THE ANALYZED OF TAR AS WASTE MATERIAL OF BITUMINOUS COAL GASIFICATION BY USING GASCHROMATOGRAPHY

Rijal Abdullah[1] dan Hengki Ade Satria[2]
[1]Department of Civil Engineering, Fakulty of Engineering, Universitas Negeri Padang
[2]Department of Mining, Fakulty of Engineering, Universitas Negeri Padang

ABSTRACT: The aims of this research is to detemine chemical compounds of TAR in bituminious coal gasification. The method used is experimental research. The coal Tar was collected by gasification process to bituminous coal which obtained from PT. NAL Sawahlunto. Commontly, the Graded of coal as much as 7.554.20 kcal/kg of calories, a flying substance of 39.62%, water content of 5.88% and ash of 4.21%. The gasification process has been carried out by using reactor tube with temperatures ranging from 800 to 1000°C with an air quantity of 6.93 l/s and a duration of testing of 2700 s. The result shows that the coal tar has 241 chemical compounds, such as benzene, heptadecane, eicosane, 2-Methyl-2-(alpha-thienyl)-1,3-dithiolane, 9-Octadecenoic acid (Z)-phenylmethyl ester (CAS) Benzyl oleate, and etc.

Keywords: *waste material,reactor tube, experiment research*

1. INTRODUCTION

The use of coal as a source of energy can be done by direct combustion, but it would be better if the coal is converted form of synthetic oil, among others by likuifikasi or gasification, because it can improve the effectiveness and efficiency.

Coal liquefaction is to convert coal into synthetic liquid fuel, by way of reacting coal with hydrogen at high temperature and pressure. While gasification is the conversion of coal into gas by way of combustion. The main product of gasification is referred to as syngas or also known as synthetic gas.

Miller (2005), Arif (2012), Sunggyu Lee (2007) gasification is a process for upgrading solid hard coal conditions by disposing of impure components and converting them into purified gases and can be utilized directly as fuel or more he continued reacted to produce other gases or liquid fuels and chemicals.

Synthesis gas as the main product of coal gasification can be utilized for the process of fischer tropsch, and to produce chemicals such as methanol and ammonia. In addition, the synthesis gas that has the combustible properties can also be utilized in the field of machining such as for combustion engines (internal combustion engine).

Arif (2012) states that in addition to producing syngas, coal gasification also produces char or charcoal and coal tar. This occurs because in the reactor design there is no source of combustion other than by simply relying on the initial combustion for the oxidation zone. Coal for gasification feeds has a coal ash content of not more than 10%. Meanwhile, the higher the volatile matter the higher the gas product, and the high fixed carbon value will enhance the performance of gasifier.

Arif (2012) Sunggyu Lee (2007) found that many tar as a byproduct that became the impurity of syngas. The more dominant tar is usually produced from bituminous coal. Tar obtained by about eight gallons per ton of coal (Speight, 2005).

Coal Tar is a mixture of complex compounds composed of several compounds with different functional groups and predominantly poliaromatic compounds. This compound causes coal tar to be a dangerous and toxic substance (B3 waste). The physical and chemical properties of tar are almost similar to petroleum but the coal tar has a high polyaromatic and impurity rate. Nevertheless tar has many benefits and uses. If the tar content is analyzed first and further processing is done then tar can be used as raw material in petrochemical industry, cosmetics, medicine, fuel, and others. Therefore tar became one of the commodity raw materials industry is quite expensive.

One of the largest tar producing countries is China, from Chongqing Jupeng Energy Co., Ltd. The tar-producing company sells coal tar at a price ranging from US $ 480 to US $ 750 / metric ton or equivalent to Rp 6,394,723.45 to Rp 9,991,755.39 /metric ton (Coal Tar Price Year 2017). While coal with 6,322 kcal / kg calories cost about US $ 86.23 /ton or equivalent to Rp 1,148,785.42 / ton. (Coal Price January 2017).

In general (Anonymous) in coal there are benzene with various derivatives that are very

useful for the industry. Toluene, benzoate Acid, Phenol, TNT, TNB, Nitrobenzene, and Paracetamol.

The high economic value of tar (as a by-product of coal gasification) should be a consideration for us to conduct a study of its potential. This is what encourages researchers to study the analysis of coal tar composition.

Fardhyanti and Damayanti, using gas chromatography tool (GC-MS) in analyzing tar from coal production of PT. KPC and PT. Arutmin, finds the results as in Table 1 below.

Table 1 Composition of Coal Tar in Kalimantan (PT. KPC dan PT.ARUTMIN).

THE COMPOSITIONS OF PT KPC COAL TAR

Peak Number	Compounds	Percentage (%)
1	Phenol	8.06
2	2 methyl phenol (o cresol)	3.42
3	4 methyl phenol (p cresol)	11.06
5	2,4-dimethyl phenol	5.13
6	3 ethyl phenol	5.33
17	1,8-dimethyl naphtalene	5.50
34	1,6-dimethyl-4-isopropyl naphtalene	8.65

THE COMPOSITIONS OF ARUTMIN-KALIMANTAN COAL TAR

Peak Number	Compounds	Percentage (%)
18	Benzene	1.53
22	Phenol	3.89
40	4-methyl phenol (p-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

Source: International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering Vol:9, No:8, 2015.

The analyzed tar is the result of the process of pyrolysis of Kalimantan sub bituminous coal from PT. KPC and PT. Arutmin. With the analysis, it can be known what components are contained in coal tar and can be utilized again in meeting the needs of petrochemical industry and other industries so that tar can have higher economic value.

Based on the two types of research mentioned above, the authors are interested to analyze the tar content resulting from the process of bituminous coal gasification of PT products. NAL Sawahlunto uses gas chromatography analyzer (GC-MS).

2. RESEARCH METHODOLOGY

2.1. Materials Research

The material used in this research is bituminous coal PT. NAL Sawahlunto with water content (ar) 5.88%, fixed carbon (adb) 52.79%, flying substance (volatile matter, adb) 39.62, ash (ash content, adb) 4.21%.

2.2. Research Stages

There are two main steps in this stage, namely Coal Analysis and Coal Gasification.

2.2.1. Coal Analysis

After obtaining coal in underground mining PT. NAL Sawahlunto as gasification experiment material, then analyzed to the coal sample. Coal analysis revealed moisture, volatile, ash, fixed carbon, and calorie values. Furthermore, preparation of coal size using jaw crusher before feeding to gasification reactor.

2.2.2. Coal gasification

In the gasification process the researchers determined experimental variables based on Arif's research (2016) with the following data (see Table 2).

Table 2. Gasification Experiment Variable

Mass of coal (kg)	d_p of coal (mm)	Amount of air (liter/s)	Measurement time (s)
1,3	15	6,93	2700

Arif (2016)

Coal Gasification Procedures

a. Open the lid of the reactor to refill the prepared coals as much as 300 grams which has been given kerosene as the initial burning in the oxidation zone, then light the fire and wait until the coal becomes red-hot.
b. After that reinsert the prepared coal until it fills the entire contents of the reactor. Close the reactor and turn the oxidizing gas flow into the reactor. Right at that time the thermocouple was in a state of being measured.
c. Turn the air flow into the reactor
d. Let the gasification process proceed until the formation of brownish smoke as a sign that the sistesis and tar gases have formed.
e. When synthesis gas is still formed, the valve is opened in the sampling pipe to take a sample of tar that is connected to the pipe into a container that has been filled with water.
f. The gasification ends at 2700 seconds. Wait a while until the reactor temperature is low, then move the tar from the water-filled container to the provided sample container. open the lid of the reactor and remove the coal char.
g. Perform the same procedure for the next gasification test to add tar.
h. After all tests are completed, take the tar sample to the laboratory for analysis using a gas chromatographic tool.

2.2.3. Gas Chromatography (GC-MS)

Before tar was analyzed by gas chromatography (GC-MS) the samples were first prepared using toluene. The prepared tar is 0.05 grams with toluene 0.5 ml. Tar injected into a 2 micron GC-MS gas chromatograph.

The test variables are based on previous research conducted by D.S Fardhyanti and A. Damayanti as seen in Table 3 below.

Table 3. Chromatographic Experiment Variables Gas

Temperature of injection	583 K
Temperature of colom	313-578 K
Pressure of colom	10 kPa
Temperature do detector	583 K
Curren of colom	0,54 ml/menit

In the tar analysis process using GC-MS tool, it is tested three times, by distinguishing the injection temperature. Injection temperature used ie 290^0 C, 300^0C, and 310^0C.

Gas Chromatography Testing Procedure

a. Before the operation, the instrument is checked, whether the column is as desired. Is the septum in the injection port still good not leaking. Is the detector already installed according to the desired and others.
b. The gas stream starts with a low flow rate by opening the main and secondary valves of the carrier gas tank to indicate a 15 psi needle, this allows the carrier gas flow of 2-5 ml / min for the gasket column or 0.5 ml / min for the capillary column. Next check whether there is leakage of gas at the connection to the column and exit the column using soap spray.
c. The column is heated to the desired initial temperature, the detector temperature is set to 10-25 ° C higher than the column temperature, as well as the injection port temperature.
d. The velocity of the gas stream is then increased to 25-30 ml / min or until an optimum gas flow rate is reached.
e. The detector used is Mass Spectroscopy with helium gas as the carrier phase.
f. The volume of the injected sample is 2 microns. During elution ie during the sample trip from the injection port to the detector, if the column temperature is maintained constant, such elution is called Isothermal Elution. While Elusi with programmed temperature (temperature programming) is over elusi the column temperature is set up gradually at a certain rate, or set to rise at a certain temperature and held to its temperature. (linear and increase varied).
g. The signal from this detector will be recorded as a chromatogram on a simple or microprocessor-treated recorder displayed on the monitor screen.
h. In the chromatogram displayed by the microprocessor at once can know the level of each component by performing qualitative and quantitative analysis..
i. The results of composition analysis of coal tar as a by-product of bituminous coal gasification PT.NAL Sawahlunto.

The gasification process is done by using fixed bed reactor with 1,3 kg of coal mass with 6.93 L / s air quantity, measuring time for 45 minutes (2700 seconds) and testing temperature up to 1000oC. The tar analysis was performed using GC-MS under the brand Shimadzu GC-2010 Plus. Conditions running using wiley type library, injection temperature 310 ° C using Rtx-5MS capillary column with 40 ° C to 305 ° C, the carrier gas used is helium gas with a pressure of 10 Kpa and a total flow of 0.54 mL / min and samples are injek as much as 2µL. Based on the results of the experiment it is known that benzene compounds and derivatives are more dominant in coal tar. As seen in the table of each of the following experiments.

Experiment I

Table 4. Dominant Components in Coal Tar Trial One

Peak	Compound		Percent
	Name	Type	(%)
2	Benzene (CAS) Phene	Aromatic	0,33
6	9-Octadecenoic acid (Z)-phenylmethyl ester (CAS) Benzyl oleate	Aromatic	
12	Benzene, ethyl- (CAS) EB	Aromatic	
13	Benzene, 1,2 dimethyl- (CAS) o-Xylene	Aromatic	
30	Benzaldehyde (CAS) Phenylmethanal	Aromatic	
45	Benzenemethanol (CAS) Benzyl alcohol	Aromatic	
133	Benzeneacetic acid, alpha, 3,4-tris[(trimethylsilyl)oxy]-,trimethilsilyl ester (CAS) TETRAKISTRIMETHYL	Aromatic	
139	1,2-Benzenedicarboxylic acid, dioctyl ester (CAS) Dioctyl phthalate	Aromatic	
Total			13,08

Experiment II

Table 5. The Dominant Components in Coal Tar In the second testing

Peak	Compound		Percent
	Name	Type	(%)
41	9-Octadecenoic acid (Z)-phenylmethyl ester (CAS) Benzyl oleate	Aromatic	4,76
48	Benzene, ethyl- (CAS) EB	Aromatic	1,36
49	Benzene,1,2-dimethyl-(CAS) o-Xylene	Aromatic	0,83
55	Benzene,1,2-dimethyl-(CAS) o-Xylene	Aromatic	0,52
67	Benzaldehyde (CAS) Phenylmethanal	Aromatic	2,40
214	Benzeneacetic acid, alpha,3,4-tris[(trimetylsylil)oxy]-, trimethylsilyl ester (CAS) TETRAKISTRIMETHYLSI	Aromatic	0,43
223	1,2-Benzenedicarboxylic acid, dioctyl ester(CAS) Dioctyl phthalate	Aromatic	0,26
Total			10,56

Percobaan III

Tabel 6. Komponen yang Dominan dalam Tar Batubara Percobaan Tiga

Peak	Compound		Percent
	Name	Type	(%)
4	Benzene (CAS) Phene	Aromatic	0,34
18	Benzene, ethyl-(CAS) EB	Aromatic	1,52
19	Benzene, 1,2-dimethyl-(CAS) o- Xylene	Aromatic	1,18
23	Benzene, 1,2-dimethyl-(CAS) o- Xylene	Aromatic	0,55
35	Benzaldehyde (CAS) Phenylmethanal	Aromatic	2,53
187	Benzenaecetic acid, alpha,3,4-tris[(trimethylsilyl)oxy]-, trimethylsilyl ester (CAS) TETRAKISTRIMETHYLSI	Aromatic	0,56
195	1,2-Benzenedicarboxylic acid, dioctyl ester (CAS) Dioctyl phthalate	Aromatic	0,36
Total			7,04

3. CONCLUSIONS AND SUGGESTIONS

Based on the analysis of tar by-product of bituminous coal gasification PT. NAL Sawahlunto using GC-MS tool was known that the more dominant component in tar is benzene compound.

Based on the research that has been done, there needs to be gasification testing for various levels of coal and analyzing the composition of tar produced, and the need for economic study of the tar.

4. REFERENCES

[1] Algifari, Arif. (2016). *Studi Eksperimen Pengaruh Luas Permukaan Batubara dan Laju Alir Udara Terhadap Pembentukan Syngas pada Rancangan Reaktor Gasifikasi Fixed Bed*. Skripsi 1-45. Padang: Universitas Negeri Padang.

[2] Anonim. *Manfaat dan Kegunaan Benzena dan Turunannya*. [Online] Tersedia: http://kimiastudycenter.com/kimia-xii/39-manfaat-kegunaan-benzena-dan-turunannya#ixzz4VC0UA4zR [Tanggal akses 8 Januari 2016] [23:48]

[3] Fadhyanti, D.S dan Damayanti, A. (2015). *Analysis of Coal Tar Compositions Produced from Sub-Bituminus Kalimantan Coal. International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering* (Vol:9, No:8, Tahun 2015).

[4] Lee, Sunggyu. 2007. *Handbook of Alternative Fuel Technology*. Boca Raton: CRC Press.

[5] McNair, Harold M dan Bonelli, Ernest J. 1988.*"Dasar Kromatografi Gas"*. Bandung: ITB Bandung