Bio Oil Production:Pyrolysis of Saw Dust in an Auger Reactor

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Abstract: Pyrolysis of saw dust from babul plant in a fluidized bed reactor for production of bio oil was reported. Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), ultimate analysis and proximate analysis were performed on the saw dust. The FTIR analysis showed the presence of C-H bonds and the ultimate analysis showed a high percentage of carbon which demonstrated its potential as a raw material for the production of bio oil. The process parameters of the reactor namely the residence time, reactor temperature and feed rate were optimized. Maximum yield of 20.4% was reported at a temperature of 600 °C, feed rate of 5kg/h and at a residence time of 90 seconds.

Keywords: Pyrolysis, biomass, bio oil, residence time, yield, loading rate.

1. Introduction

The current problem of environmental pollution and a shortage of conventional fossil fuels has increased the importance of biomass for meeting the rapid economic growth. [1-3].Utilizing the energy obtained from agricultural wastes or agricultural by-products which is a form of renewable energy does not add carbon dioxideto the environment. There is a lesser chance of health risk and environmental pollution compared to fossil fuels as the biomass contains fewer amounts of nitrogen and sulfur [4-5]. A huge impact can be created on CO$_2$ reduction by substituting the use fossil fuels with energy obtained from biomass [6-7].Plant biomass mainly comprises of cellulose, hemicelluloses and lignin making it an ideal source of renewable energy for the producing power and heat [8-9]. However, biomass availability may be seasonal in nature, thus utilizing biomass along with coal for combustion is more feasible [10].

Several factors like environmental benefit, economic benefit and availability of source need to be considered for selection of proper alternative energy. Thus biomass is identified as the potential source capable of responding to all the challengesof factors. Biomass is an abundant resource that can be found in diverse forms like wood residues, agricultural residues, municipal solid wastes and dedicated energy crops.It is the only form of renewable energy that can be converted into several types of fuels, including liquid, char and gas which also promises flexibility in production and marketing. Generally, pyrolysis is chosen to achieve this goal. It can produce the highest liquid yield of up to 75 wt% with conditions of moderate temperature (~500°) and short vapor residence time (~1s) [11].Due to their, high combustion efficiency, fuel flexibility, high heat transfer and low emission of SOx, NOxand CO$_2$ neutral, a lot of attention has been given to combustion and co-combustion of renewable energy sources. [12-13].

Parveen et al. carried out the pyrolysis of sugarcane bagasse in a fixed-bed fire-tube heating reactor to determine the role of feed size, final temperature and sweeping gas flow rate on the product yields under different conditions of pyrolysis. It was concluded that pyrolysis by means of a fixed-bed fire –tube reactor was a good option for converting biomass solid wastes into bio oils [14].Abnisa et al. demonstrated that the use of palm shell as an agricultural residue can be used for the production of bio oil through pyrolysis process. The

study was carried out at different operating conditions. Optimization of theflow rate of N_2, temperature, reaction time and particle sizewas carried out and the maximum yield of 47.3 (wt%)was obtainedat a flow rate of 2 L/min of N_2 at an operating temperature of 500 °C and a reaction time of 60 minutes. [15]. Tsai et al. prepared a series of pyrolysis oils and chars from agricultural by-product rice husk by lab-scale fast pyrolysis system using induction heating. The process parameters such as heating rate, pyrolysis temperature, holding time, condensation temperature, nitrogen gas flow rate and particle size on the pyrolysis product yields and their chemical composition were examined. The optimum yield of 40% of pyrolysis oil was achieved at the pyrolysis temperature of >500°C, heating rate of >200°/min, holding time of >2min, condensation temperature of <-10°C and particle size of <0.50mm. The yield of pyrolysis oil was not affected by the flow rate of nitrogen (sweeping ga)[16]. Kader et al. performed the production of bio oil through pyrolysis of tamarind seed into using a fixed bed fire-tube heating reactor, liquid condenser and collector. At an operating temperature of 400 °C, the maximum yield of 45 (wt%) was obtained. The corresponding gas flow rate obtained was 6 L/min with 3200 um feed size and 30 mins of running time [17].Kim et al. carried out the comparison of pyrolysis of construction waste wood by means of fluidized bed reactor and batch reactor in the temperature range of 450–550 °C. The maximum yield was obtained at a temperature of 500 °C. The fluidized bed reactor gave higher yields than the batch reactor while were found to be less temperature dependent. Improved oil quality and reduced moisture content was also obtained through the fluidized bed reactor by reducing the dehydration and secondary condensation [18].

Veeresh et al. carried the FTIR analysis of agricultural wastes like, saw mill dust, press dug, ground nut husk, castor seed cake, jatropa seed cake, and tamarind fruit shell. The results showed that structures of alkyne C-H bend, sulfur compounds S=O, aliphatic amines C-N, methylene C-H bends, secondary amides N-H bend, methylene symmetric C-H stretch, amines N-H stretch and urethanes amides were commonly found in all the samples but the intensity in each sample varied. [19]. Tanneru et al. carried out the Fourier transform infrared spectroscopy of a hydrocarbon mixture. The finding were found to be in agreement with the physical and chemical properties of the boiler fuel and oxidized product [20].

Peng Fu et al. used thermogravimetric analyzer and Fourier transform infrared (FTIR) analyzer to study the pyrolysis mechanism of rice straw, maize stalk and cotton straw. The highest thermal reactivity was shown by maize stalk. The three materials were found to have similar pyrolysis gases namely CO, CO2, methane, ethylene and ethane. The major nitrogen containing product was found to be HCN[21].

Yang et al. characterized the pyrolysis of cellulose, hemicellulose and lignin using a thermogravimetric analyzer (TGA) with a pack bed and differential scanning calorimeter (DSC). Pyrolysis of hemicellulose occoured at a temperature of 220 – 315 °C and was found to be easily degraded. At a temperature range of 150 – 900 °C, lignin underwent pyrolysis while cellulose degraded mainly at a temperature of 315 °C [22].

Saw dust is commonly used in making particle board and wood pulp. It was chosen as it has higher carbon content and easily available.In the present work, bio oil production from saw dust was reported. The characterization of the oil was carried out and its properties were also studied.

2. Experimental

The saw dust was obtained from babul plant(*Vachellianilotica*)from the biomass power plant located in VIT University, Vellore, India.The samples were initially dried under the sun to remove most of the moisture content. Grinding of the saw dust was carried out in the grinding mill to obtain fine particles. Concentrated sulfuric acid, potassium sulfate, sodium hydroxide, acetonitrile and 1,3propanediol were the principle chemical used in this study. All the chemicals were of analytical grade.

2.1.Reactor

The dried saw dust was added to the hopper from where it was fed into the reactor at a feeding rate between 3 kg/h to 7 kg/h. The auger was inside a stainless steel tube with length and diameter of 1200 mm and 300 mm respectively. It was heated by a furnace which had a heating capacity of 1000°C with a maximum heating rate of 150°C per minute. However, a heating rate of 30°C per minute was used with a maximum temperature limited to 600°C. The biomass was pushed through the reactor by means of a screw feeder driven by a 1 hp variable speed motor at a reduction ratio of 1:100 resulting in a speed band of 15 – 60 rpm.Sand was used as a heat carrier and was mixed with the saw dust in the ratio of 2:1. Nitrogen was used as a carrier gas.

A water sealed receiver tank was provided at the end of the reactor furnace to separate the charred saw dust in a separate container by means of gravity. The vapor from the reactor was cooled to a temperature of 10 °C in the quenching cooler of the first collection tank. The vapor from the first collection tank was subjected to ambient cooling in the second tank. Finally, the vaporwas again subjected to another quenching cooler at 8 °C in the third tank. This increased the yield of the bio oil.The line diagram and schematic representation of the reactor have been shown in figure 1 and figure 2 respectively.
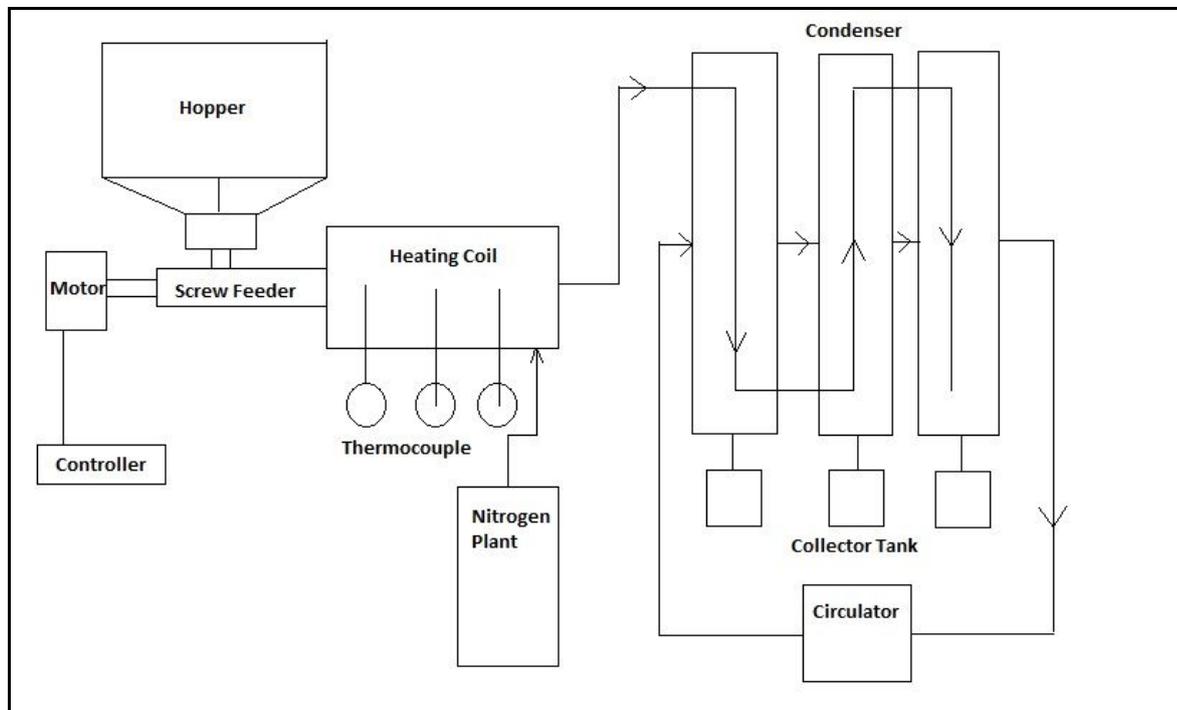

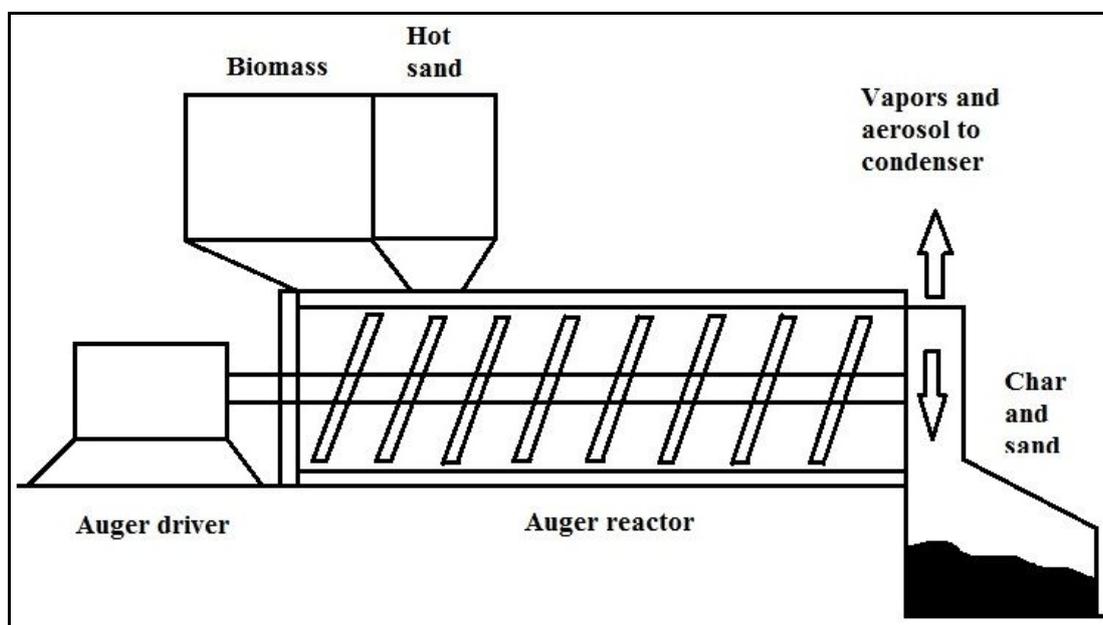**Fig. 1.Line diagram of fluidized bed reactor**

Fig. 2. Schematic of fluidized bed reactor

2.2. Ultimate analysis

Chemical composition of the saw dust was determined. Determination of carbon, hydrogen and nitrogen was reported.

2.2.1.Total carbon

The total carbon was calculated using Equ. 1.

$$\text{Calculated \% carbon} = \frac{(\text{Weight of sample} \times \text{\% carbon}) + (\text{Weight of spike} \times \text{\% carbon})}{\text{Total weight}}$$

(1)

2.2.2. Nitrogen

The Nitrogen was calculated using Kjeldahl method. 1g of the sample was dissolved in 15 mlconcentrated sulfuric acid. 7g of potassium sulfate was added along with copper as a catalyst. The mixture was boiled at a temperature of 370°C~400°C.the mixture was heated until white fumes appeared. The heating was carried out for another 60-90 min. 250 ml of water was added to the mixture followed by 45% NaOH solution.The ammonia gas generated was passed through a trapping solutiongiving ammonia ions. The content was titrated against NaOH solution and the volume of the neutralizing base was noted.

The percentage nitrogen was calculated using Equ. 2.

$$\text{\% Nitrogen} = \frac{\text{moles of nitrogen} \times \text{atomic mass}}{\text{gms sample}} \times 100$$

(2)

2.3. Proximate analysis

Composition of the material was analyzed. Determination of moisture, ash, volatile matter and fixed carbon was reported.

2.3.1. Moisture

The mass of the porcelain evaporating dish of capacity 100ml was measured. 50 gm of the saw dust was placed in the dish. The thickness of the peat in the container was kept below 3cm and lump formation was avoided. It was covered with aluminium foil and the mass was recorded to the nearest 0.01 g. It was allowed to dry at 106°C for duration of 2 hours. The weight of the specimen was measured after every 30 minutes interval. The moisture percentage was found using Equ. 3.

$$\text{Moisture content (\%)} = \left(\frac{a - b}{a} \right) \times 100$$

(3)

Where,
a= initial mass of sample as delivered
b= mass of sample after drying

2.3.2. Volatile matter

The mass of the sample after heating it to 440 °C was measured and was subtracted from the original weight (50 g) of the sample. The percentage of volatile matter present in the sample is calculated using Equ. 5.

$$\text{Volatile matter (\%)} = \frac{\text{Original mass of sample} - \text{mass of charred sample}}{original\,mass\,of\,sample} \times 100$$

(4)

2.4. Fourier Transform Infrared Spectroscopy (FTIR)

PerkinElmer apparatus was used for the FTIR analysis. The sample was mixed with KBr and made into a pellet. The radiation generated from the source passed the sample through the interferometer. The signal was received by the detector, amplified and converted to digital signal by the analog to digital converter. Finally the signal was transferred to a computer where Fourier transform was carried out. The results in the mid-infrared region (i.e., 400~4000 cm^{-1}) was graphically represented.

2.5. Thermogravimetric Analysis (TGA)

2.6410 mg of the sample was weighed and placed in the crucible of the SDT Q600 V20.9 Build 20analyser followed by reinstalling the crucible and wire basket on the hang down wire. The weight of the samplewas allowed to stabilize till the moisture content reduced. Nitrogen was used as the sample purge gas in this experiment. The analysis was carried out in the temperature range of 0 - 500°C.

3. Results and Discussion

3.1. Proximate analysis

3.1.1. Moisture content

The weight of the sample decreases from 1.02 g to 0.968 g as the time increases till 120 min. At 106 °C, the moisture escaped to the atmosphere. The trend of loss of moisture over a period of time has been shown in figure 3.
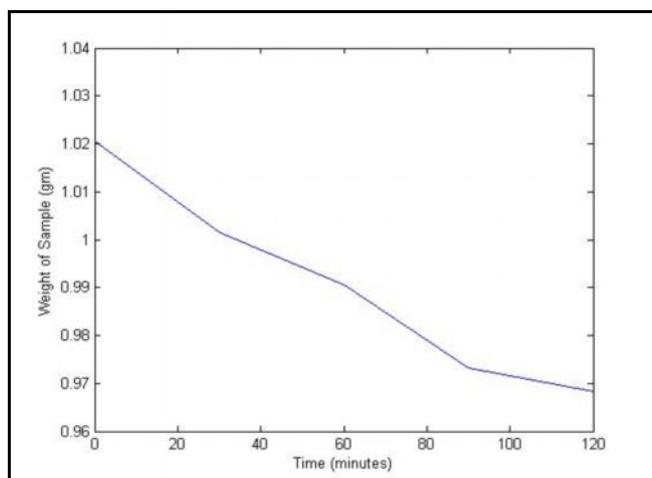

Fig. 3. Moisture loss on heating over a period of time

3.1.2. Volatile matter

0.052 g of volatile matter was found to be present in the sample. Thus the sample was found to contain 5.09% of volatile matter.

3.2. Ultimate analysis

From table, the percentage of carbon, hydrogen and nitrogen was found as 37.49%, 5.9% and 0.36% respectively. The results indicated that the sample has higher content of carbon which makes it a potential source for production of bio oil.

Table 1. Ultimate analysis and higher heating value

Ultimate analysis	Rice husk wt%	Saw dust wt%	Bio-oil wt%	Bio-char wt%
Carbon	40.64	46.2	39.64	81.7
Hydrogen	5.09	6.6	6.9	1.4
Nitrogen	0.63	3.4	0.2	Trace
Oxygen	53.64	43.8	53.25	-
O/C	1.32	0.948	1.34	-
H/C	0.13	0.143	0.17	0.017136
HHV (MJ/Kg)	17.02	12	17.95	27.9

S. Murugavelh *et al* /Int.J. ChemTech Res. 2015,8(6),pp 349-357.

354

3.3.FTIR Spectra Analysis

The FTIR of the saw dust was conducted for a wide range from 4500 cm-1 to 500 cm-1. The results indicated that the sample has different functional groups. The peak at 3217 cm-1 and 3178 cm-1 indicated the presence of OH group. The peak at 2900.94 cm-1corresponds to the C-H bonding. The peak at 1028, 1049 cm-1 and 1103 cm-1 indicated the C-O bonds. Peaks were observed near 599 cm-1 to 577 cm-1 which indicated the presence of phenyl group (Table 1). C=O bonds were found to be present at a peak of 1728.22 cm-1.

Apart from the C-H and C-O bonding, a peak at 659.66 cm-1 indicated the presence of Si-O bonds and the presence of aliphatic amine C-N bond at a peak of 1236 cm-1 was observed. At a peak of 2900.94 cm-1, methylene symmetric C-H bond was found to be present [19].

From the FTIR spectrum it was observed that the saw dust has carbon and hydrogen bonding as well as carbon and oxygen bonding. This indicated that the saw dust has great potential to be used for bio oil production through pyrolysis. The figure 4 shows the FTIR spectra of the saw dust sample.
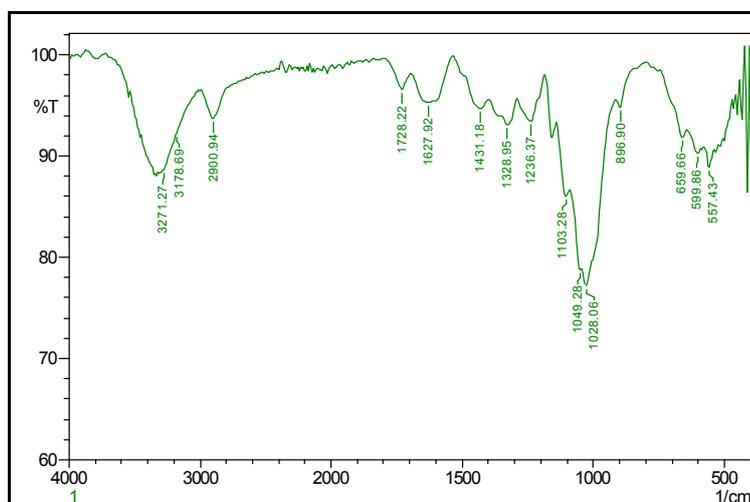

Fig. 4. FTIR Spectra of saw dust

### 3.4. Thermogravimetric Analysis

From TGA/DTG graph it was observed that the increase in temperature from 25 °C to 100 °C resulted in escaping of moisture from the saw dust. In the next stage the larger compounds like cellulose and hemicellulose breaks into smaller compounds (200 °C to 400 °C). This constitutes to the large portion of biooil. At 350°C there was a high rate decomposition of biomass, this was mainly due to the decomposition of lignin at that temperature range. Lignin is a ring shaped molecule and needs higher energy to break the bonds, The reason for biochar formation was due to the decomposition of lignin at temperature above 400C.
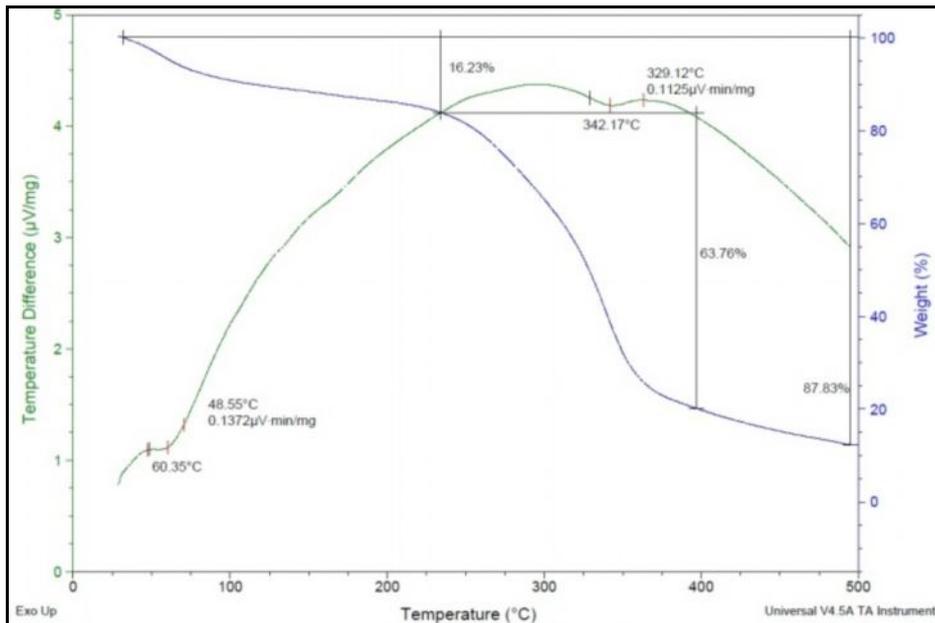
Fig. 5. TGA analysis of saw dust

3.5. Effect of temperature

From figure 6, maximum yield of 20.4% was reported at a temperature of 600 °C. At other temperature ranges of 450 °C, 500 °C, 650 °C and 700 °C the corresponding yields obtained were 17%, 19.4%, 19.5% and 19% respectively. The maximum yield was obtained at 600 degree as disintegration of the C-H bond occurred at 600°C. The yield was low at 500°C to 550°C degree as the pyrolysis was not complete as compared to 600°C. The decrease in yield at 700°C was due to the formation of char which affected the volatile gas formed which got trapped in the char.
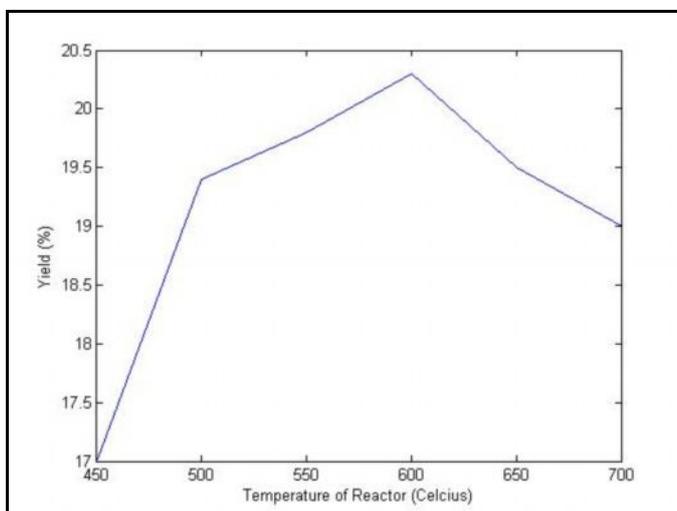
**Fig. 6.Effect of reactor temperature on yield**

3.6. Effect of loading rate

The empty bed volume was calculated to be 84.823 litres on the basis of the empty bed volume (V_e) the feed rate was optimized. It can be observed from figure 7that maximum yield of 15% was reported. It can also be observed that as the feed rate was increased the yield was found to be increase up to 5 kg /h. As the feed rate was increased further up to 6 kg/h, the yield decreased to 14%. It can be attributed to the fact that the contact area availablefor the biomass to the heating surface was reduced as the bulk biomass formed a thick bed which resisted the uniform transfer of heat. The free flow of material was affected when the feed rate was increased beyond 5 kg/h. The lower yield reported for 3 kg/h and 4 kg/ h was due to the fact that the production of volatile compound was low as the biomass available for pyrolysis was low.
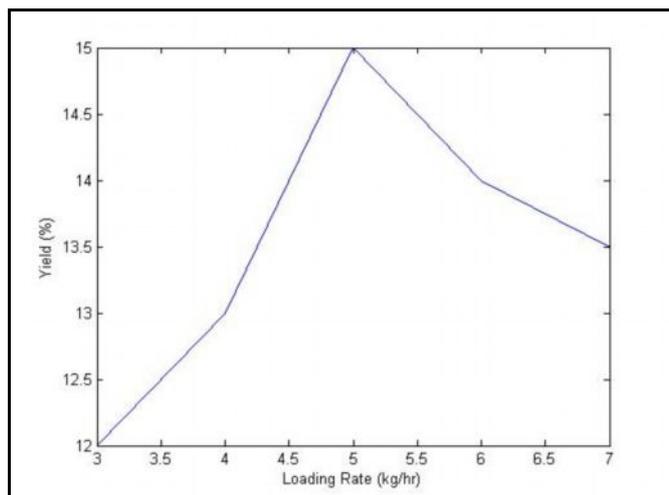
Fig. 7.Effect of loading rate on yield

3.7. Effect of residence time

The Residence Time(RT) ofthe sample was varied between 40 sec to 120 sec. figure8 indicated the residence time plays a major role on pyrolysis. As the time increased, the yield increased up to 90 sec.It was due to the factthat the reactor acts as a plug flow reactor connected in series. The complete cracking of the saw dust occurred at 90 sec which resulted in maximum yield of 20.4%. As the residence time was increased from 90 sec the yielddecreased as the secondary cracking took place. Below 90 secs, the yield decreased as the saw dust did not attain the required pyrolysis temperature of 600 °C.
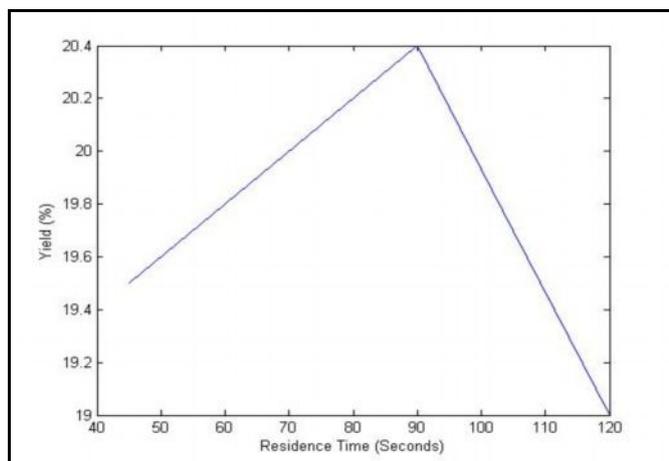
Fig. 8. Effect of residence time on yield

4. Conclusion

The characterization of saw dust showed that, it is a potential source for bio oil production. Modified Auger reactor with nitrogen is a suitable reactor for pyrolysis of saw dust as it increases the heat transfer efficiency. The process parameters for bio oil production in the auger reactor have been optimized. The maximum yield of 20.4% was obtained at the reactor temperature of 600 °C and a loading rate of 5kg/h. The total time to obtain the maximum yield was optimized to 120 minutes.

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