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Catalytic co-pyrolysis of coal and polypropylene plastic into liquid fuel

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ABSTRACT

The decline in fossil fuel sources has sparked research interest in renewable fuels. Ongoing efforts are directed towards discovering alternative energy sources that offer high efficiency and environmental sustainability. By addressing current challenges, investigating the co-pyrolysis of coal and polypropylene (PP) plastic into liquid fuel emerges as an intriguing pursuit. This study examined the co-pyrolysis process of coal with polypropylene plastic by investigating the effects of variations in the ratio of raw materials coal/PP plastic and the ratio of CaO catalyst/raw material used. The results showed that with the reduction in the ratio of coal/plastic, the yield of liquid fuel increased. Co-pyrolysis of coal: PP plastic with a ratio of 25:75 with the addition of 20% CaO catalyst obtained 37.56% liquid fuel yield with the characteristics of density of 0.839 g/mL, viscosity of 2.51 cSt, calorific value of 46.813 MJ/kg and pH of 2.9. Based on the findings of this study, the liquid fuel exhibited a high heating value but had a low pH, necessitating a reduction in acidity.

1. Introduction

Oil and Gas imports in Indonesia continue to increase along with the increasing public energy demand. Population growth and an increase in the number of vehicles have driven an increase in domestic oil and gas demand. In June 2021, Oil and Gas imports increased by 11.44% to US$ 2.3 billion. The increase in the value of crude oil imports of 489.5 million US$ or 101.48% became a trigger for the increase in gas import. The increase in both population and industrial activities has made fossil energy consumption being inversely proportional to available fossil energy reserves [1]. For this reason, to cope with this problem, alternative energy sources, some of which are coal and plastic waste, are required then.

Coal is a material containing hydrocarbon compounds. Here, Indonesia becomes the fifth largest producer and exporter of coal in the world. In 2021, coal production was targeted to reach 625 million tons. From this amount, domestic coal demand or Domestic Market Obligation (DMO) was targeted to reach 137.5 million tons. Meanwhile, in 2020, Indonesia's actual coal production was at 558 million tons. It was approximately 134 million tons used to meet the domestic needs. With total reserves of 38.84 billion tons, it will last for approximately 65 years if no other coal reserves are found. Efforts are continually made to gradually decline the coal exports, considering the increasing use of domestic coal [2].

In the utilization of coal into liquid raw material, it needs to do energy diversification to convert coal into liquid fuel through liquefaction technology. This process, however, requires a solvent and hydrogen gas at relatively high pressure [3]. For this, other processes are then required to convert coal into liquid fuel, which is more effective and relatively affordable.

Pyrolysis refers to a technology for the decomposition of solid fuel into liquid by means of heating without the presence of oxygen at atmospheric pressure [4,5]. But, the coal pyrolysis process still produces a low yield of liquid products. The co-pyrolysis method of coal with other materials that have a higher (H/C)eff is an effort to increase the yield of liquid products. Polypropylene plastic has (H/C)eff =2.05, while coal has (H/C)eff=0.76 [6,7].

The use of catalysts in pyrolysis is critical to improve the quality of liquid products [8]. Calcium oxide (CaO) is an alkaline earth metal used as a catalyst for biomass pyrolysis. Conducted the fast pyrolysis of cotton stem biomass by using calcium oxide and the results showed the decrease of the acid compounds in the liquid product, and the increase of the ketone and hydrocarbon content [9]. Therefore, research was carried out on the co-pyrolysis of coal and polypropylene plastic with a CaO catalyst. The aim of this research is to determine the effects of the ratio of coal: polypropylene (PP) plastic and CaO catalyst concentration on liquid fuel yield and characterization of liquid fuel products.

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2. Materials and Methods

2.1. Preparation of \raw materials

Initially, the coal to be used was washed with water and dried under the sun within 4 hours. It was then crushed and sieved with a 50-mesh sieve. Polypropylene (PP) plastic wastes were collected and cleaned prior to be cut into 1x1 cm in size. Finally, it was dried under the sun.

2.2. Co-pyrolysis process

The production of liquid fuel was carried out by inserting materials in the form of coal, PP plastic and CaO catalyst into the co-pyrolysis reactor (Figure 1) at a temperature of 400°C without the presence of oxygen by flowing nitrogen gas at a flow rate of 100mL/minute for 60 minutes. Co-pyrolysis products are the non-condensable gas, charcoal and liquid fuel. The organic vapor formed would be condensed using a condenser to produce liquid fuel. Liquid fuel products were then characterized by conducting physical analysis by determining density, viscosity, pH and heating value. Whereas, chemical analysis used gas chromatography-mass spectroscopy (GC-MS) to determine the components contained in the resulting products.

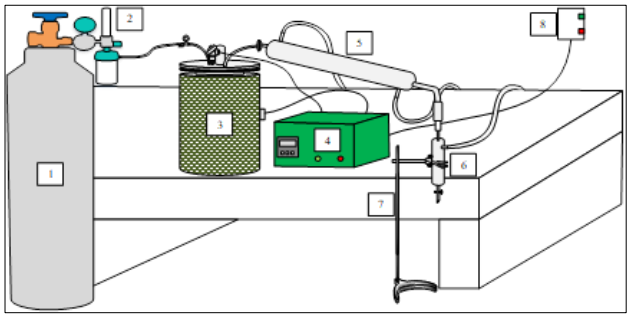

Fig. 1. Co-Pyrolysis equipment series

Remarks:
1.Nitrogen tube 2. Regulator 3. Reactor 4. Temperature Control
5. Condenser 6. Separator 7. Clamp Stand 8. Current Sources

2.3. Result analysis

Chemical analysis and physical analysis were conducted to the product results obtained. Chemical analysis was carried out using GC-MS (Gas Chromatography Mass Spectrometry) and physical analysis included density test, viscosity test, pH test and heating value test.

3. Results and Discussion

3.1. The effects of the ratio of coal and polypropylene plastic on liquid fuel yield

The research process was carried out with polypropylene plastic/coal ratios at 0/100, 25/75, 50/50, and 75/25 at an operating temperature of 400°C. Figure 2 shows the results of liquid fuel yield using various raw material ratios.

Yield refers to the ratio between the product mass and the mass of the initial material. Figure 2 shows the relationship between the percentage of a mixture of polypropylene plastic and coal on the product yield produced at a temperature of 400°C. With more polypropylene plastic added to the co-pyrolysis process, the yield of liquid fuel produced increased. This was because polypropylene plastic contains more hydrogen elements, so this hydrogen can be a donor in coal. In this way, coal is more easily decomposed into liquid product, as proven by the more decreasing char product. In this research, the polypropylene/coal plastic variable with the highest yield was a polypropylene/coal plastic ratio of 75/25 with a liquid fuel yield value of 45.38%. At a polypropylene plastic/coal ratio of 0/100, the liquid fuel produced experienced a significant decrease due to the absence of a hydrogen supply, which could increase the yield of liquid fuel. The results of this research are in accordance with what was conducted with slow pyrolysis of coal and plastic at plastic mixture variables of 0%, 10% and 20% in which there was an increase in the percentage of pyrolysis results in liquid products of 13%, 18% and 19% respectively [10]. Based on these results, it can be seen that the addition of the percentage of plastic in the co-pyrolysis of polypropylene plastic and coal can increase the yield of the liquid fuel produced.

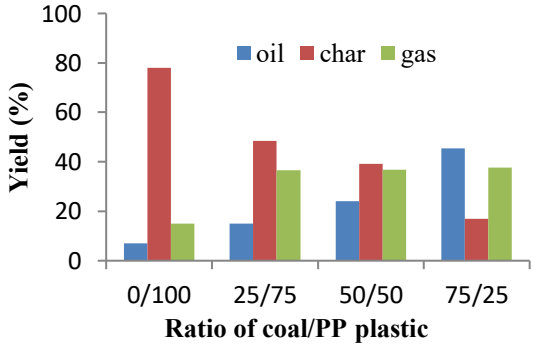

Fig. 2. Effects of the ratio of coal and PP plastic on product yield

3.2. Effects of CaO catalyst concentration on liquid fuel yield

This co-pyrolysis research used raw materials in the form of PP plastic and coal with a ratio of 75: 25 and a variable CaO catalyst concentration. The ratios of CaO catalyst to raw materials used were at 10%, 15%, and 20%. Figure 3 shows the effects of the ratio of CaO catalyst and raw materials on the liquid yield obtained.

Figure 3 shows that as the CaO catalyst concentration more increases, more liquid fuel is produced. The highest liquid fuel yield was obtained at a catalyst ratio of 20%. However, the yield of liquid fuel in the co-pyrolysis process without a CaO catalyst was found greater than that of with a catalyst. Wang et al. [11] stated that the decrease in liquid fuel yield is related to the large number of non-condensable gas products being formed, resulting in the production of more light hydrocarbon fractions that could not be condensed. This type of hydrocarbon has a lower boiling point than ambient temperature does.

Char production increases with the increasing CaO catalyst concentration. The occurs as CaO as a catalyst absorbs CO2 gas during the co-pyrolysis process [12]. The more CaO

catalyst used, the more CO2 gas will be absorbed. This then causes char production in the co-pyrolysis process to increase, while gas production decreases.

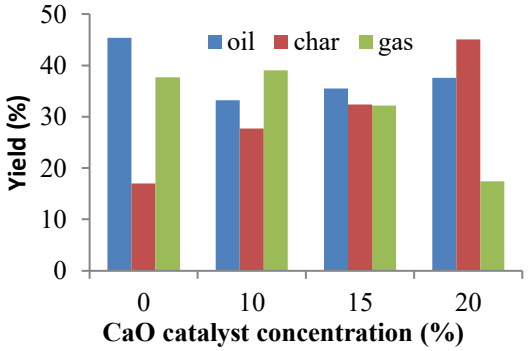

Fig. 3. The effects of the ratio of CaO catalyst and raw materials on the liquid fuel yield obtained

3.3. Characteristics of liquid fuel

The co-pyrolysis process uses polypropylene (PP) plastic and coal as raw materials to produce products in the form of liquid fuel, char and gas. Liquid fuel with the largest yields is characterized based upon physical and chemical properties. The characterization of the physical properties of liquid fuel consists of testing density, viscosity, heating value and pH. Also, the chemical properties of the liquid fuel obtained were analyzed using Gas Chromatography-Mass Spectroscopy (GC-MS) to determine the chemical components formed in the liquid fuel.

3.4. Results of physical analysis

The characterization of the physical properties of this liquid fuel is in the form of analysis of density, viscosity, heating value and pH. Table 1 presents the comparison of liquid fuel produced from polypropylene plastic/coal 75/25, polypropylene plastic/coal 75/25 with 20% catalyst, and diesel.

Table 1. The comparison of physical properties from liquid fuel

Parameter	BBC from PP Plastic /coal (R = 75/25)	BBC from PP Plastic/ coal (R = 75/25) with CaO 20%	Diesel Oil (Sunarno, *et. al*, 2022b)
Density (g/mL)	0,818	0,839	0,815-0,87
Viscosity Kinematic (cSt)	2,16	2,51	2-4,5
Heating value (MJ/kg)	40,84	46,813	42,75
pH	2,24	2,9	5,5-8

Density refers to the amount of mass per volume of liquid. It is a physical characteristic that can be used as an indication in knowing the type of certain product or compound. The test was carried out using a clean and dry pycnometer. The empty pycnometer was weighed and the results were recorded. It was filled with liquid fuel and closed until it overflowed and there were no air bubbles. Subsequently, the pycnometer containing liquid fuel was weighed and the results were recorded. Table 1 shows that the density of liquid fuel produced at a polypropylene/coal plastic feed ratio of 75/25 is 0.818 g/mL while the density of liquid fuel produced at a polypropylene/coal plastic feed ratio of 75/25 with a catalyst of 20 % of 0.839 g/mL. The results of this test showed that the density of liquid fuel resulting from co-pyrolysis of polypropylene plastic/coal fell within the density characteristics of diesel oil at 0.815-0.870 g/mL

Viscosity is an important physical component of fuel that must be considered. It is related to the viscidness of a fluid and the frictional force between fluid layers when one layer moves over another one. The increase in viscosity value is determined by the density value. In other words, the higher the density value, the thicker the product produced [13]. The viscosity of the liquid fuel produced in this study was at a polypropylene/coal plastic feed ratio of 75/25 of 2.16 cSt, while the viscosity of the liquid fuel produced at a polypropylene/coal plastic feed ratio of 75/25 with a 20% catalyst was 2 .62 cSt. This value corresponded to the viscosity of diesel fuel, i.e. 2-4.5 cSt.

Table 1 depicts that the heating value of liquid fuel was at a polypropylene/coal plastic feed ratio of 75/25 is 40.84 MJ/kg, while with the addition of a 20% catalyst there was an increase in the heating value, i.e. 46.813 MJ/kg. This heating value was found higher compared to liquid fuel produced from co-pyrolysis of 25% empty palm fruit bunches and 75% LDPE plastic with a 3% CaO catalyst which has a heating value of 43.5 MJ/kg [3]. Similarly, the heating value of liquid fuel from co-pyrolysis of empty palm fruit bunches and polypropylene plastic was 43.2 MJ/kg [14]. From the results of this test, the heating value obtained was found greater than that of diesel oil, i.e. 42.75 MJ/kg.

In this research, the liquid fuel produced had a degree of acidity (pH) at a polypropylene/coal plastic feed ratio of 75/25, i.e. 2.24, but with a 20% catalyst the liquid fuel produced increased to 2.9. The CaO catalyst can reduce the acid compound content in the liquid product resulting from pyrolysis. However, the pH of liquid fuel from polypropylene plastic and 75/25 coal with a 20% catalyst is still below the acidity (pH) for diesel oil in the range of 5.5 – 8 [15].

3.5. Results of chemical analysis

Figure 4 and Figure 5 illustrate the results of the chromatogram of liquid fuel with a coal/polypropylene plastic ratio of 25/75 and coal/polypropylene plastic 25/75 with the addition of 20% catalyst at a temperature of 400°C. Figure 4 shows 30 peaks with different area percentages, while Figure 5 shows 15 peaks.

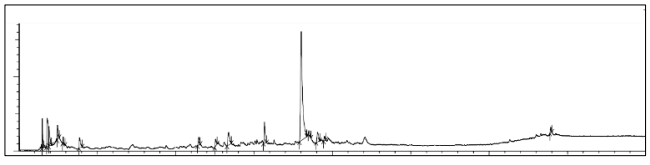

Fig. 4. The chromatogram results of liquid products resulting from co-pyrolysis of coal and PP plastic without a catalyst

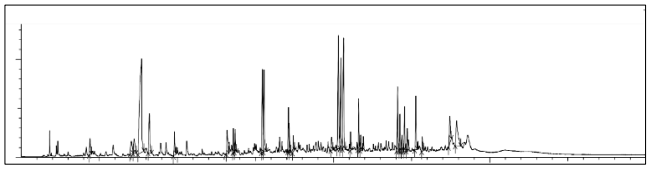

Fig. 5. The chromatogram results of coal and PP co-pyrolysis liquid products

with the addition of 20% catalyst

Table 2. Compounds contained in liquid fuel with and without a catalyst

Component	%Area (without catalysts)	%Area (with catalysts)
Hydrocarbon	**56,7**	**57,52**
4 Methyl Heptane	1,03	-
1,3,5 Trimethyl Cyclohexane	1,83	-
1,2,4 Trimethyl Cyclohexane	3,44	-
2,6 Dimethyl nonane	1,27	-
2,6 Dimethyl nonane	1,22	-
2,4 Diethyl 1 methyl cyclohexane	0,96	-
4,4,5 Trimethyl 2 hexene	1,79	-
7 Methyl 1 andesene	1,99	-
1 Pentadecene	6	-
1 Hexadecane	0,99	-
1 Tridesen	9,37	-
1 Heptadecene	6,2	-
1 Tridesen	8,05	-
1 Nonadecent	3,99	-
Hydraction of methyl cyclododecane	2,86	-
9 ecocene	5,71	-
1,3,3,4 Tetramethyl 2 oxabicyclo hexane	-	51,26
1,3,3,4 Tetramethyl 2 oxabicyclo hexane	-	1,38
Methyl oxirane	-	3,85
Germacrane-b	-	1,03
Alcohol	**24,65**	**13,48**
2,4,6 Methanol	2,54	-
2,4,6 Methanol	1,38	-
1 Tridesanol	0,91	-
2,4,6 Trimethyl cyclohexyl methanol	1	-
3,7,11,15 Tetramethyl 1 hexadecanol	2,19	-
3,7,11,15 Tetramethyl 1 hexadecanol	1,27	-
3,7,11,15 Tetramethyl 1 hexadecanol	2,79	-
3,7,11,15 Tetramethyl 1 hexadecanol	1,38	-
1,2,2 Docosanodiol	3,48	-
2,2,6,6 Tetramethyl cyclohexyl methanol	0,94	-
Tridecanol	2,6	-
2 Hexyl 1 decanol	4,17	-
1,2,3 propanetriol	-	10,26
2 butenol	-	3,26
Ketones	**1,6**	**23,15**
3 Acetyl oxymethyl 3,4 dimethyl 2 pentanone	1,6	-
2 propanone	-	3,76
2 butanone	-	4,93
2 pentanone	-	1,39
3 pentanone		3,06
2,5 hexanedione		2,16
3 methyl 2 cyclopentanone		1,84
5 Hydroxypentanone		4,85
6 Methyl 7 octanone		1,16
Aldehyde	**17,05**	**-**
2 Heptanol	17,05	-
Carboxylic acid	**-**	**5,85**
2 ethyl 2 hydroxybutyric acid		5,85

The data in Table 2 showed a comparison between liquid fuel products of co-pyrolysis with and without 20% CaO catalyst. The compound with the highest area was hydrocarbon at 56.7% (process without catalyst). Meanwhile, by using a 20% CaO catalyst, the area of hydrocarbon compounds increased to 57.52%. Other compounds dominating in the liquid fuel resulting from this research without a catalyst were 24.65% alcohol, 1.6% ketones and 17.05% aldehydes.

While, other compounds with the addition of 20% catalyst were 13.48% alcohol, 23.15% ketones, and 5.85% carboxyic acid. By adding the CaO catalyst, the alcohol content could be significantly reduced because during the co-pyrolysis process with the CaO catalyst it was able to neutralize the acid, called as deacidification, resulting in the splitting of the O atom so that it turned into alcohol, aldehyde, ketone and acid compounds. Deacidification also had an impact on the increase of the amount of hydrocarbons, as indicated by the increasing heating value.

4. Conclusion

The addition of polypropylene plastic in co-pyrolysis with coal helped to increase the yield of liquid fuel. Co-pyrolysis with a polypropylene plastic/coal ratio of 75/25 obtained a yield of 45.38%. The addition of the CaO catalyst helped to improve the quality of the liquid product. Liquid fuel produced from co-pyrolysis of polypropylene plastic/coal with a ratio of 75/25 and 20% catalyst had a kinematic viscosity of 2.62 cSt, density of 0.839 g/mL, heating value of 46.813 MJ/kg and pH of 2.9, with a composition 57.52% hydrocarbon, 13.48% alcohol, 23.15% ketone, and 5.85% carboxylic acid.

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