Biomass Char Gasification with Carbon Dioxide As An Alternative Energy

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Abstract. Currently, the main energy source are fossil based fuel. Utilisation of conventional fossil fuel is contributing to greenhouse gas emissions which causes climate change. Attention to renewable energy sources has increased nowadays to reduce the high dependence on fossil fuel which is considered not renewable. Biomass seems to be a promising and environmental friendly feedstock that can be converted into useful products (biochar, bio-oil and syngas). One of the method to convert biochar to syngas is through the gasification technology. When biochar is reacted with gasifying agent like CO$_2$ and H$_2$O at high temperatures, syngas which is rich in hydrogen can be produced. The main objectives of this work are to study the gasification behaviour of pineapple peels in Thermogravimetric Analyzer (TGA) using CO$_2$ as its gasifying agent. The effect of temperature towards char reactivity and carbon conversion were determined. In conclusion, this study provides information on utilisation of biomass waste as an energy source through gasification technology.

Keyword: Biochar, Biomass, Char reactivity, Carbon conversion, Gasification

Introduction

A report by the Intergovernmental Panel on Climate Change (IPCC) showed that global emissions of greenhouse gases have risen to exceptional levels although there are growing number of policies to reduce climate change [1]. Greenhouse gases include water vapor, methane, nitrous oxide, ozone, chlorofluorocarbons, hydrofluorocarbons, and carbon dioxide (CO$_2$). With increasing amount of greenhouse gases above normal values, it has a negative effect on Earth’s temperature where the heat gets trapped leading to high-temperature values that contributes to global warming and climate change [2]. According to IPCC (2014), by mid-century, greenhouse gas emissions must be lowered by 40 to 70% compared to 2010 values and by and by the end of the century, the value to be lower to near-zero [1]. This is to limit the increase in global mean temperature to 2 °C. In Paris Agreement, a range between 1.5 °C and 2 °C was established. However, reaching 2°C would already mean reaching to worst climate change consequences [2]. The Fourth National Climate Assessment Report in year 2018 announced to make a significant impact on carbon dioxide reductions [3]. IPCC also reported that the energy supply sector is the largest contributor to global greenhouse gas emissions, which accounted for almost 50 % of all greenhouse gas emissions [1]. On the other hand, biomass also emits significant amounts of greenhouse gases adding to global warming and threatening the environment in other ways [4]. To
overcome this problem, current dependence on fossil fuel has to reduced and shift to alternative energy which is renewable. Biochar production from biomass can act as a powerful tool for clean energy conversion and atmospheric carbon sink in order to counteract climate changes [5]. Biochar can be derived from biomass or agricultural wastes like rice husk, coconut husk, sugarcane bagasse, empty fruit bunch, ground nut shell etc. Biomass can be converted into biochar through thermochemical conversion method called pyrolysis. This process is carried out at high temperatures between 300 and 700 °C under oxygen-limiting conditions producing biochar, a carbon rich, fine-grained, porous substance [6]. The carbon rich biochar can be further reacted through gasification process, in a controlled supply of CO2 or H2O to produce syngas [7]. Syngas like hydrogen can be directly converted into electric energy by using fuel cells and it seems like hydrogen could play an important role as an energy vector in the coming decades [8]. In this study, the gasification behaviour of pineapple peels in Thermogravimetric Analyzer (TGA) using CO2 as its gasifying agent. The effect of temperature towards char reactivity and carbon conversion were determined.

Material and methods

Reactivity of char with CO2 was determined using Thermogravimetric Analyzer (TGA). CO2 was used as the gasifying agent as it was most compatible with TGA. The char samples heated in nitrogen at 50 °C min⁻¹ to the targeted temperature: 600, 700, 800, 900 and 1000 °C. When the sample reached the target temperature, the gas was switched to CO2 and the particular temperature was held for one hour. Percentage of sample lost under CO2 exposure and the devolatilisation losses incurred before reacting with CO2 was calculated using Equations (1) and (2):

\[
\text{Devolatilisation} \text{(%)} = \frac{W_0 - W_1}{W_0} \times 100
\]

\[
\text{Sample lost during CO2 exposure} \text{(%)} = \frac{W_1 - W_2}{W_0} \times 100
\]

where

\[W_0\] is the mass in milligrams, of the char at the start (time=0);
\[W_1\] is the mass in milligrams, of the char when switched to CO2;
\[W_2\] is the mass in milligrams, of the residue after reacting with CO2.

The carbon fraction of char reacts slowly with CO2. Char reactivity, R, and carbon conversion, X, was based on the reactive portion of char, which was the weight of solid remaining at the time switched to CO2 less the weight of ash. They were calculated from the derivative thermogravimetric (DTG) data provided by the TGA software based on the Equations (3) and (4):

\[
R = -\frac{1}{W_0} \frac{dW}{dt}
\]

\[
X = \frac{W_0 - W}{W_0 - W_a}
\]

where

\[W_0\] is the mass, in milligrams, of the char at the start (time=0);
\[W\] is the mass, in milligrams, of the char at any given time;
\( W_a \) is the mass, in milligrams, of the ash.

Results and discussion

Percentage of weight loss of sample under CO\(_2\) exposure is summarized in Table 1. The devolatilisation losses incurred before reacting with CO\(_2\) was calculated using Equation 1. For pineapple peels, devolatilisation loss was around 22.27 to 50.12 % wt before attaining targeted temperature. For gasification temperatures of 1000 °C, it is worth noting that the char samples lost 50 % of its initial sample weight during devolatilisation, leaving only half of the char sample to react with CO\(_2\). Increasing weight loss was observed during one hour exposure in CO\(_2\) when the gasification temperature was increased from 600 to 800 °C. However at 900 and 1000 °C, total weight loss during CO\(_2\) exposure decreased. Sample lost during CO\(_2\) exposure was calculated using Equation 2. Highest percentage weight loss was observed at temperature 800 °C for the char referring to the initial weight of char inserted to the TGA. The highest weight loss percentage observed for pineapple peels was 59.13 %wt. The results indicate that the char reacts well with CO\(_2\) producing a high gas yield. However, this is purely based on the weight loss of the char observed in the reactivity tests. At gasification temperatures of 800 °C to 1000 °C, 50 % of the biomass sample weight loss was observed during devolatilisation before reacting with CO\(_2\). This could mean that a good gas yield can be achieved even before reacting the char with CO\(_2\) due to high volatile matter content in the char sample.

**Table 1.** Percent weight loss of pineapple peels during devolatilisation and 1 hour exposure to CO\(_2\)

| Temperature (°C) | Devolatilisation (% wt) | CO\(_2\) exposure (% wt) |
|------------------|--------------------------|--------------------------|
| 600              | 22.27                    | 2.55                     |
| 700              | 25.01                    | 30.35                    |
| 800              | 28.25                    | 59.13                    |
| 900              | 36.78                    | 51.47                    |
| 1000             | 50.12                    | 37.60                    |

The relationship between char reactivity and gasification time is shown in Figure 1. The chars were not gasified satisfactorily under lower temperatures. For each char gasified at 600 and 700 °C, the reactivity was very small almost none during the one hour exposure with CO\(_2\) producing flat line in the figure. The char reacted significantly with CO\(_2\) at temperature 800 °C onwards producing the highest rate at 1000 °C. As the gasification temperature increased, the char reactivity increased making shorter time taken to complete gasification. This is to say higher temperature gasification can be adopted for batch gasification as less time required for the char to complete react with CO\(_2\). However, the char would have mostly decomposed in the devolatilisation stage before reacting with CO\(_2\) at targeted temperature of 1000 °C. Continuous gasification process can be run under lower temperature like 800 °C as longer time needed to complete gasification, so feedstock can be supplied continuously for the gasification process.
Reactivity of pineapple peel char was 0.07 min\(^{-1}\) at 800 °C and the sample depleted within 17 minutes exposure to CO\(_2\). At 900 °C, an average at the peak showed reactivity of 0.24 min\(^{-1}\) and within 9 minutes the sample depleted. Highest rate was found for temperature 1000 °C which was around 0.48 min\(^{-1}\) and the duration taken for the sample to deplete was only 3 minutes. The char reactivity was found to be more pronounced at high temperatures (900 and 1000 °C), with the majority of char being lost within the first few minutes spent in the TGA.

The curves of the carbon conversion against gasification time are plotted in Figure 2. It can be seen that the carbon conversion increased as the gasification time increased. At a particular time, it also shows that the carbon conversion was higher as the gasification temperature increased except for some overlaps between 600 and 700 °C. A similar trend were reported for Binxian char gasified under CO2 at temperature ranging from 1000 to 1300 °C [9]. According to Adschiri et al. change in the conversion rate among the chars is attributed to the physical change of the pore structure of char and change in char reactivity [10]. Conversion ratio changes are also related to the inherent properties of the parent biomass sample and the porosity and surface area characteristics of the chars obtained after pyrolysis [11]. Gasification rates are influenced by a number of process variables, such as particle size and size distribution, char porosity, the mineral content of the char, temperature and the partial pressure of the gasifying agents [12].
Figure 2. The relationship of char gasification time and carbon conversion

The curves of the char reactivity versus carbon conversion of the char at different temperatures are shown in Figure 3. Char reactivity increased as the gasification temperature increased and shows a parabolic trend with carbon conversion. The char reactivity increased as carbon conversion increased, attaining a maximum and remained at maximum throughout certain carbon conversion and finally decreased with increasing carbon conversion.

Figure 3. The effect of temperature on char reactivity and carbon conversion

It was stated by Ollero et al. that for most chars of coal, lignite and peat reactivity decreases with increasing conversion, while for most chars of biomass the reactivity increases [13]. Each char or coal sample is found to have its own characteristic rate curve. The different rate characteristics of coals and chars are apparently due to the difference in their pore characteristics, which again change with conversion and temperature [14]. Apart from that, gasification of chars from the pyrolysis of biomass is affected by the biomass properties such as the contents of ash and fixed carbon and the constituents present in the ash [11]. Thus low ash content and high fixed carbon content biomass materials are recommended to be used in the gasification processes when char from pyrolysis is used as a feedstock.
Conclusions

Studies using pineapple peels for gasification to produce valuable gasses are scarce and much of the issues involved are less explored. In this study, pineapple peels was reacted with CO$_2$ to understand its gasification behaviour. From the results, pineapple peels showed that at temperature of 800 °C and above, the char reacts significantly with CO$_2$. Highest reactivity was observed at 1000 °C which was 0.48 min$^{-1}$.

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