

# Analysis of Coal Tar Compositions Produced from Sub-Bituminous Kalimantan Coal Tar

D. S. Fardhyanti, A. Damayanti

**Abstract**—Coal tar is a liquid by-product of coal pyrolysis processes. This liquid oil mixture contains various kinds 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. The coal tar was collected by pyrolysis process of coal obtained from PT Kaltim Prima Coal and Arutmin-Kalimantan. The experiments typically occurred at the atmospheric pressure in a laboratory furnace at temperatures ranging from 300 to 550°C with a heating rate of 10°C/min and a holding time of 1 hour at the pyrolysis temperature. The Gas Chromatography-Mass Spectroscopy (GC-MS) was used to analyze the coal tar components. The obtained coal tar has the viscosity of 3.12 cp, the density of 2.78 g/cm<sup>3</sup>, the calorific value of 11,048.44 cal/g, and the molecular weight of 222.67. The analysis result showed that the coal tar contained more than 78 chemical compounds such as benzene, cresol, phenol, xylene, naphthalene, etc. The total phenolic compounds contained in coal tar are 33.25% (PT KPC) and 17.58% (Arutmin-Kalimantan). The total naphthalene compounds contained in coal tar is 14.15% (PT KPC) and 17.13% (Arutmin-Kalimantan).

**Keywords**—Coal tar, pyrolysis, gas chromatography-mass spectroscopy.

## I. INTRODUCTION

COAL can be defined as flammable sedimentary rock, formed from organic sediments, particularly on plan waste and formed through coalification. The main elements of coal consist of C, H, and O. Based on the level of the coal formation process which is controlled by pressure, heat and time; coal is generally divided into seven classes, namely: peat, lignite, sub-bituminous, bituminous, steam coal, anthracite, and graphite.

Generally, coal utilization technologies are divided into combustion, pyrolysis, liquefaction and gasification. Pyrolysis technique is a technique of heating coal in high temperature (500-1000°C), which produce coke (coal with high calorific combustion), gas and tar [1]. When coal pyrolysis and distillation are conducted by heating without contact with air, the coal will be converted into solid, liquid, and gas. The amount and nature of the products depend on the pyrolysis temperature and the type of coal used. One of products of the pyrolysis 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 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 aromatic compounds (benzene, toluene, xylene, naphthalene, anthracene, etc.), phenolic compounds (phenol, cresol, xylenol, catechol, resorcinol, etc.), heterocyclic nitrogen compounds (pyridine, quinoline, isoquinoline, indole, etc.), and oxygen heterocyclic compound (dibenzofuran, etc.), which all have been 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.) [2]. Therefore, a detailed analytical study on the composition and chemical structure of coal tar will be advantageous to its processing and utilization. Furthermore, paraffinic and oleophinyc compounds which can be used as liquid fuel are also contained in coal tar. When being processed, the very complicated compounds of the coal tar will be splitted to simple products with higher economic value [3].

This purposes of the research are expected to drive the next research on coal in Indonesia especially in Kalimantan to produce components which are still have high economic value. Although lots of studies related to coal utilization have been conducted, studies concerning coal tar are relatively rare. Some researchers have studied the coal pyrolysis and coal tar component separation [4]-[14].

This research studied the pyrolysis process of coal to obtain the characteristics of Kalimantan coal tar. It is believed that GC-MS can carry out analysis of the complex composition of coal tar. In this study, an experimental research on coal pyrolysis was conducted in a pyrolysis reactor furnace, with coking-coals as the feeding material. A detailed composition analysis was carried out on the coal tar generated in the experiment, therefore a satisfactory analytical result obtained, which offers a referable theoretical foundation for the further processing and utilization of coal tar.

## II. MATERIALS AND METHOD

### A. Material

The coal samples was obtained from PT Kaltim Prima Coal and Arutmin-Kalimantan (density: 1.34 g/cc; color: black; shape: granular; size: 10-20 mesh). Other supporting materials

D. S. Fardhyanti and A. Damayanti are with the Department of Chemical Engineering, Faculty of Engineering, Semarang State University, Semarang 50229, Indonesia (phone: +62-24-8508101 Ext.114; fax: +62-24-8508101 Ext.109; e-mail: dewiselvia@yahoo.com).

are such as glasswool and N<sub>2</sub> gas.

### B. Experimental

The schematic diagram of coking-coals pyrolysis is shown in Fig. 1.

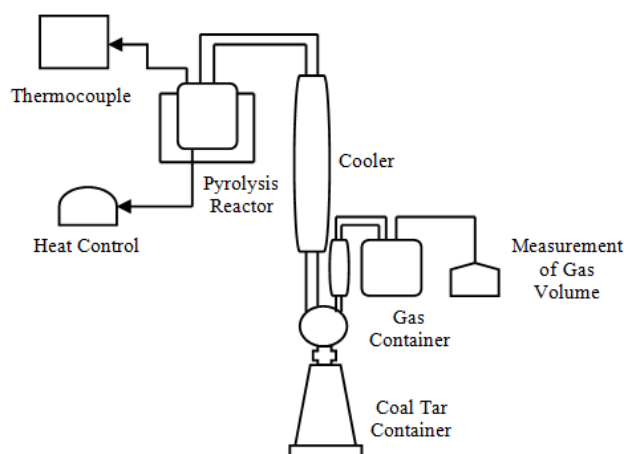


Fig. 1 Equipment of Coal Pyrolysis and Products Separation

Pyrolysis process is conducted by following the procedures that have been used by [15]. A number of coals are crushed into 10-20 mesh size, afterwards are dried. Coal sample is weighed as much as 1,350 g, and is used as feed. The coal feeds are fed into pyrolysis reactor and heated gradually. The increasing temperature of 30°C per minute and N<sub>2</sub> gas flow rate of 100 mL per minute. Nitrogen gas has been used to obtain the inert condition and to carry the gaseous pyrolysis products. The gas was condensed and the liquid containing oil/tar and water was obtained. The temperature attained at 400°C and settled for 15 minutes, then it raised up to 500°C. After the temperature attained at 650°C, the heating process is stopped and the coal tar is obtained. The reactor temperature decrease with N<sub>2</sub> carrier gas is still turned on, so there is still a residual gas which can come out. Tar is collected in a container with ice cooling system. The results are stored in the refrigerator and used for the next step. Coal tar is analyzed for its components and concentration by using GC-MS. From the analysis by GC-MS on coal tar, it will be obtained the concentration of each component i. eventually, the coal tar was analyzed its compositions using GC-MS. The principal conditions of this analysis are shown in Table I.

### III. RESULTS AND DISCUSSION

The pyrolysis process of 1,350 g coals produced 360.5 mL coal tar and the product conversion was 36.70% (w/v) (PT KPC) and 25.77% (w/v) (Arutmin-Kalimantan). The process took 3 hours, produced liquid compound consisting of two layers. The top layer was black and the bottom one was yellow. The coal tar has so many various components and it depends on the time and temperature of the process. The components of coal tar were also very complex which have various types of hydrocarbon compounds with a lot of

molecular weight range.

TABLE I  
CONDITIONS OF ANALYSIS USING GC-MS  
GC-MS: GCMS-QP2010S Shimadzu

Column: Rastek RXi-5MS		
Column:		
Inner diameter	[m]	2.5 x 10 <sup>-4</sup>
Length	[m]	30
Carrier gas	-	He
Split ratio	[-]	153
Flow rate	[cm/sec]	26.6
Sample volume	m <sup>3</sup>	1.10 <sup>-9</sup>
Injection temp.	[K]	583
Column temp.	[K]	313 – 578
Pressure column	kPa	10.0
Column flow	mL/min	0.54
Detector (FID) temperature	[K]	583

The pyrolysis process is not a simple destructive reaction; the result of thermal degradation products depends on of the process conditions. Pyrolysis reaction of coal to produce tar was occurred in several stages, called degasification or decomposition. The first stage of decomposition was the breaking of the carbon bonds alifatis (at low temperature), followed by the breaking of C-H bonds and the elimination of the complex hetero ring. The maximum decomposition occurred at temperatures between 450-700°C. If the pyrolysis process temperature was 450-700°C, a process called low temperature carbonization; when temperatures above 900°C were called high temperature carbonization. The low temperature carbonization produced less gas and more liquid substance but the high temperature carbonization produced more gas and less liquid substances. Low temperature carbonization produced liquid substances that was very different of liquid substances was produced by the high temperature carbonization, although it was used the same coal. Liquid substances that were produced by low temperature carbonization contained more tar acids and tar bases than liquid substances were produced by the high temperature carbonization.

The pyrolysis reaction needed a specific time, the decomposition would not be complete in a short time reaction (more reactions on the decomposition stage were not complete). But the long time reaction effected on the amount of gas released. The pyrolysis time increased the possibility of the products collided each other and on the reactor wall. It caused the formation of molecules with higher hydrocarbon chains (secondary reaction of destructive distillation, where it produced a larger compound). It made very difficult to split back and caused the conversion products of coal tar low [16].

The time of pyrolysis also caused so many volatile substances in the coal tar were released and produced a lot of heavy fraction compounds; the upper layer was called the asphaltene. It will reduce the process efficiency because the processing was much more difficult and the product contained many impurities, such as inorganic compounds, sulfur and

other substances. The pyrolysis transformed organic materials into gaseous components, small quantities of liquid, and a solid residue (coke) containing fixed amount of carbon and ash. The composition of gas which is produced from the pyrolysis is carbon monoxide, hydrogen, methane, and other hydrocarbon compounds.

Coal pyrolysis is processed (at low temperature, 450-600°C) to obtain coal tar and to find out the components

contained in the coal tar so that the artificial coal tar that will be used in the study has a composition which is similar to the real coal tar. The obtained coal tar has the viscosity of 3.12 cp, the density of 2.78 g/cm<sup>3</sup>, the calorific value of 11,048.44 cal/g, and the molecular weight of 222.67. The chromatograms of GC-MS analysis are showed in Figs. 2 and 3.

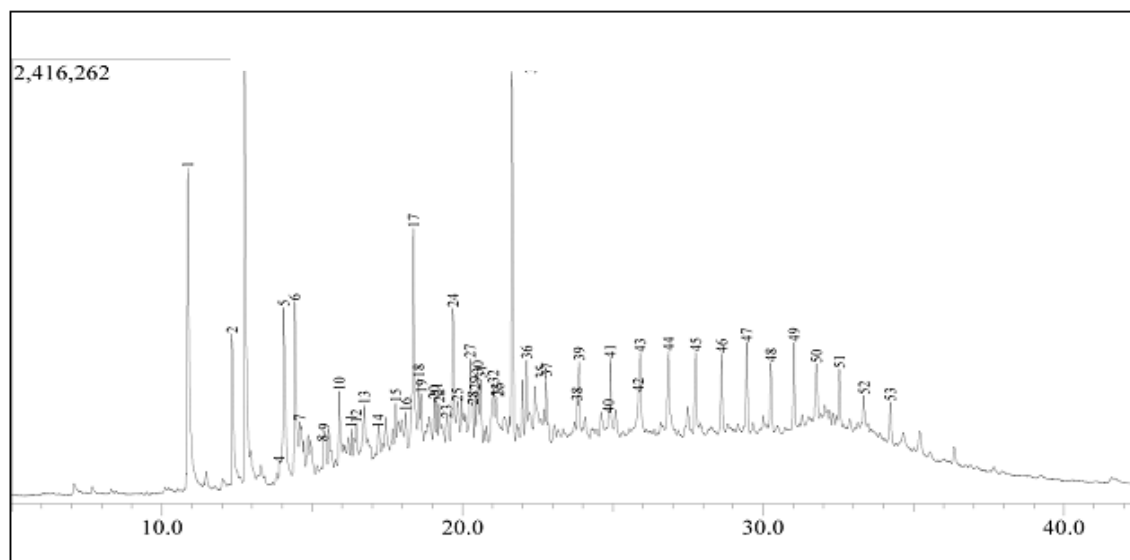


Fig. 2 Typical gas chromatogram of the components of PT KPC coal tar

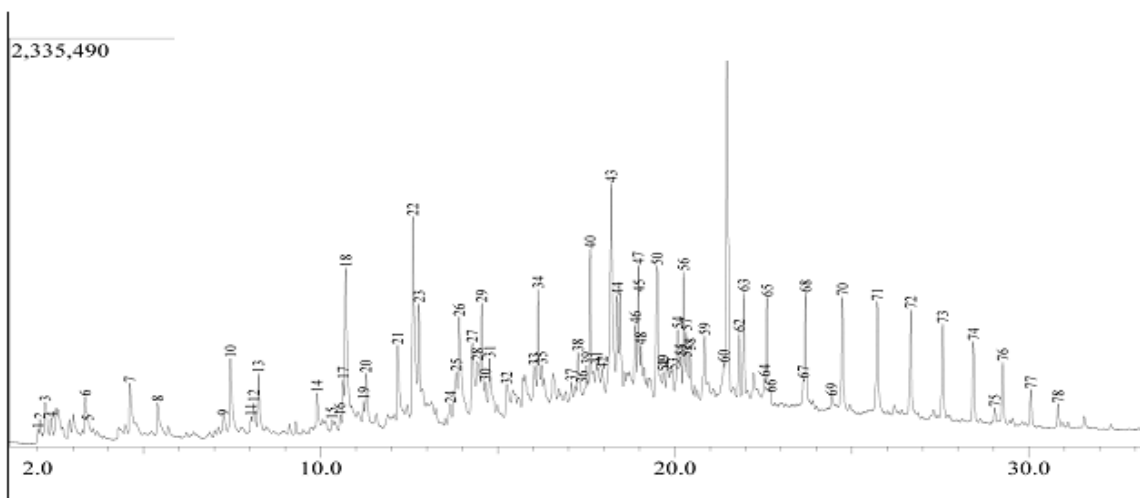


Fig. 3 Typical gas chromatogram of the components of Arutmin-Kalimantan Coal Tar

The results of GC-MS analysis of the coal tar showed that it contained more than 78 chemical compounds such as benzene, phenol, naphthalene, and others. The main components of each coal tar are showed in Tables II and III. Tables I and II represent that PT KPC and Arutmin-Kalimantan coal tar contain more than 5 main components.

They are phenolic compounds and naphthalene compounds.

It showed that coal tar contains so many tar light oil and tar creosote oil. 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 78 components. The total phenolic compounds which contained in coal tar are 33.25% (PT KPC) and 17.58% (Arutmin-Kalimantan). The total naphthalene compounds which

contained in coal tar are 14.15% (PT KPC) and 17.13% (Arutmin-Kalimantan). It was caused of the pyrolysis process is carried out at a temperature of 450-700°C (low temperature carbonization) which will produce a substance that contains more tar acid and tar base [17].

TABLE II  
THE COMPOSITIONS OF PT KPC COAL TAR

Peak Number	Compounds	Percentage (%)
1	Phenol	8.06
2	2-methyl phenol ( <i>o</i> -cresol)	3.45
3	4-methyl phenol ( <i>p</i> -cresol)	11.06
5	2,4-dimethyl phenol	5.13
6	3-ethyl phenol	5.55
17	1,8-dimethyl naphtalene	5.50
34	1,6-dimethyl-4-isopropyl naphtalene	8.65

TABLE III  
THE COMPOSITIONS OF ARUTMIN-KALIMANTAN COAL TAR

Peak Number	Compounds	Percentage (%)
18	Benzene	1.63
22	Phenol	3.89
40	4-methyl phenol ( <i>p</i> -cresol)	4.90
43	1,8-dimethyl naphtalene	5.94
50	1,2,3,4-tetrahydro-1,1,6-trimethyl naphtalene	3.08
61	1,6-dimethyl-4-isopropyl naphtalene	8.11

#### IV. CONCLUSION

Coal tar is a significant product generated from coal pyrolysis. Using a method of gas chromatograph/mass spectroscopy (GC/MS), this work presents a composition of Kalimantan coal tar generated in the experiment. The analysis offers a referable theoretical foundation for the further processing and utilization of coal tar.

The obtained coal tar has the viscosity of 3.12 cp, the density of 2.78 g/cm<sup>3</sup>, the calorific value of 11,048.44 cal/g, and the molecular weight of 222.67. The results of GC-MS analysis of the coal tar pyrolysis results indicate that coal tar contains more than 53 components. The total phenolic compounds contained in coal tar are 33.25% (PT KPC) and 17.58% (Arutmin-Kalimantan). The total naphtalene compounds contained in coal tar is 14.15% (PT KPC) and 17.13% (Arutmin-Kalimantan). This is logical, since the pyrolysis process was carried out at a temperature of 450-700°C (low-temperature carbonization) which will produce a substance that contains more tar acid and tar base.

#### ACKNOWLEDGMENT

Authors would like to thank the Directorate General of Higher Education, Ministry of National Education, Indonesia, for financial support of this work through the research grant of "Hibah Bersaing" Universitas Negeri Semarang (UNNES) 2015.

#### REFERENCES

- [1] R. K. Hesley, J. W. Reasoner, and J. T. Riley, *Coal Science, An Introduction to Chemistry Technology and Utilization*, Mc Graw-Hill Publishing Company Limited, London (1986).
- [2] R. Egashira, M. Nagai, and C. Salim, Separation of Nitrogen Heterocyclic Compounds Contained in Coal Tar Absorption Oil Fraction by Solvent Extraction. *6<sup>th</sup> World Congress of Chemical Engineering*. Melbourne. Australia (2001).
- [3] J. Hayashi, S. Amamoto, K. Kusakabe, and S. Morooka, Evaluation of Vapor Phase Reactivity of Primary Tar Produced by Flash Pyrolysis of Coal, *Energy & Fuels*, vol. 9, pp. 290-294, 1995.
- [4] A. Matsumura, S. Sato, and I. Saito, Solvent Extraction of Hetero-Compounds from Coal liquid, *Nippon Enerugi Gakkai Sekitan Kagaku Kaigi Happpo Ronbunshu*, vol. 35, pp. 415-418, 1998.
- [5] B.C. Elina, and N.F. Iraj, Quantitative Analysis of Phenol and Alkylphenols in Brazilian Coal Tar, *Quim Nova Journal*, vol. 27, no. 2, pp. 193-195, 2004.
- [6] Y. Kodera, K. Ukegawa, Y. Mito, M. Komoto, E. Ishikawa, T. Nakayama, Separation of Phenolic Compounds from Coal Liquids, *Fuel*, vol. 70, no. 6, pp. 765, 1991.
- [7] A.P. Catherine, and G.L. Richard, G.L., Semiempirical Thermodynamic Modelling of Liquid-liquid Phase Equilibria: Coal Tar Dissolution in Water-Miscible Solvents, *Environmental Science Technology*, vol. 28, no. 7, pp. 1331-1340, 1994.
- [8] J. Jianfang, W. Qiyu, W. Yingyu, T. Weicheng, and X. Bo, GC/MS Analysis of Coal Tar Composition Produced from Coal Pyrolysis, *Bulletin Chemical Social Ethiopia*, vol. 21, no. 2, pp. 229-240, 2007.
- [9] B. Setiaji, I. Tahir, and D. Wahidiah, Pemisahan Komponen Tar Batubara dengan Kolom Fraksinasi Menggunakan Fasa Diam Zeolit-Mn, *Berkala MIPA*, vol. 16, no. 1, pp. 11-18, 2005.
- [10] W.B. Sediawan, H. Sulisty, and Widyastuti: Perengkahan Termal Parafin-parafin Rantai Panjang dari Tir Batubara, *Forum Teknik*, vol. 24, no. 1, pp. 10-19, 2000.
- [11] N. Rokhati, S. Warnijati, and I.M. Bendiya: Pirolisis Tir Batubara secara Sinambung, *Teknosains*, vol. 12, no. 2, pp. 135-149, 2000.
- [12] R. Egashira, and J. Saito: Solvent Extraction of Coal Tar Absorption Oil with Continuous Countercurrent Spray Column, *Journal of the Japan Petroleum Institute*, vol. 50, no. 4, pp. 218-226, 2007.
- [13] R. Egashira, and C. Salim: Separation of Coal Tar Distillate by Solvent Extraction – Separation of Extract Phase Using Distillation, *Journal of the Japan Petroleum Institute*, vol. 49, no. 6, pp. 326-334, 2006.
- [14] R. Egashira, C. Salim, and J. Saito: Separation of Coal Tar Fractions by Solvent Extraction – Extraction/Solvent Separation by Secondary Extraction, *Journal of the Japan Petroleum Institute*, vol. 48, no. 1, pp. 60-66, 2005.
- [15] L. Suyanti, *Kinetika Reaksi Pirolisis Tir Batubara dengan Menggunakan Katalis*, Tesis Program Pasca Sarjana, Universitas Gadjah Mada, Yogyakarta (2000).
- [16] A.A. Lappas, D. Pappavasilou, K. Batos, and L.A. Vasalos, Product Distribution and Kinetic Prediction on Greek Lignite Pyrolysis, *J. Fuel Chem*, vol. 69, pp. 1304-1308, 1990.
- [17] R.S. Ebbe, C.E. Dennis, G.R. Franklin, and J.W. Robert, Coal-Tar Chemicals and Syncrude Oil Production from Low-Rank Coals Using Mild-Temperature Pyrolysis, *AIChE Spring National Meeting*, Houston, Texas, April 22-26 2007.