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Study of Palm Oil Shell Utilization as Metallurgical Coke with Variation of Bondcrete Additive

Asful Hariyadi*, Dinda Khoirunnisa Hidayat, Moch. Purwanto

Department of Chemical Engineering, Institut Teknologi Kalimantan, Jl. Soekarno Hatta KM 15 Balikpapan 76127, Indonesia

ABSTRACT

Coke, an essential ingredient in the steel and metallurgical industries, is typically derived from bituminous coal. However, in Indonesia, where bituminous coal is rare, coke production is dependent on coal imports due to the high moisture content of local coal. An alternative approach is to use biomass, such as palm oil processing waste, for "biomass coke" to produce a more environmentally friendly coke with lower greenhouse gas emissions. Palm kernel shell waste rich in lignocellulose proved suitable for this purpose due to its compressive strength and carbon content. Pyrolysis, a technique for creating porous micro-structured carbon from palm kernel shells, was used to produce this coke substitute, offering a more sustainable energy source with a lower carbon footprint than fossil fuels. Bio-coke exhibits low moisture content (5.84%) and ash content (13.20%) due to the moisture and ash reduction effects of bondcrete adhesive during combustion. It also demonstrates substantial compressive strength (14 mPa), a high calorific value (6795 cal/g), and a favorable pore structure with a large surface area, indicating a positive influence of bondcrete adhesive on coke properties without compromising energy potential.

***Keywords*:** Coke, iron ore, palm kernel shell, pyrolisis, smelter.

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1. INTRODUCTION

Coke is a product resulting from the thermal processing of coal that is typically used in the steel and metallurgical industries. The coal used in making coke should be coking coal, which is bituminous coal [1]. Characteristics of bituminous coal include moderate carbon content, varying moisture levels, and calorific values that also vary depending on the quality [2]. In Indonesia, bituminous coal can be found, but this type of coal tends to be rarer than subbituminous and lignite coal [1]. Most of the coal in Indonesia is coal with high water content, so to produce coke it is necessary to import from abroad such as Japan, China and Taiwan.

An alternative to coke is to utilize the potential of biomass. Biomass is organic material derived from plants or other living things, such as palm oil processing waste, wood, straw, litter and organic waste [3]. Biomass has high moisture, variable ash content, and usually a lower calorific value compared to bituminous or anthracite coal [4]. Due to these characteristics, biomass is not suitable for producing high-quality coke. The idea of utilizing biomass as one of the feedstocks in the coal coking process is known as "biomass coking". In this process, biomass is blended with coal to produce coke that has more environmentally friendly characteristics, such as lower greenhouse gas emissions. However, this process is more complex than conventional coke-making and requires a specialized arrangement.

Material properties that need to be considered in order for biomass to qualify for the Indonesian National Standard (SNI) for coke are that it must have a high calorific value (8,000 cal/kg), hard, bulky, and porous to allow the passage of gases in the furnace. The mechanical strength of biomass is still low compared to coal, so it is necessary to modify the process to improve the physical

*Corresponding author: Asful Hariyadi
Department of Chemical Engineering, Institut Teknologi Kalimantan
Jl. Soekarno Hatta KM 15 Balikpapan76127, Indonesia
E-mail: asful.hariyadi@lecturer.itk.ac.id

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construction of the resulting char to withstand the pressure when used in the Blast Furnace. If the strength modulus is low, biomass char easily collapses during compression [5].

Oil palm shell waste or PKS is suitable to be utilized as raw material for coke reductors because it has a high lignocellulose content and a tough structure so it has the appropriate compressive strength and carbon content [6]. The utilization of technology to produce carbon with pore microstructure from PKS is pyrolysis. Pyrolysis is defined as the thermal degradation of solid fuels under conditions without or with limited amounts of oxygen/air. Pyrolysis is the most widely used energy conversion method to utilize biomass to produce high energy products, such as char (solid), tar (liquid) and gaseous products [7]. The solid product in the form of char has specific specifications such as carbon content and compressive strength and is therefore referred to as coke. In addition, energy produced from organic matter has a minimal carbon footprint when compared to fossil fuels [8].

2. MATERIAL AND METHOD

2.1. Material

Palm kernel shell (PKS) waste used as raw material for the manufacture of coke comes from Penajam, East Kalimantan. Meanwhile, bituminous coal was obtained from PT Bukit Asam Tbk. Low-rank iron ore was obtained from Sebuku, South Kalimantan.

2.2. Preparation of PKS

Preparation of PKS begins with drying the material in the oven at 110°C for 12 hours to remove moisture content. The PKS is then crushed using a milling machine and sieved using a 100 mesh sieve.

2.3. Pyrolysis Process of PKS

8,000 g of palm kernel shell (PKS) waste was carbonized using a furnace reactor at 600°C for 2 hours. In this pyrolysis process, the biomass is fast heated at 5°C/s to a high temperature in an oxygen-free state. The equipment used is a multi-purpose reactor that can be used for pyrolysis and corbonization of solid fuels, both coal and biomass.

2.4. Briquetting Process of PKS

The carbonated PKS went through a blending process by adding bituminous coal with various compositions (4:0, 3:1, 2:2) as listed in Table 1. PVA-based bondcrete must be diluted with a ratio of 1:20 (bondcrete: water). Bondcrete adhesive of various masses (10, 15, 20 grams) was added to each variable. The mixture is then molded into cylindrical coke briquettes with a diameter of 30 mm * 50 mm with a forging pressure of ±100 kPa.

Table 1. Coke briquette composition variable.

Code	PKS (gram)	Coal (gram)	Adhesive (gram)	Adhesive fraction (%)
A			10	9,1
B	100	0	15	13,0
C			20	16,67
D			10	9,1
E	75	25	15	13,0
F			20	16,67
G			10	9,1
H	50	50	15	13,0
I			20	16,67

2.5. Characterization of Coke Briquettes

The results of coke briquette molding were then proximate tested to determine the chemical characteristics of coke briquettes. Proximate Analysis ASTM D3172 aims to evaluate calorific value, moisture content, ash content, and volatile matter content.

Cross-sectional and elemental examinations were conducted utilizing a scanning electron microscopy (SEM) device that featured an energy-dispersive X-ray spectroscopy (EDS) system (JEOL, JSM-6510LA) with settings of 15 eV and 3 nA acceleration. The primary objective of this approach was the detection and characterization of carbonaceous substances found within the carbon-infiltrated goethite ore samples.

Quantification of specific surface area and pore volume was performed through N_2 adsorption analysis using a Quantachrome NOVA 2000 instrument. Furthermore, the data obtained was assessed using BET and BJH techniques to evaluate the impact of the heating process. Initially, the samples were subjected to a vacuum drying period of one hour at 108°C in a glass container. Afterwards, high purity (>99.9999%) N_2 gas was adsorbed and desorbed in liquid nitrogen at -196°C. This analytical procedure was duplicated to ensure replication of results.

3. RESULTS AND DISCUSSION

3.1 Proximate Analysis of PKS and Bituminous Coal

The following are the proximate test results for PKS raw materials before carbonation and bitimous coal shown in Table 2. The calorific value contained by PKS and BC is still far from the target of ≥ 6000 cal/g refer to SNI 4931: 2010.

To produce good coke briquettes, raw PKS are carbonated using a furnace reactor. The mass of PKS decreased from the test mass by 68.11% and obtained a yield percentage of 31.89%. The yield calculation aims to determine the level of charcoal productivity resulting from the carbonization process on palm kernel shells. The carbonized PKS was then tested again with proximate analysis with the test results in Table 3 as follows.

The production of coke briquettes can be carried out using the blending method, which is mixing carbonated PKS with bituminous coal which aims to improve the chemical characteristics of carbon products and increase the compressive strength of the material after forging. The following are the results of proximate analysis for coal before carbonation.

Table 2. Proximate Test Results of Palm Kernel Shell Raw Materials.

Materials	Moisture content (%)	Ash content (%)	Volatil matter content (%)	Fixed Carbon (%)	Calorific value (cal/g)
PKS	9,37	1,68	70,76	18,19	4.698
Bituminous coal	28,50	2,0	12,16	63,50	5.994,5

Table 3. Proximate Test Results of PKS after Carbonation.

Materials	Moisture content (%)	Ash content (%)	Volatil matter content (%)	Fixed Carbon (%)	Calorific value (cal/g)
PKS	5,84	10,36	25,20	58,60	5.870

3.2 Chemical Characterization of Coke Briquettes

The proximate analysis of palm kernel shell waste (PKS) aims to understand how variations in the mixture ratio between PKS and coal, as well as variations in adhesive composition affect values such as moisture content, ash content, volatile matter content, bound carbon content, and calorific value of coke. In addition, a compressive strength test was conducted to determine the strength limit of the coke to withstand the load when pressurized.

The results of the treatment of several variable codes showed that the composition of raw materials and adhesive mixture influenced the moisture content, ash content, volatile mattter content, bound larbon content and calorific value shown in Table 4.

Table 4. Proximate Test Results of Coke Briquettes Based on Treatment Code.

Materials	Moisture content (%)	Ash content (%)	Volatil matter content (%)	Fixed Carbon (%)	Calorific value (cal/g)
A	5,48	13,36	19,34	61,82	6.126
B	5,27	12,58	20,37	61,78	6.084
C	2,94	12,88	22,03	62,15	6.165
D	3,16	13,48	15,14	68,22	6.464
E	3,74	12,76	16,22	67,28	6.453
F	2,06	12,36	17,72	67,86	6.598
G	4,67	13,69	10,92	70,72	6.570
H	3,31	14,02	11,96	70,71	6.622
I	5,84	13,20	14,49	70,29	6.795

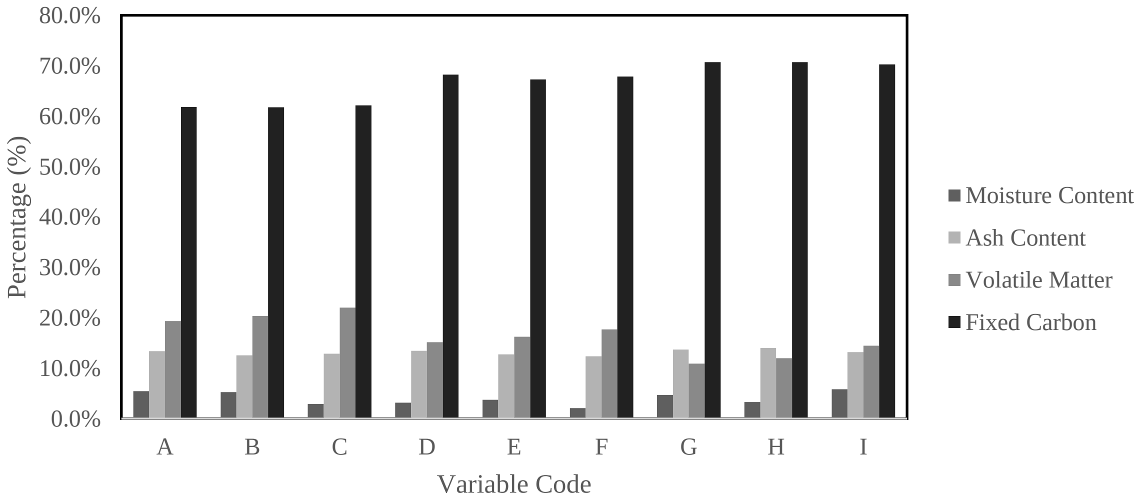

Figure 1. Results of Proximate Analysis of Coke Briquettes

The use of calorific value aims to measure the level of heat generated by coke combustion. In addition to pressure strength, calorific value is the most important quality parameter for coke as a reductor material, so the quality of coke is strongly influenced by calorific value. The higher the calorific value of charcoal, the better the quality of coke produced [9].

Figure 1 shows an overall increase in calorific value along with the addition of coal composition and percentage of adhesive in coke briquettes. The calorific value of coal before carbonization is higher when compared to PKS so the addition of coal composition will further increase the calorific value after both materials are carbonated. In addition, bondcrete as an adhesive is a polar resin composed of polyvinyl acetate homopolymer so it also provides additional calorific value to the material.

Water content has a significant influence on the calorific value or heat produced. High water content will cause a decrease in heating value. This is due to the heat that is first used to evaporate the water in the briquette before the heat is used for combustion. As a result, the measured calorific value will be low [10]. In accordance with the addition of coal composition, the highest calorific value is obtained in the results of variable I with a calorific value of 6,795 cal/g and has met SNI 4931: 2010 with a minimum standard of above 6,000 cal/g. When referring to the AISI (American Iron and Steel Institute) standard, a good calorific value for the ferroalloy industry is in the range of 6,800 - 7,169 cal/g.

The overall content of fixed carbon shows an increase in all samples which is influenced by the increasing composition of coal in the raw material and the addition of the amount of adhesive fraction in coke briquettes which also affects the increase in the value of flying matter in coke briquettes. When the value of flying matter is higher, the fixed carbon content tends to be lower, and vice versa [8]. However, the highest fixed carbon value was obtained in variable H with 70.71%. The value of fixed carbon will be in line with the calorific value produced. If referring to AISI for the ferroalloy industry, the value of fixed carbon is good if in the range of 85-90%. The low content of fixed carbon can also be caused by an incomplete carbonization process which is influenced by the stability of temperature, heating rate and carbonation time on palm shells, which results in the high content of fly substances produced [5].

Volatile matter, which includes compounds other than water, ash, and carbon, consists of hydrocarbons, methane, and carbon monoxide. The presence of hydrocarbons in the volatile matter will lead to an increase in the volatile matter content, which in turn makes the coke briquettes more flammable [11].

Figure 1 also shows an increase in the value of volatile matter content in all samples which is influenced by the addition of coal composition in the raw material and the increase in the amount of adhesive fraction in coke briquettes. One of the reasons is that the presence of adhesives composed of polyvinyl acetate homopolymer resin will add elements of volatile organic fractions, thus affecting the content of volatile matter [12].

Based on Figure 1, there is an increase in water content for all sample variation codes. This can be due to the mixing of PKS charcoal with coal which has a different moisture content and the addition of adhesives that have water content can increase the amount of moisture content in the printed coke briquettes.

According to Surup et al. [8], there is a tendency for the moisture content of briquettes to increase in each raw material mix composition when the particle size gets smaller. If we consider the particle size, the sieving process used to achieve a 50 mesh size produces coke briquettes with a greater number of pores. This larger number of pores in the coke briquettes has a tendency to absorb water from the surrounding air, because the ability to absorb water is influenced by the surface area and pores of the coke briquettes.

However, there are anomalies in the data generated. The moisture content tends to decrease with the addition of adhesive composition. This is because the adhesive used is a type of polar resin that causes the hydration reaction with the adhesion caused by the adhesive to be higher so that the coke briquette will tend to be more difficult to evaporate water due to its pores being clogged by the adhesive. The author's initial hypothesis predicts that the composition above 10% already exceeds the water requirement for the hydration reaction of charcoal, so that most of the water in the adhesive is not attached to the charcoal. This in turn causes this unbound water to tend to easily evaporate during post-treatment drying. However, this prediction is not absolute, so further literature review is needed..

The different moisture content values in PKS and Coal coke have a significant impact on the ease with which the coke can reduce metals. The higher the moisture content, the more difficult it is for the coke to perform the reduction process. Conversely, the lower the moisture content, the easier the coke will be to reduce metal minerals. In addition, the moisture content in coke also affects its hardness. The higher the moisture content, the more brittle the coke will be [10].

Based on the results obtained, all samples have met the classification in SNI 4931: 2010 with a moisture content value below 12%. The lowest moisture content was obtained in variables C and F. When referring to AISI (American Iron and Steel Institute), the value of moisture content for high-quality coke briquettes is below 5% and coke briquettes in all blending variations have fulfilled this aspect.

Based on Figure 1, the overall ash content of coke briquettes is influenced by the composition of PKS and Coal raw materials which have different ash content values. In coke briquettes with full composition of PKS or not mixed with coal (A, B, C), the ash content produced is lower than coke briquettes with the addition of coal composition (D, E, F, G, H, I). This is due to the hydrocarbon composition of PKS which is a type of cellulose. On the other hand, although Coal contains cellulose molecular structure, the process of dissolution causes an increase in silica content which is the main element in Coal. Coal ash is a residue from coal combustion consisting of amorphous fine particles. The ash is formed as inorganic material due to mineral changes that occur during the coal combustion process [13].

The increase in ash content occurs due to the silica content which is the main element in coal and adhesive which also has a small portion of silica content. All variables have met the aspects set by SNI 4931:2010 with a maximum ash content composition not exceeding 20%. However, if referring to AISI, the ash content value is set in the range of 9-10%. The ash content produced in all samples tends to fluctuate in the range of 12-14% so that the changes produced do not have a significant impact.

3.2 Physical Characterization of Coke Briquettes

The compressive strength of coke has a very important value because it affects the ability of coke to withstand the load in the smelting furnace of metal minerals, as well as maintaining the integrity of the coke during the distribution process. The physical characterization of coke briquettes were showed in Table 5.

Based on Figure 2, it can be seen that the compressive strength increases at the same coke briquette composition with an increasing amount of adhesive composition. The increase in compressive strength is due to the increase in hardness with the amount of adhesive composition given. In addition, the compressive strength of coke is also affected by moisture content, where high moisture levels make coke more brittle, and vice versa. When the coke is dried, the water trapped in the pores of the coke will evaporate, so that when pressed, the coke becomes more easily destroyed [8].

Table 5. Analysis of Coke Briquette Compressive Strength Test

Code	PKS composition (gram)	Coal composition (gram)	Adhesive (gram)	Adhesive fraction (%)	Load (MPa)
A			10	9,1	11,61
B	100	0	15	13,0	13,20
C			20	16,67	14,08
D			10	9,1	**rupture**
E	80	20	15	13,0	11,53
F			20	16,67	13,64
G			10	9,1	**rupture**
H	60	40	15	13,0	13,75
I			20	16,67	14

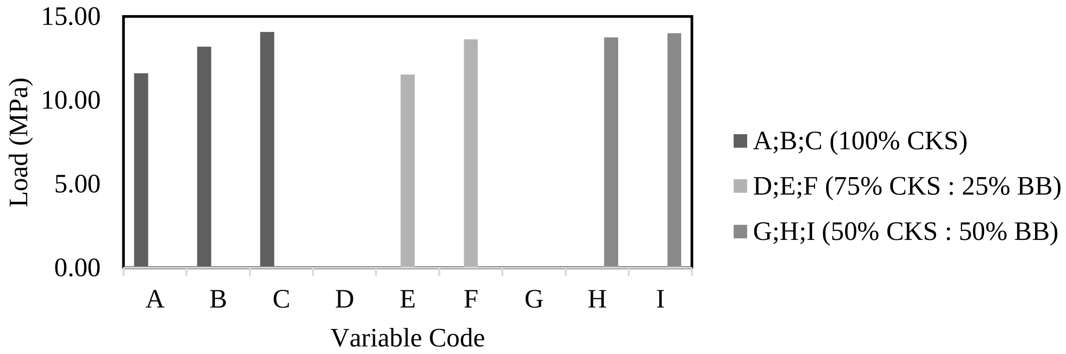

Figure 2. Coke Briquette Compressive Strength Test Results

The adhesive used is water-based resin so that it affects the water content. However, there are 2 samples (Variable D and G) that cannot be measured because the compressive strength produced is below the minimum specification of the testing equipment so that the sample breaks during the compression test. This is predicted because the amount of binder given is too small so that it is not able to bind the maximum of all charcoal particles, and in accordance with the proximate test that the small amount of binder is directly proportional to the increased water content so that it makes the coke briquette brittle.

In addition to the compressive test, the physical characteristics of coke briquettes were also determined by morphological analysis of activated carbon (Table 6). Morphological analysis of carbon surface was carried out using SEM instrument at 3,000x magnification. Referring to Figure 3, it is obtained that the surface morphology of carbon produced by the carbonation of PKS has a homogeneous pore area and looks more fragile than the pore surface on coal which looks more heterogeneous.

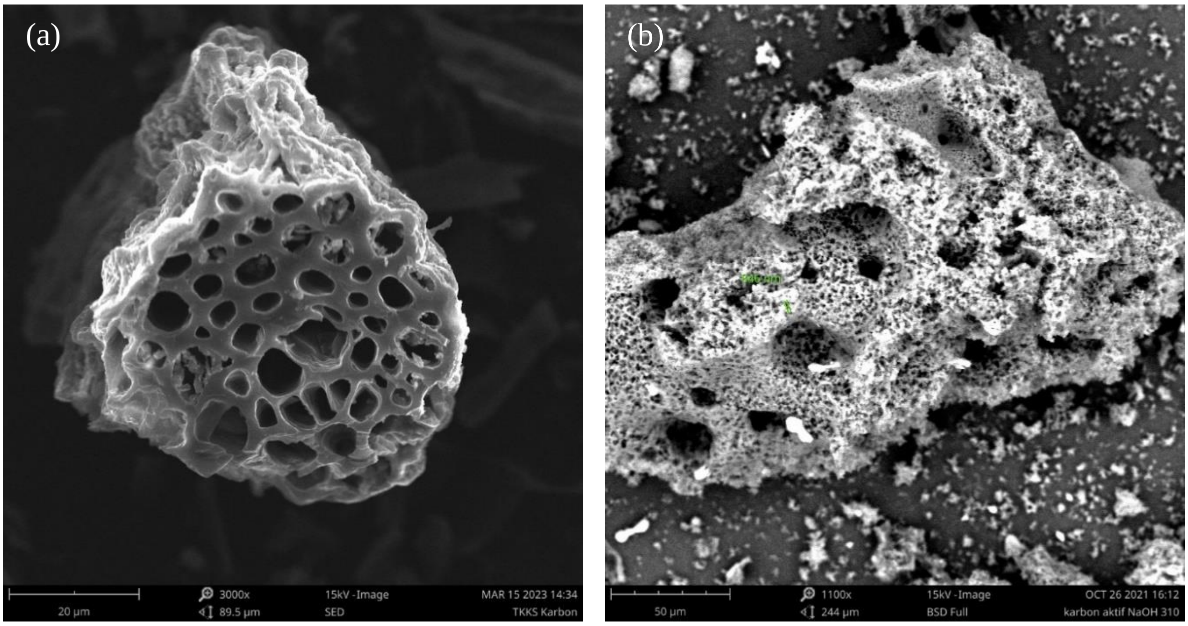

Figure 3. Pore morphology (a) Carbonated PKS; (b) Carbonated coal.

The reactivity of coke is strongly influenced by the pore microstructure formed during the production process. The existence of many pore structures will cause the surface area to be larger and the gas diffusion process to be faster so that the metal mineral reduction process can run optimally [14]. Surface Area Analyzer (SAA) testing was conducted to determine the adsorbent surface area, pore volume, and pore radius. SAA testing with the BJH method using nitrogen gas as adsorp/inert gas was conducted for sample I (60% Carbonized PKS with 16.67% adhesive). The pore diameter is classified into 3 types, namely macropores (d > 50 nm), mesopores (2 < d < 50 nm), and micropores (d < 2 nm) and the carbon produced has a pore size of 62,46 Å or about 6,246 nm and belongs to the mesopore type [15].

Coke briquettes with mesoporous structures that have a large surface area have advantages in reactions in gas furnaces due to their ability to increase the contact between fuel and gas, and accelerate the chemical reaction process. The formed mesoporous structure allows for increased gas diffusion and better penetration into the coke material, improving fuel utilization efficiency and production of desired products, improving the yield and quality of the final product in the metallurgical process [16].

Table 6. Pore Characterization Result for Sample I.

No	Parameters	Results
1	Surface area	123,666 m^2/g
2	Pore volume	0,739 cc/g
3	Average pore radius	62,46 Å

4. CONCLUSION

The chemical and physical characteristics of coke briquettes from carbonated palm kernel shells and bituminous coal are influenced by the composition of the constituent raw materials and the adhesive used. Based on the research conducted, sample I with a composition of 60 grams CKS, 40 grams coal, and 20 grams bondcrete adhesive (16.67%) showed the best coke results. Sample I has a low moisture content of 5.84%, as well as a fairly low ash content of about 13.20%, which can be explained by the effect of bondcrete adhesive in reducing moisture and ash formation during combustion. In addition, this sample has a significant compressive strength of up to 14 mPa, a high level of calorific value of about 6795 cal/g, as well as a beneficial pore structure with a large surface area, indicating that the bondcrete adhesive exerts a positive influence on the coke properties without compromising the energy potential.

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