Performance evaluation of Pyrolysis system (1-5 kg/h) at different temperature

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Abstract
The objective of this work is to perform experimental and theoretical analysis to produce bio-oil through Pyrolysis of sawdust and pine wood pellets (8mm) in fixed bed reactor using slow Pyrolysis. The experiments are performed at five different Pyrolysis temperatures 400, 425, 450, 475 and 500 °C at constant heating rate 10 °C/min in self-Pyrolysis environment. Bio-oil is found to have distinct properties of being acidic, high water content to be considered as a fossil fuel, but can be used as a replacement for the furnace oil. The characterization of bio-oil carried out like calorific value, viscosity, pH, density, flash point, fire point and water content. The characterization of bio-char and Pyro-gas is also carried out. Bio-char obtained is having higher calorific value similar to bituminous coal and hence can be used for cogeneration and synthesis of activated carbon. In the Pyro-gas composition, carbon monoxide (CO), hydrogen (H₂) and methane(CH₄) combustible gases obtained which can be used for thermal applications.

Keywords: Thermochemical process, biomass, pyrolysis, bio-char

Introduction
In 21st century, Energy and Pollution are important concerns for the world. The demand of energy is increasing because of economic empowerment. Sustainable energy solution is one of the most important challenges posed before mankind. Renewable energy technologies can provide a viable solution to the demand of energy production and pollution reduction leading to mitigation of adverse effect of global warming and climate change.

Biomass Feedstocks
Every region has its own locally generated biomass feedstocks from agriculture, forest, and urban sources. A wide variety of biomass feedstocks are available and biomass can be produced anywhere that plants or animals can live. Furthermore, most feedstocks can be made into liquid fuels, heat, electric power, and/or bio based products. This makes biomass a flexible and widespread resource that can be adapted locally to meet local needs and objectives. Some of the most common (and/or most promising) biomass feedstocks are:

- Grains and starch crops – sugar cane, corn, wheat, sugar beets, industrial sweet potatoes, etc.
- Agricultural residues – Corn stover, wheat straw, rice straw, orchard pruning, etc. Food waste – waste produce, food processing waste, etc.
- Forestry materials – Logging residues, forest thinnings, etc.
- Animal byproducts – Tallow, fish oil, manure, etc.
- Energy crops – Switchgrass, miscanthus, hybrid poplar, willow, algae, etc.
- Urban and suburban wastes – municipal solid wastes (MSW), lawn wastes, wastewater treatment sludge, urban wood wastes, disaster debris, trap grease, yellow grease, waste cooking oil, etc.

Ways to extract energy from Biomass
There are three different ways to extract energy from biomass. 1) Direct Combustion, 2) Bio-chemical conversion, 3) Thermo-chemical conversion

Direct Combustion
It is a quite obvious and straightforward way for extracting the energy from biomass. The major disadvantage associated with it is most of the heat will be wasted because of the open burning which results in lower efficiency of the process and it also contributes to pollution.
Bio-chemical Conversion
It involves a process of anaerobic digestion under the action of micro-organisms which converts biomass into a gaseous fuel known as biogas which is a mixture of methane and carbon dioxide. The major drawback of this method is high capital investments associated with it and requirement of longer digestion periods.

Thermo-chemical Conversion
It involves conversion of biomass into more useful forms like charcoal, liquid and gaseous products. Gasification, Pyrolysis, Combustion and Torification are the various methods of thermo-chemical conversion.

Review of literature
Selection of Biomass for Pyrolysis
In fixed bed reactor with simple and reliable design various types of biomass used asa fuel to produce valuable end products. Biomass may vary in its physical and chemical properties due to its diverse origin and types so based on proximate analysis, chemical analysis and ultimate analysis, the fuel for Pyrolysis selected. Different types of biomass such as agricultural, forestry, municipality waste and industrial waste can utilize.

Biomass characterization depends upon proximate analysis, chemical analysis and ultimate analysis. From these analyses, the effects of biomass on product yields measured. Proximate analysis is the simplest and quickest way of investigating the fuel quality of solid material [Nayan et al., 2013] [12]. Proximate analysis gives weight percentage of moisture, volatile, fixed carbon and ash. Green biomass contains 50% of moisture [Asadullah et al. 2007] [6], however for Pyrolysis moisture free (3% to 5% wt) biomass required otherwise bio-oil yield contains water as a part of moisture. Volatile materials mainly derived from cellulose and hemicelluloses which converted to bio-oil yield [Asadullah et al. 2007] [6]. High volatile content indicates that material is more volatile than solid fuel and loss in fixed carbon during Pyrolysis is less [Nayan et al., 2013] [12]. The fixed carbon which is converted to char so fixed carbon was responsible for production of char in Pyrolysis [Asadullah et al. 2007] [6]. The ash content particularly potassium favors the secondary reactions which in turn increases terequate phase, char and gas yield while decreases the liquid oil yield [Siu Hua Chang, 2014] [14]. Cellulose, hemicelluloses and lignin are the three main components of biomass [Akhtar and Amin, 2012]. In Pyrolysis, cellulose and hemicelluloses decomposes in a short interval of temperature 573K to 673K because of homogeneous structure and it is contributed for production of bio-oil yield [Hiliodhari et al., 2014] [11]. While lignin does not decompose uniformly constantly up to 973K and it produced charcoal [Hiliodhari et al., 2014] [11]. The aim of all these analysis was to provide ratio of combustible to incombustible substance of biomass [Siu Hua Chang, 2014] [14].

Effects of pyrolysis temperature and residence time
Bio-char is carbon-rich product generated from biomass through batch type slow pyrolysis. The effects of pyrolysis temperature and residence time on the yield and properties of bio-chars obtained from shredded cotton stalks were investigated. Makavana et al. (2020a) [7] safely said that the quality of biochar of shredded cotton stalk obtained at 500°C temperature and 240 min is best out of the all experimental levels of variables of temperature and residence time. At this temperature and residence time, the quality of bio-char in terms higher heating value (8101.3cal/g or 33.89 MJ/kg), nitrogen (1.56%), Carbon (79.30%), and C/N ratio (50.83) respectively. The quality of bio-char for various applications is discussed along with different quality parameters. The bio-char could be used for the production of activated carbon, in fuel applications, and water purification processes. Average bulk density of whole cotton stalk and shredded cotton stalk was found as 29.90 kg/m3and 147.02 kg/m3 respectively. Thus density was increased by 3.91 times. The value of pH, EC and CEC of shredded cotton stalk biomass was found as 5.59, 0.03 dS/m and 38.84 cmol/kg respectively. Minimum and maximum values pH, EC and CEC of its bio-char was found as 5.85 to 9.86, 0.04 to 0.10 dS/m and 38.02 to 24.39 cmol/kg at 200°C and 60 min and; 500°C and 240min temperature and residence time respectively. Moisture content, ash content, volatile matter and fixed carbon of shredded cotton stalk biomass were found as, 12.5, 5.27, 80.22, and 14.51 (% d.b) respectively. The minimum and maximum value of bio-char in terms of ash content, volatile matter and fixed carbon of bio-char were found as 5.5 to 15.56, 48.02 to 79.48 and 15.02 to 36.40 (% d.b) respectively. Calorific value of cotton stalk biomass was found as 3685.3 cal/g. The minimum and maximum higher heating value of its bio-char was found as 4622.0 cal/g and 8101.3 cal/g at 200°Cand 60 min and; 500°C and 240 min temperature and residence time.

Effect of Size of feed particles
Biomass is a poor conductor of heat so there is an issue of heat transfer during Pyrolysis [Akhtar and Amin, 2012]. It is an important parameter as it is controlling rates of drying and primary Pyrolysis during biomass decomposition [Gunay Ozbay, 2015] [4]. The size of feed particles play an important role on the yield and properties of liquid oil produced and it also affect the heating rate as larger particles heats up more slowly so expected volatile less [Beis et al., 2002] [13]. Small particle sizes are preferred in Pyrolysis system as smaller particles heat up uniformly with short time. The Pyrolysis oil vapors gets enough time for secondary reactions so it produces more gas yield and less char and liquid yield [Bharadwaj Rangarajan, 2014] [3]. While incase of larger particles, due to poor heat transfer, it heats up very slowly and releases less volatile matter so it produced more char and less liquid yield. So optimum size of feed particles should be chose for Pyrolysis process to get maximum amount of liquid yield.

Methodology
Determination of chemical composition of biomass using proximate, chemical and ultimate analysis. Drying of biomass in oven for 24 hours to remove initial moisture from biomass. Performance analysis of fixed bed reactor by varying different operating temperature. Analysis of end products of Pyrolysis such as bio-oil, bio-char and pyro-gas. Simulation of fixed bed pyrolyzer. Sawdust and Pinewood Pellets has been selected as a material for Pyrolysis. It has high bulk density, easily available, easy to feed and has lower moisture content. It also facilitates storage and transport.
To determine the various characteristics of sawdust pellets following analysis carried out.
1) Proximate analysis, 2) Chemical analysis, 3) Ultimate analysis

**Proximate analysis**
Proximate analysis carried out to know the moisture content, volatile content, ash content and fixed carbon of biomass. It gives the quality of fuel which is useful to select the material for Pyrolysis. Proximate analysis of sawdust pellets carried out as per ASTM standards. ASTM E870-82 (2013).

**Results**
This chapter involves the results obtained during experiment and its discussion. It also involves results of proximate, chemical and ultimate analysis of sawdust and pinewood pellets.

**Experimental data**
The pre-treated 3 kg pellets taken for each experiment.

Experiments performed at five temperatures 400, 425, 450, 475 and 500 °C. Each experiment repeated three times to get the results. Other details of experiments are given in table 1.

| Material          | 8mm Sawdust pellet | 8mm Pinewood pellet |
|-------------------|--------------------|---------------------|
| Weight of biomass (kg) | 3                  |                     |
| Heating rate (°C/min) | 10                 |                     |
| Coolant           | Chilled water      |                     |
| Coolant temperature (°C) | 10                 |                     |

**Chemical composition of pellets**
The results of proximate, chemical and ultimate analysis of sawdust and pinewood pellets are shown in table 2. The calorific values of sawdust and pinewood pellets are respectively 17.96 MJ/kg and 19.30 MJ/kg. The bulk densities of sawdust and pinewood pellets are 613 kg/m³ and 625 kg/m³. Aalso find Makavana et al., 2020c [9] the Effect of Pyrolysis Temperature and Residence Time on Bio-char Obtained from Pyrolysis of Shredded Cotton Stalk.

| 8mm Sawdust pellet | 8mm Pinewood pellet |
|--------------------|--------------------|
| **Proximate Analysis** |                    |
| Moisture content (%) | 7.86               | 6.84               |
| Volatile content (%db) | 73.81             | 67.58             |
| Ash content (%db) | 2.98               | 3.89               |
| Fixed carbon (%db) | 10.66              | 12.37              |
| **Chemical Analysis** |                    |
| Cellulose (%) | 43.26              | 40.19              |
| Hemicellulose (%) | 17.77              | 14.75              |
| Lignin (%) | 24.21              | 31.55              |
| Mineral (%) | 8.88               | 8.35               |
| **Ultimate Analysis** |                    |
| Carbon (%) | 42.78              | 40.64              |
| Hydrogen (%) | 5.98               | 4.76               |
| Oxygen (%) | 48.92              | 51.37              |
| Nitrogen (%) | 0.47               | 0.59               |

The experiments performed with Pinewood pellets by taking same experimental conditions as sawdust pellets. The same trend observed in case of Pinewood pellets also as in case of Sawdust pellets. The yield obtained at different temperatures reported in table 3 and 4. In case of Pinewood pellet, the maximum bio-oil yield obtained 34.60% at 450 °C. So, in our experiment at 450 °C, we obtained optimum bio-oil yield for both pellets. Pinewood pellets has higher bio-oil yield compared to Sawdust pellets. After that increase in temperature results into decrease in bio-oil yield and increase in gas yield which is not desirable.
Products of Pyrolysis.
The products of Pyrolysis are bio-oil, bio-char and pyro-gas. The detailed description of products is given below. As per our support in shown table 5.

Table 5: Percentage of Bio-char, bio-oil and pro-gas yield of temperature and residence time Makavana et al. (2020b) [10].

| Run No. | Temperature (°C) | Residence time, min | Bio-char yield (%) | Bio-oil yield (%) | Pyro-gas yield (%) |
|---------|------------------|----------------------|-------------------|------------------|-------------------|
| 1       | 200±15           | 60                   | 70.2              | 15.2             | 14.6              |
| 2       | 200±15           | 120                  | 68.6              | 18.2             | 12.6              |
| 3       | 200±15           | 180                  | 65.8              | 18               | 16.2              |
| 4       | 200±15           | 240                  | 64.8              | 14.4             | 20.8              |
| 5       | 300±15           | 60                   | 42.4              | 16.4             | 41.2              |
| 6       | 300±15           | 120                  | 44.4              | 18.4             | 37.2              |
| 7       | 300±15           | 180                  | 44.4              | 17.2             | 38.4              |
| 8       | 300±15           | 240                  | 44.2              | 20.8             | 35                |
| 9       | 400±15           | 60                   | 37.6              | 14.4             | 48                |
| 10      | 400±15           | 120                  | 37.8              | 12               | 50.2              |
| 11      | 400±15           | 180                  | 36.8              | 10.4             | 52.8              |
| 12      | 400±15           | 240                  | 37.2              | 15.6             | 47.2              |
| 13      | 500±15           | 60                   | 36.4              | 7.6              | 56                |
| 14      | 500±15           | 120                  | 36.2              | 7.2              | 56.6              |
| 15      | 500±15           | 180                  | 34                | 7.2              | 58.8              |
| 16      | 500±15           | 240                  | 34                | 7.2              | 58.8              |

*Bio-char yield is considered as torrefied biomass*

Bio-oil
Bio-oil consists of water and organic compounds [Asadullah et al. 2007] [10]. Bio-oils are dark brown, highly viscous, high density and comprised of highly oxygenated compounds [2015 World Energy Issues Monitor]. Bio-oils consist of 15% - 30% water and organic compounds are acids, alcohols, aldehydes, ketones, esters, phenols, guaiacols, syringols, sugars, furans, alkenes, aromatics, nitrogen compounds and miscellaneous oxygenates. Bio-oil used as furnace oil and byproduct techniques can be used as a fuel. Also measured Makavana et al. (2020b) [10].

Bio-char
Char is the other major pyrolysis product. Depending on temperature, the char fraction contains inorganic materials ash, carbon content to varying degrees, any unconverted organic solids and carbonaceous residues, produced on thermal decomposition of the organic components, in particularly lignin. Char can be used as an adsorbent and solid fuel due to its higher calorific value. Also measured Makavana et al. (2020b) [10].

Pyro-gas
The Pyrolysis contains carbon based non-condensable gases like CO, CO2, methane, ethane, ethene, propane and propene and minor amounts of higher gaseous compounds and water vapor. The pyro-gas has a sufficient higher heating value which can be used for biomass heating or in the internal combustion engine. Also measured Makavana et al. (2020b) [10].

Characterisation of Bio-oil
Bio-oil consists of water and organic compounds. Bio-oil consists of complex mixture of cellulose, hemicelluloses and lignin. The bio-oil can be used as furnace oil. The bio-oil obtained through experiment characterized by density, pH, water content, calorific value, viscosity, flash and fire point. The obtained properties of bio-oil through different analysis reported in following table 6 and table 7. Makvana et al., (2018) [8] also found the Engineering properties of various agricultural residue.

Table 6: Characterisation of bio-oil for sawdust pellet

| Temperature (°C) | 400 | 425 | 450 | 475 | 500 |
|------------------|-----|-----|-----|-----|-----|
| CV (MJ/kg)       | 21.58 | 22.61 | 23.74 | 24.82 | 25.33 |
| Density (kg/m3)  | 1029.10 | 1028.20 | 1027.34 | 1026.42 | 1024.13 |
| Viscosity (cSt) @ 40 °C | 14.87 | 15.17 | 15.98 | 16.57 | 18.38 |
| pH               | 4.10 | 3.81 | 3.56 | 3.10 | 3.08 |
| Water content (%) | 8.60 | 8.10 | 7.85 | 7.21 | 6.98 |
| Flash point (°C) | 108 | 102 | 100 | 101 | 100 |
| Fire point (°C)  | 171 | 168 | 162 | 158 | 156 |

Table 7: Characterisation of bio-oil for pine wood pellet

| Temperature (°C) | 400 | 425 | 450 | 475 | 500 |
|------------------|-----|-----|-----|-----|-----|
| CV (MJ/kg)       | 24.60 | 24.84 | 25.49 | 25.68 | 26.27 |
| Density (kg/m3)  | 1045.21 | 1040.77 | 1039.79 | 1043.89 | 1045.13 |
| Viscosity (cSt) @ 40 °C | 15.23 | 16.27 | 17.21 | 17.89 | 18.21 |
| pH               | 3.89 | 3.78 | 3.67 | 3.51 | 3.15 |
| Water content (%) | 7.65 | 7.64 | 7.61 | 7.59 | 7.51 |
| Flash point (°C) | 108 | 105 | 103 | 99 | 102 |
| Fire point (°C)  | 180 | 172 | 168 | 160 | 158 |

Characterisation of Bio-char
The characterisation of bio-char carried out. Proximate analysis of bio-char gives theash, volatile and fixed carbon content. The volatile content of bio-char decreased as the temperature increases that we can say from analysis. As the temperature increases, more volatile expelled out from biomass pellet and less volatile matters left in biomass pellet. Hence, higher Pyrolysis temperature resulted in higher fixed carbon. The fixed carbon content of char found after volatile matters removed from bio-char. The volatile content decreased as the temperature increases. With the decrease in volatile content, fixed carbon increases. Also the calorific value of bio-char increases with the increase in temperature. The analysis data for both pellets reported in table 8 and 9. Also find Makavana et al., 2020c [9] the Effect of Pyrolysis Temperature and Residence Time on Bio-char Obtained from Pyrolysis of Shredded Cotton Stalk.

Table 8: Characterisation of Bio-char of sawdust pellet

| Temperature (°C) | 400 | 425 | 450 | 475 | 500 |
|------------------|-----|-----|-----|-----|-----|
| Ash (% wt)       | 2.38 | 2.77 | 3.18 | 2.98 | 2.21 |
| Volatile (% wt)  | 18.88 | 17.87 | 14.14 | 13.91 | 13.10 |
| Fixed carbon (% wt) | 77.87 | 78.21 | 79.22 | 80.10 | 82.33 |
| CV (MJ/kg)       | 30.21 | 30.97 | 31.27 | 33.29 | 34.16 |
Characterisation of Pyro-gas

After interval of ten minutes, the sample of gas collected in balloon. The gas composition analysed in gas-chromatograph with repetition. Hydrogen, methane, carbon monoxide and carbon dioxide detected in GC. It observed that hydrogen and methane gases increases with time and temperature while carbon monoxide and carbon dioxide decreases as shown in graph (fig.) 3. The flame temperature and calorific value of gas measured during experiment as shown in Table 10. The gas composition graph is shown in figure 3.

Table 9: Characterisation of Bio-char of pinewood pellet

| Temperature (°C) | 400 | 425 | 450 | 475 | 500 |
|-----------------|-----|-----|-----|-----|-----|
| Proximate Analysis |     |     |     |     |     |
| Ash (%wt) | 8.51 | 8.56 | 8.98 | 9.10 | 10.12 |
| Volatile (%wt) | 28.16 | 27.50 | 26.70 | 25.56 | 24.22 |
| Fixed carbon (%wt) | 62.19 | 65.78 | 68.85 | 69.37 | 70.31 |
| CV (MJ/kg) | 27.10 | 27.39 | 28.42 | 29.31 | 31.10 |

Table 10: Characterisation of Pyro-gas

| Temperature (°C) | Sawdust Pellet | Pinewood Pellet | Flame temperature (°C) |
|-----------------|---------------|----------------|------------------------|
| 400 | 9.36 | 8.37 | 674 |
| 425 | 10.02 | 9.86 | 680 |
| 450 | 10.75 | 9.46 | 707 |
| 475 | 11.00 | 10.15 | 721 |
| 500 | 11.97 | 10.57 | 749 |

**Fig 3: Gas composition graph**

**Conclusion**

The article covers the description of biomass any waste material, known as bio-char and its physicochemical properties along with its proximate analysis. The potential biomass wastes that can be used for bio-char production are presented. Various production routes of bio-char have been discussed. Among those, pyrolysis, Torrefaction, slow pyrolysis, intermediate pyrolysis, fast pyrolysis, flash pyrolysis, hydrothermal carbonization, and microwave assisted pyrolysis are discussed with their operating conditions and specifications. Bio-chars have a tremendous range of physical and chemical properties, which greatly affect their wide applications. The physical, chemical and mechanical properties of bio-chars depend on the feedstock type and pyrolysis operating conditions. The experiments results showed that maximum bio-oil yield is obtained 34.86% wt and 35.61% wt respectively for sawdust and pinewood pellet at 450 °C

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