



Characteristics of Hybrid Coal from Co-Pyrolysis of Lignite and Corn Cob

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Abstract

Lignite is the lowest rank coal which has less economic value. Corn cobs are solid waste biomass as a by-product of corn processing. The processing of these two materials can produce a product in the form of hybrid coal through the co-pyrolysis process. This study aims to determine the optimum temperature and mixing ratio of co-pyrolysis of lignite and corn cob and to characterize the hybrid coal produced by co-pyrolysis. The lignite is dried and crushed to a particle size of 20-50 mesh. Corn cob was cleaned, cut into pieces, and sieved to a size of 0.4-2 mm. Then it was dried using an oven at 105°C for 24 hours. Lignite and corn cob were mixed with a ratio of 3:1, 1:1, and 1:3 (mass of lignite: mass of corn cob). The mixture of materials is inserted into the pyrolysis reactor as much as 400 grams. The pyrolysis process was carried out at temperatures of 350°C, 400°C, 450°C, 500°C, and 550°C for 1 hour by flowing nitrogen gas into the reactor with a flow rate of 1.5 L/minute. The results showed that increasing the mixing ratio and co-pyrolysis temperature would decrease the yield of hybrid coal. Increasing the pyrolysis temperature will increase the calorific value of hybrid coal. Still, the effect of the mixing ratio of lignite and corn cob shows a decrease in heating value at a mixing ratio of 1:1 and an increase in a mixing ratio of 1:3. Other parameters such as moisture content and volatile matter content decreased with increasing temperature and mixing ratio. In contrast, ash content and fixed carbon content increased. So, an optimum temperature and mixing ratio of 450°C and 1:3 is the best condition to get hybrid coal that met the requirements to be a solid fuel.

INTRODUCTION

Coal is one of Indonesia's energy sources. Potential coal reserves in Indonesia are mostly found on the islands of Kalimantan and Sumatra. Indonesia's coal reserves are 88.21 billion tons, Kalimantan holds most of the total reserves at 25.84 billion tons or 62.1% (Meyliawati et al., 2022). Coal is classified into different grades according to the quality of its combustion. As energy demand continues to increase, the focus is shifting to low-rank coals despite constraints of low calorific value, high moisture content, and high CO₂ emissions. In addition, in some countries, including Indonesia and China, low-rank coals (lignite and sub-

bituminous) are in ample supply compared to high-grade coals (Tahmasebi et al., 2016).

For combustion in pulverized coal burners, low-rank coals require additional processing to deal with excess moisture content. In some applications, high-temperature tail gas is used for thermal drying to remove moisture from low-rank coals. These extra treatments lowers the overall efficiency of the power plant (Xu et al., 2015).

Low rank coal can be used as fuel with a mixture of biomass. Among renewable energy sources, biomass-based energy sources are considered carbon-neutral because the amount of carbon dioxide released into the atmosphere during combustion is equal to the amount of carbon dioxide absorbed by plants through photosynthesis

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during their life cycle (Xiu & Shahbazi, 2012). Biomass energy in the form of corn cob waste is widely used due to the high corn production in Indonesia, especially at Balangan Regency in South Kalimantan. In 2020, Balangan Regency's corn planting area is 2896 hectares and yields 1856 tonnes (Herlinawati et al., 2022). The resulting corn cob waste accounts for 30% of production. Corn cob contained 37.2% cellulose, 41.9% hemicellulose, and 15.3% lignin (Singh et al., 2021).

Mixing low-rank coal (lignite) with biomass can be used as a feedstock for co-pyrolysis, converting it into solid (biochar), gas, and liquid products (Li et al., 2017). Biochar products can be used as solid fuels for power plants, raw materials for activated carbon, and even as catalyst supports and supercapacitor electrodes (Kan et al., 2016; Nanda et al., 2016; Qian et al., 2015), as well as effective adsorbents (Mukherjee et al., 2014).

Several studies related to pyrolysis of low rank coal and biomass have been carried out (Akyürek, 2019; Hossain et al., 2017; Pinto et al., 2015; Uzoejinwa et al., 2019). Co-pyrolysis of lignite and biomass (rice husk) produces hybrid coal products (Sasongko et al., 2017). Some researchers (Soncini et al., 2013; Wei et al., 2011; Zhang et al., 2007) also conducts coal and biomass pyrolysis with a research focus on product distribution. Soncini et al. (2013) pyrolyzes sub-bituminous, lignite coal, and southern yellow pine as biomass and the results showed that gas and water increased with increasing the weight percentage of biomass, while the amount of remaining char decreased. Wei et al. (2011) used legume straw and pine sawdust as biomass, and Dayan lignite and Tiefs bituminous coal as pyrolysis raw materials. The results show that co-pyrolysis of legume straw/Tiefs bituminous can obtain higher liquid production rate than pine sawdust/Tiefs bituminous co-pyrolysis. The rank of coal has a significant impact on the liquid yield of co-pyrolysis. And used legume straw and Dayan lignite as raw materials at a pyrolysis temperature of 500 – 700 °C, the results showed that as the pyrolysis temperature and the mixing ratio of legume straw/Dayan lignite increased, the char yield decreased and, correspondingly, the liquid yield increased.

This study used lignite and corn cob biomass as raw materials. The raw material mixture was pyrolyzed at a pyrolysis temperature of 350 – 550 °C and a corn cob/lignite mixing ratio of 3:1, 1:1, and 1:3. Taking the charcoal product (hybrid

coal) obtained from the pyrolysis process as the main product, its calorific value, and proximate parameters were analyzed, and the effects of pyrolysis temperature and mixing ratio on the characteristics of the hybrid coal product were studied.

MATERIALS AND METHODS

Materials

The corn cob comes from the Balangan district of South Kalimantan, Indonesia. The coal was sourced from Asam-Asam in the Tanah Bumbu district of South Kalimantan, Indonesia. The coal used is lignite, which is a low-rank coal.

Pre-treatment of Raw Material

The coal was crushed and sieved to 0.3-1 mm. Corn cobs cleaned, cut into small pieces and sieved into a size of 0.4-2 mm. The material was then dried in an oven at 105°C for 24 hours. This process was to remove moisture, thereby preventing decay. The lignocellulose content, proximate analysis, and calorific value of the raw materials were analyzed.

Pyrolysis of Coal and Biomass

Lignite and corn cob were mixed in a mass ratio of 3:1, 1:1, 1:3, lignite: corn cob. 400 g of the raw material mixture was placed in the pyrolysis reactor and heated at a temperature of 350°C, 400°C, 450°C, 500°C, and 550°C for 1 hour with a nitrogen flow rate of 1.5 L/min. After the reaction was complete, the reactor was cooled to room temperature and the char was collected. Then the proximate and calorific value analyses were carried out. As a comparison, lignite and corn cobs were pyrolyzed without mixing at 500°C. The sample codes used in this study are shown in Table 1.

Table 1. Experimental operating condition and codes.

Temperature (°C)	Mixing Ratio (Lignite: Corn cob)		
	3:1	1:1	1:3
350	H11	H21	H31
400	H12	H22	H32
450	H13	H23	H33
500	H14	H24	H34
550	H15	H25	H35

Tabel 2. Calorific value and proximate analysis of raw material.

Analysis	Lignite			Corn Cob		
	This study	Baganuur coal ^(a)	Aduunchuluun coal ^(a)	This study	Shariff et al ^(b)	Biswass et al ^(c)
Calorific value	4,765.295	n/a	n/a	4,247.320	3,9314.035	3,8215.344
Proximate Analysis						
Moisture Content	23.250	n/a	n/a	3.800	7.14	12.77
Ash content	3.935	7.45	10.6	2.455	1.05	2.30
Volatile matter	10.995	41.6	47.1	67.360	87.76	91.16
Fixed Carbon	61.820	78.5	73.3	26.385	11.19	6.54

(a) (Byambajav et al., 2018); (b) (Shariff et al., 2016); (c) (Biswas et al., 2017)

Table 3. Yield char, calorific value and proximate analysis of hybrid coal.

Codes	Yield Char (%)	Calorific value (cal/g)	Proximate Analysis (%)			
			Moisture content	Ash content	Volatile Matter	Fixed Carbon
LP	71.54	5,770.5615	5.306	5.1615	36.601	52.9315
CP	57.92	6,397.332	2.8925	6.1055	26.0315	64.9705
H21	83.00	4,793.4265	6.7365	4.1735	50.602	38.488
H22	78.25	4,953.458	6.156	5.4305	45.1805	43.233
H23	73.52	5,375.2935	5.0755	6.0075	41.0945	47.9225
H24	62.06	5,568.3835	5.0195	6.1335	33.132	55.715
H25	61.81	5,749.3505	4.771	6.395	33.6775	55.1565
H14	70.08	5,704.2755	5.268	5.7795	35.0775	53.875
H34	62.06	5,865.7415	4.9805	5.782	32.412	56.8255
SNI*	-	5,000-6,000	max 12	max 15	max 22	> 30

LP = pyrolyzed lignite

CP = pyrolyzed corn cob

* SNI 13-4931-2010: Coal Briquettes

Characterization

The calorific value of hybrid coal samples was quantified using a bomb calorimeter (Gallenkamp Adiabatic Bomb Calorimeter CBA-305). Also, proximate analysis is determined according to ASTM D3172-07a.

RESULTS AND DISCUSSION

Corn cob were analyzed for lignocellulosic content. Corn cob consist of hemicellulose (36%), cellulose (36.58%) and lignin (15.88%). The results of the calorific value and the proximate analysis of raw material are shown in Table 2. The results from this study are also compared with the results from other literature. Then the results of hybrid coal analysis from co-pyrolysis of lignite and corn cob are shown in Table 3.

Effect of Pyrolysis on The Characteristics of Lignite and Corn Cob

Table 2 shows the calorific value and approximate properties of lignite and corn cob

before pyrolysis and Table 3 shows these number after the pyrolysis process. The raw material analysis results in Table 2 show that the calorific values of lignite and corn cob before pyrolysis are 4,765.29 cal/g and 4,247.32 cal/g, respectively. This indicates that the calorific value of lignite and corn cob does not meet the charcoal briquetting quality standard of SNI 13-4931-2010, which is 5,000-6,000 cal/g. The calorific value for pyrolysis of lignite is 5,770.56 cal/g. The corn cob value after pyrolysis was 6,397.33 cal/g. This indicates that pyrolysis increases the calorific value of lignite about 21.0956% and corn cob about 50.6204%. Klaas et al (2020) carried out pyrolysis of corn cob at 300°C and obtained an increase in the calorific value of 19.4805%, where the calorific value of the raw material was 3,678.227 cal/g and increase to 4,394.765 cal/g after pyrolysis (Klaas et al., 2020). In this study, a greater increase in heating value was obtained because it used a higher pyrolysis temperature, 500°C.

It can be seen from Table 2 that corn cob has high volatile matter content. Due to the high

content of volatiles in corn cob, corn cob was suggested to be a suitable feedstock for thermochemical transformation processes such as pyrolysis. The high volatile content also makes biomass a highly reactive fuel that burns faster. It also can be observed that the ash content of corncob is quite low compared to lignite. A low ash content in the biomass feedstock can reduce slagging and fouling in furnaces used in thermochemical conversion processes caused by the alkali content in the ash-rich biomass. The different analysis results of corn cob from the literature may be due to some factors, such as different types of corn, different weather conditions for growing corn and different soil types for growing corn. As well as the different characteristics of lignite coal due to different mining locations in different countries (Shariff et al., 2016).

The instant analysis results of lignite and corn cob before and after the pyrolysis process in Table 3 show that the pyrolysis process reduces the moisture content of the product and increases the ash content of the product. The decrease in water content is due to the evaporation of more water due to the high pyrolysis temperature. The increase in ash is due to the presence of combustion residue. The ash content indicates that the inorganic components in the raw materials exist in the form of metal oxides (Mohammed et al., 2017). In addition, there was an increase in lignite volatile matter but it decreased in corn cob. The level of volatile matter in the material is caused by the perfection of the carbonization process, and is also affected by the time and temperature of the decomposition process (Wang et al., 2020).

The Effect of Co-Pyrolysis Temperature on The Yield and Characteristics of Hybrid Coal

Yield Char

The co-pyrolysis product is influenced by several factors, namely the nature of the material, the type of reactor, the residence time, heating rate and temperature of the co-pyrolysis (Garcia-Nunez et al., 2017; Kan et al., 2016; Sasongko et al., 2017). The results of this study indicate that temperature differences affect the yield of solid products (hybrid coal). The effect of co-pyrolysis temperature of lignite and corn cob on hybrid coal yield is shown in Figure 1.

Figure 1 shows that the yield of hybrid coal (char) is inversely proportional to temperature. Hybrid coal yield decreases with increasing co-

pyrolysis temperature. Yield obtained at temperatures of 350°C, 400°C, 450°C, 500°C and 550°C respectively were 83.00%; 78.25%; 73.52%; 62.06% and 61.81%. This shows that the yield of hybrid coal has decreased from 83.00% at 350°C to 61.81% at 550°C. This study is in accordance with previous research conducted by Zullaikah (2015) where hybrid coal decreased from 37.16 grams (37.16%) at a temperature of 300°C to 18.44 grams (18.44%) at a temperature of 700°C. The decreasing yield of hybrid coal indicates that the raw material decomposes more with increasing temperature.

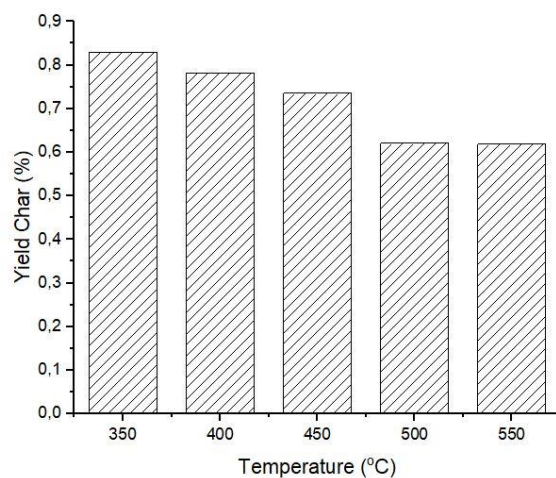


Figure 1. Yield char of co-pyrolysis of lignite and corn cob at various temperature.

Calorific Value

The higher the co-pyrolysis temperature, the higher the calorific value of the hybrid coal (Qiram et al., 2015). The effect of co-pyrolysis temperature of lignite and corn cob on hybrid coal calorific value is shown in Figure 2.

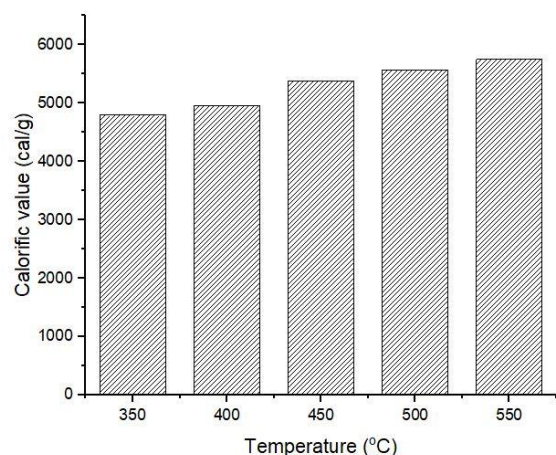


Figure 2. Calorific value of hybrid coal at various co-pyrolysis temperatures.

Figure 2 shows the calorific value of hybrid coal increases with the increase in co-pyrolysis temperature so that the highest heating value is obtained at a temperature of 550°C, which is 5,749.35 cal/g. Meanwhile, the lowest calorific value was 4,793.43 cal/g in the sample with a temperature variation of 350°C. The calorific value at 450°C, 500°C and 550°C corresponds to the quality standard of coal briquettes, which is 5,000-6,000 cal/g. But at 350°C and 400°C, the calorific value does not meet the quality standard of coal briquettes. At temperatures of 300-400°C, carbonization begins, releasing carbon monoxide, carbon dioxide and other short hydrocarbons. Carbonization above 400°C can significantly increase the calorific value of the hybrid coal (Sasongko et al., 2017). The calorific value has a major influence on the quality of the briquettes produced. The calorific value of briquettes describes the value of the heat of combustion that the briquettes can produce (Abdelsayed et al., 2019).

Proximate Analysis

From the data in Table 3, it can be seen that the higher the co-pyrolysis temperature, the lower the moisture content and volatile matter and increase the ash content and fixed carbon of hybrid coal. This is due to thermal decomposition releasing low molecular weight components (water and volatiles) leaving solids that fix carbon and ash (Jeong et al., 2014). The reduction in water content is due to the high pyrolysis temperature allowing more water to evaporate. The water contained in the solid product affects the quality of the briquettes produced. The moisture content of the briquettes should be as low as possible to generate a high calorific value and to burn easily (Saeed et al., 2020).

The Effect of Raw Material Mixing Ratio on The Yield and Characteristics of Hybrid Coal

Yield Char

In biomass pyrolysis, cellulose content increases tar production, lignin is the main component used to make char products, and hemicellulose contributes to tar and gas production (Naqvi et al., 2019). However, the presence of lignite as a feedstock for pyrolysis together with biomass will greatly affect the char product, especially when the lignite used has a larger composition. The yield charproducts at various

mixing ratios at constant temperature (500°C) is shown in Figure 3.

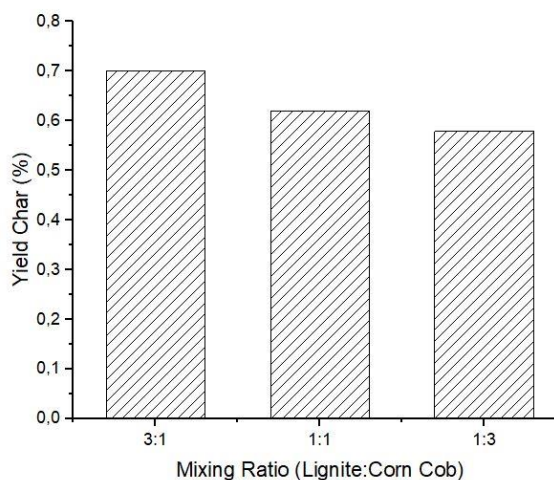


Figure 3. Yield char of co-pyrolysis of lignite and corn cob at various mixing ratio.

Figure 3 shows that the more corn cob (in a mixture of lignite and corn cob) produces less char because corn cob contain higher cellulose, the decomposition of cellulose produces more tar. The same product distribution also occurs in the pyrolysis of lignite and rice husk (Li et al., 2019). As a result, increasing the addition of corn cob resulted in a decrease in lignite as the main source of char, and consequently in char yields from lignite and corn cob pyrolysis. The resulting char yields ranged from 56.4-81.3% indicating that most of the material was converted to char.

Calorific Value

The calorific value of hybrid coal can be influenced by the composition of the raw materials (mixing ratio) shown in Figure 4.

Figure 4 shows that the calorific value of lignite typically increases to 5,865.74 after pyrolysis at a 1:3 lignite: corn cob mixing ratio. Increasing the mixing ratio or adding corn cob in the pyrolysis of lignite can increase the calorific value of the hybrid coal. However, when the mixing ratio is lower than 1:3, the calorific value decreases. Because the calorific value of corn cob is higher than that of lignite, the calorific value of the more lignite is lower because the calorific value of the produced briquette is affected by the calorific value of the raw material (Tumuluru & Fillerup, 2020). Thus, the addition of a maximum of 75% corn cob is the optimum mixing ratio to increase the calorific value of hybrid coal.

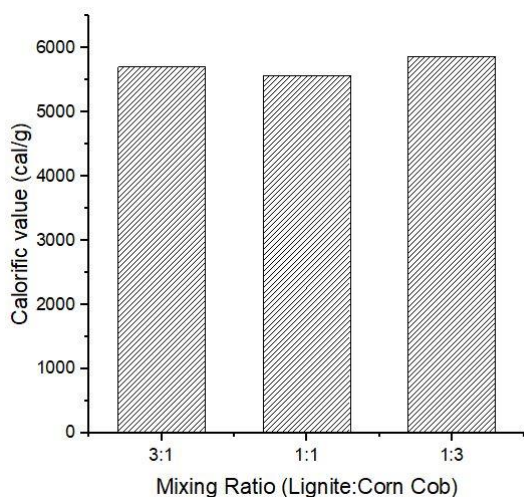


Figure 4. Calorific value of hybrid coal at various mixing ratio.

Proximate Analysis

The more mixing of corn cob with lignite will reduce the moisture content and volatile matter and increase the ash content and fixed carbon of hybrid coal produced (Table 2). The moisture content of the mixture of lignite and corn cob ranged from 4.98-5.27%, ash content 5.78-6.13%, volatile matter 32.41-35.08%, and fixed carbon 53.87-56.82%. The results of the best proximate analysis that meet the standards of SNI 13-4931-2010 were produced at a mixing ratio of 1:3, lignite:corn cob. In general, the volatile matter hybrid coal produced in this study did not meet the coal briquette standard (max 22%). The volatiles are caused by the improvement of the carbonization process and are also affected by the time and temperature of the decomposition process. The higher the temperature and burn time, the more volatiles are wasted, resulting in low volatility of the sample (Tomczyk, Sokołowska, & Boguta, 2020).

CONCLUSION

Hybrid coal from lignite and biomass is quite promising as an alternative to renewable solid fuels. Its manufacture through a co-pyrolysis process is quite simple, and efficient, and does not harm the environment. Based on the variation used in the study, it was found that the optimum temperature for obtaining large quantities of hybrid coal was 450°C, with a mixing ratio of lignite: corn cob, 1:3. Under these conditions, it also fulfills the requirements of a material to be used as fuel based

on its calorific value, which is more than 5,000 cal/g.

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