A comparative study on pyrolysis for liquid oil from different biomass solid wastes

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Abstract
Locally available different biomass solid wastes, pine seed, date seed, nutshell, hay of catkin, rice husk, jute stick, saw-dust, wheat straw and linseed residue in the particle form have been pyrolyzed in laboratory scale fixed bed reactor. The products obtained are pyrolysis oil, solid char and gas. The oil and char are collected while the gas is flared into atmosphere. The variation of oil yield for different biomass feedstock with reaction parameters like, reactor bed temperature, feed size and running time is presented in a comparative way in the paper. A maximum liquid yield of 55 wt% of dry feedstock is obtained at an optimum temperature of 500 °C for a feed size of 300-600 μm with a running time of 55 min with nutshell as the feedstock while the minimum liquid yield is found to be 30 wt% of feedstock at an optimum temperature of 400 °C for a feed size of 2.36 mm with a running time of 65 min for linseed residue. A detailed study on the variation of product yields with reaction parameters is presented for the latest investigation with pine seed as the feedstock where a maximum liquid yield of 40 wt% of dry feedstock is obtained at an optimum temperature of 500 °C for a feed size of 2.36-2.76 mm with a running time of 120 min. The characterization of the pyrolysis oil is carried out and a comparison of some selected properties of the oil is presented. From the study it is exhibited that the biomass solid wastes have the potential to be converted into liquid oil as a source of renewable energy with some further upgrading of the products.

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1. Introduction
Energy propels the society. It is the major requirement of present society for its sustainable development. The energy consumption in the world has been growing at an alarming rate. By the year 2100, the world population is expected to be more than 12 billion and it is estimated that the demand for energy would increase by five times the present demand [1]. Thus, significant consumption and depletion of fossil fuel and the evident global warming are pressing continuously to think for alternative energy sources. Under such circumstances, it has become imperative to find out some potential sources of energy that may be able to meet considerable part of the energy demand in future. Biomass has been recognized as a major renewable energy source to supplement this declining fossil fuel source of energy [2]. It is considered to be the most popular form of renewable energy. Biomass and its solid waste is attractive from the points of view of ease of availability, high carbon content, low moisture and ash content, low or even no cost, no conflict arising from alternative usage, solving solid waste disposal problems and keeping the environment clean. In some cases, it may have some existing usage; however, the better utilization and application from the point of view of energy recovery and environment need to be emphasized.

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1.1 Introduction

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Currently bio-oil production is becoming very much promising [3]. There are various biomass solid wastes available in different corners of the world including Bangladesh and Brunei Darussalam. A few examples are: date seed, pine seed, nutshell, wheat straw, linseed residue, hay of catkin, rice straw, bagasse, jute stick, sawdust, rice husk, empty fruit bunches, livestock, scrap tire, refused plastic, wastepaper etc. These carbonaceous solid wastes are renewable energy sources and therefore, the potential of converting them into useful energy such as liquid oil should be seriously considered. In this way, the wastes would be more readily usable and environmentally more acceptable. It is found from the characterization of most of these biomass solid wastes that these wastes contain higher percentage of volatile matter. This high volatile content biomass has high potential for pyrolysis liquid production [4]. Transformation of energy into useful and sustainable forms that can fulfill and suit the requirements of mankind in the best possible way is the common concern of the scientists, engineers and technologists. From the point of view of energy transformation, pyrolysis is more attractive among various thermochemical conversion processes because of its simplicity and higher conversion capability into liquid product. Pyrolysis is generally described as the incomplete thermal degradation of the carbonaceous solid materials in the complete absence of oxygen or oxidizing agent at relatively moderate temperature of 500 to 800°C to yield condensable liquid, known as bio-oil, bio-fuel, bio-crude, char (charcoal) and gaseous products (fuel gases). Pyrolysis system may be either fixed bed or fluidized bed. In fixed bed system, a fixed bed pyrolysis reactor is used. As the feedstock is kept fixed in the reaction bed (reactor), it is called fixed bed pyrolysis. In this process, the feed material is fed into the reactor and heat is applied externally at a faster rate. In this work an external biomass source heater is used. Nitrogen is used as inert gas for making inert atmosphere in the system and for helping the gaseous mixture to dispose of the reactor. From the reactor, the vaporized mixture passes through water-cooled condenser. Extracting heat from the vapor, condenser converts it into liquid product and a part of the vapor is escaped as non-condensable gas. The process of biomass pyrolysis is considered to be very complex consisting of both concurrent and consecutive reactions. A possible reaction pathway of pyrolysis of biomass solid waste is presented in Fig. 1.

![Fig. 1. A possible reaction pathway of pyrolysis of biomass solid waste.](image)

This technology is spreading with research and experimental work in many countries of the present world [5-6]. The pyrolysis oil has moderate heating value, can be easily transported, can be burnt directly in thermal power plant and in gas turbine or can be upgraded to obtain light hydrocarbons for transport fuel and for the production and recovery of chemicals [7]. In this study fixed bed pyrolysis of a number of biomass solid wastes, widely available in Bangladesh is considered to obtain bio-oil, solid char and gases. Thus, the wastes may be used for energy recovery as fuel. It is to mention that there are scopes to upgrade the oil to obtain high grade fuels and valuable chemicals. The solid char can be used for making activated carbon (AC). The char has its potential as a solid fuel as well [7]. AC production costs can be reduced by either choosing a cheap raw material or by applying a proper production method like pyrolysis system [8]. Thus, the pyrolysis conversion appears to be a new development in the alternative renewable sources of energy. Recently UK, Malaysia and India have given much attention towards the pyrolysis technology. A number of pyrolytic conversion studies using different biomass solid wastes has been carried out in the Department of Mechanical Engineering of Rajshahi University of Engineering & Technology. A comparative study on the liquid product yields and their characterization analysis has been taken into consideration in this paper.
2. Materials and methods

2.1. Materials

The feedstock raw-materials collected are pine seed, date seed, plum seed, nutshell, hay of catkin, rice husk, jute stick, saw dust, wheat straw and linseed residue. These are collected locally in Rajshahi and then milled into particles and air-dried. Finally the feedstock is oven-dried at 105-110°C for 24 hours prior to pyrolysis. The proximate analysis of the feedstock is presented in Table 1.

| Feedstock (%) | Moisture (%) | Volatile (%) | Fixed carbon (%) | Ash (%) |
|---------------|--------------|--------------|------------------|---------|
| Pine seed     | 5            | -            | -                | 4.5     |
| Date seed     | 5-10         | -            | -                | 1-2     |
| Nut shell     | 4.6          | 72.22        | 21.16            | 0.56    |
| Plum seed     | -            | -            | -                | -       |
| Rice husk     | 12           | 52.4         | 17.1             | 18.5    |
| Saw-dust      | 7.5          | 91           | -                | 1.5     |
| Jute stick    | 9.02         | 78.40        | 11.80            | 0.78    |
| Wheat straw   | 5.17         | 71.32        | 16.69            | 6.82    |
| Linseed residue | 6.7         | 77.7         | 10.7             | 5.6     |
| Hay of catkin | -            | -            | -                | -       |

2.2. Experimental

Each of the feedstock is pyrolyzed individually in externally heated stainless steel fixed bed pyrolysis reactor system. The main components of the system are fixed bed reactor, liquid condenser and ice-cooled liquid collectors. The schematic diagram of the fixed bed pyrolysis system is shown in Fig. 2.
The effective dimensions of the reactors are presented in Table 2. The reactor is heated externally by a biomass source heater at different temperatures from 400 to 600°C. The temperature is measured by means of pyrometer and mercury thermometer. Nitrogen gas is supplied in order to maintain the inert atmosphere in the reactor, and to dispose of the pyrolyzed vapor products to the condenser. Pyrolysis vapor is condensed into liquid in the condenser and collected in the ice-cooled liquid collectors. The char is collected from the reactor bed after each experimental run through the opening at the bottom of the reactor. The non-condensable gas is flared into the atmosphere.

3. Results and discussion

3.1. Product yield

The products obtained from the pyrolysis experimental studies are liquid oil, solid char and gas. The products obtained from the latest experimental study using pine seed as the feedstock are shown in Fig. 3.

![Fig. 3. Products obtained from the pyrolysis of pine seed.](image)

The maximum liquid product yields of different biomass solid wastes for different reactor dimensions and their associated reaction conditions are presented in Table 2.

| Biomass            | Pine seed | Date seed | Plum seed | Nut shell | Hay of catkin | Rice husk | Jute stick | Saw-dust | Wheat straw | Linseed residue |
|--------------------|-----------|-----------|-----------|-----------|---------------|-----------|------------|----------|-------------|-----------------|
| Reactor dimensions | 7.6 x 46  | 7.6 x 46  | 7.6 x 46  | 6.0 x 29  | 6.0 x 29      | 4.0 x 38  | 7.0 x 37.6 | 4.0 x 38 | 6.0 x 29    | 6.0 x 29        |
| Liquid product yields (%) | 40        | 50        | 39        | 55        | 44            | 40        | 50         | 41       | 53          | 30              |
| Optimum operating temperature (°C) | 500       | 500       | 520       | 500       | 450           | 450       | 425        | 440      | 500         | 400             |
| Feed size (μm) | 2.36-2.76 mm | 0.11-0.20 cm³ | 2.96-4.75 mm | 300-600 | 300-600 | <1000 | 420 | 350-450 | 300-600 | 2.36 mm |
| Running time (min) | 120       | 120       | 120       | 55        | 75            | 75        | 60         | 65       | 65          | 65              |

3.1.1. Effect of operating temperature

The effect of reaction conditions on product yields for the biomass feedstock pine seed, which was the latest experimental study is presented here. The similar trend of product yields is observed for other biomass feedstock as well. The relationship between the variation of percentage of weight of liquid, char, and gaseous products at different reactor bed temperature is presented in Fig. 4. The results show that the liquid yield increases with operating temperature and a
maximum yield of 40 wt% is obtained at 500 °C for feed particle size of 2.36-2.76 mm with a running time of 120 min. When the temperature exceeds 500 °C, liquid yield decreases. At a lower temperature of 400 °C, the liquid product is found to be 30 wt% of the dry feedstock. The higher temperature may cause secondary cracking reaction of the vapors, yielding more gas products at the cost of liquid product. On the other hand, the reason for the lower liquid yield at lower temperature may be due to insufficient temperature to complete decomposition of the feed material.

![Graph showing effect of temperature on product yield](image)

**Fig. 4. Effect of operating temperature on product yield.**

### 3.1.2. Effect of feed particle size on product yield

Fig. 5 represents the percentage weight of liquid, solid char and gas products for different feed particle size at a reactor bed temperature of 500 °C and an operating time of 120 minutes. It is observed that at 500 °C, the percentage of liquid collection is maximum at 40 wt% of total biomass feed for particle size of 2.36-2.76 mm. Liquid yield is found to be maximum for the smaller particles because the larger size particles might not be adequately heated up so rapidly causing incomplete pyrolysis.

![Graph showing effect of particle size on product yield](image)

**Fig. 5. Effect of feed particle size on product yield.**

### 3.1.3. Effect of running time on product yield

Fig. 6 shows the variation of product yield (wt%) of liquid, solid char and gas products with running time at a temperature of 500 °C for feed particle size of 2.36-2.76 mm. The maximum liquid product is found to be 40 wt% of biomass feed while the solid char product is 32 wt% of dry feed at 120 minutes. It is observed that at lower and higher
running times, the liquid product yields are not optimum that may be due to insufficient pyrolysis reaction and higher rate of gas discharge respectively.

![Fig. 6. Effect of running time on product yield.](image)

### 3.2. Characterization of pyrolysis oil

The characterization of the pyrolysis oil from different biomass solid waste is presented in Table 3. The oil is found to be a dark-color single phase liquid. The energy content of the oil in the form of higher heating value (HHV) is found to vary from 20 to 33 MJ/kg which is certainly higher than the corresponding solid biomass feedstock. Some oils are found to be heavier than water while the others are lighter, the density being in the range of 900 to 1224 kg/m$^3$. The low viscosity of the pyrolysis oils is a favorable feature for handling and transportation of the liquid oils. The oils are found to be corrosive in nature having pH values in the acidic range. The flash point is found to be reasonable.

| Properties               | Pine seed | Date seed | Plum seed | Nut shell | Hay of catkin | Rice husk | Jute stick | Sawdust | Wheat straw | Linseed residue |
|--------------------------|-----------|-----------|-----------|-----------|---------------|-----------|------------|---------|-------------|-----------------|
| Kinematic viscosity (cSt)| 12.15     | 6.63      | 1.14      | 9.72      | 10.95         | 1.20      | 12.8       | 0.98    | 9.85        | 8.72            |
| Density (kg/m$^3$)       | 1166      | 1042.4    | 940       | 900       | 900           | 960       | 1224       | 910     | 1098.6      | 1095            |
| Flash Point (°C)         | 120       | 126       | 112       | -         | -             | >70       | -          | -       | -           | -               |
| pH value                 | -         | -         | 3.19      | -         | -             | 2.22      | 2.92       | 2.23    | -           | -               |
| HHV (MJ/kg)              | 20.00     | 28.64     | 22.39     | 19.34     | 23.43         | 20.43     | 21.09      | 19.08   | 17.23       | 33.35           |

### 3.3. Comparison among pyrolysis oil, biomass oil and diesel fuel

Table 4 shows the comparison of some of the fuel properties of pyrolysis oil derived from different biomass solid waste feedstock with diesel and heavy fuel. It is evident that the density and viscosity of pyrolysis oil are favorable and closer to
The higher heating value of the pyrolysis oil is found to be in the comparable range with other reported pyrolysis oil while still being less than diesel and heavy fuel.

Table 4. Comparison of pyrolysis oil with conventional fuel

| Analysis               | Pineseed | Date seed | Plum seed | Nut shell | Hay of cattin | Rice husk | Jute stick | Sawdust | Wheat straw | Linseed residue | Diesel | Heavy fuel oil |
|------------------------|----------|-----------|-----------|-----------|---------------|-----------|------------|---------|--------------|----------------|--------|----------------|
| Kinematic viscosity at 26°C (cSt) | 12.15    | 6.63      | 1.14      | 9.72      | 10.95         | 1.20      | 12.8       | 0.98    | 9.85         | 8.72            | 2.61   | 200            |
| Density (kg/m³)        | 1166     | 1042.4    | 940       | 900       | 900           | 960       | 1224       | 910     | 1098.6       | 1095            | 827.1  | 980            |
| Flash Point (°C)       | 120      | 126       | 112       | -         | 105           | -         | >70        | -       | -            | -               | 53     | 90-180         |
| HHV (MJ/kg)            | 20.00    | 28.64     | 22.39     | 19.34     | 23.43         | 20.43     | 21.09      | 19.08   | 17.23        | 33.35           | 45.18  | 42-43          |
| pH value               | -        | -         | 3.19      | -         | 2.98          | 2.22      | 2.92       | 2.23    | -            | -               | -      | -              |

4. Conclusions

Biomass solid wastes are successfully converted into liquid oil, solid char and gas by fixed bed pyrolysis system. The maximum liquid yield is found to be the highest of 55 wt% of dry biomass feedstock for nut shell at a temperature of 500 °C for a feed size of 300-600 μm with a running time of 55 min while the lowest liquid yield is found to be 30 wt% of dry biomass feedstock at a temperature of 400 °C, for a feed size of 2.36 mm with a running time of 65 min with linseed residue as the feed material. The heating value of the pyrolysis oil is found to be in the range of 20.00 to 33.35 MJ/kg, which is either similar or higher than other biomass derived pyrolysis oils. However, the values are significantly higher than that of the corresponding solid biomass wastes. The density and viscosity of the oil are found to be higher than that of diesel and heavy fuel. Thus, the oil from the biomass solid wastes may be considered to be an important candidate of potential sources of alternative fuel that may further be upgraded.

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