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Separation of Phenolic Compounds from Coal Tar

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Abstract. Coal tar is a liquid by-product of the process of coal gasification and carbonation. This liquid oil mixture contains various kind of useful compounds such as benzoic aromatic compounds and phenolic compounds. These compounds are widely used as raw material for insecticides, dyes, medicines, perfumes, coloring matters, and many others.

This preliminary research needed to be done that given the optimum conditions for the separation of phenolic compounds from the artificial coal tar by the extraction process. The aim of the present work was to study the effect of two kinds of aqueous were used as solvents: the methanol and acetone solutions, the mass fraction of water in solvents and the mass ratio of solvent to feed for the separation of phenolic compounds from the artificial coal tar by solvent extraction.

Phenolic compounds in coal tar were selectivity extracted into the solvent phase and these components could be separated by extracted with aqueous methanol solution, mass ratio of solvent to feed, $E_o/R_o = 2$ and the mass fraction of water in solvent, $y_w = 0{,}2$. These experimental results can be used to select the solvent and the optimum conditions of the process.

Keywords: Coal tar, Solvent Extraction, Distribution coefficient, Yield.

1. Introduction

Indonesia is the country's largest coal exporter in the world and have an estimated 5 billion tons of coal reserves. It is expected to increase the use of coal as an alternative raw material of petroleum, in the manufacture of gas, coke and coal briquettes. One by-product of the process of coal gasification carbonation is tar, which is contains amount of long-chain hydrocarbons, so it needs to be able to produce compounds that have high economic value, but because the smell is sharp and unpleasant, it is often considered as waste. Tar is a primary reaction products of coal pyrolysis that has very complex polynucleous compound and it is a product of the carbonization process that has high value but still neglected. Coal tar is a liquid produced as by-products in some industrial fields such as steel, power plant, cement, and others.

Coal tar contains more than 348 types of chemical compounds, which are very valuable. Benzoid aromatic compounds (benzene, toluene, xylene, naftalene and antrasene), phenolic compounds (phenol, cresol, xylenol, cathecol and resorcinol), heterocyclic nitrogen compounds (pyridine, quinolin, isoquinolin, indole), homosiklik hydrocarbons (benzene, toluene, etilbenzena, xylene, naphthalene, 1-metilnaftalena, 2-metilnaftalena) and oxygen heterocyclic compound (dibenzofuran), which has used as raw materials or intermediates materials in various chemical industries (as anti-oxidant, anti septic, resin, softener ingredient in plastic industry, paint, perfume, medicine, etc.) are found in coal tar (Egashira *et al.*, 2005). It is also a type of raw materials from which phenols, naphthalenes and anthracene can be extracted for the production of washing oil, cementitious agents, antiseptic agents, and catalytic hydrogenated to produce gasoline, diesel oil, etc. Therefore, a detailed analytical study on the composition and chemical structure of coal tar will be advantageous to its processing and utilization, and enable it to be a chemical and power fuel materials of great value. Similarly, paraffinic and olefinic compounds which can be used as liquid fuel is also contained in coal tar. It will encourage the research of the coal tar, but due to the sharp smelling and unpleasant, it is often considered as waste. When it was processed further more, the very complex compounds of the coal tar will be split to produce simple forms with higher economic value (Hayashi *et al*., 1995).

This research were expected to do further research on coal in Indonesia in particular research on Indonesian coal tar that will get the components which is still has a high economic value. These researches on coal have been carried out, but specifically for the coal tar were so little. These researchs are expected to drive the next researchs on coal in Indonesia to produce components which are still have high economic value. Various studies on the coal have been done, but the specific researh on the coal tar is still very few. Some researchers have learned about the pyrolysis of the coal and the separation of components of the coal tar [2, 3, 5, 6, 11]. Egashira et al. [9, 10], Egashira and Saito [8], and Egashira and Salim [7] have already done the separation of absorption oil and the tar light oil fraction from the coal tar.

This preliminary research needed to be done that given the optimum conditions for the separation of phenolic compounds from the artificial coal tar by the extraction process. The phenolic compounds such as phenol, *o*-cresol, and *p*-cresol are very valuable which phenol has used as the main component in the anti septic manufacture, trichlorophenol (TCP) and cresol has used as disinfectant (known as lysol) and deodorizer. Phenolic compounds are stable but they are also non-biodegradable, toxic and corrosive. Phenolic compounds comsumption will increase by the increasing of the world industry, especially the anti septic industrial.

The aim of the present work was to study the effect of two kinds of aqueous solution were used as solvents: the methanol and acetone solutions, the mass fraction of water in solvents and the mass ratio of solvent to feed for the separation of phenolic compounds from the artificial coal tar by solvent extraction.

2. Experimental

2.1. Material

Methanol (e-MERCK), acetone (e-MERCK), aquadest, kerosene, phenol (e-MERCK), *p*-cresol (e-MERCK), *o*-cresol (e-MERCK).

2.2. Experimental

The material systems and experimental conditions for the equilibrium extraction are summarized in Table 1. The artificial coal tar was used as a feed which kerosene was used as diluent. The solute components of the artificial coal tar in this study were phenol, *o*-cresol, and *p*-cresol which were determined from the Gas Chromatography-Mass Spectroscopy (GC-MS) analysis of the coal tar. The analysis result showed that the coal tar contained more than 78 chemical compounds such as benzene, *o*-cresol, *p*-cresol, phenol, naphtalene, etc. The compositions of benzene, *o*-cresol, *p*-cresol, phenol, naphtalene in the coal tar are 1.63%, 3.50%, 8%, 6% and 2.26%, respectively.

Table 1: Material Systems and Conditions for Equilibrium Extraction

Feed		Artificial coal tar
Mass, R_o	[kg]	0,005
Composition in R_o		Phenol ($x_{p,o}$) = 0,077; *o*-cresol ($x_{oc,o}$) = 0,044; *p*-cresol ($x_{pc,o}$) = 0,094
Solvent	[-]	Aqueous of methanol solution and aqueous of acetone solution
Mass fraction of water, $y_{w,o}$	[-]	0,2; 0,5; 0,8
Mass ratio of solvent to feed, E_o/R_o		1, 2, 4
Shaking time, t	[hr]	6
Frequency of shaking	[hr^{-1}]	7200
Extraction temperature	[K]	303

The feed (artificial coal tar), R_o, and the solvent, E_o, were brought into contact in an Erlenmeyer flask with a screw cap, which was shaken in the system conditions as Table 1. After equilibration, the oil raffinate phase, R_1, and the aqueous extract phase, E_1, were poured into a separation funnel, settled for an hour and separated into each other to be weighed. All phases were analyzed by Gas-Chromatograph (GC) and determined the mass fraction of component i in extract phase, $y_{i,1}$ and in raffinate phase, $x_{i,1}$. The details of this analysis were described previously. The GC analyses determined the compositions of these phases in terms of the mass fraction of the components of interest. The mass fraction of water in the extract phase, $y_{w,1}$, was calculated as,

$$y_{w,1} = 1 - \sum_{i \neq w} y_{i,1} \tag{1}$$

By neglecting the amount of any components other than those of interest in this study.

3. Results and Discussion

The mass fractions of any components in the raffinate and extract phase, x_i and y_i, are constant with time after 6 hours and the system of the phases attained to an equilibrium. Allowing for this result and the effect of the experimental conditions, the shaking time was fixed at 6 hours for reliability in the following experiments.

3.1. Distribution Coefficient

The distribution coefficient of component i, K_i, was defined by the Eq.(2):

$$K_i = \frac{y_{i,1}}{x_{i,1}} \tag{2}$$

With the compositions of oil and aqueous phases at equilibrium. The distribution coefficients, K_i, are shown in Fig. 1 with the mass fraction of water in the equilibrium extract phase, $y_{w,1}$.

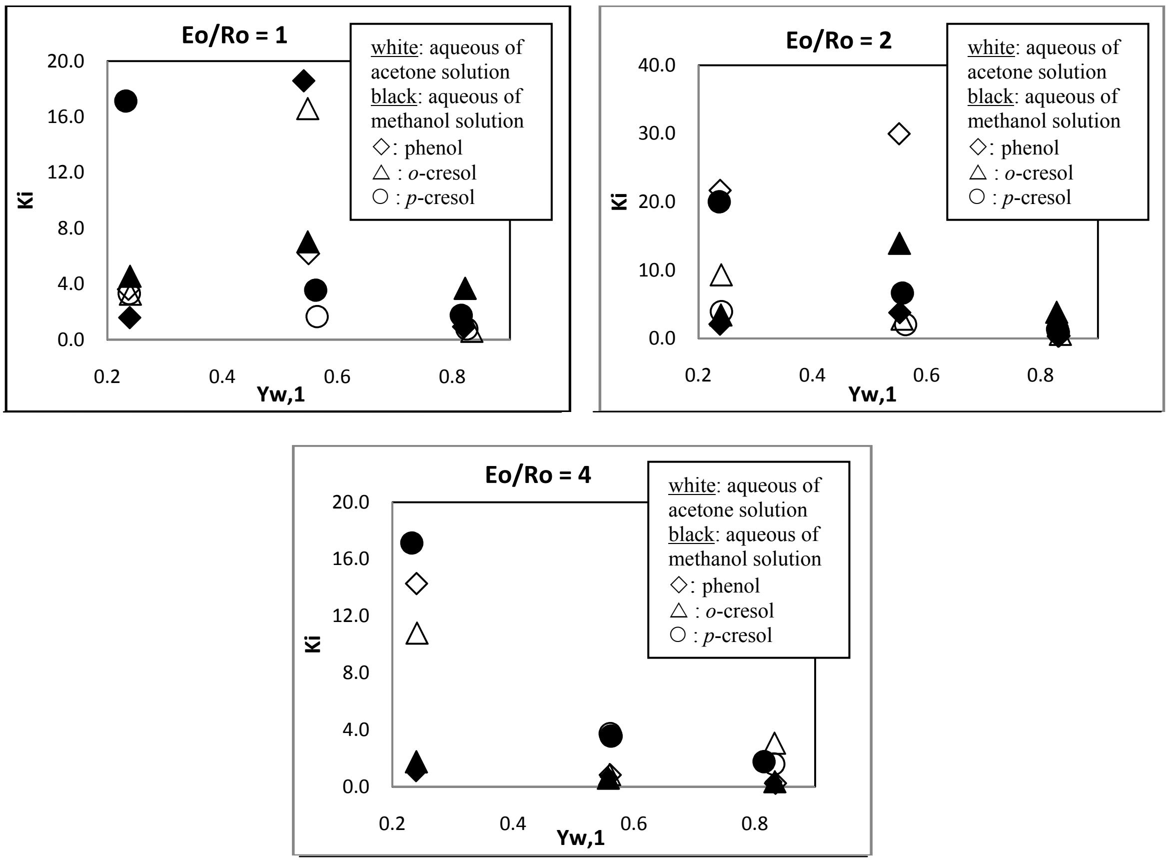

Fig. 1: Effect of mass fraction of water in extract, y_w, and mass ratio of solvent to feed, E_o/R_o, on the distribution coefficient, K_i

Figure 1 show the effects of the water content in extract phase, y_w, and the mass ratio of solvent to feed, E_o/R_o, in the distribution coefficient, K_i. Both methanol and acetone without water were completely miscible with the artificial 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 artificial coal tar. The distribution coefficients of the phenolic compounds decreased with the increase of $y_{w,i}$, mainly because the polarity of the solvent becomes higher as $y_{w,i}$ increases. The amount of water transferring from the solvent into the raffinate was negligible (Egashira, 2001). The distribution coefficient of the phenolic compounds were higher with E_o/R_o=2, which K_i in the case of aqueous of methanol solution was larger than of the case of aqueous of acetone solution. K_i value was much greater 1, these results reconfirmed that the coal tar could be separated into the phenolic compounds by extraction with aqueous of methanol solution and aqueous of acetone solution.

3.2. Yield

Yield of component i, $y_{e,i}$, transferred into the extract phase during the equilibrium extraction was defined by Eq.(3):

$$Y_{e,1} = \frac{E_1.y_{i,1} - E_o.y_{i,o}}{R_o.x_{i,o}} \tag{3}$$

The yields obtained by this equation are given in Fig. 2 with the mass fraction of water in the equilibrium extract phase, $y_{w,1}$.

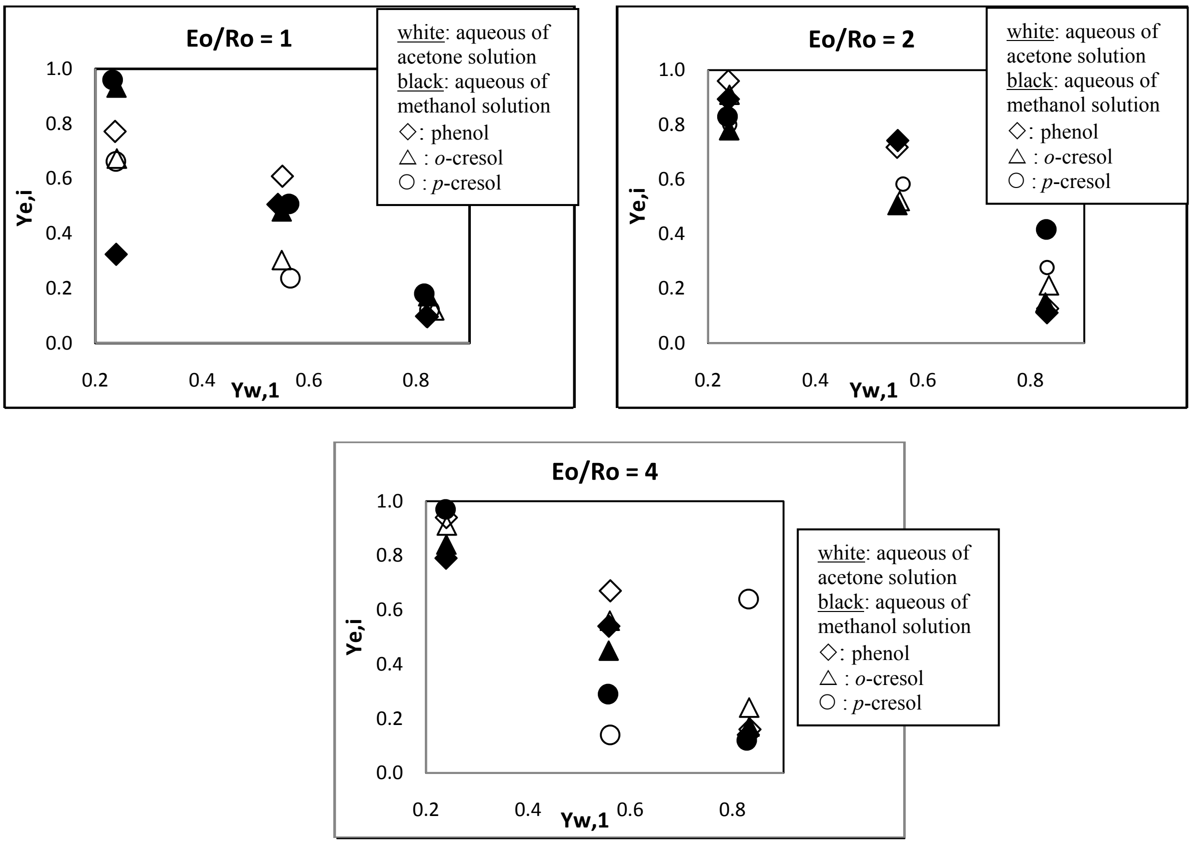

Fig. 2: Effect of mass fraction of water in extract, y_w, and mass ratio of solvent to feed, E_o/R_o, on yields, $y_{e,i}$

The yields obtained by Eq. (3), $y_{e,i}$, in the case of methanol solution and in the case of aqueous of acetone solution are given in Fig.2. Since the yi,1 of the phenolic compounds were so high, $E_o.y_{i,o}$ were negligible relative to $E_i.y_{i,1}$ in Eq. (3). The yield of phenolic compounds was higher with E_o/R_o=2, which $y_{e,i}$ in the case of aqueous of methanol solution was larger than of the case of aqueous of acetone solution.

4. Conclusions

Solvent extraction methods using aqueous of methanol solution and aqueous of acetone solution can be used to separate phenolic compounds in coal tar. The yields, $Y_{e,i}$, and selectivity, K_i, were about 0.8 and 30 at maximum, respectively. It was confirmed that phenolic compounds could be selectively separated.

Phenolic compounds in coal tar were selectivity extracted into the solvent phase and these components could be separated by extracted with aqueous methanol solution with $E_o/R_o=2$ and the mass fraction of water, $y_w=0,2$. These experimental results can be used to select the solvent and the optimum conditions of the process.

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