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Separation of arenols from a low-temperature coal tar by liquid-liquid extraction

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Abstract–Low-temperature coal tar (LTCT) is a sticky liquid mixture produced mainly from coal pyrolysis, which contains various value-added chemicals (VACs). Liquid-liquid extraction is considered as one of the green and effective ways to explore the organic composition and separate the VACs from LTCT. Herein, petroleum ether, methanol, and carbon disulfide were used to extract arenols from a LTCT. As a result, the relative content and absolute content of arenols extracted from the LTCT are *ca.* 96.3% and 85.9%, respectively. Among them, *p*-cresol is predominant, accounting for 22.2%. The isolated contents of arenols are up to 84.6%. Moreover, a kilogram-scale operation was carried out under the same conditions, which offers a potential application in industrial production.

Keywords: Arenols, Low-temperature Coal Tar, Liquid-liquid Extraction, GC/MS, FTIR

INTRODUCTION

The utilization of low-temperature coal tar (LTCT), a sticky liquid mixture produced mainly from coal pyrolysis, has attracted more and more attention [1,2]. Catalytic hydrogenation of LTCT is a feasible technology to produce clean liquid fuel, but high temperature and high pressure lead to high cost [3-13]. Separating value-added chemicals from LTCT is more attractive. For this purpose, isolating specific group components (SGCs) from LTCT and understanding the molecular compositions of the SGCs are necessary.

Various methods, such as extraction [14-29], column chromatography [30], extraction-column chromatography [31], adsorption [32-35], and chemical derivatization [36], are utilized to explore and separate some SGCs from some raw materials. Among them, liquid-liquid extraction (LLE) is a feasible approach because of its large extraction capacity and easy accessibility.

LTCT usually contains 20-30% arenols, which are important chemicals and key building blacks of synthetic fibers, engineering plastics, and dye intermediates phenolic resins [21,37-43]. Separating arenols also facilitates subsequent catalytic hydrogenation of LTCT [44,45]. As a traditional method for separating arenols from LTCT, acid-base extraction not only consumes a large amount of alkali and acid, but also releases a large amount of wastewater. To reduce these shortcomings, many other technologies, such as extraction with urea [17], ethanolamine [29], and ionic liquids [16, 25,28], forming deep eutectic solvents with phenols [14,15,18-20, 22-24,26,27], extraction-column chromatography [31], and adsorption with functionalized metal-organic framework [32], have been invented to separate arenols from LTCT. Understanding the molecular composition of LTCT and separating arenols from LTCT are of great importance for practical applications of LTCT.

Herein, we report our development of LLE for LTCT separation with petroleum ether (PE), methanol, and carbon disulfide (CDS) as the extractants. We also investigated kilogram-scale separation of LTCT using the technology.

EXPERIMENTAL SECTION

1. Materials

PE (b.p. 60-90 °C), methanol, and CDS, are analytical reagents purchased from Sinopharm Chemical Reagent Co., Ltd. in Shanghai, China. The LTCT was collected from Shaanxi Coal Industry Chemical Co. Ltd. in Shaanxi, China. The contents of carbon, hydrogen, oxygen, nitrogen, and sulfur of the LTCT are 83.6%, 8.3%, 7.2%, 0.8%, and 0.1%, respectively.

2. Arenol Separation

Arenols were separated from the LTCT by LLE at room temperature (Fig. 1). Two PE/methanol mixed solvents (PE/MMSs) were used. For convenience of description, we denote 200 mL PE and 100 mL methanol as PE/MMS 1, and 50 mL PE and 100 mL CH_3OH as PE/MMS 2. In detail, 25 g LTCT and PE/MMS 1 were mixed in a separating funnel (SF) with continuous shaking. Then, the SF was allowed to be cooled until two phases were formed clearly. Upper phase 1 (UP_1) and lower phase (LP_1) are PE- and methanol-extractable portions, respectively. After discharging LP_1 from the SF bottom, PE/MMS 2 was added to UP_1 for back extraction (BE) to obtain upper phase 2 (UP_2) and lower phase 2 (LP_2). LP_2 was discharged from the SF bottom and then incorporated with LP_1 followed by adding 300 mL CDS to the incorporated portion (IP) in the SF, which was intensively shaken, *i.e.*, the IP was extracted with

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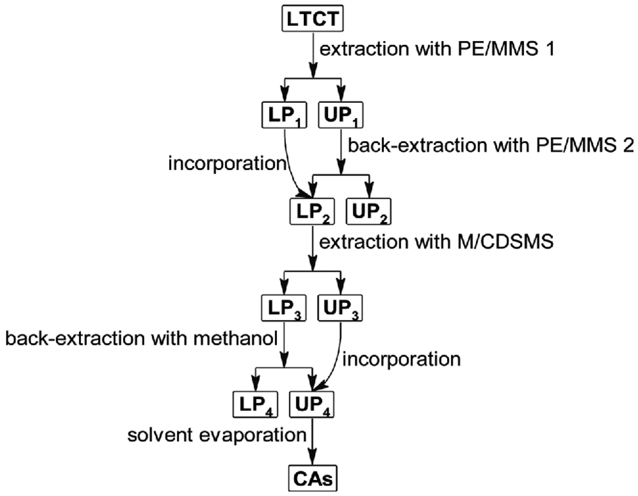

Fig. 1. Procedure for isolating CAs from the LTCT.

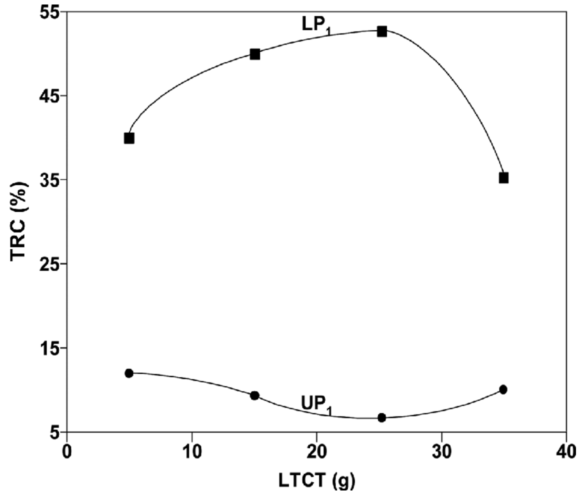

Fig. 2. TRC of arenols in UP_1 and LP_1 obtained by extracting different amounts of the LTCT with PE/MMS 1.

a methanol/CDS mixed solvent (*M*/CDSMS), and then allowed to be separated into upper phase 3 (UP_3, *i.e.*, methanol-extractable portion) and lower phase 3 (LP_3, *i.e.*, CDS-extractable portion). LP_3 was discharged from the SF bottom and then mixed with 150 mL methanol for BE to obtain upper phase 4 (UP_4) and lower phase 4 (LP_4). UP_3 and UP_4 were incorporated and then the solvents in the IP were evaporated with a rotary evaporator to obtain the crude arenols (CAs, 3.1 g). The LPs, UPs, and CAs were analyzed with a gas chromatograph/mass spectrometer (GC/MS); detailed information was introduced in Supplementary Material (Figs. S1-S4 and Tables S1-S31). All the solvents were recycled and reused.

The relative contents (RCs) of arenols in the LPs and UPs were determined by the analysis with the GC/MS. The total recovery (TR) of arenols was confirmed by analyzing the LTCT and CAs with the GC/MS, *i.e.*, $TR=m_{CAs}\ AC_{CAs}/(m_{LTCT}\ AC_{LTCT})$, where m_{LTCT} and m_{CAs} represent the masses of LTCT and CAs, and AC_{LTCT} and AC_{CAs} denote the absolute content (AC) of arenols in the LTCT and CAs, respectively, which were tested by external standard method.

RESULTS AND DISCUSSION

1. Molecular Composition of LTCT, LP_2, and UP_4

The LTCT was analyzed with the GC/MS after being dissolved in PE, since most of the GC/MS-detectable compounds in LTCT can be extracted with PE [41]. As shown in Figs. S1 and S4 along with Tables S1-S31, the LTCT mainly consists of chain alkanes, alk-1-enes, arenols, and arenes. The total RC (TRC) of arenols, one of the most abundant group components with relatively high content, is *ca.* 17.3% in the LTCT. Among the arenols, *p*-cresol (peak **8**) is the most abundant, accounting for 4.5% in the LTCT. The total AC of arenols in the LTCT is *ca.* 12.6%.

As exhibited in Fig. 2, the TRC of arenols in LP_1 increases up to *ca.* 51.2% with increasing the LTCT up to 25 g but then significantly decreases with further increasing the LTCT, while a reverse variation can be observed for the TRC of arenols in LP_1 with increasing the LTCT, *i.e.*, when using PE/MMS 1 as the solvents, the optimum amount of the LTCT is 25 g. Arenols tend be transferred into LP_1 from the LTCT due to the formation of $O\text{-}H\cdots O/O\text{-}H\cdots\pi$ bond between the arenols and methanol [46,47], while hydrocarbons (HCs), including alkanes, alkenes, and arenes, tend to be transferred into UP_1 due to the weak polarity of PE. After BE, the TRC of arenols in LP_2 is *ca.* 61.9%. The total ion chromatogram and compound distribution of LP_2 are listed in Supplementary Material (Figs. S2 and S4 along with Tables S1-S31). As Fig. S2 shows, many arenols with lower RCs, such as 3-ethylphenol (peak **21**), 2-ethyl-4-cresol (peak **29**), 4-ethyl-2-cresol (peak **31**), isopseudocumenol (peak **35**), *p*-cumenol (peak **41**), 5-indanol (peak **53**), and 2-methylnaphth-1-ol (peak **96**), detected in LP_2 were not detected in the LTCT. The main reason is that such arenols tend to form less volatile molecular clusters by the complex intermolecular interactions so that they cannot be detected with GC/MS. Therefore, the LLE effectively destroyed the clusters, facilitating the arenol detection. At the same time, there are still a large number of long-chain alkanes and alkyl-substituted condensed arenes in LP_2. For the continuity and simplicity of process, LP_2 was used for subsequent extraction.

As shown in Fig. S3, arenols are predominant in CAs, indicating that the arenols were effectively separated by extracting LP_2 with *M*/CDSMS followed by BE of LP_3 with methanol. Because of their weak polarity, the residual HCs in LP_2 tend to be transferred to LP_3 by extraction with CDS, and the residual arenols in LP_3 tend to be transferred to UP_4 by BE with methanol due to the hydrogen bonds between the arenols and methanol.

The TRC of arenols in UP_4 is higher than 96.0%, which is much higher than that in LP_2. The TRC of *p*-cresol, 2,4-xylenol, or 2,3-xylenol in UP_4 is not lower than 10.0%. As listed in Tables S1-S31, much more arenols (peaks **22**, **27**, **37**, **43**-**47**, **49**-**51**, **55**-**58**, **60**, **65**, **66**, **68**, **70**, **72**, **84**, **86**, **99**, **101**, **109**, and **110**) in UP_4 than in the LTCT were detected, suggesting that the LLE is effective for understanding the detailed composition of arenols in LTCT. The TRC of arenols in UP_4 is much higher than that in the LTCT and LP_2, implying that arenols are effectively enriched from the LTCT.

2. FTIR Analysis of LTCT, LP_2, and UP_4

As shown in Fig. 3, the absorbance of -OH stretching vibration around 3,388 cm^{-1} in UP_4 is much stronger than that in the LTCT

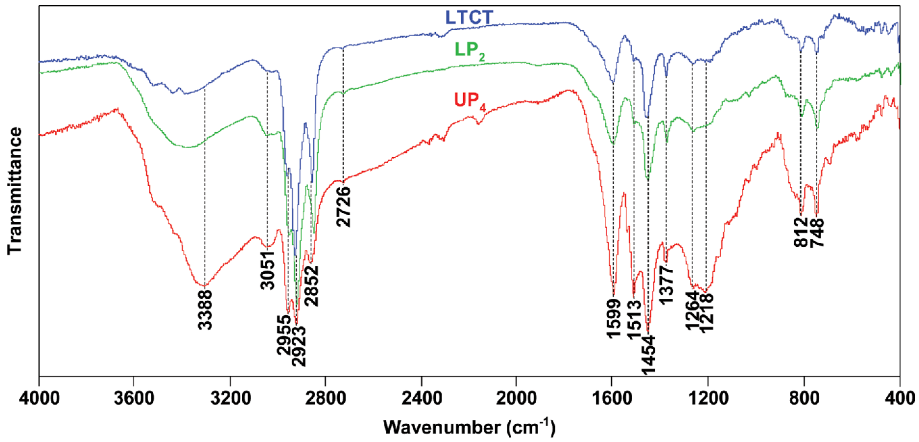

Fig. 3. FTIR spectra of the LTCT, LP_2 and UP_4.

Table 1. ACs (%) of group components in CAs

Arenol	Neutral oil	Pyridine	Ignition residue	Moisture
84.0 (83)[a]	3.2 (0.8)[a]	0.3 (0.5)[a]	0.3 (0.4)[a]	0.3 (10)[a]

[a] The national standard.

and LP_2, further proving that arenols are significantly enriched into UP_4. The absorbances resulting from aromatic rings (ARs) around 3,051, 1,599, 1,513, and 1,454 cm^{-1} in UP_4 are also obviously stronger than those in the LTCT and LP_2, because all the arenols contain AR(s). In contrast, the absorbances of aliphatic moieties around 2,955, 2,923, and 2,852 cm^{-1} in UP_4 are significantly weaker than those in the LTCT and LP_2 due to the abundant existence of alkanes and alkenes.

3. Kilogram-scale Operation

To explore the potential application of the LLE for arenol enrichment from the LTCT, a scale-up experiment was done. As a result, 120.5 g CAs were obtained and their TR is 80.4%. As listed in Table 1, all the indexes, except the AC of pyridine, meet the national standard.

CONCLUSION

CAs were effectively separated from the LTCT with commonly used solvents. Much more arenols, which were not detected in the LTCT, obtained by the LLE were detected with GC/MS. The LLE is an effective approach for understanding the detailed molecular composition of LTCT. The scale-up experiment proved the potential industrial application of the LLE for isolating CAs from LTCT. Compared with the traditional acid-base process, the LLE has advantages of lower energy consumption, higher solvent recovery, and convenient operation.

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NOMENCLATURE

AC : absolute content
AC_{CAs} : the absolute content of arenols in the crude arenols
AC_{LTMT} : the absolute content of arenols in the low-temperature coal tar
ARs : aromatic rings
BE : back extraction
CAs : crude arenols
CDS : carbon disulfide
FTIR : Fourier transform infrared spectrometer
GC/MS : gas chromatograph/mass spectrometer
HCs : hydrocarbons
IP : incorporated portion
LLE : liquid-liquid extraction
LP : lower phase
LTCT : low-temperature coal tar
m_{CAs} : the mass of crude arenols
M/CDSMS : methanol/carbon disulfide mixed solvent
m_{LTCT} : the mass of low-temperature coal tar
PE : petroleum ether
PE/MMS : petroleum ether/methanol mixed solvent
RC : relative content
SGC : specific group components
SF : separating funnel
TR : total recovery
TRC : total relative content
UP : upper phase
VACs : value-added chemicals

SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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