

Complex Extraction of Phenol, o-Cresol, and p-Cresol from Model Coal Tar Using Methanol and Acetone Solutions

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ABSTRACT

Aims: The extractive performance of two solution solvents were studied for the complex extraction of phenols from model coal tar at varying conditions and variables.

Study design: Ordinary solvent extraction can preferentially extract phenolic compounds from the other compositions in coal tar. In order to separate the phenolic compounds from coal tar, it is essential to choose an extractant that has a specific interaction with phenols but insoluble in coal tar. Toward this aim, methanol solution and acetone solution may be candidate for their following characteristic.

Place and Duration of Study: Department of Chemical Engineering, Semarang State University and Department of Chemical Engineering, Gadjah Mada University.

Methodology: For this research, the influence of temperature, mass ratio of solvent to feed, mole fraction of water in solvent, and composition of solvent in the extractability of phenols were studied for methanol solution and acetone solution using model coal tar. Model coal tar is used in which the solute is a phenol, o-cresol, and p-cresol; diluent is kerosene, and solvent are water and methanol or acetone. Methanol and acetone need to be mixed with water because their polarities are not strong enough to form immiscible mixture with kerosene. The extract phase of the each extraction processes are analyzed by GC to obtain the concentration of each component in the extract phase and the concentration of each component in raffinate phase.

Results: Maximum of solute mole fraction (0.055 phenol; 0.037 o-cresol, and 0.061 p-cresol), maximum of the distribution coefficient (2.80 phenol; 3.66 o-cresol; and 4.55 p-cresol), and maximum of the yield (0.66 phenol; 0.64 o-cresol; and 0.76 p-cresol) obtained in the mass ratio of solvent-feed is 1, temperature is 308 K, and mole fraction of water in solvent is 0.2 by using an aqueous methanol solvent.

Conclusion:

Even though the mole fractions of the solutes in the extract are relatively low, but since the boiling points of the solvents and the solutes are differ significantly, the solutes can be easily separated by evaporating the solvents.

Phenolic compounds in low temperature coal tar may be extracted efficiently by methanol and acetone solutions at ambient temperature.

Keywords: phenol, o-cresol, p-cresol, methanol, acetone, extraction, coal tar

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1. INTRODUCTION

Coal tar which is obtained by pyrolysis process at low temperature is more complicated and contained main components such as aromatic, hydrocarbon, and phenolic compounds about 10%, 60%, and 30%, respectively. Coal tar is an important source of chemicals oil and fuel oil [1].

Therefore, a detailed analytical study on the composition and chemical structure of coal tar will be advantageous to its processing and utilization. When being processed, the very complicated compounds of the coal tar will be splitted to a simple products with higher economic value [2]. It is important to obtain the phenols for the following reasons. First, phenolic compounds are of high value chemicals, and their reclamation favors the process economics of the coal processing industry. Second, phenolic compounds are important raw materials for production of bisphenol A, phenolic resin, engineering plastics, synthetic fiber, etc. And third, removal of phenolic compounds in advance can decrease the consumption of H_2 in the hydrogen treating process of coal tar for the production of fuel oils [1].

Many methods to separate the useful compounds from coal tar have been tried. Various method have been used to obtain individual phenolic compounds contained in coal tar: ordinary solvent extraction, supercritical extraction, distillation, extractive distillation, azeotropic distillation, crystallization, liquid membrane separation, adsorption, etc. Although the reactive extraction achieves good separation of coal tar fraction, it requires relatively high energy costs, since the solvent used in the reactive extraction is corrosive to the extractor and is difficult to recover and reuse [3]. Ordinary solvent extraction can preferentially extract phenolic compounds from the other compositions in coal tar. In order to separate the phenolic compounds from coal tar, it is essential to choose an extractant that has a spesific interaction with phenols but insoluble in coal tar. Toward this aim, methanol solution and acetone solution may be candidate for their following characteristic.

Model coal tar in this research is similiary with the real coal tar which is obtained by coal pyrolysis (at low temperature, 450-600°C) to find out the components contained in the coal tar so that the model coal tar that will be used in the study has a composition which is similar to the real coal tar. Coal tar produced has the following physical characteristics: dark black coloured, viscosity = 2.82 cp, density = 2.05 g/cm³, and the caloric value = 10,425.63 cal/g. Using a method of GC-MS, this work presents a composition of the coal tar generated in the experiment. The analysis shows that coal tar contains more than 53 components. The total phenolic compounds contained in coal tar is 39.44% (v/v). Of those, the largest are phenol (8.06% v/v), *o*-cresol (3.45% v/v), and *p*-cresol (11.06% v/v) [4].

In this research, the extractive performance of two solution solvents were studied for the complex extraction of phenols from model coal tar at varying conditions and variables.

Extraction is often operated at ambient temperature, higher temperature is however favorable for the efficient mass transfer especially for the viscous liquids like coal tar due to the drastically lowering viscosity and the decreasing interfacial tension. For this purpose, the influence of temperature and composition of solvent in the extractbility of phenols were studied for methanol solution and acetone solution at 298, 308, and 318K using model coal tar.

2. MATERIAL AND METHODOLOGY

2.1 Material and Experimental

2.1.1 Material

1. Aquadest
2. Solvents: methanol and acetone (products of e-MERCK).
3. Model coal tar: kerosene, phenol, *p*-cresol, and *o*-cresol (products of e-MERCK).

2.1.2 Experimental

Instruments used in this study:

1. Shaker bath, product by Memmert WB14, SV1422, Scwabach, Germany.
2. Gas Chromatography (GC), product by GC 6820 Agilent Technologies, column: Rastek RXi-5MS002E.

The variables studied in this research are:

1. Composition of solvent (mole fraction of water and solvent) : 0.2, 0.5, 0.8.
2. The type of solvent : acetone solution and methanol solution.
3. Mass ratio of solvent to feed (E_o/R_o) : 1, 2, and 3.
4. Temperature of the process : 298, 308, 318 K.

This research uses artificial coal tar solution feed with the composition:

1. 77.5% v/v kerosene(as diluent)
2. 8% v/v phenol
3. 3.5% v/v *o*-cresol
4. 11% v/v *p*-cresol

Each solution is extracted with the solvents of aqueous acetone and aqueous methanol to obtain the equilibrium data of each component.

2.2 Methodology

10 mL of the feed (model coal tar), R_o , and the solvent, E_o , were brought into contact in an erlenmeyer flask with a screw cap. The erlenmeyer was shaken in a water bath shaker with amplitudo of shaking is 35 rpm. After equilibrium attained (5 hours), the mixtures were poured into a separating funnel, settled for an hour and separated into two phases. Then the two phases were weighed. The extract phases were analyzed by Gas-Chromatograph (GC). The principal conditions of this analysis are shown in Table 1.

Table 1

Conditions of Analysis Using GC-MS

OVEN

Initial temp : 140°C (On)

Maximum temp : 300°C

Initial time : 10.00 min

Equilibration time : 0.50 min

Ramps:

Rate Final temp Final time

10.0 (Off)

Post temp : 50°C

Post time : 0.00 min

Run time : 10.00 min

FRONT INLET (SPLIT/SPLITLESS)

BACK INLET (UNKNOWN)

Mode : Split

Initial temp : 280°C (On)

Gas type : Helium

COLUMN 1

COLUMN 2

Capillary Column (not installed)

Description : HP-5 Column (P/N:19091J-413)

Max temperature : 300°C

Nominal length : 30.0 m

Nominal diameter : 320.00 μ m

Nominal film thickness : 0.25 μ m

Inlet	: Front Inlet
Outlet	: Front Detector
FRONT DETECTOR (FID)	
BACK DETECTOR (NO DET)	
Temperature	: 300°C (On)
Hydrogen flow	: Off
Air flow	: Off
Makeup flow	: Off
Makeup Gas Type	: Helium
Flame	: On
Electrometer	: On
Lit offset	: 2.0
SIGNAL 1	
Data rate	: 5 Hz
Type	: front detector
POST RUN	
Post Time	: 0.00 min

For the liquid extraction processes of the major components of coal tar, model coal tar is used in which the solute is a phenol, *o*-cresol, and *p*-cresol; diluent is kerosene, and solvent is water and methanol or acetone. Kerosene is used as diluent because it is almost similar with the real coal tar. It contains such as Carbon, Hydrogen and Oxygen. Phenol, *o*-Cresol, and *p*-Cresol are completely miscible with kerosene. Methanol and acetone need to be mixed with water because their polarities are not strong enough to form immiscible mixture with kerosene [6].

The extract phase and the raffinate phase of each extraction processes are analyzed by GC to obtain the concentration of each component.

The distribution coefficient for each component *i*, K_i , is calculated by using Equation (1) as follows [5]:

$$K_i = \frac{\text{mole fraction of solute in extract phase}}{\text{mole fraction of solute in raffinate phase}} \quad (1)$$

The yield ($Y_{e,i}$) of each component in extract phase during the extraction process are calculated with Equation (3) as follows [5]:

$$Y_{e,i} = \frac{(\text{mass of extract} \times \text{mole fraction of solute in extract phase})}{(\text{mass of feed} \times \text{mole fraction of solute in feed})} \quad (2)$$

Equation (2) is formulated based on the assumption that there is a little material loss during extraction. This assumption was laboratory checked by measuring the amount of extract and raffinate and the results were compared to the amount of initial feed and solvent. It turned out that the assumption is correct. The assumption that after 5 hours the equilibrium has been attained was checked by analyzing the compositions of the extract and raffinate at various time. The compositions after 4 hours are almost constant. So the assumption of 5 hours for equilibrium time is justified.

3. RESULTS AND DISCUSSION

3.1 The Effect of Mole Fraction Ratio of Solvent to Feed on Phenolic Compounds Extraction

Figure 1 (a) and (b) shows the effect of mole fraction ratio of solvent to feed (E_o/R_o) for mole fraction of phenol, *o*-cresol, and *p*-cresol in the extract phase and the raffinate phase at

308K and $Y_w=0.2$. Increasing the ratio of E_o/R_o decreases mole fraction of phenol, *o*-cresol, and *p*-cresol in the extract phase and in the raffinate phase. Maximum value of mole fraction of phenol, *o*-cresol, and *p*-cresol in extracts phase which are obtained by using methanol solution is 0.055; 0.037; and 0.061, respectively. Because methanol has a greater polarity than acetone that able to form a liquid-liquid heterogeneous system with kerosene at various temperatures.

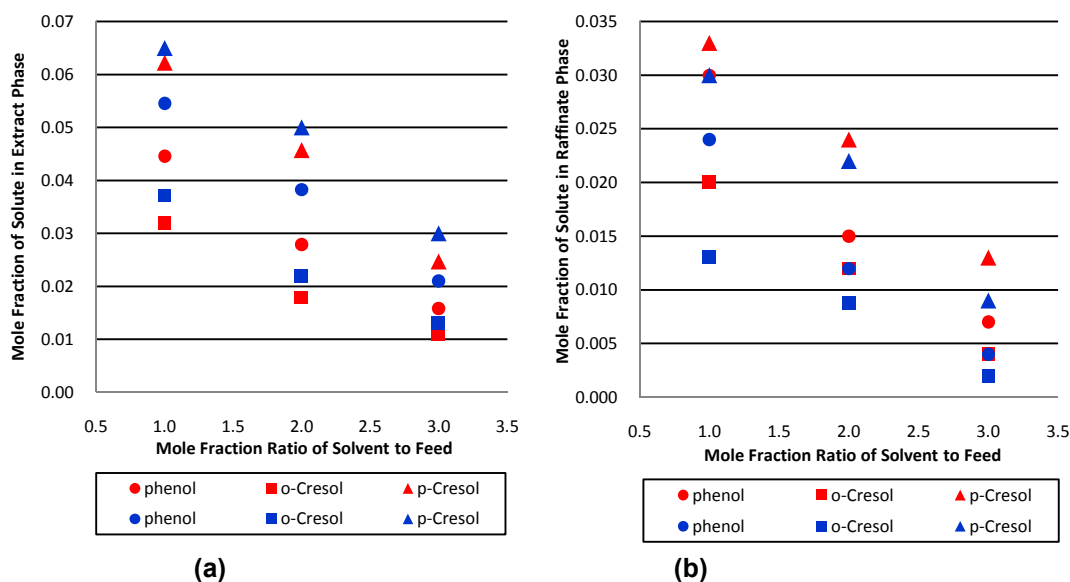


Fig. 1. The Effect of Mole Fraction Ratio of Solvent to Feed for Mole Fraction of Phenol, *o*-Cresol, and *p*-Cresol in Extract Phase (a) and Raffinate Phase (b) at 308 K and $Y_w=0.2$ with Acetone Solution (red) and Methanol Solution (blue)

3.2 The Effect of Temperature on Phenolic Compounds Extraction

Extraction is often operated at ambient temperature, higher temperature is however favorable for the efficient mass transfer especially for the viscous liquids like coal tar due to the drastically lowering viscosity and the decreasing interfacial tension. For this purpose, the influence of temperature in the extractability of phenols were studied for methanol solution and acetone solution at 298, 308, and 318 K using model coal tar. The result are presented in Figure 2 (a) and (b). Obviously, rising temperature increases mole fraction of phenol, *o*-cresol, and *p*-cresol in the extract phase and decreases mole fraction of phenol, *o*-cresol, and *p*-cresol in the raffinate phase, but at 318K it decreases mole fraction of solute in phase extract and increases mole fraction of solute in the raffinate phase. It was caused by the operation temperature approaches the boiling point of methanol (337.7 K) and acetone (329.2 K) so that there are few molecules of the solvent has turned into a vapor phase which can reduce the ability of the solvent to dissolve solutes. Maximum value of mole fraction of phenol, *o*-cresol, and *p*-cresol in extracts phase which are obtained by using methanol solution is 0.055; 0.037; and 0.061, respectively. Because methanol has a greater polarity than acetone that is able to form a liquid-liquid heterogeneous system with kerosene at various temperatures.

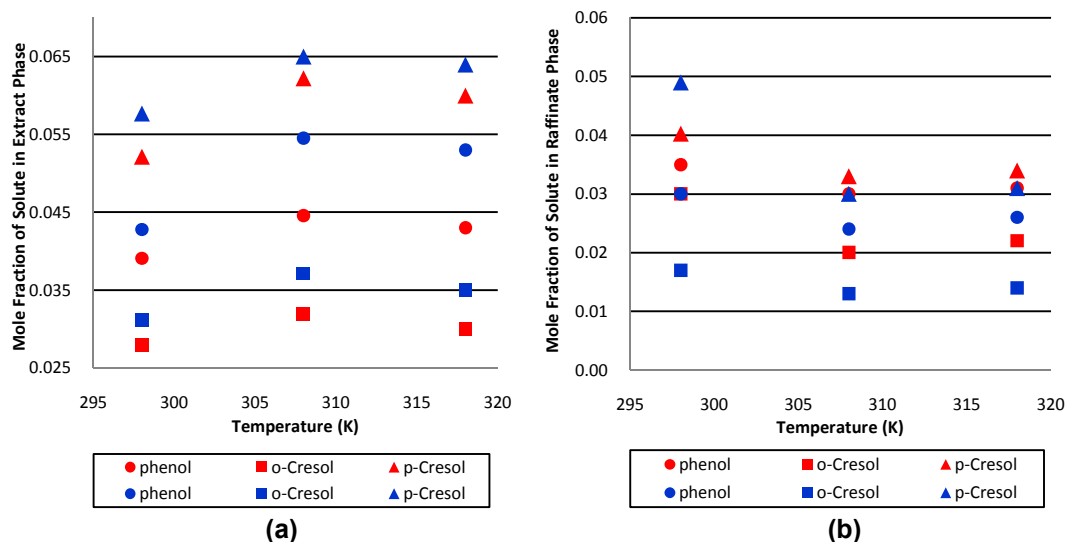


Fig.2.The Effect of Temperature for Mole Fraction of Phenol, o-Cresol, and p-Cresol in Extract Phase (a) and Raffinate Phase (b) at $E_o/R_o=1$ and $T = 308$ K with Acetone Solution (red) and Methanol Solution (blue)

3.3The Effect of Mole Fraction of Water in Solvent on Phenolic Compounds Extraction

Figure 3 (a) and (b) show the effect of mole fraction of water in solvent for mole fraction of phenol, o-cresol, and p-cresol in the extract phase and the raffinate phase at a 308 K and the ratio of $E_o/R_o = 1$. Pure acetone and pure methanol are organic solvents. Both of them without water were completely miscible with the model coal tar and could not be used as extraction solvents. Pure methanol and acetone don't have enough polarity to form two phase with the model coal tar. Therefore, the addition of water into the solvent can increase the polarity of the solvent to form a heterogeneous layer so that the extract phase (water phase) and the raffinate phase (organic phase) can be separated perfectly. Increasing mole fraction of water in the solvent decrease mole fraction of phenol, o-cresol, and p-cresol in extract phase and raffinate phase. Maximum value of mole fraction of phenol, o-cresol, and p-cresol, obtained for $Y_w = 2$ using methanol solution is 0.055; 0.037; and 0.061, respectively. Because methanol has a greater polarity than acetone that is able to form a liquid-liquid heterogeneous system with kerosene at various temperatures.

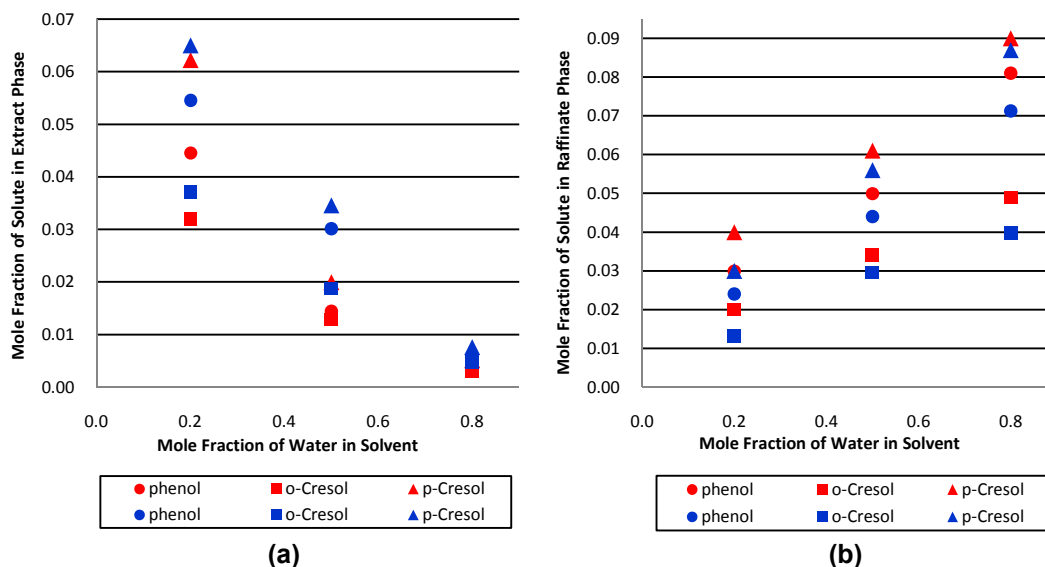


Fig.3.The Effect of Mole Fraction of Water in Solvent for the Mole Fraction of Phenol, o-Cresol, and p-Cresol in Extract Phase (a) and Raffinate Phase (b) at $E_o/R_o=1$ and $T = 308$ K with Acetone Solution (red) and Methanol Solution (blue)

3.4The Effect of Temperature for the Distribution Coefficient

Figure 4 shows the effect of temperature and ratio of E_o/R_o for the distribution coefficient of phenols at $Y_w = 0.2$ and operating temperature (298 K, 308 K and 318 K). The increasing temperature about 10° increases the distribution coefficient of phenol, o-cresol, and p-cresol, but at 318 K decreases mole fraction of solute in the extract phase and increases mole fraction of solute in the raffinate phase. It was caused by the operation temperature approaches the boiling point of methanol (337.7 K) and acetone (329.2 K) so that there are few molecules of the solvent has turned into a vapor phase which can reduce the ability of the solvent to dissolve solutes. Maximum distribution coefficient of phenol, o-cresol, and p-cresol is obtained using methanol and acetone solution at 308 K. The value of the distribution coefficient of phenol, o-cresol, and p-cresol is 2.80; 3.66; and 4.55, respectively using methanol solution as solvent. Because methanol has a greater polarity than acetone that is able to form a liquid-liquid heterogeneous system with kerosene at various temperatures.

The value of the distribution coefficient is more than 1. It indicates that the extraction process can be performed to separate phenol, o-cresol, and p-cresol from coal tar. Therefore, it should be selected as a great value of the distribution coefficient and it showed the requirement of solvent for this process.

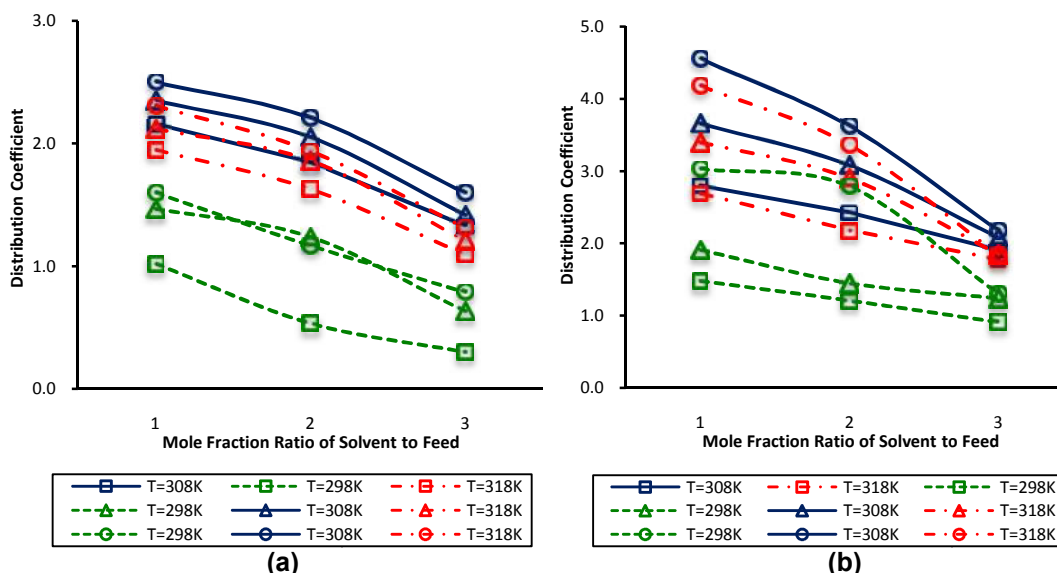


Fig.4.The Effect of Temperature and Mole Fraction Ratio of Solvent to Feed (E_0/R_0) for the Distribution Coefficient of Phenol ($\square$), o-Cresol (Δ), and p-Cresol ($\circ$) at $Y_w = 0.2$ with Acetone Solution (a) and Methanol Solution (b)

3.5The Effect of Mole Fraction of Water in Solvent for the Distribution Coefficient

The effect of water to solvent for the distribution coefficient, defined as the ratio between the mass concentration of water and mass concentration of methanol/acetone, is shown in Figure 5.

Figure 5 shows the effect of mole fraction of water in solvent and the ratio of solvent to feed (E_0/R_0) for the distribution coefficient of phenol, o-cresol, and p-cresol at 308 K. Pure acetone and pure methanol are organic solvents. Both of them without water were completely miscible with the model coal tar and could not be used as extraction solvents. Pure methanol and acetone don't have enough polarity to form two phase with the model coal tar. Therefore, the addition of water into the solvent can increase the polarity of the solvent to form a heterogeneous layer so that the extract phase (water phase) and the raffinate phase (organic phase) can be separated perfectly. However, the increasing mole fraction of water in solvent decreases the distribution coefficient of phenol, o-cresol, and p-cresol. It caused the ability of the solvent to dissolve solute. Maximum distribution coefficient of phenol, o-cresol, and p-cresol is obtained using methanol and acetone solution with mole fraction of water in solvent is 0.2. The value of the distribution coefficient of phenol, o-cresol, and p-cresol is 2.80; 3.66; and 4.55, respectively using methanol solution as solvent. Because methanol has a greater polarity than acetone that able to form a liquid-liquid heterogeneous system with kerosene at various temperatures.

The value of the distribution coefficient is more than 1. It indicates that the extraction process can be performed to separate phenol, o-cresol, and p-cresol from coal tar. Therefore, it should be selected as a great value of the distribution coefficient and it showed the requirement of solvent for this process.

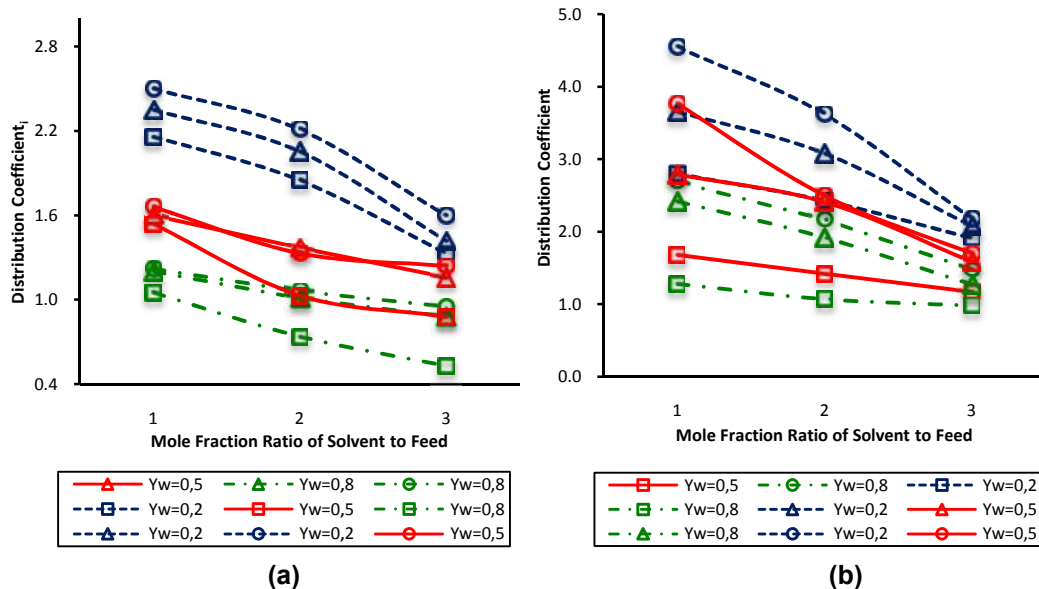


Fig.5.The Effect of Mole Fraction of Water in Solvent (Y_w) and Mole Fraction Ratio of Solvent to Feed (E_o/R_o) for the Distribution Coefficient of Phenol ($\square$), *o*-Cresol (Δ), and *p*-Cresol ($\circ$) at 308 K with Acetone Solution (a) and Methanol Solution (b)

3.6The Effect of Temperature for the Yield

Figure 6 shows the effect of temperature and the ratio E_o/R_o for the yield of phenol, *o*-cresol, and *p*-cresol at $Y_w = 0.2$. The increasing temperature increases the yield of phenolic compounds, but at 318 K decreases mole fraction of solute in the extract phase and increases mole fraction of solute in the raffinate phase. It was caused by the operation temperature approaches the boiling point of methanol (337.7 K) and acetone (329.2 K) so that there are few molecules of the solvent has turned into a vapor phase which can reduce the ability of the solvent to dissolve solutes. Maximum yield of phenol, *o*-cresol, and *p*-cresol is obtained using methanol and acetone solution at 308 K. The value of the yield of phenol, *o*-cresol, and *p*-cresol is 0.66; 0.64; and 0.76, respectively using methanol solution as solvent, because methanol has a greater polarity than acetone that able to form a liquid-liquid heterogeneous system with kerosene at various temperatures.

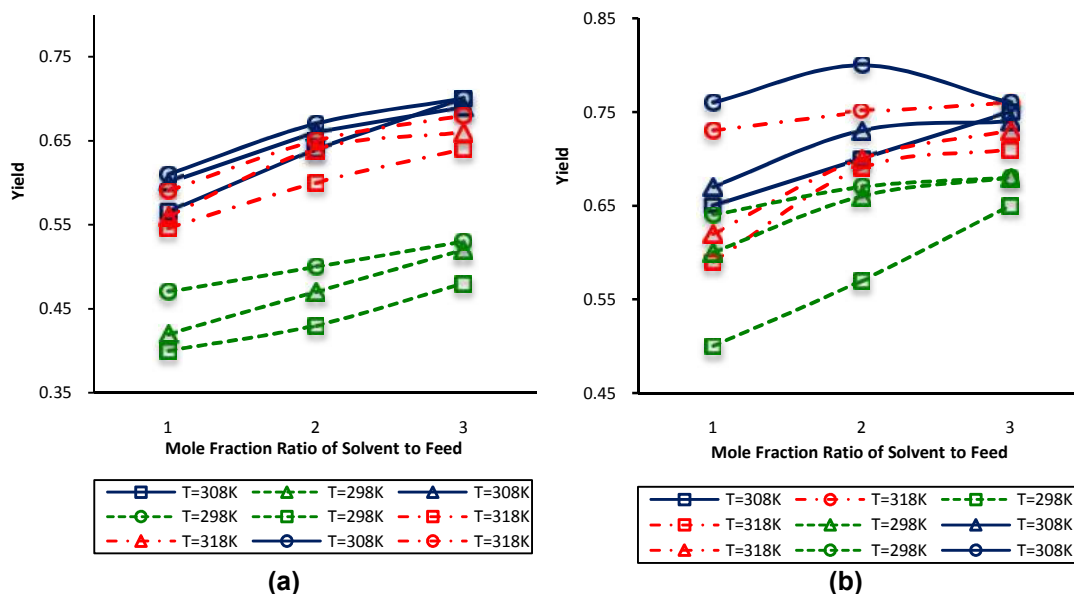


Fig.6. The Effect of Temperature and Mole Fraction Ratio of Solvent to Feed (E_o/R_o) for the Yield of Phenol ($\square$), o-Cresol (Δ), and p-Cresol ($\circ$) at $Y_w = 0.2$ with Acetone Solution (a) and Methanol Solution (b)

3.7 The Effect of Mole Fraction of Water in Solvent for the Yield

Figure 7 shows the effect of the mole fraction of water in the solvent and the ratio of E_o/R_o for the yield of phenolic compounds at 308 K. Pure acetone and pure methanol are organic solvents. Both of them without water were completely miscible with the model coal tar and could not be used as extraction solvents. Pure methanol and acetone don't have enough polarity to form two phase with the model coal tar. therefore, the addition of water into the solvent can increase the polarity of the solvent to form a heterogeneous layer so that the extract phase (water phase) and the raffinate phase (organic phase) can be separated perfectly. However, the increasing in mole fraction of water in solvent decreases the distribution coefficient of phenol, o-cresol, and p-cresol. It caused the ability of the solvent to dissolve solute. Maximum yield of phenol, o-cresol, and p-cresol is obtained using methanol and acetone solution at 308 K. The value of the yield of phenol, o-cresol, and p-cresol is 0.66; 0.64; and 0.76, respectively using methanol solution as solvent, because methanol has a greater polarity than acetone that able to form a liquid-liquid heterogeneous system with kerosene at various.

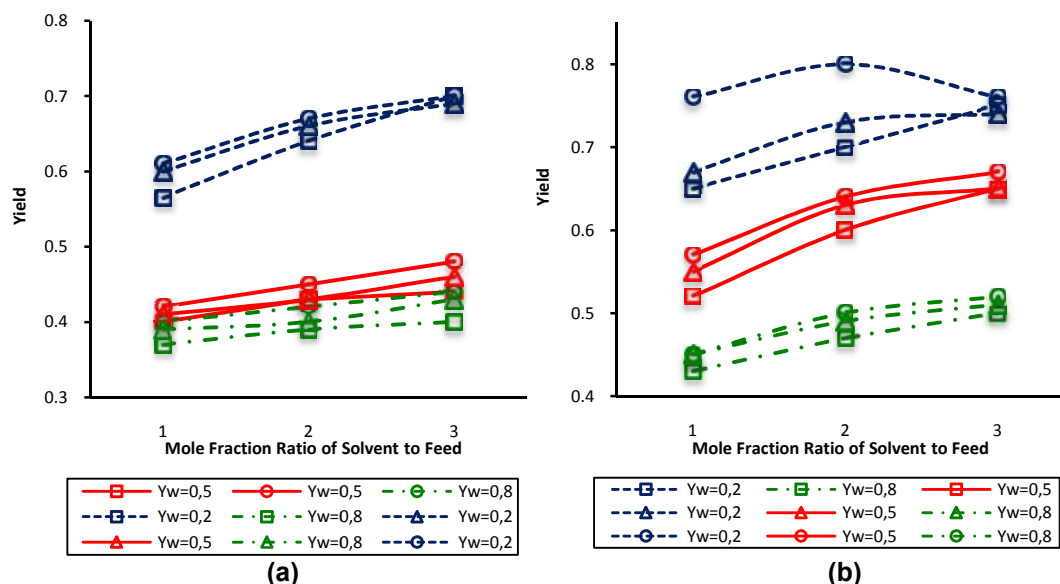


Fig.7.The Effect of Mole Fraction of Water in Solvent (Y_w) and Mole Fraction Ratio of Solvent to Feed (E_0/R_0) for the Yield of Phenol ($\square$), o-Cresol (Δ), and p-Cresol ($\circ$) at 308K with Acetone Solution (a) and Methanol Solution (b)

Eventhough the mole fractions of the solutes in the extract are relatively low, but since the boiling points of the solvents and the solutes are differ significantly, the solutes can be easily separated by evaporating the solvents.

4. CONCLUSION

Optimum process conditions for extraction process of phenolic compounds are obtained in the mass ratio of solvent-feed is 1, temperature is 308 K, and mole fraction of water in solvent is 0.2 by using an aqueous methanol solvent.

Maximum mole fraction of phenol, o-cresol, and p-cresol are 0.055, 0.037, and 0.061, respectively.

Maximum the distribution coefficient of phenol, o-cresol, and p-cresol are 2.80, 3.66, and 4.55, respectively.

Maximum the yield of phenol, o-cresol, and p-cresol are 0.66, 0.64, and 0.76, respectively.

Eventhough the mole fractions of the solutes in the extract are relatively low, but since the boiling points of the solvents and the solutes are differ significantly, the solutes can be easily separated by evaporating the solvents.

Phenolic compounds in low temperature coal tar may be extracted efficiently by methanol and acetone solutions at ambient temperature.

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338 **COMPETING INTERESTS**

339

340 "Authors have declared that no competing interests exist."

341

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343 **AUTHORS' CONTRIBUTIONS**

344

345 "Dewi Selvia Fardhyanti' designed the study, performed the statistical analysis, wrote the
346 protocol, and wrote the first draft of the manuscript. 'Wahyudi Budi Sediawan' managed the
347 analyses of the study. "Panut Mulyono" managed the literature searches. All authors read
348 and approved the final manuscript."

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351 **CONSENT (WHEREEVER APPLICABLE)**

352

353 "All authors declare that 'written informed consent was obtained from the patient (or other
354 approved parties) for publication of this case report and accompanying images. A copy of
355 the written consent is available for review by the Editorial office/Chief Editor/Editorial Board
356 members of this journal."

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