Production of bio-oil and bio-char from different biomass wastes

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Abstract. Environmental pollution is rising due to the excess use of fossil fuels causing severe global warming and acid rains. High market price and the limited amount of fossil fuels have caused energy crises worldwide especially in the underdeveloped countries. The huge amount of biomass organic wastes is being widely used as an alternative feedstock as a potential source for second generation biorefining process. In this research four different biomass wastes are used to investigate the yield of bio-oil and biochar using a conventional pyrolysis method. Rice husk, bagasse, sawdust (Dalbergia sisso Roxb.), and sawdust (Populus caspica Bornm.) are operated in a fixed bed reactor. The rationale of this study is to evaluate the effect of temperature on the yield of bio-oil and biochar at three different temperatures (300 °C, 400 °C, and 500 °C) with heating rate of 3.69 °C/min. The particle size of each biomass waste used was 0.498 mm. Sulfuric acid was used as a catalyst to enhance the rate of reaction. The proximate analysis of biomass wastes was performed in order to evaluate the moisture content, ash content, and volatile matter and fixed carbon. The results showed that with the increase of temperature, the bio-oil yield increases and biochar yield decreases. The highest yield of bio-oil (32.39%) was achieved at 500 °C from bagasse feedstock and the highest yield of biochar (37.50%) was obtained at 300 °C from rice husk feedstock.

1. Introduction

The world is facing huge energy crisis due to high prices and the limited amount of fossil fuels available. New alternatives that are sustainable and environmentally friendly can overcome energy crisis worldwide [1]. Wood wastes and agricultural residues are the significant renewable solid energy resources available which may be converted into value added products by their conversion at high temperature in the absence of oxygen to form bio-oil, biochar, and syngas. Biomass contains cellulose, hemicellulose, lignin, ash, and extractives[2]. Generally, wood wastes and agricultural wastes are different in terms of their species and structural constituents. Wood wastes mainly consist of hardwoods and softwoods. The structural composition of hardwoods waste contains 43% cellulose, 35% hemicellulose, and 22% lignin while softwoods contain about 43% cellulose, 28% hemicellulose, and 29% of lignin on an extractive free basis. The structural composition of agricultural residues such as rice husk, bagasse, and corn cob is dependent on the type of biomass species [2].

The most emerging technologies are pyrolysis that converts different kinds of biomass wastes for the synthesis of biofuels and biochemical. Organic end products of wood wastes and agricultural wastes are converted into more valuable products which find many useful applications. [3]. In the presence of the catalyst carbon-carbon bonds in biomass compounds break down. Different...
hydrocarbons, carbon dioxide, and water are extracted by the process of decarboxylation and dehydration of hydrocarbon compounds via cracking reactions[1]. Condensation of vapors forms bio-oil at temperatures of 400 °C to 500 °C as a significant product than the other pyrolysis products. The color of the oil is dark brown and has a strong acrid smell. Bio-oil is more beneficial as compared to biomass because it can be easy to use, store and transport. The intensity of energy in bio-oil is five times more than that of the initial raw material[4]. Biochar is also a significant product obtained from pyrolysis of biomass, which has more than 50% carbon. Biochar can be used not only as a fuel but also used in soil amendments. It is quite stable both biologically and chemically due to its porous structure. It remains settled in the soil for 1,000 years[5]. Therefore, from the production of biochar via pyrolysis technique the quantity of carbon dioxide is reduced in the environment. Biochar can be beneficial for adsorption and building processes[6].

Generally, catalysts are used to boost up reaction kinetics by breaking down higher molecular weight compounds into lighter hydrocarbon compounds. Therefore, various catalyst show different end products in various operating conditions[7]. The reaction mechanisms of pyrolysis of biomass feedstock are complicated but can be generally described in three stage mechanism.

\[
\text{Biomass feedstock} \rightarrow \text{Water} + \text{Unreacted solid} \quad (1) \\
\text{Unreacted solid} \rightarrow (\text{Volatile} + \text{Gases})_1 + (\text{Char})_1 \quad (2) \\
(\text{Char})_1 \rightarrow (\text{Volatile} + \text{Gases})_2 + (\text{Char})_2 \quad (3)
\]

The 1st step of feedstock degradation, which occurred between 122 °C and 202 °C, can be called pre-hydrolysis. During this stage, some internal modification such as water removal, bond breakage, a free radicals formation, and the carbonyl, and carboxyl groups formation takes place during conversion of biomass into volatiles[8]. The 2nd step of the biomass feedstock degradation correlates to the key pyrolysis technique. Starting with a high rate that ends with the formation of pyrolysis oil, solid, and gas. In the 3rd step, the char degrades at a very slow rate and carbon-rich char is left behind. At low temperature, cellulose carbonization starts with a gradual degradation and char formation on heating, and fast volatilization proceeds on pyrolysis at higher temperatures. During 1st stage degradation reactions such as depolymerization, oxidation, dehydration, and decarboxylation; the pyrolysis reactions produce nearly 62-72% liquid distillate and 10-18% charred solid [9].

During heating, the hemicelluloses reacts more readily than cellulose. The thermal degradation of hemicellulose begins above 100 °C during heating for 48 h. The hemicelluloses breaks down first, at the temperature of 197-257 °C and cellulose breaks down in the temperature range of 237 to 347 °C, with lignin pyrolyzing at temperatures of 277 to 497 °C [10]. The most significant temperature for the production of the pyrolysis products such as liquid, solid, and gas is between 377 and 527 °C.

Bio-oil has various potential applications for commercial purposes and as well as in domestic for heating purposes. Bio-oil is a complex mixture of oxygenated compounds. Functional groups of bio-oil provide the potential for utilization. Bio-oil is also significant for the production of valuable biochemicals such as furfural and derivatives of furfural. On the other hand, biochar consist of a strong carbon matrix which is known as biochar. At low-temperature pyrolysis, higher amount of biochar is obtained due to the low rates of devolatilization and low conversion of carbon. Biochar also contains hydrogen and inorganic species in two structure: stacked crystalline sheets and randomly ordered amorphous aromatic structure [7]. The potential applications are to stabilize the quality of soil and enhanced vegetative production. Biochar enables the long-term sequestration of carbon in soil due to its inert nature [11]. It is also applicable in soil amendment, co-firing power generating plant, and enhance poultry production.

In this study different types of biomass wastes such as rice husk, bagasse, sawdust (Dalbergia sisso Roxb.) and sawdust (Populus caspica Bornm.) are pyrolyzed in the presence of catalyst for the production of bio-oil and biochar at various temperatures.
2. Methodology

2.1. Sampling
The samples of raw materials; rice husk, bagasse, sawdust (Dalber gia sisso Roxb. and sawdust (Populus caspica Bornm.); were collected from the field. Air dried samples were ground and then sieved to achieve a particle size of 0.498 mm. The 100g of each sample was impregnated in water solution in the presence of the specific concentration of catalysts before the experiments for the purpose of hydrolysis.

2.2. Experimental Setup
The conventional pyrolysis experiment was conducted in a fixed bed reactor to study the effect of temperature on pyrolysis products such as bio-oil and biochar. The reactor is made up of stainless steel (SS316). The length of the furnace is 80 cm and its inside diameter is 6.3 cm. Nichrome wire is wounded throughout the furnace length as a heating element. The furnace is insulated to facilitate maximum heat utilization. All the biomass wastes samples are pyrolysed in the fixed bed reactor as shown in figure 1.

2.3. Procedure
In this study, 10 to 20 g of raw material was placed in the stainless-steel sample tube. The tube was hanged in the tubular furnace. After closing the flange and placing measuring instruments in place, nitrogen gas purging was begun. The reactor temperature was set and heating switched on. Cooled water was circulated throughout the condensers when the pump was turned on. For each run continuous flow rate of nitrogen gas was 0.15 lit/min. The vapours were condensed by a two-stage condensation using chilled water. When condensate formation stopped, the heating was continued for 20 minutes to ensure the completion of reaction. The condensate was collected in the conical flasks. The quantity of liquid was more in the first condenser than in the second condenser. The liquid obtained from both flasks was weighed and stored for characterization. Furnace could cool down which took around 1 hour. Then the tube was taken out through the flange and remaining solid was collected from the tube for mass balance. The equations (4), (5), (6), and (7) were used to calculate the conversion and yields of bio-oil, biochar, and syngas using weight of biomass and char on dry basis (db).

\[
\text{Conversion (\%)} = \left( \frac{W_{\text{Biomas} \text{ db}} - W_{\text{Solid} \text{ db}}}{W_{\text{Biomas} \text{ db}}} \right) \times 100
\]  

\[
\text{Liquid yield (wt\%)} = \left( \frac{W_{\text{Liquid} \text{ db}}}{W_{\text{Biomas} \text{ db}}} \right) \times 100
\]  

\[
\text{Solid yield (wt\%)} = \left( \frac{W_{\text{Solid} \text{ db}}}{W_{\text{Biomas} \text{ db}}} \right) \times 100
\]  

\[
\text{Gas yield (wt\%)} = 100\% - \text{liquid yield (wt\%)} - \text{solid yield (wt\%)}
\]

Where \( W_{\text{Biomas} \text{ db}} \) and \( W_{\text{Solid} \text{ db}} \) are the weights of initial biomass and remaining solid, respectively, on the dry basis.
3. Results and Discussion

3.1. Proximate Analysis

Proximate analysis was conducted using four types of feedstock. The volatile matter was high in the sawdust (Populus caspica Bornm.) and low in rice husk which is shown in Table 1. High moisture content was 6.80% calculated in rice husk while low moisture content was 1.25% reported for sawdust (Populus caspica Bornm.). High ash content was calculated 17.45% in rice husk. Lower volatile matter in biomass wastes leads to produce a rigid charcoal. The low quality of bio-oil and corrosion in pyrolysis system has been improved due to the low content of moisture.

| Biomass                  | Moisture % | Ash % | Volatile Matter % | Fixed Carbon % |
|--------------------------|------------|-------|-------------------|----------------|
| Sawdust (Dalbergia sisso Roxb.) | 5.25 ± 1.43 | 1.5 ± 0.5 | 88.25 ± 2.75 | 6.0 ± 1.95 |
| Sawdust (Populus caspica Bornm.) | 1.25 ± 0.25 | 1.5 ± 0.28 | 93.75 ± 1.43 | 3.0 ± 1.35 |
| Baggage                  | 4.25 ± 0.50 | 2.0 ± 0.50 | 89.75 ± 1.32 | 5.0 ± 0.76 |
| Rice husk                | 6.80 ± 2.06 | 17.45 ± 0.69 | 63.06 ± 1.72 | 15.85 ± 0.10 |

3.2. Effect of temperature on products yield

The conversion (%), bio-oil yield (%), Char yield (%) and gas yield(%) for the tested samples at three temperatures (300, 400 and 500°C) are presented in Table 2. The percentage of the biomass sample that is converted to vapours on heating is called conversion.

The conversion varies from 62.50% to 69.44%, 77.09% to 80.28%, 72.91% to 77.09%, and 82.40% to 83.31% for Rice husk, Bagasse, Sawdust (Dalbergia sisso Roxb.) and Sawdust (Populus caspica Bornm.) respectively. One can observe that the conversion increases with temperature for first three samples although to a different extent. The conversion declines with temperature for the fourth sample although variation is not much. The conversion is higher for bagasse (80.28%) and Sawdust (Populus caspica Bornm.) (83.31%). Rice husk undergoes lowest conversion 62.50% and 69.44% at the lowest temperature as well as at the highest temperature respectively. Where as Sawdust (Populus caspica Bornm.) undergoes highest conversion 82.40% and 83.31% at the lowest temperature as well as at the highest temperature respectively.
The bio-oil yield varies from 22.05% to 23.33%, 21.37% to 32.39%, 22.43% to 27.94%, and 21% to 24.83% for Rice husk, Bagasse, Sawdust (Dalbergia sisso Roxb.) and Sawdust (Populus caspica Bornm.) respectively. It is obvious that the yield increases with temperature but to a varying extent. Increase in yield of bio-oil for a temperature change from 300 to 500°C is relatively higher for Rice husk and Bagasse samples as compared to that of the saw dust samples. Bagasse gives highest (32.39%) and lowest (21.37%) bio-oil yields at 500°C and 300°C respectively.

The char yield varies from 37.50% to 30.55%, 22.90% to 19.71%, 27.08% to 22.90%, and 17.60 to 16.68% for Rice husk, Bagasse, Sawdust (Dalbergia sisso Roxb.) and Sawdust (Populus caspica Bornm.) respectively. It is notable that the yield decreases with temperature in all cases but to a varying extent. The maximum variation is depicted by Rice husk samples and the least decrease is shown by the Saw dust (Populus caspica Bornm.) samples. The gas yields are calculated by difference.

This effect of temperature on the yield of bio-oil is mainly due to the maximum primary and secondary degradation of the biomass and char, thus leading to a greater conversion and higher yields at higher temperatures. The yield of biochar is mainly affected by secondary cracking of pyrolysis vapors and decomposition of char at higher temperatures. The effect of temperature is not linear in terms of yields of pyrolysis gases.

Table 2. The conversion and production of bio-oil and biochar yields through pyrolysis of biomass wastes at three temperatures with the catalyst.

| Biomass Sample          | Temperature (°C) | Conversion (%) | Bio-Oil yield (%) | Char yield (%) | Gas yield (%) |
|-------------------------|------------------|----------------|-------------------|----------------|---------------|
| Rice Husk               | 300              | 62.50          | 22.05             | 37.50          | 40.45         |
|                         | 400              | 67.20          | 21.50             | 32.79          | 45.69         |
|                         | 500              | 69.44          | 23.33             | 30.55          | 46.11         |
| Bagasse                 | 300              | 77.09          | 21.37             | 22.90          | 55.72         |
|                         | 400              | 80.46          | 24.21             | 19.53          | 56.25         |
|                         | 500              | 80.28          | 32.39             | 19.71          | 47.88         |
| Sawdust (Dalbergia sisso Roxb.) | 300 | 72.91          | 22.43             | 27.08          | 50.48         |
|                         | 400              | 71.75          | 26.93             | 28.24          | 44.81         |
|                         | 500              | 77.09          | 27.94             | 22.90          | 49.14         |
| Sawdust (Populus caspica Bornm.) | 300 | 82.40          | 21.60             | 17.60          | 60.80         |
|                         | 400              | 83.17          | 24.50             | 16.82          | 58.67         |
|                         | 500              | 83.31          | 24.83             | 16.68          | 58.47         |

Gaseous products from pyrolysis are carbon monoxide, carbon dioxide, hydrogen, methane and lower hydrocarbons such as oxygen and nitrogen. At high temperatures, the large molecules in bio-oil and biochar are depolymerized into smaller molecules, which also contain the gaseous fractions [12].

Conclusion
The yield of pyrolysis products, bio-oil and char converted from different biomass wastes, using conventional pyrolysis process at different temperature (300-500 °C) was investigated in this research. Biomass wastes used in this research were rice husk, bagasse, sawdust (Dalbergia sisso Roxb.) and sawdust (Populus caspica Bornm.). They are operated at 300 °C, 400 °C, and 500 °C temperature in the presence of a catalyst. The catalyst selected for this process was sulfuric acid. The proximate analysis of biomass wastes was performed in order to evaluate the moisture content, ash content, volatile matter and fixed carbon. Yield of bio-oil obtained from bagasse feedstock at the temperature of 500 °C
is the highest as compared to others which is 32.39%. On the other hand, yield of biochar produced by rice husk feedstock at 300 °C temperature is highest among others which is 37.50%. The results reveal that the yield of bio-oil increases with increase in temperature and vice versa for the char.

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