | 17.16g | 88.30% | 68.85% |
| 3.0: 1 | 34.50g | 17.24g | 83.31% | 65.26% |

### 3.2 Influence of the Dosage of Catalyst

15g acetic acid and 17.25g ethanol reacted at 85℃ with the mixture in the drip funnel added in 1-3 seconds per drop. When the amount of concentrated sulfuric acid as the catalyst was changed as calculated in equation 8, the experimental results were shown in Table 2. The results demonstrated that the yield increased with the increase of the account of sulfuric acid. When 5mL of concentrated sulfuric acid was added, the yield was the highest. However, the yield decreased if the account of the sulfuric acid continued to increase. We guess that there were too many free water molecules in the system if too little concentrated sulfuric acid as the dehydrating agent was added in the esterification reaction, which made the synthesis reaction go in the reverse direction, due to the lower productivity. On the other hand, too much account of sulfuric acid may cause the raw material of ethanol or acetic acid carbonized seriously, which will reduce the amount of available raw materials, and eventually lead to the reduction of the yield.

$$V_{H2SO4} = (m_{HAc} * k_2)/\rho_{H2SO4} \tag{8}$$

where $V_{H2SO4}$ is the volume of concentrated sulfuric, $\rho_{H2SO4}$ is the density of concentrated sulfuric with 1.84g/mL, $m_{HAc}$ is the quality of the acetic acid, $k_2$ is the mass ratio of concentrated sulfuric acid to acetic acid.

**Table 2. Influence of the dosage of catalyst on the synthesis of ethyl acetate**

| $k_2 = m_{H2SO4} : m_{HAc}$ | $m_{H2SO4}$ | $V_{H2SO4}$ | $m_{EAC}$ | $W_i$(purity) | $Y_i$(yield) |
|---|---|---|---|---|---|
| 5% | 0.75g | 0.41mL | 11.09g | 84.29% | 42.47% |
| 10% | 1.50g | 0.82mL | 11.34g | 84.64% | 43.61% |
| 20% | 3.00g | 1.63mL | 11.66g | 89.81% | 47.58% |
| 40% | 6.00g | 3.26mL | 14.50g | 89.20% | 58.77% |
| 60% | 9.00g | 4.89mL | 17.82g | 87.75% | 71.05% |
| 80% | 12.00g | 6.52mL | 11.53g | 91.01% | 47.68% |
| 100% | 15.00g | 8.15mL | 6.36g | 89.63% | 25.90% |

### 3.3 Influence of the Temperature

15g acetic acid, 17.25g ethanol, and 5mL concentrated sulfuric acid reacted with the mixture in the drip funnel and added in 1-3 seconds per drop. When the esterification reaction temperature was changed, the experimental results are shown in Table 3. The crude product could not be steamed when the reaction temperature was lower than the boiling point of ethyl acetate at 77.1℃. The yield of ethyl acetate decreased as the esterification reaction temperature increased. In our study, when the reaction temperature was kept at 85℃, the yield reached the maximum, which is lower than the optimal reaction temperature reported in some other relevant literature. It is speculated that the higher the temperature was, the more serious the side reaction was.

**Table 3. Influence of the temperature on the synthesis of ethyl acetate**

| T(temperature) | $m_{EAC}$ | $W_i$(purity) | $Y_i$(yield) |
|---|---|---|---|
| 80-85℃ | 17.82g | 87.75% | 71.05% |
| 90-95℃ | 13.81g | 93.37% | 58.59% |
| 100-105℃ | 13.87g | 90.51% | 57.04% |
| 110-115℃ | 15.71g | 84.53% | 60.34% |

### 3.4 Influence of the Feeding Rate of Reactants

15g acetic acid, 17.25g ethanol, and 5mL concentrated sulfuric acid reacted at 85℃. If the feeding rate of reactants was changed, the experimental results are shown in Table 4. It showed that the yield of ethyl acetate was the highest when the mixture in the drip funnel was added in one second per drop. If the rate of the mixture addition was too slow, the esterification reaction time would turn out to be much longer, resulting in a serious side reaction., if the rate of the mixture addition was too fast, the ethanol was steamed without sufficient reaction, leading to the waste of the raw material, and thus the productivity of ethyl acetate would be reduced. By effectively controlling the rate of the mixture addition and reaction temperature, we tried to make the rate of the mixture addition be consistent with the evaporation rate of the crude product of ethyl acetate so that the reaction direction of the reversible reaction of synthesis of ethyl acetate can always go in the direction of the forward reaction. Through this dynamic balance, the conversion rate of various raw materials reached the maximum and the yield was the highest.

**Table 4. Influence of the feeding rate of reactants on the synthesis of ethyl acetate**

| feeding rate of reactants | $m_{EAC}$ | $W_i$(purity) | $Y_i$(yield) |
|---|---|---|---|
| Add all the mixtures once | 13.44g | 92.42% | 56.44% |
| 1s per drop | 17.82g | 87.75% | 71.05% |
| 3s per drop | 15.69g | 91.17% | 64.99% |
| 5s per drop | 8.04g | 90.05% | 32.90% |

### 3.5 Influence of the Washing Method

15g acetic acid, 17.25g ethanol, and 5mL concentrated sulfuric acid reacted at 85℃ with the mixture in the drip funnel added in 1-3 seconds per drop. 5mL of saturated washing solution of sodium carbonate was added into the separatory funnel to make the mixture neutral in order to remove the impurity of acetic acid from the crude products, and 7mL of the saturated washing solution of sodium chloride was used to separate the bicarbonate ion from the organic phase. The amount of the saturated washing solution of calcium chloride was changed to explore the most suitable amount in order to remove the ethanol completely from the crude products of ethyl acetate. The Gas Chromatogram results discovered that if the mass ratio of ethanol to acetic acid in the esterification reaction was less than 1.5, the impurity content of ethanol in the refined product was much lower, and the content of the target product of ethyl acetate was much higher with 15mL of saturated calcium chloride solution washed twice. If the proportion of ethanol and acetic acid in the esterification reaction continued to increase, the impurity content of ethanol in the crude product would increase greatly also, which would demand a more saturated calcium chloride solution to remove ethanol. However, too much saturated calcium chloride washing solution led to a high purity but a low yield of the final refined product of ethyl acetate. 8.5g ethyl acetate can be dissolved in 100g water at 15℃. The more the washing solution was added, the greater the loss was caused by the dissolution of ethyl acetate in the washing solution, resulting in a reduction of ethyl acetate.

## 4. Conclusion

Ethyl acetate was efficiently synthesized by the esterification process, using concentrated sulfuric acid as a catalyst. We discovered that that the molarity ratio of ethanol to acetic acid, the dosage of catalyst, reaction temperature, feeding rate of reactants, and washing times played a key role in controlling the yield and purity of the products. In our paper, we obtained the products of ethyl acetate with much higher yield and purity by using fewer raw materials at a much lower temperature. It would be helpful to improve the industrial application of the synthesis of ethyl acetate.

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