CHARACTERIZATION AND COMPARATIVE STUDY OF PYROLYSIS OF LOW RANK COAL AND BIOMASS

Rinny Jelita, Iryanti Fatyasari Nata, Chairul Irawan, Jefriadi, Muhammad Hafiz, Indrayati Angreini, Meilana Dharma Putra

Department of Chemical Engineering
Lambung Mangkurat University
Jl. A. Yani Km. 35 Banjarbaru 70714, Indonesia
Email: mdputra@ulm.ac.id

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ABSTRACT

Low rank coals are not used optimally, another way to increase this value is combustion without oxygen, known as pyrolysis. On the other hand, as a solid waste biomass, palm kernel shell (PKS) is a by-product of the palm oil industry that can cause environmental problems if not handled properly. In fact, the waste is plentiful and not even widely used, therefore it may also be an ideal feedstock for the pyrolysis process. This study compares the distribution of products from coal and PKS pyrolysis, and also characterizes the liquid (tar) and solid (char) products. The results show that the pyrolysis of coal produces more char, while the pyrolysis of PKS produces more gas. Higher tar yields were obtained with the pyrolysis process using PKS. GC-MS identified the main tar compounds for both materials as phenol and acetic acid, 3-methylphenol and methanol were also found in coal and PKS, respectively. The calorific value of char increased by about 5.19 % for coal and 41.12 % for PKS after pyrolysis. The other physical properties of coal and PKS are also improved after pyrolysis. Therefore, the application of pyrolysis in the use of coal and PKS can increase the added value of these two materials and contribute to alternative energy sources.

Keywords: pyrolysis, low rank coal, biomass, value-added, alternative energy.

INTRODUCTION

Low rank coals such as lignite and subbituminous have less economic value because the main composition contains volatile matter and moisture with low fixed carbon content. On the other hand, environmental problems due to waste and depletion of fossil fuels encourage researchers to develop alternative fuels based on biomass such as palm kernel shell (PKS). PKS are the residue of palm oil processing that contains a lot of chemical compounds thus having potential to be developed into fuel. A combustion process without oxygen such as pyrolysis is needed to increase the use value of these materials. Compared with other materials, biomass is environmentally providential resource and could provide renewable energy. In addition, its high thermochemical reactivity and high volatile substance content are conducive to pyrolysis reaction [1]. The solid product resulted from pyrolysis can be used as a material for fuel briquettes.

Several studies related to biomass and coal pyrolysis have been carried out [2 - 5]. Abdelsayed et al. studied the effects of temperature and microwave heating on the structural properties of the chars, tar and gaseous produced during pyrolysis [6]. Some pyrolysis of PKS are conducted with internal circulation of heavy oil [7]. Liew et al. produces the activated carbon used as catalyst support [8] and Wang et al. tried to find physico-chemical properties evolution of chars through pyrolysis of PKS [9]. Most pyrolysis processes using coal are carried out by mixing biomass as called co-pyrolysis [1, 10 - 12].

Utilization of coal and PKS through appropriate processes such as pyrolysis can produce potential products, thus it becomes interesting to develop.

Pyrolysis becomes a potential process to be an efficient route to convert biomass into bioenergy and bio-refinery products. Our research aims to compare distribution of the pyrolysis products of coal and biomass, and also to characterize the products of liquid (tar) and solid (char). This research provides a new alternative source of energy based on coal and PKS as an efficient and inexpensive product.

EXPERIMENTAL

Materials

PKS was obtained from PT. Perkebunan Nusantara XIII Pelaihari, Tanah Laut District, South Kalimantan, Indonesia. It consists of hemicellulose (18.84 %), cellulose (32.79 %) and lignin (33.745 %). Coal was obtained from Asam-Asam, Tanah Bumbu District, South Kalimantan, Indonesia.

Pre-treatment of Raw Material

The coal was milled and sifted to 0.3 - 1 mm. The PKS were cleaned, cut into pieces and sifted to a size of 0.4 - 2 mm. The materials were then dried at 105ºC for 24 h in an oven. This process was conducted to eliminate moisture content thus preventing rotting [3]. The analysis of lignocellulose content, proximate and calorific value of the raw material was conducted.

Pyrolysis of Coal and Biomass

Two hundred g of coal were put into the reactor and heated at temperatures of 400^{o}C for 1 h with 1.5 L min^{-1} of nitrogen gas flow rate. The liquid (tar) and solid product (char) resulted from co-pyrolysis were weighed. After completion of the reaction, the reactor was cooled up to room temperature and char was then collected. The same procedure was repeated for the PKS. The chemical content of tar was analysed as well as the calorific value and proximate from solid products.

Characterization

Identification of liquid compound was conducted by using Gas Chromatography- Mass Spectroscopy (GC-MS) (QP2010S SHIMADZU) equipped with Column Rastek RXi-5MS, length 30 m, ID 0.25 mm, helium carrier gas, EI ionization and 70 eV. Quantification of calorific number was performed by using bomb calorimeter (Gallenkamp Adiabatic Bomb Calorimeter CBA-305). Proximate analysis was determined according to ASTM D3172-07a.

RESULTS AND DISCUSSION

Pyrolysis Product of Coal and PKS

Fig. 1 shows the yield of distribution of tar, char and gas obtained from pyrolysis process. The products were processed by depolymerizing and fragmenting the material of coal and biomass. Pyrolysis of coal produced high char (63.7 %) and low tar (10.98 %), while yield of gas is about 25.32 %. This result of char in this research was in accordance with the pyrolysis process of Xilinhot lignite observed by Li et al. as the process yielded char (67.68 %) accompanied with the medium production of gas (17.11 %) and low production of water (9.40 %) and tar (5.81 %) [11]. The observed biomass pyrolysis temperature range is 200 to 400°C, while the coal pyrolysis temperature range is 350°C to 650°C [10]. It indicates that the pyrolysis of coal has just begun, and it is still possible to increase the yield of some of its products.

PKS pyrolysis produces gas of 52.74 %, tar of 23.63 % and char of 23.63 %. In the pyrolysis process, PKS was decomposed into tar and gas more than solid products (char) because of the higher cellulose content. The content of cellulose triggers an increase in tar yield. Lignin compound is the main component to produce the char, while the hemicellulose contributes to yield the tar and gas [13]. The yield of PKS tar produced throug this pyrolysis is lower than the research results conducted by Huang et al. as the yield of tar of 50 % and char of 34.8 % [7]. Rock et al. observed the pyrolysis of the

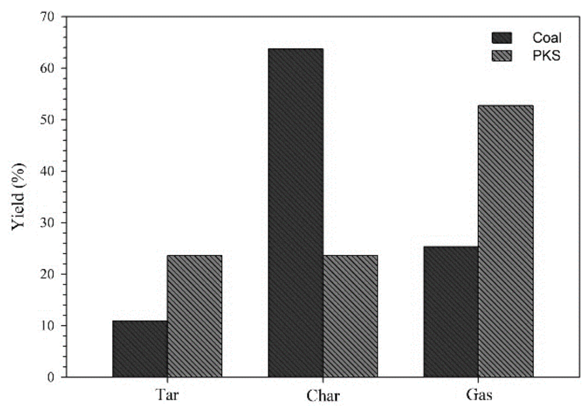

Fig. 1. Distribution of pyrolysis product.

same biomass with the char yield of 40 % [8], while the process investigated by Lam et al. resulted in a dark biochar of fruit peel with pyrolysis yield of 30.7 % - 47.7 % [2]. This difference can be explained by the different composition of the raw materials as the value of tar yield is dependent on the type of raw material used. On the other hand, the value of the tar yield highly depends on the temperature, heating rate, particles, type, and composition of the raw materials [4, 14].

Characterization of Tar

The liquid product (tar) resulted from the pyrolysis of coal and PKS has characteristic of blackish brown in color with a pungent odor. The liquid product contains an organic phase and higher water content. To find the composition of the compound from the tar produced by pyrolysis of coal and PKS, the mixture of compounds was passed through gas chromatography (GC) and then separated into individual components. The results of the GC-MS analysis of tar are shown in Figs. 2 and 3.

As observed in Figs. 2 and 3, the coal tar chromatogram consists of 26 peaks and PKS tar chromatogram consists of 47 peaks. Those indicate the number of compounds contained in the tar product. Each peak represents the compounds contained in tar; the component was identified by matching the compounds stored in the data bank. The major components identified in the tar product are presented in Table 1. It shows the compounds found in coal tar and PKS as those consist of phenolic compounds, acids, aldehyde, esters, alkanes and ketones. The composition of the raw material structure affects the results in co-pyrolysis product, it was observed that some of the chemical compounds in PKS tar were not found in coal, vice versa. The pyrolysis

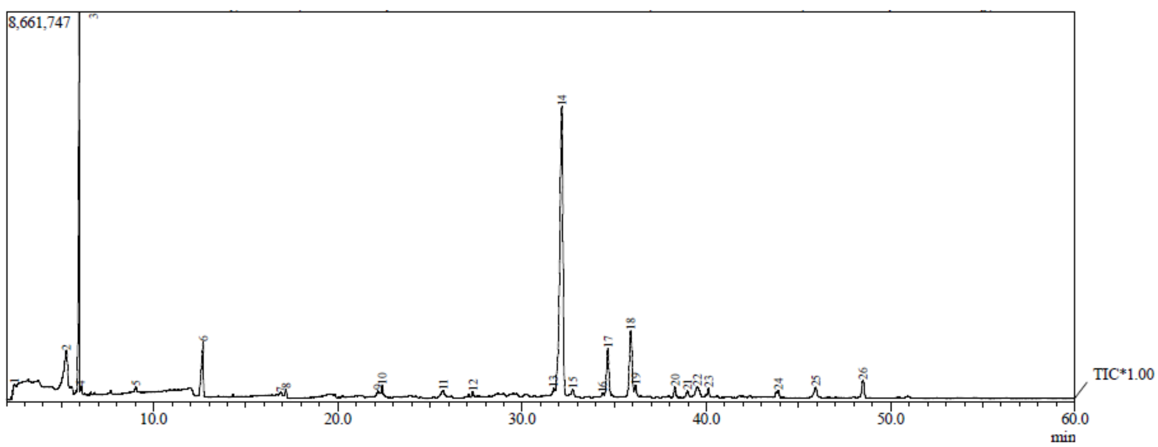

Fig. 2. Chromatogram of the tar produced by pyrolysis of coal.

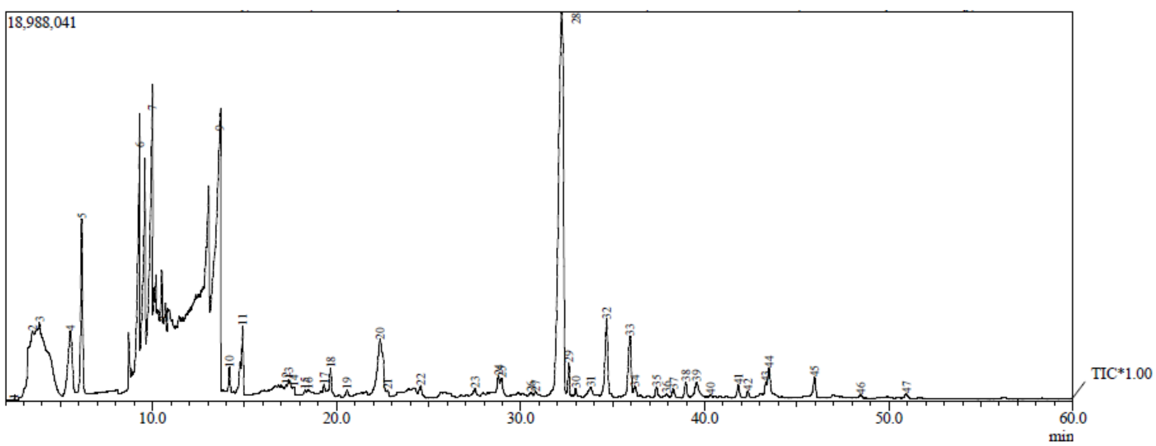

Fig. 3. Chromatogram of the tar produced by pyrolysis of PKS.

process from PKS could produce more than 400 active compounds; pyrolysis of hemicellulose is degraded to alcohol and carboxylic acid (such as acetic acid) at low temperature (200°C - 300°C); the cellulose is decomposed into carbonyl and heterocyclic compound (furfural) at medium temperature (300°C - 400°C). Furthermore, the lignin is degraded to monomeric phenolic compounds (phenol) and light aromatic hydrocarbon (benzene) at high temperature (250°C - 500°C) [15, 16]. There was no benzene found for both tar because the process using lower temperature (400°C).

The tars studied consist of compounds with the distribution of the number of carbon atoms C1-C16 and the more dominant compounds are with the number of carbon atoms C2-C7. The pyrolysis of the compounds consisting of coal tar and PKS leads to the formation of compounds with short to medium carbon chains, so that the tar is dominated by compounds with light to medium fractions. The main compounds (written in bold) identified in coal tar were phenol, acetic acid and 3-methyl phenol, while in PKS tar were acetic acid, phenol and methanol. Coals were made from plant decompose over millions of years [17]. Therefore, phenol can be the biggest compound of tar coal due the content of lignin from plant and cell walls matrix to stabilize the structure [18]. Meanwhile, cellulose in plants is completely decomposed so that no furfural compounds are found in tar coal. Based on the chemical contant in the bio-oil, it can be utilized into various products. The presence of aliphatic compounds in bio-oil allows oil to be used as fuel because in general, aliphatic compounds are flammable and are often used as fuel [19]. However, the direct use of bio-oil as a substitute for fossil fuels still encounters obstacles. Bio-oil has significant oxygen (O) content in addition to carbon (C) and hydrogen (H). This results in bio-oil having a low calorific value and less stable properties, thus limiting its direct use for fuel [20]. Therefore, the calorific value of bio-oil from lignite and PKS in this study was 62.813 cal g^{-1} and 389.447 cal g^{-1}, respectively, and this value did not meet the requirements as fuel. However, the content of aliphatic and alicyclic compounds in bio-oil can be further processed into other chemicals.

Characterization of Char

Solid product from the pyrolysis of coal and PKS is in the form of black powder. For biomass, during the formation of biochar, the lignocellulosic components (i.e. lignin, cellulose, and hemicellulose) present in PKS may undergo several reactions such as the breaking of alkyl-aryl bonds, cellulose and hemicellulose depolymerization, fragmentation, and dehydration

Table 1. Tar Compound identified by GC-MS.

Compounds	Chemical Formula	Peak (%)	
		Coal	PKS
Acetaldehyde	C_2H_4O	0	3
Methanol	CH_4O	1.1	**7.02**
Hydroxy acetone	$C_3H_6O_2$	0.53	1.47
Methyl acetate	$C_3H_6O_2$	0	2.59
Acetic acid	$C_2H_4O_2$	**17.98**	**51.36**
Acetone	C_3H_6O	6.45	2.04
Furfural	$C_5H_4O_2$	0	2.43
Nonane	C_9H_{20}	1.05	0
Phenol	C_6H_6O	**43.29**	**13.99**
o-Cresol	C_7H_8O	5.6	1.58
3-methyl phenol	C_7H_8O	**8.54**	1.27
Dodecane	$C_{12}H_{26}$	3.11	0.06
2,3-Dimethylphenol	$C_8H_{10}O$	3.23	0.25
2,6-Dimethoxyphenol	$C_8H_{10}O_3$	1.4	0.36
Hexadecane	$C_{16}H_{34}$	1.95	0.06

of ingredients; thus producing a biochar matrix that could contain polyaromatic hydrocarbon structure with cellulose and hemicellulose polymer units [8].

The calorific value of a briquette describes the value of the heat of combustion that can be produced by briquettes [21]. The calorific value increases about 5.19 % for coal and 41.12 % for PKS after pyrolysis (Fig. 4(a)). In the temperature range of 0°C - 200°C, only water evaporation occurs. In the temperature range of 200°C - 300°C, the biomass undergoes devolatilization and carbonization, which changes the calorific value significantly. At a temperature of 300°C - 400°C, carbonization begins, releasing carbon monoxide, carbon dioxide and other short hydrocarbons [22]. The

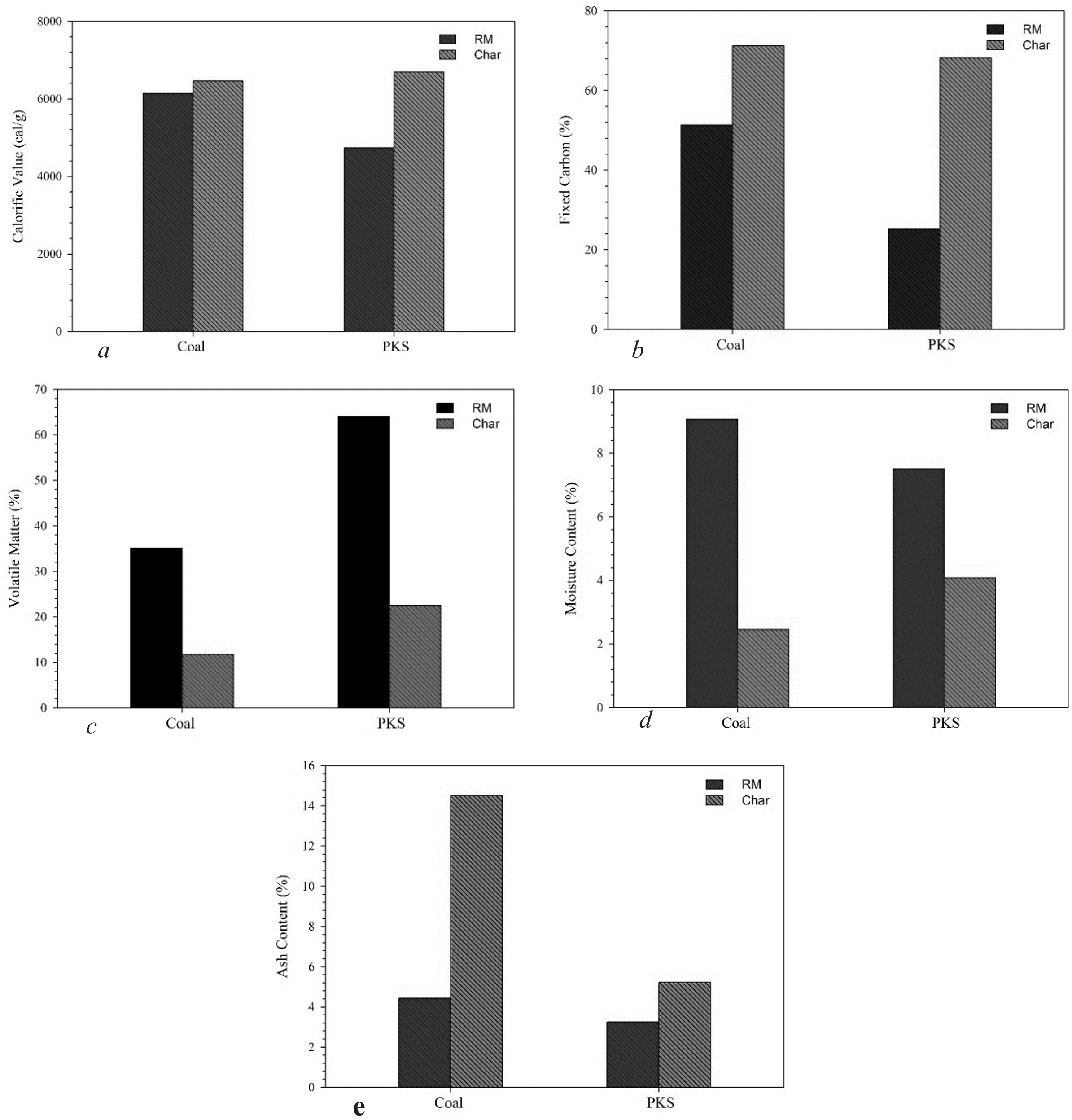

Fig. 4. Calorific value (a), fixed carbon (b), volatile matter (c), moisture (d), and ash (e) content of coal and PKS (RM - raw material, char - after pyrolysis).

increase in calorific value also indicates an increase in the fixed carbon content. Fixed carbon content affects the calorific value, where the greater fixed carbon content thus calorific value will increase. The fixed carbon content of char increased about 38.77 % for coal and 171.07 % for PKS. At the beginning, fixed carbon content of coal has a higher value compared to PKS, but it comes to almost same value after pyrolysis (Fig. 4(b)).

The fixed carbon content is inversely proportional to the amount of volatile matter in the material [18]. From Figs. 4(b) and 4(c), it can be seen that materials with high value of volatile matter have low fixed carbon values. The high and low levels of volatile matter in materials are caused by the perfection of the carbonization process and are also influenced by the time and temperature of the decomposition process. The higher the temperature and combustion time, the more volatile matter is wasted, so that during the test it will produce samples with low volatile matter [23]. The high volatile matter content in the briquettes will cause more smoke but easier to combust [24]. Low volatile matter content are more preferable in use because less smoke is produced [25, 26]. Both the fixed carbon and calorific value of the coal and PKS increased after the pyrolysis process, whereas the volatile matter and moisture content decreased dramatically. Volatile matter decreased about 66.45 % for coal and 64.89 % for PKS (Fig. 4(c)), while moisture content decreased about 72.92 % for coal and 45.68 % for PKS (Fig. 4(d)).

The best raw material for pyrolysis must have a moisture content of less than 10 % for heat to occur quickly [18]. It can be seen at Fig. 4(d) that both of feedstock met this requirement. The water contained in solid product will affect the quality of the briquettes produced. The water content of the briquettes should be as low as possible in order to produce a high calorific value and easily ignited for combustion [12]. The other physical property of solid product is ash content that increased significantly after pyrolysis process as the value of 60.39 % for PKS and 227.97 % for coal (Fig. 4(e)). Ash content indicates the presence of inorganic components in the raw material in the form of metal oxides. The high amount of ash content in the fuel causes corrosion, fouling and reducing the calorific value [26]. It means that the higher ash content produced, the lower quality of the briquettes.

Both the coal and PKS showed high fixed carbon content after pyrolysis; in addition, PKS also has lignin as potential material for conversion into carbon-dense material such as biochar. Comparing coal and PKS in this research, coal is better to develop to be a briquette because it has higher calorific value and more increase after pyrolysis. The other important physical property is moisture content of coal. This reduced significantly and the value is lower than PKS.

CONCLUSIONS

The pyrolysis process was successfully improved the quality of low rank coal and PKS by converted to some products. The result shows that coal produced more char and PKS produced more gas. The greater tar yield was obtained by using PKS with the largest tar compounds for both materials were phenol and acetic acid. The calorific value of char increased about 5.19 % and 41.12 % for coal PKS after pyrolysis, respectively. The other physical properties were also improved, so the application of pyrolysis could enhance the value-added of coal and PKS as well as a contribution to the alternative energy, especially for char product. Tar products cannot be used directly as fuel because of its low calorific value, but can be further processed into other chemicals.

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