

[Research Note]

Extraction of Phenol in Water Phase Using Liquefied Dimethyl Ether

Shinya SATO* and Akimitsu MATSUMURA

Advanced Fuel Research Gr., Institute for Energy Utilization, National Institute of Advanced Industrial Science and Technology, AIST Tsukuba West, 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, JAPAN

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The applicability of liquefied dimethyl ether (DME) was evaluated as an extractant for phenol, a polar substance, in water. The phenol extraction ratio was 79% from 5.45 wt% phenol solution, and 67% from 0.11 wt% phenol solution using a liquefied DME/water volume ratio of 1.5 : 1. Phenol could be isolated from the DME phase by extraction with a water phase containing an initial phenol concentration of 1.09 wt% or more. Based on these results, a concept of the extraction process was constructed with a pressure swing method for recycling the DME extractant.

Keywords

Phenol, Extraction, Dimethyl ether, Aqueous solution

1. Introduction

Some liquid fuels contain high amounts of polar compounds. Isolation of such polar compounds for use as raw materials for the petroleum industry would lead to more effective use of resources. For example, coal tar and coal-derived liquids usually include large amounts of phenols. These phenols have been isolated commercially by base extraction. Such polar compounds are usually extracted using a water-based solvent, alkaline solution or methanol-water mixture, etc., but must be separated from the water phase after the extraction. An easier method of extraction from water would increase the efficiency of production of chemical materials using these substances.

Through the Bituminous Coal Liquefaction Project¹⁾ managed by the New Energy and Industrial Technology Development Organization (NEDO), the authors have developed a process to recover phenols from the coal-derived naphtha fraction by a methanol-mediated extraction method^{2)~4)}. Our prior study⁵⁾ extracted phenols from water with toluene followed by removal of the toluene by distillation. Distillation usually requires a relatively large amount of energy, so is preferably replaced by other processes requiring less energy such as a pressure swing process, which can extract phenols at lower cost.

This study investigated the extraction of phenol from water using two liquefied gases, butane and dimethyl ether (DME), which are suitable for a pressure swing

extraction system.

Although DME is attracting more attention as an alternative to diesel fuel than as an extractant, several studies and patents have concerned the use of DME for the dehydration of solid materials or the extraction of natural products^{6)~8)}. However, few studies have investigated the recovery of organic substances from water. Our study is also considered beneficial to the development of uses for DME other than as a fuel.

2. Experimental**2.1. Materials and Extraction Apparatus**

The model solution was prepared by dissolving phenol (Waco Pure Chemical Industries, Ltd.) in pure water. Butane was obtained from Tokyo Chemical Industry, Ltd. DME was obtained from NKK (now JFE) involved in the DME direct synthesis technology development financially supported by the Ministry of Economy, Trade and Industry.

2.2. Extraction

The extraction apparatus was a 13 ml pressure glass tube cylinder (Hyperglass cylinder, Model 01, Taiatsu Techno Corp.) with 2 double pipe-type valves (**Fig. 1**). Liquefied butane or DME (2-6 ml) was added to model solution (4 ml) containing 0-5.45 wt% phenol through Valve A, followed by vigorous shaking for one min. Then the apparatus was turned upside down and set aside. After complete separation of the contents, the water phase was collected through Valve B. The weight of collected water was defined as the amount of the recovered water phase, and the remaining solvent in a cylinder was defined as the recovered liquefied gas

* To whom correspondence should be addressed.

* E-mail: s-sato@aist.go.jp

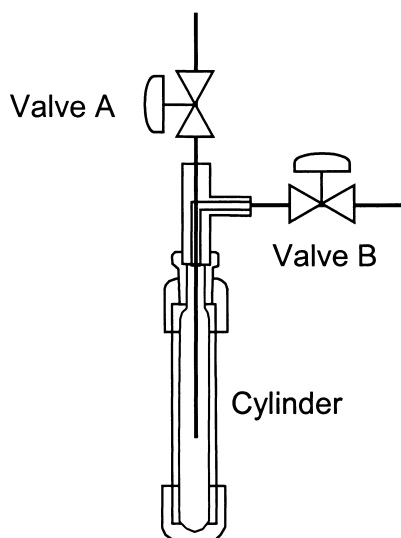


Fig. 1 Simplified Illustration of the Experimental Apparatus

(butane or DME) phase. The extract was recovered by vaporizing the liquefied gas under ambient temperature and pressure, followed by dissolving in ethanol.

2. 3. Analysis

All water was transferred to a volumetric flask and the volume adjusted to 20 ml by adding ethanol. Extracts in the liquefied gas phase were also diluted to 20 ml with ethanol. Phenol concentration was determined by a high-performance liquid chromatograph equipped with a Silica-ODS column (Nucleosil C-18, 2.0 mm ϕ \times 250 mm) and UV detector, using methanol solvent. The extraction ratio of phenol was defined as the percentage of phenol extracted from the water phase to that extracted from the liquefied gas phase based on the charged phenol.

3. Results and Discussion

3. 1. Extraction by Liquefied Butane

Butane has a boiling point of -0.5°C and remains in the gaseous state at room temperature and ambient pressure, but is liquid at about 0.6 MPa. Liquefied butane has a low density (approximately 0.6 g/ml at 20°C) and low solubility in water (3.25 ml/100 ml at 20°C). These properties indicate that a pressure swing extraction process can be operated at less than 1 MPa by using butane as a recycled extractant. This process requires no high-pressure equipment and probably lower energy than a distillation process.

At first, the performance of liquefied butane was tested for the extraction of phenol in water using 3.2 wt% phenol-water solution, based on the content of phenols (including cresols and dimethylphenols) in the water phase in the methanol-mediated extraction process in our previous paper⁵). Liquefied butane:

Table 1 Extraction of Phenol in Water by Liquefied Butane and Dimethyl Ether

		Butane		DME	
		0.5	1	1	1.5
Solvent/water ratio	[vol/vol]	0.5	1	1	1.5
	[wt/wt]	0.29	0.55	0.76	1.07
Total recovery	[wt%]	99	99	80	80
Recovery of phase					
	Butane/DME phase [wt%]	113	107	72	71
	Water phase [wt%]	95	95	86	91
Phenol content					
	Butane/DME phase [wt%]	1.80	0.85	4.52	3.33
	Water phase [wt%]	2.76	2.87	0.85	0.42
Extraction yield	[%]	18	16	77	79

Feed: 3.2 wt% phenol-water soln.

water weight ratios were 0.29 : 1 and 0.55 : 1 (volume ratios 0.5 : 1 and 1 : 1) (Table 1).

The recovery ratio was 99 wt% for the whole system, which is the percentage of recovered water phase + remaining butane phase in the cylinder based on the charge, and 95 wt% for the water phase. The difference may be caused by a small quantity of water dissolved in the liquefied butane phase. The extraction ratio of phenol was only 16 to 18%. These results indicate that liquefied butane is not suitable for phenol extraction.

3. 2. Extraction by Liquefied DME

Butane was not effective because butane is a non-polar compound in the paraffin series. A more polar extractant is required for more effective extraction but must also be liquefied at room temperature and less than 1 MPa and insoluble in water. DME has a boiling point about -25°C and condenses under 0.6 MPa at room temperature. Based on the phase equilibrium data⁹), the solubility of DME in water is estimated to be 35 wt% at 25°C and 0.55 MPa, and 4-10 wt% at normal pressure and room temperature. The solubility of water in liquefied DME is about 7 wt% at 25°C and 0.55 MPa. Although a considerable amount of DME is dissolved in water, liquefied DME and water form a binary phase system. Therefore, DME is suitable for a pressure swing process at less than 1 MPa. Liquefied DME should have a high affinity for phenol in contrast to liquefied butane, because DME is an ether type compound. In addition, DME is expected to be available as an alternative gas oil in large quantities and at a low price.

The extraction was carried out using liquefied DME by the same method as that using liquefied butane. DME (6 ml) was added to water phase (4 ml) and shaken. The volume of the water phase increased to 6 ml due to the solubility of DME in water. The recovery ratio of the water phase was 86-91 wt%, whereas that of DME phase was only 71-72 wt% (Table 1). These low recovery ratios were caused by the mutual dissolu-

Table 2 Extraction of Phenol in Water Phase Using Liquefied DME

Initial phenol content [wt%]	5.45	1.09	0.55	0.11
DME/water ratio [wt/wt]	1.04	1.04	1.02	1.04
Phase recovery				
DME phase [wt%]	69	60	55	57
Water phase [wt%]	90	94	96	96
Phenol in water phase [wt%]	1.20	0.33	0.16	0.04
Extraction yield [%]	79	71	72	67
K	6.9	5.1	5.7	4.9

K: Ratio of phenol concentration in DME/water system.

tion and release of dissolved DME in the water phase as a gas when the water phase was recovered. This was also the cause of low total recovery ratio of 80 wt%. The extraction ratio of phenol was as high as 77-79%, showing the effectiveness of liquefied DME for phenol recovery from water.

Next, the effect of phenol concentration was examined using 0.11 to 5.45 wt% of phenol solution with a DME: water volume ratio of 1.5 : 1. The extraction ratio of phenol was 79% when the initial concentration of the solution was 5.45 wt%, and decreased with lower initial concentration, but was 67% even if the concentration was as low as 0.11 wt% (Table 2). With an initial concentration of 1.09 wt% or higher, water and phenol extracted by liquefied DME formed two phases after the DME was evaporated. However, no phase separation was observed at concentrations lower than 1.09 wt%.

Using liquefied DME, the extraction of phenol was 67-79 wt% but that of water was only 7 wt%. The phenol concentration in water phase was reduced to 1.2-0.04 wt% after the extraction.

The phenol concentration in the extracted water increased to about 10 times as much as the original phenol solution. When the amount of extracted phenol exceeded the saturation solubility in the extracted water, two phases were formed. Therefore, phase separation was observed in the original solution with a phenol concentration of 1.09 wt% and more. Under such conditions, phenol could be instantly isolated from water. Even if the phase separation does not occur, phenol could be concentrated approximately 10 times, suggesting the isolation of phenol by re-applying the extraction.

The concentration ratio of phenol, the concentration of phenol in organic phase divided by that in water phase, tended to be larger at higher initial phenol concentration, at 6.9 with 5.45 wt% initial concentration, and 4.9 with 0.11 wt%. According to the equilibrium data of the phenol-water-toluene system¹⁰⁾, the concentration ratios are 1.72 and 2.25 for 1.17 wt% and 6.06 wt% of toluene phase concentration of phenol at the equilibrium state, respectively. Therefore, extraction

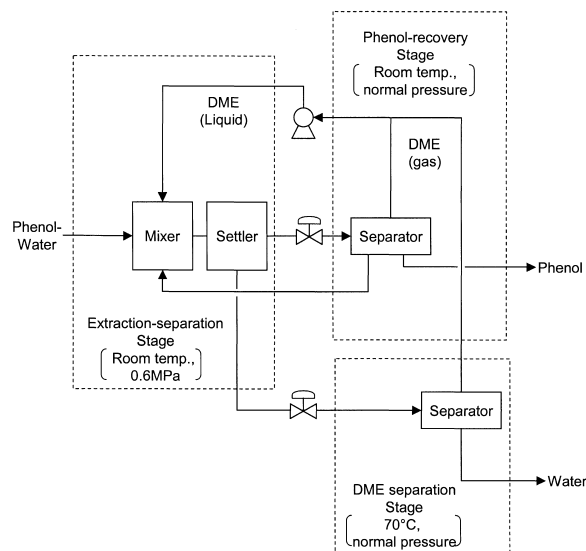


Fig. 2 Simplified Flow Diagram of the Phenol Extraction Process Based on Liquefied Dimethyl Ether

by DME should be more effective than with toluene as proposed in the previous study⁵⁾.

To determine the DME remaining in the water phase accurately, total organic carbon (TOC) concentration was measured with water containing DME but no phenol. After leaving the recovered water phase at ambient temperature or at 70°C for one hour, the TOC became 310 ppm and 200 ppm, respectively, whereas that of pure water containing no DME was only 4 ppm. From these results, the concentrations of DME in water phase were assumed to be 595 ppm and 384 ppm based on the carbon content of DME (52.1 wt%), indicating some removal of DME from water.

3. 3. Recovery Process of Phenol by DME

From the above results, a conceptual flow diagram of a phenol extraction process using DME was proposed (Fig. 2), consisting of three stages. The first extraction-separation stage is operated under 0.6 MPa and room temperature. The second phenol recovery stage removes DME by releasing the pressure, and phenol and water are recovered in two phases, phenol is isolated as an extract, and water containing saturated phenol is returned to the first stage. The third DME separation stage releases the DME dissolved in water by heating under normal pressure. Separated DME gas in each stage is collected and condensed again under pressure for recycling.

4. Conclusion

The applicability of liquefied DME was evaluated as an extractant for phenol, a polar substance, in water. The phenol extraction ratio was 79% using 5.45 wt% phenol solution, and 67% using 0.11 wt% phenol solu-

tion using a liquefied DME/water volume ratio of 1.5 : 1. Phenol could be isolated from the DME phase by extraction of a water phase containing phenol of 1.09 wt% or more. Based on the results, a concept of the extraction process was designed with a pressure swing method for recycling DME as the extractant.

DME is promising as an alternate fuel to gas oil, and is anticipated to be available at a price comparable to gas oil in the future. Therefore, DME will become an inexpensive, novel extractant. Extraction using liquefied DME is applicable to broad areas, including production of chemical materials from coal tar or coal-derived liquids, and the extraction of organic compounds other than phenol in water.

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要 旨

液化ジメチルエーテルによる水中のフェノールの抽出

佐藤 信也, 松村 明光

産業技術総合研究所 エネルギー利用研究部門新燃料開発研究グループ, 305-8569 茨城県つくば市小野川 16-1 つくば西

水中の極性有機物を効率的に回収し, 化学原料として供給する方法を開発するため, 液化ジメチルエーテル (DME) による水中のフェノールの抽出を検討した。

水相の 1.5 倍容量の液化 DME による水中のフェノール抽出では, フェノール濃度 5.45 wt% の水溶液の抽出率は 79%,

0.11 wt% の水溶液の抽出率は 67% であった。原料の初期濃度が 1.09 wt% 以上の場合は, DME 相を常圧にすることにより, 1 段でフェノールを単離することができた。これらの結果より, DME リサイクル系における圧力スイング法フェノール回収プロセスの概念を考案した。