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Zeolite Effect on Solid Product Characteristics in Hydrothermal Treatment of Household Waste

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Abstract. The number of primary energy sources in Indonesia will run out quickly. Therefore, innovation is required to provide renewable energy sources (NRE) that accommodate the increasing energy necessities. Hydrothermal is the potential degradation process of plastic waste to generate NRE. This study aims to examine the effectiveness of the hydrothermal process in breaking down bulky raw materials and the role of zeolite as a catalyst to upgrade the quality of hydrochar as a novel solid fuel by evaluating the essential parameters through proximate and ultimate analysis. The addition of zeolite in the hydrothermal process can increase the water content, ash content, and volatile matter and slightly decrease the calorific value and fixed carbon. The condition to obtain the best characteristics was temperature of 220 °C and the addition of 20 % zeolite.

Keywords: Hydrochar, Hydrothermal, Waste Treatment, Zeolite

INTRODUCTION

In the Press Release of the Ministry of Energy and Mineral Resources of the Republic of Indonesia Number 311.Pers/04/SJI/2020, on October 22, 2020, the Minister of Energy and Mineral Resources declared that the fossil energy crisis due to continuous use has pushed for a complete transition from fossil energy to new renewable energy (NRE). Based on the Handbook of Energy and Economic Statistics of Indonesia 2020, the total energy availability owned by Indonesia was 218,292,073 TOE (Tons of Oil Equivalent), of which 80,960,474 TOE (37.09 %) from coal, 69,090,070 TOE (31.65 %) petroleum, 36,706,710 TOE (16.82 %) natural gas, and the rest in the term of hydropower, geothermal, wind, and others. However, Indonesia's total energy consumption in 2020 had reached 131,326,721 TOE (60.16 % of total energy available in the same year), of which coal consumption was 13.44 %, petroleum at 26.36 %, and natural gas at 11.53 %. If energy consumption continues without any renewal, it is predicted that the amount of oil in Indonesia will run out in the next nine years, natural gas in 22 years, and coal in the next

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65 years. Therefore, innovation is required to support the government's attempts to provide renewable energy sources that can continuously accommodate the increasing energy necessaries of the inhabitants.

The potential source of renewable energy is quite large, in particular waste. Based on data in the National Waste Management Information System from the Ministry of Environment and Forestry, Indonesia's total waste generation in 2021 was 22,905,248.45 tons/year, of which 35.27 % is unmanaged. Meanwhile, West Kalimantan contributed 441,177.29 tons/year, with Pontianak City as the most significant waste producer, with 144,651.25 tons/year. Of the total waste in West Kalimantan, the highest percentage composition is food waste 48.58 %, plastic 23.44 %, wood 6.80 %, and others from paper, glass, rubber/leather, cloth, and metal. Food waste is organic waste that can be degraded biologically. However, plastic waste demands an enduring time to be completely degraded. Chamas et al. (2020) estimated the half-life of degradation of various types of plastic in the soil involving PET > 2500 years, HDPE (plastic bottles) 230-280 years, HDPE (pipe) 4600-5500 years, PVC > 2500 years, LDPE 4.6 years, and PS > 2500 years. Therefore, it constrains the treatment; thus, the rising amount of plastic waste can be restrained and converted into NRE.

The potential degradation process of plastic waste to generate NRE is the thermal process (thermolysis). The thermolysis comprises hydrothermal operated at temperatures of 180-350 ^{o}C (Román et al. 2012; L. Zhang et al. 2010), pyrolysis at 400-550 ^{o}C, and gasification at 800-1200 ^{o}C (Kammann and Funke, 2017; L. Zhang et al. 2010). This comparison reveals hydrothermal is a thermolysis process with the lowest operating temperature. Furthermore, hydrothermal is a thermal conversion process that can be conducted even though the sample is soaked with high water content. This process employs water as an environmentally friendly and abundant solvent in the decomposition process (Yuliansyah et al. 2010). Hence, this technology is appropriate to be applied in Indonesia, where most of the waste is wet because it is still not separated between organic and inorganic waste. During the hydrothermal process, the plastic polymer sample wrapped in high pressurized water will be decomposed into smaller molecules with a high calorific value, referred to coal-like material as hydrochar (Román et al. 2012).

Currently, the catalyst performance in hydrothermal liquefaction (HTL) has been intensively explored to upgrade product quality. Based on the most recent studies, homogeneous catalysts such as HCOOH, NaOH, KOH, K_2CO_3, Na_2CO_3, KH_2PO_4, K_2HPO_4, K_3PO_4, and metal supported heterogeneous catalysts such as Ni/C, Ru/C, Pt/C, Pd/C, $Ni/SiO_2–Al_2O_3$, Ru/Al_2O_3, and Pt/Al_2O_3 did not increase the bio-oil yield. This outcome contradicted the favorable performances of heterogeneous metal oxide catalysts such as CeO_2, La_2O_3, SiO_2, and hierarchical Fe-Co-ZSM-5, which promoted the bio-yield (Govindasamy and Kumar, 2022).

Even the less expensive metal oxides, such as red clay and red mud, enhanced the biocrude yield with a higher heating value (HHV) much greater than the uncatalyzed HTL (Cheng et al. 2020). Moreover, Hao et al. (2023) loaded the non-nobel metals Ni, Cu, and Co onto activated carbon (AC) to construct Ni/AC, Ni-Co/AC, and Ni/Cu/AC, which were subsequently employed in the HTL process of municipal waste. Compared to non-catalytic HTL, Ni-Co/AC and Ni-Cu/AC catalysts raised the bio-crude HHV and significantly reduced sulfur content. Mukundan et al. (2022) recognized this finding for a mixture of Prosopis juliflora (PJ) biomass and polypropylene (PP) plastic waste utilizing alumina-supported metal oxide (Mo, Ni, W, and Nb) catalysts in HTL. The Nb/Al_2O_3 catalyst worked great, exhibiting exceptional recyclability, bio-oil yield, high deoxygenation, and carbon recovery.

However, there has yet to be a thorough investigation into the behavior of natural zeolite in hydrothermal treatment carbonization (HTC) which then known as hydrothermal treatment (HT). One of the ubiquitous minerals with the most diverse uses is zeolite, whose microstructure provides a wide range of potential applications. Due to its physical and chemical properties, zeolite can act as an absorbent, an ion exchanger, a molecular filter, and a catalyst. Moreover, the geological position of Indonesia among the world's volcanoes contributes to the widespread availability of zeolite. Kusdarto (2008) from the Center for Geological Resources (PSDG) of the Geology Agency in the Ministry of Energy and Mineral Resources confirmed that Indonesia has a tremendous natural zeolite commodity, approximately 447,490,160 tons. Therefore, this research aims to investigate the performance of zeolite as a catalyst and the effect on the solid product of HT of a mixture of sawdust biomass and polyethylene terephthalate (PET) plastic waste.

MATERIALS AND METHODS

Materials

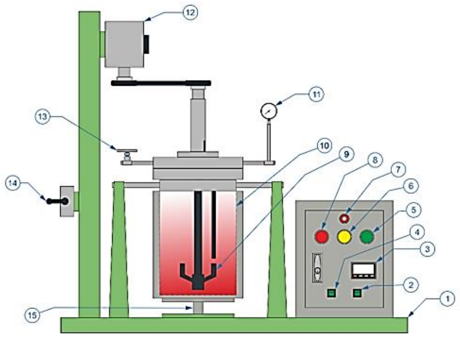
The representative samples of household waste in this research constituted sawdust biomass gathered from the nearby sawmill industry as shown in Figure 1 and polyethylene terephthalate (PET) plastic bottles collected from a waste management plant under the Agrotechnology Innovation Center at Universitas Gadjah Mada, Yogyakarta. In addition, water was used as a solvent, and natural zeolite of the mordenite type as exhibited in Figure 2, which functioned as a catalyst, was sourced from Klaten, Central Java, Indonesia. Sawdust and zeolite were previously analyzed utilizing TG-DTA (Maleiva et al., 2020), revealing the following compositions of sawdust: 49.33 % d.b. cellulose, 29.49 % d.b. lignin, and 5.11 % d.b. hemicellulose; and zeolite: 70.750 % Si, 12.381 % Al, 7.385 % Ca, 4.127 % Fe, 2.919 % K, 1.131 % S, and 0.552 % Ti.

Fig. 1: Sawdust

Fig. 2: Mordenite natural zeolite

Equipment

A two-liter batch reactor was used to process the hydrothermal treatment. This reactor was built of stainless steel material with an isolated system. The reactor was also facilitated with a pressure gauge and temperature controller, as used by Abidin et al. (2018).



1. Chassis
2. On/off switch
3. Temperature controller
4. Heater switch
5. Heater indicator
6. Motor indicator
7. Alarm
8. Power indicator
9. Stirrer
10. Reactor
11. Pressure gauge
12. Motor
13. Pressure valve
14. Motor switch
15. Reactor base

Fig. 3: Hydrothermal batch reactor

Procedures

Before use, sawdust was sieved through standard 12-by-20-mesh sieves and then dried in an oven, while PET bottles were washed and shredded into 5-mm fragments. Meanwhile, zeolite was calcined at 350 °C for three hours to activate the surface and remove impurities. The samples were then placed into a reactor with a weight-to-water ratio of 1:10. Zeolite was included in as much as 0, 10, 20, and 30 % of the total weight of the sample. The process was run at a temperature of 180-220 ºC for a half hour. The hydrochar characteristics were then characterized through proximate and ultimate analysis.

RESULTS AND DISCUSSION

The hydrothermal process is generally carried out using water under subcritical conditions as a reactant simultaneously as a catalyst that leads to the degradation of raw materials into simpler molecules (Hrnčič et al. 2016). The product was then analyzed to evaluate the catalytic activity of the zeolite in this thermal conversion process. Yield is one of the essential parameters that exhibits the percentage ratio between the initial mass and volume of raw materials with the final amount obtained for each type of product. The solid yield value decreased with increasing temperature. This phenomenon was because, at higher temperatures, the more water molecules were hydrolyzed, the more raw materials were decomposed through a cellulose bond-breaking reaction. The chain cleavage reaction can also occur in long-chain polymers into lower molecular weight oligomers.

In the thermal degradation process, the radical chain process is a sequential effect of various stages of radical initiation, chain propagation, and radical termination. Since the decomposition temperature of the biomass was lower than that of plastic, the cellulose in the biomass initiates radical formation and polymer chain cleavage. Plastic bottle contains 4.5 wt% hydrogens in their structure. The transfer of this hydrogen from polyolefin chains to radicals derived from biomass results in higher weight % reduction and lower yields of solid products (hydrochar) (Chattopadhyay et al. 2016). The results of the termination of this polymer chain can further reduce the yield value of hydrochar and increase the liquid yield because the decomposed oligomers can be dissolved into the liquid (Yuliansyah et al. 2010).

Based on Figure 4, it can be proved that an increase in decreases solid yield. However, adding more zeolite causes the solid yield to increase at various operating temperatures. As demonstrated in Figure 4, the solid yield value at the highest temperature (220 ºC) enhanced significantly from 66.86 % with the hydrothermal process without the addition of zeolite to 75.44 %, 85.31 %, and 85.83 % with the addition of zeolite of 10, 20, and 30 % respectively. These results indicate that zeolite affects the degradation process of raw materials.

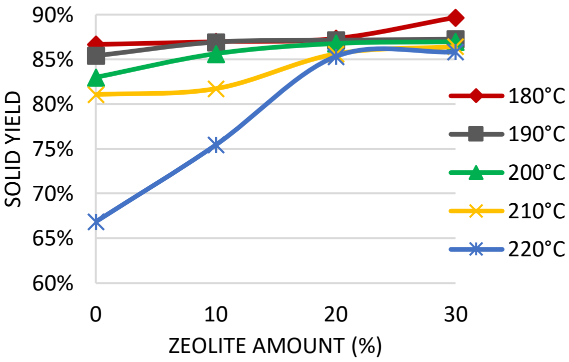


Fig. 4: Solid Product Yield of Hydrochar at Various Temperatures and Zeolite Amounts

The addition of zeolite in the hydrothermal process can drive competition between zeolite solids and raw materials to interact with water molecules. Zeolite involved in silica and alumina atoms has lower ionization energy than the oxygen atom in the water molecule. The smaller the ionization energy, the more electropositive a molecule is; hence the electronegativity gets smaller. This electropositivity can cause OH^- ions from water molecules with a larger electronegativity to be more attracted to interact with the zeolite, as exhibited in Figure 5.

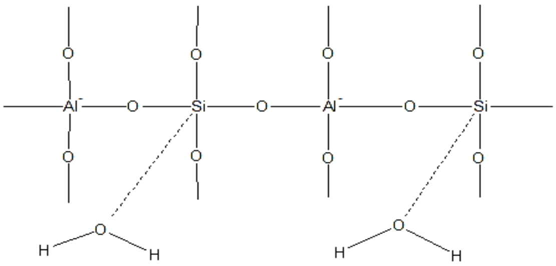


Fig. 5: Reaction of Zeolite with Water Molecules

Figure 5 shows that the covalent bonds formed between Si in zeolite and O in water molecules can further reduce the number of OH^- ions required to degrade raw materials.

In addition, the continuous increase in temperature will also increase the active Lewis acid site in the zeolite molecule (Zhang et al. 2003). Lewis acid is a species that acts as a free pair electron acceptor. This promotes the active site on the surface of the zeolite to be filled with water molecules because more free pairs of electrons from the oxygen atom in the water molecule are received by the zeolite. This further inhibits and reduces the possibility of reacting OH^- ions from water molecules with raw materials to be decomposed. Therefore, the addition of zeolite in the hydrothermal process can raise the solid yield value, and the presence of zeolite can weaken the ability of water to degrade raw materials. This is supported by the results of the analysis of the calorific value of solids, as shown in Figure 6.

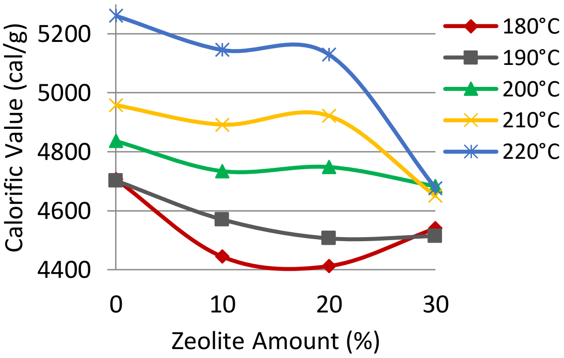


Fig. 6: Calorific Value of Hydrochar at Various Temperatures and Zeolite Amounts

Based on Figure 6, it can be seen that the calorific value increased with increasing temperature so that 220 °C becomes the optimum temperature that can produce the most significant calorific value in each hydrothermal process with the addition of zeolite. However, the calorific value of hydrochar decreased with the addition of more zeolite. This was affected by the grade of degradation as Figure 6 represents that the most hydrochar added zeolite was the least degraded hydrochar, so the calorific value was also low.

However, all hydrochar generated by the addition of zeolite during the process can produce a higher heating value than the raw materials' (biomass of 4489.21 Cal/g; plastic bottle of 4054.41 Cal/g) prior to the hydrothermal process. Moreover, the calorific value at all the highest temperatures can also exceed the calorific value of coal by 4776.92 Cal/g (Nurdiawati et al. 2015). As shown in Figure 6, hydrothermal treatment without adding zeolite at a temperature of 220 °C produced the least yield that can then be applied as fuel even though it has the best degradation quality with the highest heating value 5261 Cal/g. However, hydrothermal treatment with the 20 % addition of zeolite produced a beneficial hydrochar quality with a calorific value of 5130 Cal/g. Thus, a temperature of 220 °C and the addition of 20 % zeolite can be the most optimum hydrothermal treatment because it can produce a high calorific value and the highest yield compared to other treatments.

Proximate Analysis

Furthermore, the value of water content is one of the crucial parameters that affect the quality of hydrochar. The lower the water content value, the higher the calorific value, so the better the quality of the hydrochar produced. The effect of this zeolite catalytic activity can be observed with variations in the percentage addition of natural zeolite, as performed in Figure 7.

Figure 7 represented that the increasing temperature with zeolite addition can lower the water content value in all treatments. However, in this study, there was also an increase in water content at higher temperatures and the addition of more zeolite. This can be caused by the presence of water molecules that obstruct the surface of the zeolite; hence the process of breaking the macromolecular bonds of the raw material cannot take place properly and induces the water content of the raw material to not escape as the first product when degradation occurs.

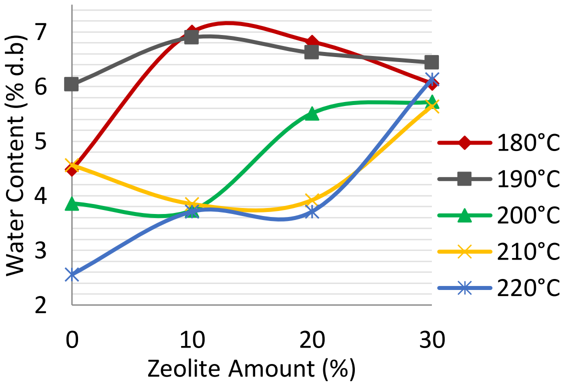


Fig. 7: Water Content of Hydrochar at Various Temperatures and Zeolite Amounts

Ash content is inorganic minerals found in the form of oxide compounds such as SiO_2, Na_2O, K_2O, MgO, SO_3, P_2O_5, Al_2O_3, and Fe_2O_3 g (Lahijani & Zainal, 2011). This ash content also affects the quality of hydrochar as a fuel. The higher the level, the lower the calorific value of hydrochar. The results of hydrochar ash content analysis at various temperatures and the amount of zeolite can be presented in Figure 8.

Figure 8 reveals that the ash content decreased with increasing temperature but increased at higher temperatures and added more zeolite. At a temperature of 220 °C, the ash content of hydrochar increased drastically to 4.92 with the addition of zeolite 30 % because, at the higher temperature, the biomass as one of the raw materials became more porous due to the wholly reacted hemicellulose and cellulose. This pore structure absorbs inorganic compounds leading to an increase in ash content. Moreover, this can also be due to the relative percentage of ash content, which other constant elements seem to increase due to a significant decrease in other inorganic oxide compounds (Nurdiawati et al. 2015). Due to the high boiling point, inorganic compounds are usually left in the ash. Besides alkaline inorganic oxide compounds, Si is biomass's most dominant inorganic component. After the hydrothermal process, Si remained remarkably stable in the form of $SiO_2.nH_2O$, which is covalently bound in the biomass matrix (Saddawi et al. 2012; Kalapathy, 2002). On the other hand, the high ash content can also be due to the natural zeolite formed by volcanic activity; thus, there are still many impurities in the form of inorganic minerals on the surface. According to Maleiva et al. (2020), carbonized natural zeolite has the highest Si content in a zeolite (70.75 %), followed by other minerals that the pore structure of the biomass may also absorb. Inorganic minerals other than Si in zeolite and biomass can also be left behind and cause the ash content to increase, even though the hydrothermal process has been carried out at high temperatures.

Furthermore, higher volatile substances can diminish the combustion efficiency and calorific value of hydrochar as fuel. The effect of temperature and the addition of zeolite on the volatile hydrochar substances can be seen in Figure 9.

Figure 9 illustrates that the concentration of volatile hydrochar substances fluctuated due to the increase in temperature or the addition of zeolite. Incomplete degradation processes and macromolecular cracking may cause this phenomenon due to the enclosed zeolite pores by water molecules and inorganic compounds absorbed in the biomass pores; hence volatile substances cannot evaporate during the degradation process.

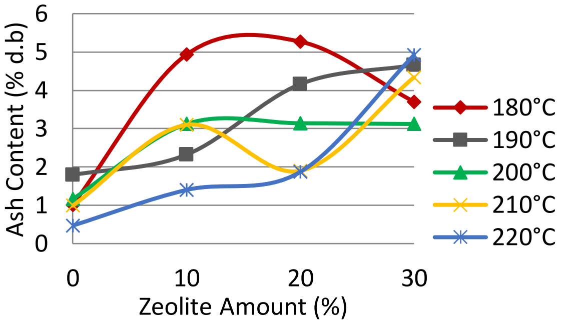


Fig. 8: Ash Content of Hydrochar at Various Temperatures and Zeolite Amounts

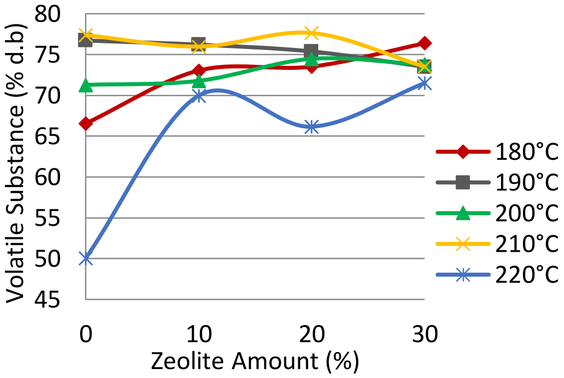


Fig. 9: Volatile Substance of Hydrochar at Various Temperatures and Zeolite Amounts

Due to the decrease in ash content and volatile substances in hydrochar by increasing temperature, the fixed carbon content and the calorific value rose. This is why fixed carbon is also a critical parameter determining the quality of hydrochar as a fuel. The value of fixed carbon at various temperatures and the addition of the amount of zeolite can be exhibited in Figure 10.

Like the ash and volatile matter, the fixed carbon content also fluctuated. These fractions influence each other, so if the ash content and volatile substances cannot decrease due to a poor degradation process, the amount of fixed carbon also cannot increase.

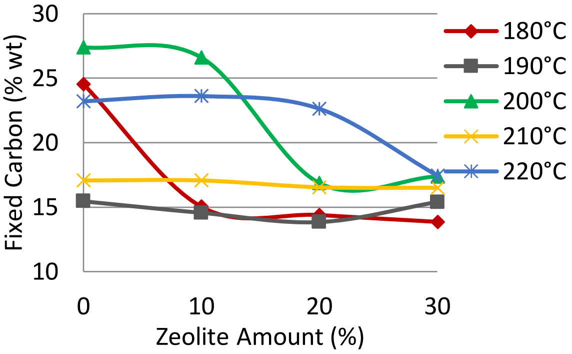


Fig. 10: Fixed Carbon of Hydrochar at Various Temperatures and Zeolite Amounts

Ultimate Analysis

After all, temperature variations and the amount of zeolite also affect the C, H, O, N, and S content in hydrochar, as provided in Table 1.

Table 1 indicates that the higher the temperature, the H, O, N, and S content tends to decrease due to breaking the hydroxyl, carboxyl, amine, and sulfonate bonds in the polymer raw materials, increasing the carbon content of the hydrochar. This is supported by Mckendry (2002) that explained the calorific value increases along with the increase in carbon content. The increase in carbon content can be proven by the higher dissociation energy of the carbon-carbon bonds so that when the carbon-oxygen and carbon-hydrogen bonds are broken with lower dissociation energies, the number of carbon chains is rearranged.

However, the percentage of C decreased, and the levels of H, O, N, and S increased with more zeolite added. This can be explained by the same reason that the breaking of hydroxyl, carboxyl, and all macromolecules of raw materials entering the zeolite is blocked by water molecules on the pores so that degradation cannot occur properly.

Table 1. C, H, O, N, and S of Hydrochar at Various Temperatures and Zeolite Amounts

Zeolite Amount	**T (°C)**	**Concentration (%)**				
		C	**H**	**N**	**S**	**O**
0 %	180	48,480	6,190	0,080	0,022	44,218
	190	50,180	5,960	0,050	0,010	42,010
	200	53,900	5,560	0,040	0,008	39,332
	210	52,920	5,730	0,060	0,004	40,296
	220	57,100	5,180	0,030	0,003	37,217
10 %	180	47,020	5,900	0,110	0,008	42,032
	190	48,600	6,090	0,100	0,006	42,884
	200	51,080	5,400	0,030	0,004	40,366
	210	52,710	5,510	0,040	0,012	38,628
	220	46,580	4,540	0,010	0,002	47,468
20 %	180	46,790	5,880	0,050	0,010	42,000
	190	47,730	6,040	0,060	0,008	42,002
	200	50,600	5,820	0,050	0,011	40,379
	210	53,920	5,510	0,030	0,004	38,636
	220	53,900	5,010	0,020	0,001	39,199
30 %	180	48,560	5,900	0,060	0,014	41,766
	190	48,030	5,900	0,050	0,014	41,346
	200	50,260	5,790	0,060	0,016	40,754
	210	49,730	5,640	0,030	0,008	40,252
	220	52,310	5,060	*	0,002	37,708

*not detected

CONCLUSION

The addition of zeolite in the hydrothermal process can increase the water content, ash content, volatile matter, and the elements of H, O, N, and S, but decrease the calorific value, fixed carbon, and the element of C compared to the products without zeolite addition which led to unbeneficial quality of the products as fuel. However, the temperature of 220 °C and the addition of 20 % zeolite were considered as the best condition to achieve the great performance of hydrothermal process regarding most of the parameters.

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