International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:7, No:6, 2013

Extraction of Phenol, *o*-Cresol, and *p*-Cresol from Coal Tar: Effect of Temperature and Mixing

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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 kinds of useful compounds such as phenol, *o*-cresol, and *p*-cresol. These compounds are widely used as raw material for insecticides, dyes, medicines, perfumes, coloring matters, and many others.

This research needed to be done that given the optimum conditions for the separation of phenol, *o*-cresol, and *p*-cresol from the coal tar by solvent extraction process. The aim of the present work was to study the effect of two kinds of aqueous were used as solvents: methanol and acetone solutions, the effect of temperature (298, 306, and 313K) and mixing (30, 35, and 40rpm) for the separation of phenol, *o*-cresol, and *p*-cresol from coal tar by solvent extraction.

Results indicated that phenol, *o*-cresol, and *p*-cresol in coal tar were selectivity extracted into the solvent phase and these components could be separated by solvent extraction. The aqueous solution of methanol, mass ratio of solvent to feed, E_o/R_o=1, extraction temperature 306K and mixing 35 rpm were the most efficient for extraction of phenol, *o*-cresol, and *p*-cresol from coal tar.

***Keywords*—**Coal tar, Distribution coefficient, Extraction, Yield.

I. Introduction

INDONESIA is one of the largest countries of coal exporter in the world. It is also predicted to have 5 billion tonnes of coal resources reserve. 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 of products of the coal gasification and carbonation process is tar, which contains the amount of long-chain hydrocarbons so that it can produce the compounds that have high economic value. However, it has a characteristic sharp and unpleasant odor so it is often considered waste. Tar is a primary reaction product 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 fieldsuch as steel, power plant, cement, and others.

One of the by-products of the process of coal gasification and carbonation is tar, which 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 product 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. They are benzoid aromatic compounds (benzene, toluene, xylene, naftalene and antrasene), phenolic compounds (phenol, cresol, xylenol, cathecol and resorcinol), heterocyclic nitrogen compounds (pyridine, quinolin, isoquinolin, indole), and oxygen heterocyclic compound (dibenzofuran), which all have been used as raw materials or intermediates materials in various chemical industries (as anti-oxidant, antiseptic, resin, softener ingredient in plastic industry, paint, perfume, medicine, etc.) [9]. 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 are also contained in coal tar. When being processed furthermore, the very complex compounds of the coal tar will be splited into a simple product forms with have higher economic value [7].

These researches are expected to drive the next researches on coal in Indonesia to produce components which are still having high economic value. Various studies on the coal have been done, but the specific research 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 [3]-[6], [8]-[10].

This research is needed to be done for getting the optimum conditions for the separation of phenol, *o*-cresol, and *p*-cresol from the coal tar by the extraction process. These compounds are very valuable component which phenol has been used as the main component for the antiseptic manufacture, trichlorophenol (TCP) and cresol has been used as disinfectant

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(known as lysol) and deodorizer. Phenol, *o*-cresol, and *p*-cresol are stable but they are also non-biodegradable, toxic and corrosive. Phenol, *o*-cresol, and *p*-cresol consumption will increase by the increasing of the world industry, especially the antiseptic industrial.

Furthermore, phenol, *o*-cresol, and *p*-cresol are susceptible to oxidation. High temperature and alkaline environment caused their degradation. In spite of the development of new extraction techniques, classic extraction dominates in many laboratories mainly due to its simplicity and low economic outlay. The efficiency of the process can be widely regulated here by the selection of suitable solvents and optimum conditions of the extraction process [2].

The aim of the present work has been to examine the effects of the extraction parameters: solvent, temperature, and mixing. Extraction was performed with aqueous solution of methanol and acetone, at three temperature, 298, 306, and 313K, through three different mixing 30, 35, and 40rpm.

II. Materials and Method

A. Material

Aquadest, kerosene, methanol, acetone, phenol, *p*-cresol, *o*-cresol were purchased from e-Merck (Germany).

B. Experimental

The material systems and experimental conditions for the equilibrium extraction are summarized in Table I. 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 I
Material Systems and Conditions for Equilibrium Extraction

Symbol		Quantity
	feed	artificial coal tar
R_o	mass, Ro	0.005 kg
X_o	composition in Ro	phenol (Xp,o) = 0.077 *o*-cresol (Xoc,o) = 0.044 *p*-cresol (Xpc,o) = 0.094
	solvent	methanol solution acetone solution
$Y_{w,o}$	mass fraction of water	0.2[1]
E_o/R_o	mass ratio of solvent to feed	1, 2, and 3
t	shaking time	6 hr [1]
	mixing scale	30, 35, and 40 rpm
T	temperature	298, 306, and 313 K

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 a water bath shaker (Memmert WB14, SV1422, Scwabach, Germany) with the system conditions as Table I. 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-Chromatography (GC) and determined the mass fraction of component i in extract phase, y_i and in raffinate phase, x_i. 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, was calculated as, [4], [5].

$$Y_w = 1 - \sum_{i \neq w} Y_i \quad (1)$$

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

III. Results and Discussion

In this research the most influential experimental variables on the extraction of phenol, *o*-cresol, and *p*-cresol from coal tar, solvents (aqueous of methanol and aqueous of acetone), temperature (298, 306, and 313K) and mixing (30, 35, and 40 rpm) were evaluated to increase the extraction selectivity and attain to equilibrium. Generally, all extracts are rich source of phenol, *o*-cresol, and *p*-cresol but their mass fraction significantly depends on extraction conditions: solvents, temperature and mixing.

Both methanol and acetone without water were completely miscible with 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. This result was accordance with previous reports suggesting that a binary solvent system are more efficient than mono solvent (pure methanol or pure acetone) in the extraction of phenol, *o*-cresol, and *p*-cresol form coal tar in regard ti their relative polarity [4], [5].

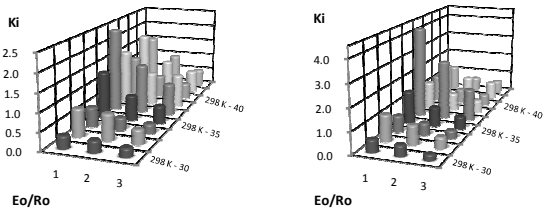
The mass fractions of any components in the raffinate and extract phase, x_i and y_i, are constant after 6 hours processing and the system of the phases attained to an equilibrium. Allowing for this result and the effect of the experimental conditions, the mixing time was fixed at 6 hours for reliability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

A. Distribution Coefficient

The distribution coefficient of component i, Ki, was defined by [4], [5]:

$$K_i = \frac{Y_i}{X_i} \quad (2)$$

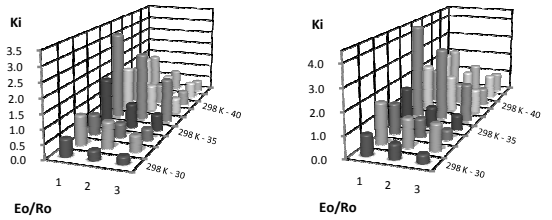
With the compositions of oil and aqueous phases at equilibrium. The distribution coefficients, K_i, are shown in Figs. 1, 2, and 3.



(a) (b)

Fig. 1Effect of temperature, mixing and mass ratio of solvent to feed, E_o/R_o, of phenol extraction by acetone solution (a) and methanol solution (b) for the distribution coefficient, K_i

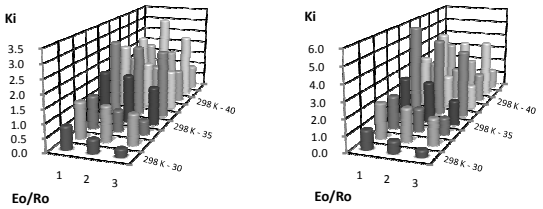
Fig. 1 shows the effects of temperature, mixing, and the mass ratio of solvent to feed, E_o/R_o, of phenol extraction by acetone solution (a) and methanol solution (b) for the distribution coefficient, K_i. The distribution coefficients of the phenol increased with the increasing of temperature and mixing but decreased at temperature 313K, mixing 40rpm and the increasing of mass ratio of solvent to feed. The amount of water transferring from the solvent into the raffinate was negligible [5]. The distribution coefficient of the phenol was higher with E_o/R_o=1, than E_o/R_o=2 or E_o/R_o=3. Extraction of phenol at temperature 306K and mixing 35rpm in the case of aqueous of methanol solution gave higher distribution coefficient K_i= 4.24 while extraction in the case of acetone solution resulted the decrease of K_i (K_i= 4.24).Temperature above 306 K caused the decreasing of K_i due to possible a degradation of phenol and increased the loss of solvent by evaporation at high temperature.



(a) (b)

Fig. 2 Effect of temperature, mixing and mass ratio of solvent to feed, E_o/R_o, of *o*-cresol extraction by acetone solution (a) and methanol solution (b) for the distribution coefficient, K_i

Fig. 2 shows the effects of temperature, mixing, and the mass ratio of solvent to feed, E_o/R_o, of *o*-cresol extraction by acetone solution (a) and methanol solution (b) for the distribution coefficient, K_i. The distribution coefficients of the *o*-cresol increased with the increasing of temperature and mixing but decreased at temperature 313K, mixing 40rpm and the increasing of mass ratio of solvent to feed. The amount of water transferring from the solvent into the raffinate was negligible for these components too [5].The distribution coefficient of the *o*-cresol was higher with E_o/R_o=1, than E_o/R_o=2 or E_o/R_o=3.K_i value was larger (K_i= 4.42) at temperature 306K and mixing 35rpm in the case of aqueous of methanol solution than in the case of acetone solution (K_i =3.14).Temperature above 306K caused the decreasing of K_i due to possible to a degradation of *o*-cresol and increased the loss of solvent by evaporation at high temperature.



(a) (b)

Fig. 3 Effect of temperature, mixing and mass ratio of solvent to feed, E_o/R_o, of *p*-cresol extraction by acetone solution (a) and methanol solution (b) for the distribution coefficient, K_i

Fig. 3 shows the effects of temperature, mixing, and the mass ratio of solvent to feed, E_o/R_o, of *p*-cresol extraction by acetone solution (a) and methanol solution (b) for the distribution coefficient, K_i. The distribution coefficients of the *p*-cresol increased with the increasing of temperature and mixing but at temperature 313K, mixing 40rpm and the increasing of mass ratio of solvent to feed. The amount of water transferring from the solvent into the raffinate was negligible for these components too [5].The distribution coefficient of the *p*-cresol was higher with E_o/R_o=1 than E_o/R_o=2 or E_o/R_o=3. K_i value was larger (K_i= 5.75) at temperature 306K and mixing 35rpm in the case of aqueous of methanol solution than in the case of acetone solution (K_i = 2.78).Temperature above 306 K caused the decreasing of K_i due to possible to a degradation of *p*-cresol and increased the loss of solvent by evaporation at high temperature.

Generally, distribution coefficient, K_i, value for all the components was larger than 1, it means that the extraction of phenol, *o*-cresol, and *p*-cresol should be done for the best extraction conditions in coal tar extracts obtained by using an aqueous solution of methanol at temperature 306 K, mixing 35 rpm, and mass ration of solvent to feed E_o/R_o=1.

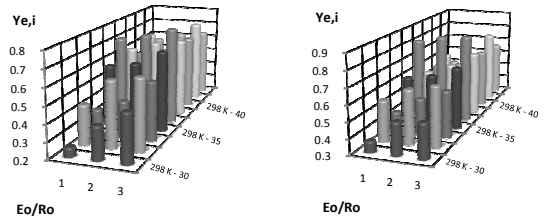
B. Yield

Yield of component i, $Y_{e,i}$, transferred into the extract phase during the equilibrium extraction was defined by[4], [5]:

$$Y_{e,1} = \frac{E_1.Y_{i,1} - E_o.Y_{i,o}}{\mathrm{R_o}.X_{i,o}} \quad (3)$$

The yields obtained by this equation are given in Figs. 4, 5, and 6.

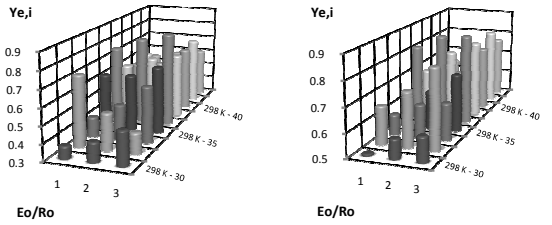
The yields obtained by (3), $Y_{e,i}$, in the case of methanol solution and in the case of aqueous of acetone solution are given in Figs. 4, 5, and 6. Since the y_i of the phenol, *o*-cresol, and *p*-cresolwere so high, $E_o.y_{i,o}$ were negligible relative to $E_i.y_{i,1}$ in (3).



(a) (b)

Fig. 4 Effect of temperature, mixing and mass ratio of solvent to feed, E_o/R_o, of phenol extraction by acetone solution (a) and methanol solution (b) for the yield, $Y_{e,i}$

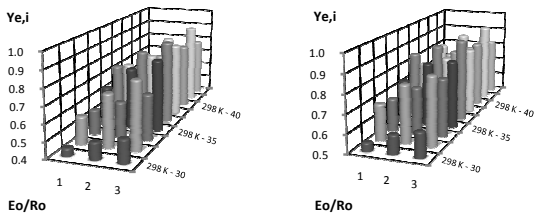
Fig. 4 shows the effects of temperature, mixing, and the mass ratio of solvent to feed, E_o/R_o, of phenol extraction by acetone solution (a) and methanol solution (b) for the yield, $Y_{e,i}$. The yield of the phenol increased with the increasing of temperature, mixing and mass ratio of solvent to feed but decreased at temperature 313K and mixing 40rpm. The yield of the phenol was higher with E_o/R_o=3than E_o/R_o=1 or E_o/R_o=2.Extraction of phenol at temperature 306K and mixing 35rpm in the case of aqueous of methanol solution gave higher yield, $Y_{e,i}$= 0.86 while extraction in the case of acetone solution resulted the decrease of $Y_{e,i}$ ($Y_{e,i}$= 0.79).Temperature above 306 K caused the decreasing of $Y_{e,i}$ due to possible a degradation of phenol and increased the loss of solvent by evaporation at high temperature.



(a) (b)

Fig. 5 Effect of temperature, mixing and mass ratio of solvent to feed, E_o/R_o, of *o*-cresol extraction by acetone solution (a) and methanol solution (b) for the yield, $Y_{e,i}$

Fig. 5 shows the effects of temperature, mixing, and the mass ratio of solvent to feed, E_o/R_o, of *o*-cresol extraction by acetone solution (a) and methanol solution (b) for the yield, $Y_{e,i}$. The yield of the *o*-cresol increased with the increasing of temperature, mixing and mass ratio of solvent to feed but decreased at temperature 313K and mixing 40rpm. The yield of the *o*-cresol was higher with E_o/R_o=3than E_o/R_o=1 or E_o/R_o=2. $Y_{e,i}$ was larger ($Y_{e,i}$= 0.88) at temperature 306K and mixing 35rpm in the case of aqueous of methanol solution than in the case of acetone solution ($Y_{e,i}$= 0.86).Temperature above 306K caused the decreasing of $Y_{e,I}$ due to possible a degradation of *o*-cresol and increased the loss of solvent by evaporation at high temperature.



(a) (b)

Fig. 6 Effect of temperature, mixing and mass ratio of solvent to feed, E_o/R_o, of *p*-cresol extraction by acetone solution (a) and methanol solution (b) for the yield, $Y_{e,i}$

Fig. 6 shows the effects of temperature, mixing, and the mass ratio of solvent to feed, E_o/R_o, of *p*-cresol extraction by acetone solution (a) and methanol solution (b) for the yield, $Y_{e,i}$. The yield of the *p*-cresol increased with the increasing of temperature, mixing and mass ratio of solvent to feed but decreased at temperature 313K and mixing 40rpm. The yield of the *p*-cresol was higher with E_o/R_o=3than E_o/R_o=1 or E_o/R_o=2. $Y_{e,i}$ value was larger ($Y_{e,i}$= 0.95) at temperature 306K and mixing 35rpm in the case of aqueous of methanol solution than in the case of acetone solution ($Y_{e,i}$= 0.91). Temperature above 306K caused the decreasing of $Y_{e,I}$ due to possible a degradation of *p*-cresol and increased the loss of solvent by evaporation at high temperature.

These results reconfirmed that the coal tar could be separated selectively into phenol, *o*-cresol, and *p*-cresol by extraction in the case of aqueous of methanol solution. The yield, $Y_{e,i}$, was higher for *p*-cresol than phenol and *o*-cresol.

IV. Conclusion

This study demonstrates that it is essential to optimize systematically the extraction solvent compositions, extraction temperature and mixing for accurate and reproducible assay of phenol, *o*-cresol, and *p*-cresol. Our results showed that solvent extraction methods using aqueous of methanol solution and aqueous of acetone solution can be used to separate phenol, *o*-cresol, and *p*-cresol in coal tar. The yields, $Y_{e,i}$, were about 0.86, 0.88, and 0.95 at maximum and selectivity, K_i, were about 4.24, 4.42, and 5.75 at maximum, respectively. It was confirmed that phenol, *o*-cresol, and *p*-cresol could be selectively separated.

This study confirmed that the aqueous solution of methanol, mass ratio of solvent to feed, E_o/R_o = 1, extraction temperature 313K, and extraction mixing 35 rpm were the most efficient for extraction of phenol, *o*-cresol, and *p*-cresol from coal tar. These experimental results can be used to select the solvent and the optimum conditions of the process.

Acknowledgement

We thank the Directorate General of Higher Education, Ministry of National Education, Indonesia, for financial support of this work through the scholarship of doctorate program (BPPS) at University of Gadjah Mada to Dewi Selvia Fardhyanti.

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