

Synthesis of 2-Ethylhexyl Acetate by Transesterification of Methyl Acetate with 2-Ethylhexanol

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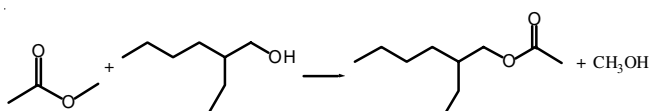
In order to explore a new application field of methyl acetate which is of limited industrial importance, one of the possibilities to obtain the desired products would be the transesterification of methyl acetate with 2-ethylhexanol. The choice of catalyst and the determination of the best experimental conditions for the transesterification were investigated in this paper. Strongly acidic cation-exchange resin NKC-9 was chosen as the catalyst in this reaction. The reaction time, the effects of the reaction temperature, the catalyst loading and the molar ratio of methyl acetate to 2-ethylhexyl acetate on the conversion of 2-ethylhexyl acetate were discussed. This paper describes an optimization study on the transesterification reaction based on nine well-planned orthogonal experiments. The maximum conversion of 2-ethylhexanol was found at a NKC-9 catalyst loading of 20 wt. %, a molar ratio of methyl acetate to 2-ethylhexanol of 4:1, a reactive time of 3 h and a reaction temperature of 80 °C. The product yield and the conversion of 2-ethylhexanol under optimal conditions reached 90.90 and 79.64 %, respectively. The structure of the product 2-ethylhexyl acetate has been confirmed by IR and ¹H NMR.

Keywords: Methyl acetate, Transesterification, NKC-9, Orthogonal experiment.

INTRODUCTION

Methyl acetate is a byproduct during the production of polyvinyl alcohol. From 1 ton of polyvinyl alcohol, about 1.68 tons of methyl acetate is produced^{1,2}. It is generally hydrolyzed by a catalyst to obtain acetic acid and methanol, which is the conventional method of treating methyl acetate in industry. However, it became not particularly economical since the price of acetic acid had decreased rapidly in recent years. Furthermore, the hydrolysis of methyl acetate has many disadvantages, such as the high requirement for the equipment and more energy extensive in the process. The transesterification of methyl acetate with 2-ethylhexanol (2-EH) is therefore a sustainable option of the applications of the methyl acetate. The coproduct formed, methanol, can undergo alcoholysis reaction once again to form polyvinyl alcohol and get recycled back for transesterification, while 2-ethylhexyl acetate (2-EHA) is a high boiling retarder solvent with limited water solubility, commonly used to promote flow and retard blushing in formulations such as lacquers, lacquer emulsions, screen inks, baking enamels and air-dry enamels. It is also an excellent solvent for nitrocellulose and widely used in the leather industry³.

Reaction equation can be presented as:



Many catalysts have been suggested therefore for use in the transesterification step, the conventional inorganic acid catalyst used in transesterification is concentrated sulfuric acid. Xu *et al.*⁴ have reported on the advantages of the heterogeneous catalyst strongly acidic cation-exchange resin NKC-9. Cui *et al.*⁵ reported the kinetic behavior and chemical equilibrium of the transesterification of methyl acetate with *n*-butanol catalyzed by an ionic liquid. Hence, these catalysts are considered good candidates for the transesterification of methyl acetate with 2-ethylhexanol.

Although there are many studies on transesterification reactions, any information about the transesterification of methyl acetate with 2-ethylhexanol has not been found in the literature. In this paper, a new method for producing 2-ethylhexyl acetate by transesterification of methyl acetate with 2-ethylhexanol was performed. In addition, the most suitable catalyst was chosen from the concentrated sulfuric acid, ion-exchange resin NKC-9 and 1-heptyl-3-methylimidazole acetate.

EXPERIMENTAL

Methyl acetate (AR grade) and 2-ethylhexanol (AR grade) were obtained from Tianjin Institute of Fine Chemicals Retrocession. Strong-acid cationic exchange resin NKC-9 was obtained from Anhui Sanxing Resin Technology Co. Ltd., NaOH (AR grade) was obtained from Shenyang Chemical Reagent No. 3 Factory. *n*-Heptane (AR grade) was obtained

from Tianjin Kemiou Chemical Reagent Co., Ltd. Other chemicals are also analytical grade.

Transesterification reaction procedure: All the experiments were conducted in a 4-neck round bottom flask of volume 250 mL equipped with a stirrer, a thermometer, a condenser pipe and a pressure-equalizing dropping funnel. The 4-neck round bottom flask was dipped in a constant temperature water bath which was equipped with a temperature sensor. 2-Ethylhexanol and NKC-9 were put into the 4-neck round bottom flask. The temperature in the reactor was maintained within ± 1 °C with respect to the desired temperature. The measured quantities of 2-ethylhexanol and NKC-9 were charged into the 4-neck round bottom flask and methyl acetate was charged to the constant pressure drop funnel. Once the desired temperature was achieved, the methyl acetate was being dropped into the reactive mixture over a 2 h period. After the dropping was finished, the temperature is maintained at the desired temperature for the fixed time. NKC-9 and the reactive liquid were separated by vacuum filtration when it cooled down and the NKC-9 was recycled at the same time. Finally the fraction between 130 and 140 °C was collected by reduced pressure distillation and weighed this fraction.

Gas chromatography was applied to study the components of the reaction mixture. The conversions of 2-ethylhexanol and the components of all samples were analyzed by gas chromatography (GC7890F) equipped with hydrogen flame ionization detector (FID). (N_2 as carrier gas, a quartz capillary column packed with PEG-20M 30 m \times 0.53 mm \times 0.5 μ m, oven temperature 80 °C, injector temperature 220 °C, detector temperature 240 °C, injecting sample volume 0.2 μ L; retention times: methyl acetate 0.9 min, methanol 1.1 min, 2-ethylhexyl acetate 7 min, 2-ethylhexanol 12.5 min).

Product spectroscopic characterization: Infrared spectra of the reaction product 2-ethylhexyl acetate (KBr pellets) was recorded on Spectrum One-B (Perkin Elmer®) FT-IR spectrometer. 1H NMR spectra was measured in $CHCl_3-d_1$ using TMS as internal standard with a Varian® INOVA spectrometer (400 MHz for 1H).

RESULTS AND DISCUSSION

Catalyst and reaction time choices: Choice of catalyst is important and results were obtained with different catalysts for the transesterification. According to literature, the suitable catalyst loading of concentrated sulfuric acid was chosen as 2 wt. % (by mass of methyl acetate)⁶, NKC-9 was 20 wt. % (by mass of methyl acetate)⁴, 1-heptyl-3 methyl imidazole acetate was 5 wt. % (by mass of methyl acetate)⁷.

The catalytic effect of the three different catalysts is illustrated in Fig. 1. According to Fig. 1, it can be observed that the catalytic effect: $H_2SO_4 > NKC-9 > 1$ -heptyl-3 methyl imidazole acetate. When acidic catalyst catalyzed, the reaction mechanism of transesterification is that proton firstly combines with the carbonyl of methyl acetate to form the intermediate of carbocation. Then protophilic 2-ethylhexanol combines with carbocation to form the intermediate. Finally this intermediate is resolved to 2-ethylhexyl acetate and methanol. As H_2SO_4 is stronger acidity than NKC-9, it showed better catalytic result than NKC-9. But the concentrated sulfuric acid may cause

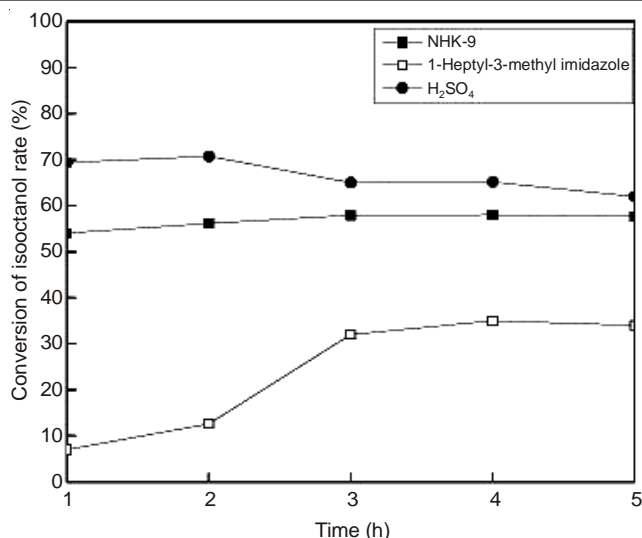


Fig. 1. Conversion of 2-ethylhexanol of the three different catalysts (reaction temperature = 80 °C, methyl acetate/2-ethylhexanol = 3:1)

equipment corrosion and difficult to separate from the reaction mixtures. Supported on the results above, the concentrated sulfuric acid is not suitable for industrial production and the catalytic activity of 1-heptyl-3 methyl imidazole acetate is lower than others, thus, the strong-acid cationic exchange resin NKC-9 proved to be the optimal catalyst in the transesterification reaction of methyl acetate with 2-ethylhexanol.

Transesterification is a reversible reaction. The reactive rate of reserve reaction changes with time. Fig. 1 also showed that when the reaction time was 3 h, NKC-9 obtained the highest conversion about 57 %. It was determined that 3 h was chosen as the suitable reactive time.

Therefore, the catalyst used in the following experiments in this paper was the strong-acid cationic exchange resin NKC-9 and the reaction time was 3 h.

Optimization of reaction conditions

Effect of the reaction temperature: Temperature has a significant effect on transesterification. To investigate the effect of the reaction temperature, operations were carried out at 60, 70, 80, 90 and 100 °C. The initial molar ratio of methyl acetate and 2-ethylhexanol was 3:1, reactive time was 3 h and the catalyst loading was 20 wt. % (by mass of methyl acetate). As shown in Fig. 2, at the beginning, with the increasing of temperature, the conversion of 2-ethylhexanol increased, because the increase of temperature led to more successful collisions. These successful collisions had sufficient energy (activation energy) to break the bonds and form products and thus resulted in higher conversion of 2-ethylhexanol. However, when the temperature reached 80 °C, the conversion of 2-ethylhexanol was the highest point and then decreased with the increase of temperature. Therefore, 80 °C was chosen as the most fixed reaction temperature.

Effect of catalyst loading: The catalyst loading was expressed as the weight ratio of the catalyst to the weight of methyl acetate. The effect of catalyst loading on the conversion of 2-ethylhexanol was tested varied from 0 to 20 wt % (by mass of methyl acetate) at reaction temperature of 80 °C, reactive time of 3 h and methyl acetate to 2-ethylhexanol molar

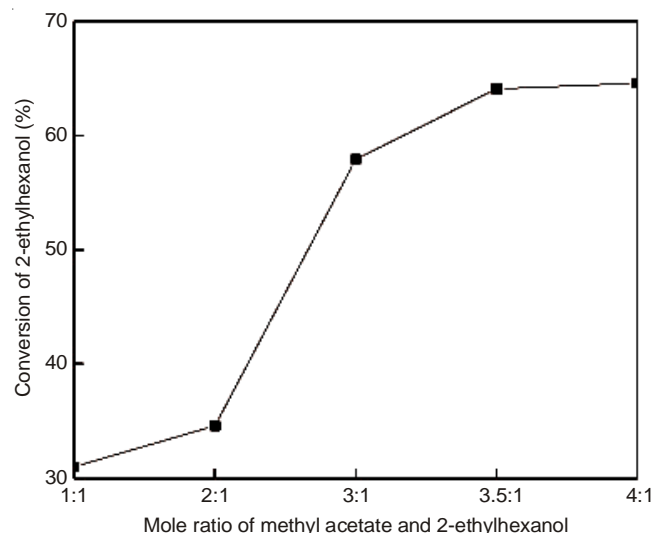


Fig. 2. Effect of the initial molar ratio of methyl acetate to 2-ethylhexanol on the conversion of 2-ethylhexanol (reaction time = 3 h, NKC-9 catalyst loading = 20 wt. %, 80 °C)

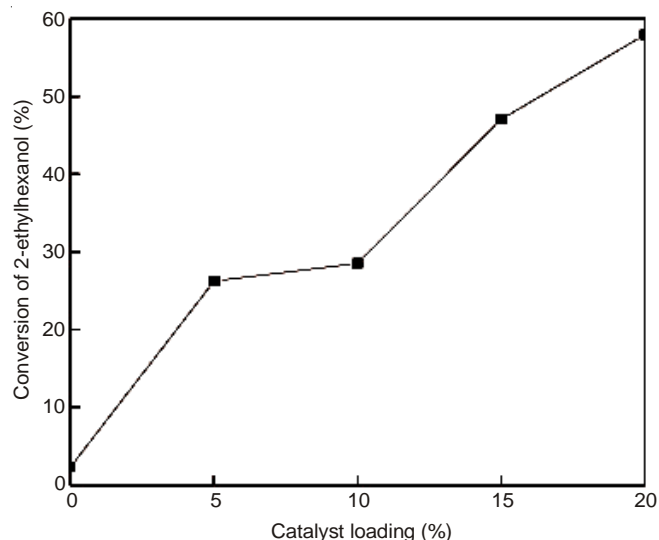


Fig. 4. Effect of catalyst loading on conversion of 2-ethylhexanol (reaction time = 3 h, methyl acetate/2-ethylhexanol = 3:1, NKC-9 catalyst loading = 20 wt. %, 80 °C)

ratio of 3:1. The effect of catalyst loading on the conversion rate of 2-ethylhexanol is given in Fig. 3. It can be observed that the conversion of 2-ethylhexanol increased with the increase of catalyst loading. It was due to the fact that the increase of catalyst loading corresponded to more available active sites for the transesterification reaction, resulting in higher conversion.

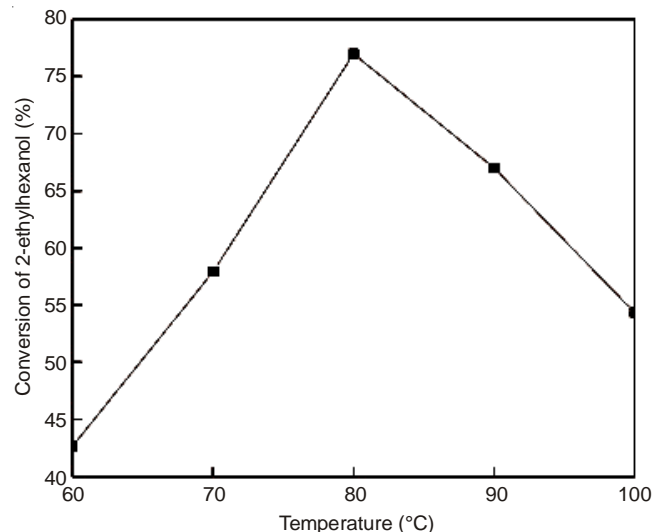


Fig. 3. Effect of reaction temperature on the conversion of 2-ethylhexanol (reaction time = 3 h, methyl acetate/2-ethylhexanol = 3:1, NKC-9 catalyst loading = 20 wt.%)

Effect of molar ratio of 2-ethylhexanol to methyl acetate:

According to the principle of chemical equilibrium, it is useful for the forward reaction to increase the amount of reactant. Therefore, the effect of different initial reactant molar ratio of methyl acetate to 2-ethylhexanol from 1:1 to 4:1 was determined at 80 °C, reactive time 3 h and loading catalyst of 20 wt. % (by mass of methyl acetate). Fig. 4 showed that the conversion of 2-ethylhexanol increased with increasing molar

ratio of methyl acetate to 2-ethylhexanol. Transesterification of methyl acetate with 2-ethylhexanol is an equilibrium controls the amount of product formed, therefore, the use of an excess of methyl acetate increased the conversion of 2-ethylhexanol.

Product spectroscopic characterization: The chemical structure of the product 2-ethylhexyl acetate was characterized by the combined methods of IR, ^1H NMR. The results of the IR, ^1H NMR spectra were consistent well with the proposed structure.

IR spectrum of 2-ethylhexyl acetate: IR spectrum data: $\nu(\text{C}=\text{O})$: 1744.69 cm^{-1} , $\nu(\text{C}-\text{O})$: 1037.07 cm^{-1} , $\nu(\text{C}-\text{H})$: 2861.33 cm^{-1} , 2930.76 cm^{-1} , 2960.39 cm^{-1} , $\delta(\text{C}-\text{H})$: 1365.53 cm^{-1} , 1383.61 cm^{-1} , 1463.63 cm^{-1} , $\nu(\text{C}-\text{C})$: 1235.07 cm^{-1} , $\gamma(\text{C}-\text{H})$: 606.04 cm^{-1} , 728.35 cm^{-1} , 771.74 cm^{-1} .

^1H NMR of 2-ethylhexyl acetate: ^1H NMR data: δ_{H} : 3.96 (d, 2H, OCH_2), 2.04 (s, 1H, CH), 2.03 (t, 3H, $\text{CH}_3\text{C}=\text{O}$), 1.25 (m, 8H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 0.87 (q, 6H, CH_3).

Orthogonal experiment: The orthogonal experiment design may provide a useful guidance to determine design parameters and improve conversion of 2-ethylhexanol and find the optimal combination for the demand of wholesale industrialization. The orthogonal experiment Table L9(3)⁴ was selected, which contained four factors three levels and nine experiments. Four factors are the reaction time, reactive temperature, catalyst loading and the initial molar ratio of methyl acetate to 2-ethylhexanol. These are considered as principal process parameters. It was found that the order of significant factors for the the conversion of 2-ethylhexanol is reaction time > catalyst loading > the initial molar ratio of methyl acetate and 2-ethylhexanol > reactive temperature. Based on the results of the range analysis, the maximum conversion of 2-ethylhexanol was found at a NKC-9 catalyst loading of 20 wt. %, a molar ratio of methyl acetate to 2-ethylhexanol of 4:1, a reactive time of 3 h and a reaction temperature of 80 °C. The product yield and the conversion of 2-ethylhexanol under optimal conditions reached 90.90 and 79.64 %, respectively.

Conclusion

The transesterification of methyl acetate and 2-ethylhexanol, which is a new highly potential and sustainable method to treat with the methyl acetate, leading to 2-ethylhexyl acetate and methanol catalyzed by NKC-9 has been studied experimentally. Strongly acidic cation-exchange resin NKC-9 was chosen as the most suitable catalyst in this reaction. The reaction time, the effects of the reaction temperature, the catalyst loading and the initial molar ratio of methyl acetate to 2-ethylhexanol on the conversion of 2-ethylhexanol were discussed. The orthogonal experiment design is adopted to investigate the optimal combination. Based on the results of the range analysis, the maximum conversion rate of 2-ethylhexanol was found at a NKC-9 catalyst loading of 20 wt. %, a initial molar ratio of methyl acetate to 2-ethylhexanol of 4:1, a reactive time of 3 h and a reaction temperature of 80 °C. The product yield and the conversion of 2-ethylhexanol under optimal conditions reached 90.90 and 79.64 %, respectively. This method possesses that procedure is simple, less demand for equipment, low cost

of production and propitious to the demand of wholesale industrialization.

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