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Research article

Separation of coal liquid distillate by dimethyl sulfoxide

Wen-Jun Fan, Jie Feng *, Mei-Xiang Wu, William Turmel, Wen-Ying Li *

Key Laboratory of Coal Science and Technology for Shanxi Province and Ministry of Education, Taiyuan University of Technology, Taiyuan 030024, PR China
Training Base of State Key Laboratory of Coal Science and Technology Jointly Constructed by Shanxi Province and Ministry of Science and Technology, Taiyuan 030024, PR China

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ABSTRACT

Efficient separation of different chemical components in liquid hydrocarbons from direct coal liquefaction is a meaningful process. This paper aims to separate the 150–180 °C coal liquid distillate into three fractions: aromatics, alkanes, and phenolics. The coal liquid distillate is composed mostly of hundreds of single-ring compounds and is not easy to study directly. Therefore, a model of the distillate on a molar ratio was defined as 1 t-butylbenzene (TBB): 1 t-butylcyclohexane (TBC): 1 phenol. And dimethyl sulfoxide (DMSO) was selected as the solvent to separate them from each other. The model compounds' vapor–liquid equilibrium shows that DMSO's effectiveness is obvious. In TBB-TBC-phenol ternary system, DMSO can entrain TBB into the light fraction and keep phenol in the heavy fraction, while TBC is in the middle fraction, which isn't affected. DMSOs' influence was studied and divided as follow: the hydrogen bond terminator between TBB and phenol, an entrainer for TBB, and an extractant for phenol. Finally the 150–180 °C coal liquid distillate is separated via batch distillation into three fractions: 150–160 °C fraction (containing 79.17 *wt.%* aromatics and 20.25 *wt.%* alkanes), 160–185 °C fraction (containing 81.30 *wt.%* alkanes and 17.69 *wt.%* aromatics) and a bottom product (containing 27.95 *wt.%* phenolics and 72.05 *wt.%* DMSO).

1. Introduction

The direct coal liquefaction process (DCL) has been studied for more than 100 years. The coal liquid, which was originally designed to replace liquid fuels and petrochemicals, contains lots of aromatics, cycloalkanes, and phenolics, and can actually be used to produce other fuels and chemicals. Coal-derived naphtha (150–180 °C distillate fraction) is one of the main products, mainly consisting of aromatics, cycloalkanes, and phenolic compounds. Among them, the phenolics were always retained in the coal liquid distillates as a deterioration agent, which hindered the hydrogenation refining process and reduced the fuel characters [1]. Meanwhile, the aromatics are also limited to use in fuels [2]. Thus a separation process is required for extracting from the raw products to get the phenolic chemicals, jet fuel [3] and aromatic products respectively [4].

However it is difficult to separate these compounds by distillation due to the existence of various azeotropes, e.g. phenolics and aromatics. Present separation methods rely on a two-step extraction process, including phenolic compounds removal and aromatics extraction. Briefly, phenolics are removed first by aqueous alkaline solutions (e.g. aqueous NaOH) and then collected by acidifying the extract with mineral acids (e.g. aqueous H_2SO_4). The coal liquid without phenolics (dephenolized oil) is processed to produce fuels and aromatics by extractant. Drawbacks of these methods are obvious, such as water pollution, oil/phenolics loss, base/acid waste generation, and huge solvent consumption [5]. Therefore, novel separation methods of coal liquid are expected.

Batch distillation is an important unit operation to deal with uncertainties in feed stock or product specification flexibly. A simple procedure, batch distillation requires the least amount of capital for separating relatively pure components and handles several mixtures just by switching the column's operating conditions [6]. Currently extractive distillation is an efficient industrial process to separate compounds from a close boiling point mixture or an azeotrope, e. g. aromatics/non-aromatics, diolefins/olefins, olefins/paraffins, and cycloalkanes/paraffins [7,8]. Extractive batch distillation may be an ideal separation for such complicated and uncertain distillates of coal liquid; however, the operating modes for such processes are more complicated, the number of column configurations tends to be very high, and the batch rectifier configuration may be very restrictive and expensive [9–12]. The employed solvent plays the most important role in this process, for its discrepant affinities with different components enhances the relative volatility fundamentally [13,14]. As various azeotropes in the coal liquid distillates hindered the distillation, solvent is added expectedly to eliminate the intermolecular forces, for example, the force from hydrogen bond (HB). In this case, the traditional criteria of solvent screening [8, 15] is no longer applicable in such a complicated mixture that contains tens of compounds with an over 30 °C range of boiling point without a typical compound of abundant content. In addition, the solvent mechanism is not clear, which is another problem to hinder the solvent screening.

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* Corresponding authors.
E-mail addresses: fengjie@tyut.edu.cn (J. Feng), ying@tyut.edu.cn (W.-Y. Li).

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Therefore, it is impossible to separate 150–180 °C aromatics, alkanes, and phenolics from the 150–180 °C coal liquid distillate by conventional distillation. An effective solvent is expected to vary their relative volatilities (RV) from each other by discrepant intermolecular forces. In this paper, the solvent's screening, function mechanism and behavior are investigated.

2. Experimental

2.1. Chemicals

Dimethyl sulfoxide (DMSO, ≥99.5 *wt.%*), phenol (≥99.5 *wt.%*), t-butyl benzene (TBB, ≥99.5 *wt.%*), and t-butyl cyclohexane (TBC, ≥99.5 *wt.%*) were obtained from Aladdin Industrial Corporation. The coal liquid was originally made from China Shenhua Coal to Liquid and Chemical Co., LTD. The 150–180 °C coal liquid distillate (CLD) was processed and supplied by China Coal Research Institute.

2.2. Measurement procedures and phase equilibrium

The liquid–liquid equilibrium (LLE) experiments were performed by mixing 2 mL of the TBB-TBC mixture with 1 mL of DMSO in 10-mL jacketed glass vessels. The vessels were placed into a shaking machine. The time of equilibration was typically 5 min, after which the two phases were allowed to settle for 30 min, and then the extract and raffinate phase were taken by a 1 mL syringe. These samples are analyzed by the GCand the LLE of TBB-TBC-phenol is drawn.

Vapor–liquid equilibrium (VLE) experiments have been done in this paper. Fig. 1 shows the designed equipment of VLE measurement. The mixture of feed and solvent was heated in a reboiler A, the overheated vapor was directed into a vapor–liquid separation chamber C, then the vapor phase was condensed by a cooling jacket F and once again went back into the reboiler via a vapor phase collection vessel D, while the liquid phase was directly sent back to the reboiler A through the liquid phase collection vessel B. Equilibrium time usually lasts for 1 h to ensure the constituent was stable, then vapor and liquid samples were taken from each vessel. Operation temperature was measured simultaneously by a thermocouple in the thermometer jacket E.

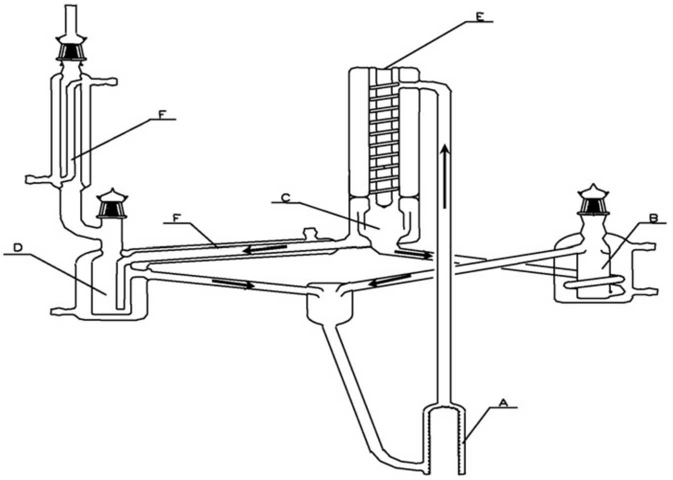

Fig. 1. Vapor–liquid equilibrium equipment. (A. reboiler, B. liquid phase sample room, C. vapor and liquid phase separation room, D. vapor phase, E. thermometer jacket, F. cooling jacket).

For each run, the solvent ratio (SR) is calculated by mole fraction for model compounds, and by mass fraction for coal liquid:

$$\mathrm{SR}_{\mathrm{BP}}=\frac{c_{\mathrm{DMSO}}}{c_{\mathrm{TBB}}+c_{\mathrm{phenol}}};\quad \mathrm{SR}_{\mathrm{BC}}=\frac{c_{\mathrm{DMSO}}}{c_{\mathrm{TBB}}+c_{\mathrm{TBC}}};\quad \mathrm{SR}_{\mathrm{phenol}}=\frac{c_{\mathrm{phenol}}}{c_{\mathrm{DMSO}}};$$

$$\mathrm{SR}_{\mathrm{BCP}}=\frac{c_{\mathrm{DMSO}}}{(c_{\mathrm{TBB}}+c_{\mathrm{TBC}}+c_{\mathrm{phenol}})};\quad \mathrm{SR}_{\mathrm{oil}}=\frac{w_{\mathrm{DMSO}}}{w_{\mathrm{oil}}}$$

where c is an initial mole fraction of a compound and w is initial mass fraction.

The relative volatility (RV) of compound 1 to compound 2 is calculated from the observed data according to the following equation:

$$\mathrm{RV}_{12}=\frac{y_1/x_1}{y_2/x_2}$$

where x_1 and x_2 are mole fractions of 1 and 2 in the liquid phase; y_1 and y_2 are those in the vapor phase. All compositions were measured or calculated on a solvent-free basis. As regards the solvents' function on different compounds, the solvent ratio and relative volatility equations are different and show as below.

$$\mathrm{RV}_{\mathrm{BP}}=\frac{y_{\mathrm{TBB}}/x_{\mathrm{TBB}}}{y_{\mathrm{phenol}}/x_{\mathrm{phenol}}},\quad \mathrm{RV}_{\mathrm{PC}}=\frac{y_{\mathrm{phenol}}/x_{\mathrm{phenol}}}{y_{\mathrm{TBC}}/x_{\mathrm{TBC}}},\quad \mathrm{RV}_{\mathrm{BC}}=\frac{y_{\mathrm{TBB}}/x_{\mathrm{TBB}}}{y_{\mathrm{TBC}}/x_{\mathrm{TBC}}}$$

2.3. Instrumental analysis experiment

0.1 μL portions of the distillate samples were taken and diluted with 1.2 mL of methanol, and then analyzed using a GC-2014 gas chromatograph equipped with a hydrogen flame detector, and a 30 m × 0.33 mm Rtx-5 column. The oven temperature was set at 80 °C for 10 min, then temperature-programmed heated to 200 °C at 5 °C/min. Samples are analyzed under a condition of 200 °C with a 1:180 split ratio, 0.2 μL injection volume.

0.1 μL coal-liquid samples were taken and diluted with 1.2 mL of methanol, and then analyzed using a 7890B Gas Chromatograph-5977 A Mass Spectrum (GC–MS). The oven temperature was held constant at 40 °C for 10 min, followed by an increase to 300 °C at 5 °C/min, and then held constant at 300 °C with a 1:180 split ratio, 0.2 μL injection volume. The GC–MS interface and mass spectrometry ion source were set at 280 °C and 250 °C, respectively. The MS was at 70 eV electron energy with a 300 mA ion current and scanned from 35 to 500 amu once per 0.5 s.

2.4. Separation apparatus of coal liquid distillate

The coal liquid distillate separation is performed on a simple distillation apparatus. It mainly consists of a 250 mL flask, a glass cooling tube, and a receiving flask. There isn't any packed material in this apparatus. The number of theoretical plates is 1.1, which is determined at total reflux. The coal liquid distillate is mixed with DMSO in the flask before heating, and fractions are collected after cooling tube. Fraction samples are then analyzed by the GC–MS (detailed information on the GC–MS analysis are in Section 2.3).

3. Results and discussion

3.1. The component of 150–180 °C coal liquid distillate

As a main DCL product, the 150–180 °C coal liquid distillate (CLD) contains abundant aromatics, alkanes, and phenolics. The composition of CLD is determined by the GC–MS, and the results are shown in Table 1. It can be seen that the CLD contains more than 24 compounds, and there are 50.81 *wt.%* alkanes, 35.82 *wt.%* phenolics, and 13.32 *wt.%*