Bio-oil production from a lignocellulosic biomass and its fuel characteristics

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Abstract. A wide research is going on in the field of renewable energy resources to shelter the scarcity of conventional fossil fuels. As we look back, from the beginning of Earth's formation, a tremendous amount of the energy stored inside the earth. Until the start of 19th century man was unaware of this treasure and used lignocellulosic biomass / wood biomass as an energy source of which people unaware of its true potential. But, as fossil fuel sources were discovered, the excavation started to meet the energy demand which obviously replaced the biomass. Then from the petroleum crude oil, petrochemicals took birth and the industrial revolution changed the prospective of entire world. Now, in this first quarter of the 21st century when the population is gigantic and demand for energy sources has increased to the enormous level, fossil fuels are being consumed like never before and now they are diminishing with very fast rate leading towards the energy crisis. So, to overcome this problem; need for the replacements, blends of fossil fuels arises and as a result we are going back in time to utilize another huge source of energy i.e. Biomass. Lignocellulosic biomass can be thermally converted into biofuels by various technologies. One of such most effective and lucrative technology is pyrolysis. Pyrolysis of lignocellulosic biomass convert it into bio-oil, bio-char and pyrolysis gas, these all have high energy content and potential in them. In this deliberated work, authors conducted a pyrolysis experiment on a lignocellulosic biomass which is available as a solid waste on long and far terrestrial region though barely investigated. Temperature of the reaction was set at 500 °C at which the bio-oil resulted its highest heating value of 17.093 MJ/kg and that of bio-char is 30.768 MJ/kg. Fourier Transform Infrared Spectroscopy (FTIR) showed number of functional groups present and Gas Chromatography-Mass Spectroscopy (GCMS) resulted in huge number of chemical compounds present in the bio-oil. Then we studied flow behaviour of bio-oil by Interfacial Rheometer and it demonstrated Shear-thinning behaviour. Thus, the study reveals fuel potential of untouched biomass in terms of bio-oil and its transport phenomenon.

1. Introduction
Petroleum depletion over a period of time, climate change and other environmental concerns triggered by consumption of fossil fuels and the need of value added petrochemicals drives a force to develop fruitful technologies [1]. For production of fuel grade chemicals and precursors to the specialty grade chemicals within a cost effective and environment friendly frame, biomass as a renewable feedstock plays a dynamic role. Mainly two routes are popular i.e., thermochemical conversion and biological conversion which produce biofuel in the form of solid, liquid (bio-oil) and gas from biomass which can be consumed as fuel and source for manufacturing of value added chemicals [2–5]. In thermochemical conversion process various technologies are developed to transform biomass into bio-fuels such as pyrolysis, gasification, hydrothermal gasification, hydrothermal liquefaction, chemical looping
combustion etc.; [3]. Among these thermo-chemical technologies, pyrolysis is an economical way for transforming biomass into bio-fuels and has qualified with an impending effect on pilot scale as well as in the form of bio-refinery [2,6].

Pyrolysis is a process of thermal degradation of the biomass in absence of oxygen to produce bio-fuels [7]. Renewable bio-fuels such as bio-oil, biochar and volatile gases are produced by the pyrolysis of biomass which can deliver our expected fuel grade chemicals and energy platform [8]. Lignocellulosic biomass is the readily available source of biomass which also contribute to solid waste at various locations but in terms of energy it is a solid fuel [9]. The process depends on the operating parameters and condition, reactor design and material, feed size, reaction atmosphere, heat transfer rate and flow rate of reacting gas medium. The main product after the pyrolysis process is bio-oil which is obtained by condensed gas and non-volatile components of the gas mixture present at the time of reaction. For lignocellulosic biomass degradation of cellulose and hemicellulose comprises of more oxygenates whereas degradation of lignin gives aromatics [10–12]. Thus, the quality of bio-oil can be represented on the basis of its C, H, N, S, O content and mainly on its calorific value [11,13]. The product distribution of this process leads to the carbon neutral system which is attributed to overcome the environmental concern [1,14]. According to the Government of India’s national policy on biofuels from renewable biomass feedstock, structural development is required to provide addition in conventional energy sources to meet the energy needs of India [15].

In this prescribed work, authors experimented pyrolysis of a solid waste lignocellulosic biomass which is present in a huge amount in the campus of Indian Institute of Technology Guwahati. Delonix Regia is the source of solid fuel for us but heavily ignored till date and hence wasted the energy content in it. We used this biomass material to produce bio-fuels. On the basis of its elemental analysis and calorific value determination we came to know that the Delonix Regia biomass has a tremendous energy potential stored in it. From thermo-gravimetric analysis we have its degradation pattern and determined the operating temperature range and thus, we set the operating temperature for pyrolysis of Delonix Regia as 500 ºC. The estimated calorific value of Delonix Regia biomass is 16.832 MJ/kg. Thus, it has a great fuel potential. To confirm its functionality we utilized some advanced characterization techniques for bio-oil characterization such as Fourier Transform Infrared Spectroscopy (FTIR) [16,17] and Gas Chromatography Mass Spectroscopy (GCMS) [18–22]. To determine its flow behavior and rheological characteristics we have studied the bio-oil using Interfacial Rheometer [23]. FTIR shows number of functional group present in bio-oil and GCMS confirms the compounds present in the percentage amount in obtained bio-oil at 500 ºC. Rheological characterization of bio-oil shows that the fluid is Non-Newtonian at steady condition resulting in shear thinning fluid but after applying a particular shear rate it performs as a Newtonian fluid which implies to its property for transporation fluid. Hence, by using above mentioned techniques it is clear that the bio-oil generated from solid waste biomass of Delonix Regia contains fuel characteristics as well as it can be useful as transporation fuel. The bio-char is characterized for its calorific value and it gives a good energy content in it. Thus this particular experimented research work confirms the ability of Delonix Regia as a solid fuel and processed to get bio-fuels which also have lucrative fuel prospective.

2. Experimental Insight

2.1. Raw Biomass
For the research study on pyrolysis of lignocellulosic biomass we have chosen Delonix Regia (DR) as a solid fuel. The DR biomass is locally available as a solid waste material which is of no use than to burn it directly. Burning this waste in atmosphere causes pollution and is likely to destroy the huge amount of energy extractable from this biomass material as solid fuel and in other form. The collected raw biomass is crushed down using wood cutter followed by grinding. The grinded biomass material is then sieved below 800-micron size and the sieved material is kept for moisture removal in hot air oven for 2 hours. After that the DR biomass raw material is ready to be fed into the reactor. We firstly researched its fuel potential by Ultimate analysis, Proximate analysis and Calorific value (CV) which is
shown in Table 1. From the results obtained, we can pursue the prospective nature of this biomass to generate bio-fuels and thus to confirm its degradation pattern we employed an advance technique of thermo-gravimetric analysis by using thermo-gravimetric analyzer (TGA). TGA study shows a seamless degradation profile over a period of time and increasing temperature including moisture of biomass removal to give parameters for pyrolysis process. Based on this particular tests, we confirmed this solid waste biomass as a solid fuel to deliver bio-fuels in form of solid, liquid and gas state by thermal degradation.

| Table 1. Ultimate and Proximate analysis of Delonix Regia biomass and its Calorific value. |
|---------------------------------|-----------------|-----------------|---------|
| Elemental Composition (wt. %)   | Proximate Analysis | CV (MJ/kg)      |
| C                               | H               | N               | O       |
| Moisture (%)                   | (%)             | (%)             | (%)     |
| Volatiles (%)                  | (%)             | (%)             | (%)     |
| Fixed Carbon (%)               | (%)             | (%)             | (%)     |
| Ash (%)                        | (%)             | (%)             | (%)     |
| 45.43                          | 5.95            | 1.25            | 47.37   |
| 9                               | 72.2            | 1.2             | 17.6    |
| 16.832                         |                 |                 |         |

2.2. **Pyrolysis of Delonix Regia biomass**

Pyrolysis is the thermal degradation of biomass material in an inert medium over maintained operating conditions. The raw biomass is collected from streets of IIT Guwahati which are broken trunks and barks of DR tree. The biomass is grinded to make it ready for feeding it into the reactor, as the reactor is a fixed bed, batch type made up of Inconel tube having an approximate capacity of 100 ml volume. The reactor is attached to the gas inlet system in its prefix and it is attached with the condenser, gas-liquid separator and liquid collection assembly in its suffix. A K-type thermocouple is inserted inside of the reactor to record the temperature inside of the reactor. Whereas a pressure transmitter is also incorporated in the system to show the exact pressure of the system. The thermocouple and transmitter is attached with the PID controller in a control panel to show the live readings. The schematic of experimental setup is directed in Figure 1.

![Figure 1: Schematic representation of fixed bed pyrolysis reactor.](image)

The reactor tube is fitted with the gas inlet line and fixed in a ATS furnace. Then the nitrogen gas is passed through the system to maintain the pressure of 1 bar inside the system as it is an open to
atmosphere system. Later, we set the process temperature at 500 °C with the heating rate of 20 °C/minute as per the TGA results. As the temperature reaches the set point i.e., 500 °C we noted down the time and from that very second the residence time of the reaction is set at 2 hours. Volatile gas is collected in tedler bag and analysed on GC. As soon as the reaction is completed, inlet gas flow and furnace is switched off and liquid product i.e., bio-oil is collected in a liquid collection assembly. Immediately after the collection we measure its amount and pH. After the reactor cooled down to room temperature, reactor tube is dislocated from the furnace and the solid pyrolytic residue remain is collected as biochar.

This experiment is carried out for three times to know the trend of reproducibility and it is showing a proper repeatability of data over an error bar of 5 %. The products obtained from the reaction are then sent for characterization.

2.3. Characterization of feed and product material

2.3.1. Delonix Regia Biomass. The DR biomass is characterized by elemental analyzer (EuroEA CHN3000 Analyzer, Italy) at Guwahati Biotech Park. It is an ultimate analysis of the biomass and thus gives elemental configuration of material. The proximate analysis of the biomass material is characterized by the ASTM standards using box furnace (VB Ceramic Consultants Chennai, India). The higher heating value (HHV) or the calorific value of material is determined on Toshniwal Bomb Calorimeter (IS 1350 -1, India). Then the thermo-gravimetric analysis of DR biomass sample was done using Thermo-Gravimetric Analyzer (TG 209 F1 Libra Netzsch, Germany) and also we studied the differential thermo-gravimetric profile of the raw material which gives the maximum degradation temperature.

2.3.2. Bio-oil. Bio-oil is tested for its pH by Eutech benchtop pH meter (pH 700 Thermo Fisher Scientific, India) and its HHV is determined using Toshniwal Bomb Calorimeter (IS 1350 -1, India). Fourier Transform Infrared Spectroscopy (FT-IR) analysis is carried out for the determination of functional groups present in bio-oil using FT-IR instrument (IRAffinity-1 Shimadzu, Japan). Gas Chromatography and Mass Spectroscopy determined the number components or the compounds present in the bio-oil (450-GC, 240-MS Varian, Netherland). The rheological characteristics of bio-oil are determined by Interfacial Rheometer (MCR 301 Anton Parr, Austria) and gives a brief idea about the flow behaviour of bio-oil and its transport mechanism. This advance characterization instruments are available with departmental analytical lab, IIT Guwahati.

2.3.3. Bio-char. Bio-char is analysed by elemental analyzer (EuroEA CHN3000 Analyzer, Italy) at Guwahati Biotech Park for its elemental composition determination and the calorific value is determined by Toshniwal Bomb Calorimeter (IS 1350 -1, India).

3. Result and Discussion

3.1. Properties of Biomass

Delonix Regia biomass has CV of 16.832 MJ/kg, this biomass is then taken into the TGA crucible on ‘dry basis’ having 7 mg weight. Atmosphere for the reaction is of nitrogen with flow rate 20 ml/min., the constant heating rate is set at 20 °C/minute. The thermogravimetric analysis and differential thermogravimetric analysis of the Delonix Regia biomass is shown in Figure 2. From the TGA plot we can observe the weight loss pattern, from 0 to 150 °C the moisture content of the material is removed. The hemicellulose and cellulose degradation takes place till 400 °C whereas the lignin content is degraded till the complete course of time i.e., till 750 °C. From DTG plot we can see that the maximum degradation temperature is around 375 °C. Thus, from this very informative data of properties of Delonix Regia biomass triggers the interest of experimenting this solid waste to multiply its energy content.
3.2. Properties of Bio-oil

The maximum bio-oil yield is 40.54 % and it has pH of around 3.5 which demonstrates its high acidic nature. Calorific value of bio-oil is evaluated on bomb calorimeter which is 17.093 MJ/kg, i.e., slightly more than that of raw biomass and thus it states the potential of this process as a positive energy recovery system. Figure 3 shows FT-IR analysis result of obtained bio-oil in % transmittance mode whereas the downward peaks represent the transmission of IR rays over a particular wave number. Each wave number represents particular functional group thus, from obtained peak values we can enlist following groups presented in Table 2. The occurrence of given functional groups represents the specific class of compounds available in bio-oil. From the associated figure and table, it is now confirmed that this bio-oil contains very valuable class of compounds such as alkanes, alkenes, alkynes ketones, aldehydes, carboxylic acids, primary, secondary, tertiary alcohols, phenol, ester, ether, aromatic compound, naphthalene and ring in benzene derivative. This analytical characterization proven the worth of DR bio-oil as a potential measure.

Table 2. Functional group present in DR bio-oil at particular wave number.

| Wave number (cm\(^{-1}\)) | Group               | Class of compound                           |
|---------------------------|---------------------|---------------------------------------------|
| 3358                      | O-H stretching      | Polymeric O-H, water impurities             |
| 2020                      | C=O stretching      | Alkynes                                     |
Gas Chromatograph and Mass Spectrometer (GC-MS) is an analytics device where GC separates the mixture of compounds and MS identifies the mass of molecule. It gives perfect idea of molecules exists on the basis of mass determination. The measurable volume of 0.2 microliter of DR bio-oil is inserted to the GC, the total program was set to 29 minutes having two ramps; first up to 140 ºC and second is from 140 to 210 ºC. Helium is used as a carrier gas inside the column.

**Figure 4.** GC-MS chromatogram of Delonix Regia bio-oil obtained at 500 ºC.

**Table 3.** Major compounds list present in DR bio-oil at 500 ºC given by NIST library.

| Sr. No. | Compound                          | Retention time | Molecular weight | Chemical formula | Area (%) |
|---------|-----------------------------------|----------------|------------------|------------------|----------|
| 1       | Benzene                           | 3.944          | 78               | C6H6             | 13.55    |
| 2       | 1,2-Propanediol, 2-acetate        | 4.064          | 118              | C5H10O3          | 1.74     |
| 3       | N,N,O-Triacetylhydroxylamine      | 4.967          | 159              | C6H6NO4          | 0.404    |
| 4       | Hexane, 2,2,4-trimethyl-           | 5.043          | 128              | C9H2O            | 0.341    |
| 5       | Pilocarpine                       | 5.972          | 208              | C11H16N2O2       | 1.746    |
| 6       | 1H-Imidazole-4-methanol           | 6.273          | 98               | C4H6N2O          | 2.247    |
| 7       | Furan, 2-ethyl-5-methyl-          | 7.257          | 110              | C7H1O            | 0.844    |
| 8       | 2-Furancarboxyaldehyde, 5-methyl- | 8.272          | 110              | C6H6O2           | 0.25     |
| 9       | 2,4-Dimethylfuran                 | 8.411          | 96               | C6H8O            | 0.569    |
| 10      | Phenol                            | 8.578          | 94               | C6H6O2           | 1.365    |
| 11      | Furan, 2-butyltetrahydro-         | 9.037          | 128              | C8H16O           | 0.553    |
| 12      | 1,2-Cyclopentanediene, 3-methyl-  | 9.633          | 112              | C6H8O2           | 1.594    |
| 13      | Phenol, 2-methyl-                 | 10.062         | 108              | C7H8O            | 0.526    |
| 14      | p-Cresol                          | 10.504         | 108              | C7H8O            | 1.674    |
| 15      | 2-Octen-4-ol                      | 10.669         | 128              | C8H16O           | 0.632    |
| 16      | Phenol, 2-methoxy-                | 10.865         | 124              | C7H8O2           | 4.435    |
| 17      | 2-Cyclopent-1-one,3-ethyl-2hydroxy| 11.546         | 126              | C7H1O2           | 0.818    |
and Technology (NIST) database library gives most plausible compounds likely to present. Thus, this is the most accurate and suitable technique to do the molecular level analysis of bio-oil sample. Generated chromatogram from GC-MS analysis of bio-oil showing number of peaks given in Figure 4. There are around 100 compounds are identified in the DR bio-oil sample by NIST library. Here, we are providing the list of major compounds in Table 3 with the area % of total volume. From the list, it is clear that the GCMS given compounds belongs to the FTIR mentioned class of compounds.

Further to understand the flow characteristics of produced bio-oil, we have carried out its flow behaviour analysis with varying shear rate by using rheometer. A significant decrease in the viscosity has been observed with an increase in the shear rate, which signifies the shear thinning behaviour of bio-oil. Basically, the existence of solid compounds present in bio-oil are responsible for the decline in the viscosity of bio-oil [23]. It has been observed that with increasing the viscosity these compounds break-down into small particles which eventually reduces the frictional forces and hence reduces the viscosity. Thus, the rheological study of DR bio-oil shows that this fluid is good for transportation and handling.

![Figure 5. Schematic representation of DR bio-oil showing shear-thinning behaviour.](image-url)
3.3. Properties of bio-char

The maximum yield of DR bio-char obtained at 500 °C is 36.702 weight % having CV of 30.768 MJ/kg. The elemental analysis gives its composition as, C-73.93 %, H-3.34 %, N-1.66 %, O-21.01 %. These properties of bio-char gives us information about the potential of bio-char as a charcoal and its energy value shows that it can be used as feedstock for energy production. The amorphous nature of bio-char leads to its valuability to make it activated and can be used as filter media for water remediation.

4. Conclusion

The HHV of bio-oil is 17.093 MJ/kg and that of bio-char is 30.768 MJ/kg which is more comparative to biomass and thus corresponds to energy recovery rate of more than 60 %. The FT-IR and GC-MS results showed the worth of this bio-oil obtained from DR biomass by presence of functional group and corresponding chemical compounds. Rheology of bio-oil presented its transport mechanism which showed the bio-oil exhibits shear-thinning behaviour i.e., Non-Newtonian fluid. Obtained bio-char can be utilized for carbon sequestration and water remediation and the non-condensable gas can deliver a high energy content as producer gas which can be used for energy production.

Finally, to conclude that this scarcely researched Delonix Regia is a profitable biomass to produce bio-fuels by pyrolysis as a gateway technique. The produced bio-oil shows the fuel properties and the chemical composition of bio-oil shows that it can be utilized for production of bio-based petrochemicals. The bio-oil can further be upgraded for fuel grade to use as transportation fuel. The process is entirely economical and eco-friendly. Thus we endorse that, the Delonix biomass has a huge energy potential which can generate a good revenue by means of pyrolysis process for producing bio-fuels.

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