Hydrothermal carbonization of rice husk for fuel upgrading

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Abstract. The biomass is popularly used as renewable energy. In Thailand rice is the most consume agricultural products. Agricultural residues from rice husk can be an energy resource. However, alkali and alkali earth materials (AAEMs) in biomass ash are the causes of corrosion and erosion problem in the heat exchanger equipment, while the acidity of ash affects the slagging agglomeration problem. Reduction of alkali and alkali earth materials can minimize the problem. In order to challenge the reduction of alkali and alkali earth materials in biomass ash, hydrothermal carbonization process was selected. Thai rice husk was used as sample to compare the result of treatment. The rice husk was heated under the condition of different temperature ranged from 180°C to 250°C, at operate pressure ranges from 12 bar to 42 bar with residence holding reaction time 1 hour. The results of proximate analysis show that the percentage by mass of fixed carbon are increased 2 times, but volatile matter is decreased by 40% and ash content is decreased by 11% due to the increment of temperature. Meanwhile, the X-Ray fluorescence (XRF) analysis results show the decreasing of alkali and alkali earth materials are reduced.

1. Introduction

The renewable energy was invented to fulfill the energy consumption demand due to population which is growing up day by day. The biomass is the renewable energy with the advantages, the biomass is green energy and biomass can be found in everywhere. While the combustion produces CO₂, agriculture biomass consumes CO₂. The CO₂ transfers in cyclic and it is not added to the atmosphere, with the CO₂ cyclic the biomass were classified to the green energy. The biomass can be found in everywhere and this is the advantage over the fossil fuel. Because of the fossil need the proper environment to discover, so its take more value than biomass.

Combustion is the oldest and easiest method to convert the biomass to energy. However, use of biomass as an energy resource in combustion process has some disadvantages due to high moisture content, uncertainty of heating value, and high ash (alkali metal) content resulting in fouling and corrosion problem in the boiler.

In 2016, Thailand consumes 2,862 kilotons of rice husk to produce energy which is 5.78% of total biomass used as an energy resource. [1] Generally, rice husk has high alkaline in composition. The case of low effective when use in the direct combustion process. Hydrothermal is one of treatment processes to
improve quality of solid fuels. The study of hydrothermal carbonization applied to coconut fiber and eucalyptus leaves in two different temperature range, 150°C-300°C and 300°C-375°C. Hydro-char fuel properties were significantly improved compare to feedstock biomass [2]. The acidity component in tropical woody biomass ash was minimized by using the hydrothermal carbonization pretreatment in mild subcritical condition [3, 4].

The objective of this paper is to study the effect of temperature to properties of Thai rice husk treated under hydrothermal process.

2. Material and Methods

2.1. Material

Rice husk is the agricultural residue products from rice production obtained in Thailand. The 1cm sizes of rice husk (figure 1.) were dried in large batch at 95°C with 24hr residence time.

2.2. Methods

The hydrothermal carbonization process was performed via Parr reactor model 4857 (figure 2.), under the variety operating temperature 180, 200, 220 and 250. The 50g (dry basis) of raw material was put and 500ml deionized water was added, with the purpose of control the pressure range from 12 bar to 42 bar in the reactor vessel. Then, seal the reactor and purge residual air by using the Nitrogen gas. Then heating the reactor with electric coil to the desired temperature and maintains residence time for 1 hour. After the reactor cools, the bio-gas was removed, the bio-char and bio-oil were separated by a filter. The bio-char was dried before analyze process.

3. Result and Discussion

3.1. Proximate and ultimate analysis

Proximate analysis was done under the ASTM D7582. CHN analyzer (LECO Corporation, 628 Series: CHN) was used in the ultimate analysis. Proximate analysis of bio-char result from table 1 shows the decrease of moisture content from 8.75% to 3.26%. Also, the volatile matter content is reduced from 67.44 to 23.23%. In the opposite, the fixed carbon is increased from 12.81% to 25.91% as shown in Figure 3. The ultimate analysis shows that the percentage of carbon is slightly up from 37.76% to 40.27%. The hydrogen is slightly down from 5.12% to 4.57% and the oxygen is also decreased from 37.09% to 28.23%. The effect from the thermal decomposition of hemicellulose which the most sensitive components of three main components is first decomposition compound related to the lower of H, O and moisture when the temperature increase. In the opposite the retained lignin and cellulose fraction generates the non-condensable gases such as H₂, CO, CO₂ and CH₄ from char that relate to the increment of carbon content.
The lower in volatile matter and higher carbon at higher temperature of hydrothermal carbonization are satisfied to the study of conversion sewage sludge into hydro-char at 200°C hydrothermal carbonization process was studied by Chao He [5]. The heating value increased at higher temperature from the study of D. Kalderis [6] also satisfy with this study.

However, the hydrothermal carbonization pre-treatment causes the weight loss in biomass which related to loss in energy, the proximate analysis results were weighted by mass loss as shown in figure 3. The ash component in entire samples remains the same as raw material. While the increment of hydrothermal temperature the volatile matter and oxygen content trends go down. In the opposite, the fixed-carbon trends are raised. Whereas the carbon content form ultimate analysis weighted by mass loss cannot see the significant different.

Table 1. The result of proximate analysis and ultimate analysis

| Temperature | Proximate (% d.b.) | Ultimate (% d.b.) | Mass loss (%) |
|-------------|---------------------|-------------------|---------------|
|             | Moisture (w.b., %)  | Ash               | Volatile Matter | Fixed-Carbon | %C | %H | %N | %O |
| Raw Rice husk | 8.75 19.75 67.44 12.81 | 39.01 5.73 0.21 35.29 | 0 |
| 180°C | 5.19 22.99 63.32 13.68 | 39.57 5.10 0.31 32.02 | 23.60 |
| 200°C | 4.23 25.34 61.35 13.30 | 41.23 4.76 0.36 28.30 | 26.58 |
| 220°C | 4.19 26.48 57.52 16.00 | 42.03 4.77 0.45 26.25 | 31.40 |
| 250°C | 3.26 31.99 42.09 25.91 | 46.64 3.96 0.69 16.70 | 44.80 |

Figure 3. Proximate and ultimate analysis weighted by mass loss

3.2. Energy

The energy loss was concerned with purpose of fuel uses. Heating value trends are increased due to the increase of temperature, but the mass yield trend goes down (figure 3). The correlation between mass yield and heating value were specified in term of energy loss. The highest heating value of solid is 19.96 MJ/kg at 250°C, but the mass yield is the lowest at 55.19%. However, the energy loss is maximum at 250°C but minimum at 180°C

Table 2. Energy and mass yield

| Temperature | HHV (d.b., MJ/kg) | Mass yield (%) | Energy loss (%) |
|-------------|-------------------|----------------|-----------------|
| Raw material | 16.77 | 100 | 0 |
| 180°C | 15.92 | 76.40 | 4.60 |
| 200°C | 15.69 | 73.42 | 5.25 |
| 220°C | 17.03 | 68.60 | 5.08 |
| 250°C | 19.96 | 55.19 | 5.75 |
3.3. Ash component analysis

The use of X-Ray fluorescence (XRF) analysis with an X-Ray fluorescence spectrometer (Bruker, model S8-Tiger) to obtain the ash component in term of oxide compound. The chart of CaO, K₂O and P₂O₅ and residence temperature trend are decreasing (figure 5-8.). The significant downward trend of alkaline at 180°C indicated that the alkaline was pulled out at lower temperature. Therefore, at the higher temperature the alkaline quantities are remained approximately. These results correlated with the study of C.A. Cuilias [3] in tropical woody biomass treated by hydrothermal carbonization at 175°C-350°C. Whereas the change of temperature affect the reduction of alkaline in biomass ash but slightly affect to the reduction of metal as in the figure 9. Shown the fairly constant quantities of Fe₂O₃. The summary of ash compound quantities in term of slagging index revealed that there are not significant change at temperature above 200°C (table 3.).

| Sample | MgO  | CaO  | Na₂O | K₂O  | P₂O₅ | TiO₂    | Fe₂O₃   |
|--------|------|------|------|------|------|---------|---------|
| Raw material | 0.443 | 0.470 | N/A  | 2.17 | 0.683 | N/A      | 5.99E⁻⁴ |
| 180°C  | 0.133 | 0.376 | N/A  | 0.652 | 0.205 | N/A      | 4.26E⁻⁴ |
| 200°C  | 0.135 | 0.167 | N/A  | 0.453 | 0.119 | N/A      | 3.79E⁻⁴ |
| 220°C  | 0.136 | 0.184 | N/A  | 0.507 | 0.17  | N/A      | 4.86E⁻⁴ |
| 250°C  | 0.128 | 0.123 | N/A  | 0.556 | 0.177 | N/A      | 4.58E⁻⁴ |

Figure 4. Mass yield, HHV and energy loss of hydrothermal carbonization at different temperature.

Table 3. Ash component form XRF analysis
Figure 5. Quantities of MgO at different temperature.

Figure 6. Quantities of CaO at different temperature.

Figure 7. Quantities of K$_2$O at different temperature.

Figure 8. Quantities of P$_2$O$_5$ at different temperature.

Figure 9. Quantities of Fe$_2$O$_3$ at different temperature.
3.4. Fuel classification

The H/C and O/C plot in figure 10. show the steadily decrease due to the increment of temperature. The treated rice husk properties trends go toward to the coal and anthracite. The data indicate that the treated rice husk fuel properties were upgraded.

![Figure 10. The O/C and H/C classification plot](image)

4. Conclusion

The change of hydrothermal carbonization temperature in these study indicate that the alkaline component in ash were treated at low temperature of the process. Then the higher temperature process does the slightly effect on the alkaline component in ash. However, the combustion properties are getting better due to the increase of temperature. As the fuel uses, hydrothermal carbonization at 180˚C is the lowest percentage energy loss of energy.

References

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