



A new separation method for phenolic compounds from low-temperature coal tar with urea by complex formation



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ABSTRACT

A new reaction agent (urea) was used to efficiently separate the phenol and cresols from low-temperature coal tar (model oil) through complexing. The effects of contact time, reaction temperature, and initial concentration were investigated. The phenols content of the upper layer was analyzed by using gas chromatography. The separation mechanism was determined by analyzing the chemical bond of the complex for urea and m-cresol using Fourier transform infrared spectrometer. Finally, urea can be recovered through reaction with diethyl ether, and the phenols removal efficiencies can remain constant after three cycles.

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Introduction

Phenol and its related o-, m-, and p-cresol isomers, usually called hydroxyl toluenes or methylphenols, are members of the class of aromatic organic compounds, and are used as raw materials on the ever-expanding synthesis of industrial organic chemicals [1,2]. For example, epoxy resins, precursors of dye intermediates, pharmaceuticals, and adducts are synthesized using o-cresol; disinfectants, preservatives, and explosives are formed by m-cresol; and p-cresol is used to produce light-resistant antioxidants and dyes [2,3]. The major sources of phenolic compounds include coal liquefaction oil, coal tar and petroleum, and biomass by pyrolysis [4,5]. Low-temperature coal tar distillates typically account for 20–30% of phenolic compounds; thus, separating them from neutral oils is valuable [6].

The traditional method for separating phenolic compounds from coal tar oils uses the principle of acid-base neutralization. The disadvantages of this method include the use of large amounts of both strong alkalis and acids and the production of excessive

amounts of waste water containing phenols. Amen-Chen et al. [4] further separated phenolic compounds from the oil by liquid-liquid extraction using alkali and organic solvents. The disadvantage of removing of phenols was more efficient under highly alkaline conditions. Venter et al. [7] separated m-cresol from neutral oils by liquid-liquid extraction. In this research, the liquid-liquid equilibrium for the systems m-cresol and neutral oil systems has been determined at 313.15 K. Although tetraethylene glycol as a high-boiling solvent is suitable for the proposed separation of m-cresol from neutral oils, the process of recovery has never been mentioned. Reaction also can be used for the separation. For example, Kun et al. [8] found that choline chloride with phenols can form deep eutectic solvents to separate phenols from oils at room temperature. Guo et al. [9] studied a variety of quaternary ammonium to separate phenols from model oils, and discussed the different effects of the phenol removal efficiency on their cation and anion. Crystallization is also an important method for separating mixtures, especially when a pure product is desired [10]. Two crystallization processes, namely, dissociation extractive and adductive, have been reported in literature [11]. However, separating phenolic compounds from neutral oils by crystallization has been rarely reported.

Urea has particular features for separation; however, the efficient and economical use of urea for separating phenolic compounds from neutral oils is less reported. Therefore, this article

Abbreviations: FT-IR, Fourier transform infrared spectrometer; GC, Gas chromatograph.

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Notations

List of symbols

C_o	original oil concentration (g L^{-1})
V_o	original oil volume (mL)
C_f	oil concentration after reaction (g L^{-1})
V_f	oil volume after reaction (mL)

Subscripts

o	original data
f	data after reaction

discusses the separation of phenol and its related isomers by efficient and economical urea adduction.

Experiment

Reagents

Phenol with a purity >99.9% in mass fraction, and o- and p-cresol isomers with a purity >99.5% respectively and m-cresol isomer with a purity >99.0% in mass fraction, were purchased from Sinopharm Chemical Reagent Company, Ltd. Hexane with a purity >99.5% in mass fraction, was also provided by Sinopharm Chemical Reagent Company, Ltd. Urea was purchased from Xilong Chemical Co., Ltd. All other chemicals used in the experiments were A.R. grade. The water was distilled before use.

Reaction

Hexane, phenol and its related o-, p-, and m-cresol isomers were used to prepare the model oil. The mixing ratio of phenol and its related o-, p-, and m-cresol isomers, phenols in the model oil was set at 2:1:1:1 in the bulk density. Therefore, 80.40 g of phenol, 40.56 g of o-cresol, 40.38 g of p-cresol, and 40.03 g of m-cresol were dissolved in 500 mL of hexane at 303.15 K in a beaker with continuous shaking. After the complete dissolution of the phenolic compounds, the solution was transferred to a 1000 mL volumetric flask, and then added with another 500 mL of hexane. Three different initial phenol contents were prepared with the same method. In this paper, the solution prepared only by one kind of phenol or cresol in oils is described with monophenol. Monophenol was also prepared to check the reaction of mechanism.

The reaction experiments were performed as follows: a known amount of urea was dissolved in the model oil in an Erlenmeyer flask. For each operation, the model oil was stirred using a magnetic stirrer at a certain speed for at least 60 min, then white complex appeared at the bottom of flask. After reaction they were allowed to settle at constant temperature for at least 60 min in a bath fitted with a temperature controller within ± 0.1 K. And they turned into liquid phase and solid phase; the two phases were separated using vacuum filtration. The phenols removal efficiencies could be investigated through the phenols content of the upper layer using gas chromatography. The solid was dried before decomposition. Diethyl ether was added in the solid complex to decompose the complex and recycle urea. After stirring a certain time, the upper liquid layer appeared after settling which was constituted mainly by phenols and diethyl ether. The lower solid layer was mainly urea. The recycled urea could be reused several times.

After the operation was attained, the oleic phase was carefully separated using a Bush funnel or separating funnel.

Analysis methods

The analysis of the oleic phase containing hexane, phenol, and the related o-, p-, and m-cresol isomers were performed using a gas chromatograph (GC) with flame ionization detection. The analytes were identified using a $50 \text{ m} \times 0.20 \text{ mm } \varphi$ capillary column, Shinwa ULBON WCOT with a constant temperature program. The oven temperature was controlled at 130 °C. The injector and detector temperature were both controlled at 250 °C. Samples were injected directly into the GC inlet to minimize the loss of the oil components. The complex was measured by infrared spectrometer (Nicolet 380, Thermo Fisher Scientific, USA). The spectra were recorded at room temperature. Infrared spectrometer was used to ensure the structural formula of the complex.

Results and discussion

The concentration of phenol and cresols in the oleic phase was analyzed using a gas chromatograph. The removal efficiency of the phenol and the related o-, p-, and m-cresol isomers in the oleic phase was calculated by using the difference between the concentration before and after the reaction.

The removal efficiency for each phenol and cresols could be calculated using Eq. (1):

$$\text{Phenol removal efficiency} = \left\{ \frac{C_o V_o - C_f V_f}{C_o V_o} \right\} \times 100\% \quad (1)$$

where C_o and C_f represent the concentration before and after reaction for phenol or cresols (g L^{-1}). V_o and V_f represent each volume of solution before and after reaction for phenol or cresols (mL).

Effect of various parameters on the reaction

Effect of reaction time and temperature

The effect of reaction time has been thoroughly investigated. All reactions were carried out using phenols oil (20 mL, initial phenol content in hexane, 201.37 g L^{-1}) and urea of 4.00 g at the reaction temperature of 273.15 K and pressure of 1 atm. The effect of reaction time on the phenol removal efficiency from hexane was investigated at five different times: 15, 30, 60, 90, and 150 min, respectively. The result is shown in Fig. 1, the phenols concentration decreased sharply from 15 to 30 min, and then became stable as the reaction time continually increasing. The reaction time was fixed at 90 min to make the reaction sufficient and the concentrations of the oleic phase for phenol, o-, p-, and m-cresol were 9.74, 6.65, 4.84, and 4.86 g L^{-1} , respectively. Temperature is a critical factor in affecting the traditional reaction and other type of liquid–solid system. Thus, controlling the temperature is recommended in all partitioning experiments. The significant parameter of temperature on the phenols concentration of the oleic phase was investigated in the range of 273.15–323.15 K with the fixed reaction time of 90 min and the pressure of 1 atm, the effect is illustrated in Fig. 2. As can be seen, the results showed that the phenols contents decreased with increasing of temperature from 273.15 to 303.15 K and increased with increasing of temperature from 303.15 to 323.15 K. The lowest phenols contents were obtained at the reaction temperature of 303.15 K, near room temperature for the reaction. The phenol and the related o-, p-, and m-cresol isomer concentrations in the oleic phase after the reaction were up to 10.83, 7.54, 5.32, and 5.38 g L^{-1} , respectively. Thus, reaction temperature of 303.15 K was used in the following experiments.

The effects of reaction temperature and time on the reaction process of phenolic compound with urea formed complex suggest

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