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Pyrolysis of Bagasse (*Saccharum officinarum*) Waste for Bio-Oil Production.

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ABSTRACT

Pyrolysis is generally known as destructive distillation of organic waste at higher temperatures in the absence of oxygen. This paper reports the pyrolysis of bagasse waste into a controlled temperature for production of bio-oil, and pyrolysis byproducts are char and pyro gases. Bagasse waste (*Saccharum officinarum*) is collected for this study from the local region of Indore, Madhya Pradesh in India. Firstly, bagasse waste characterized for cellulose, hemicellulose and lignin test, proximate, ultimate, alkali test for determination of Na and K with using different ASTM methods. Pyrolysis experiment performed into a batch type tubular reactor at 600 °C temperatures with heating rate 20 °C/min. and nitrogen flow rate 20 ml/min. and produced bio-oil (12.2 %), charcoal (31%) and pyro gas (56.81%). Bagasse waste has good fuel properties it has calorific value 3186 Kcal/Kg and higher volatile matter 75.7 % and less moisture 19 %. Thermogravimetric analysis also performed for the analysis of kinetic parameters by using Coats and Redfern method, it is a non-isothermal kinetics method, by using this method calculated activation energy (E) 13.49 Kcal/mol , frequency factor (A) $0.25 \times 10^{-8} \text{ S}^{-1}$ and kinetic rate constant (K) $0.018 \times 10^{-8} \text{ min}^{-1}$. This study motivates to use bagasse waste for energy production with using pyrolysis technique.

Keywords: Pyrolysis, bio-oil, charcoal and pyro gas, activation energy and frequency factor

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INTRODUCTION

Depletion of natural energy sources like petroleum, diesel and natural gases increased day by day due to the higher consumption and demand due to the increased population of consumers [1]. It also increases pollution rate due to the emission of Nox and Sox contents in environment in developing countries like India. Biomass can be providing a promising option due to the eco-friendly nature, easy availability and biodegradable nature [2]. In ancient time agricultural waste directly burned into open environment due to the storage problems in many part of India but it created environmental problems. But now it can be converted into useful form of energy by using thermochemical conversion process. Thermochemical conversion process played a wider role of conversion of biomass into energy (bio-oil or flue gas) by pyrolysis, gasification, combustion and liquefaction but pyrolysis is the main part of thermochemical conversion, it can be converted biomass into gases or liquid fuels [3-4].

Liquids from biomass obtained through thermo chemical conversion processes are expected to play an important role in the future as high value energy carriers and value-added chemicals. These products may offer many advantages over raw solid biomass as an energy source. Furthermore, the energy density of liquids is higher than that of raw biomass because of their chemical and physical characteristics. The bulk density of solid biomass is much less than that of liquids, since plant structures have high porosity besides, there is ease of transportation in the case of liquids [5-6]. The thermo-chemical processes of pyrolysis are available for converting the biomass to a more useful energy. Pyrolysis process is the heart of all thermo-chemical fuel conversion processes and is assumed to become an avenue to petroleum type products from renewable biomass [7-8].

In this article bagasse (sugarcane residue after juice extracted) is selected for study, its botanical name is *saccharum officinarum* and it is a part of *Graminae* botanical family. It has high volatile matter (75.7%) and high carbon content (42.39 %) and higher holocellulose contents make it a combustible solid fuel for gasification and pyrolysis.

MATERIAL AND METHODS

Physio-chemical characterization of biomass

The American Society for Testing and Materials consists of a tubular fixed bed pyrolysis reactor, mesh and (ASTM) standards for coal and coke was utilized for condenser arrangement for the supply and control of proximate analysis of biomass materials and charcoal. This method covers moisture content (ASTM method D3173), ash (ASTM method D3174) and volatile matter (ASTM D3175). Fixed carbon analysis was carried out by weight difference method [9-10]. Ultimate analysis of biomass was carried out by using CHNS (O) analyzer (Flash EA 1112 series model, Thermo Fennigan, (Italy sustainability at higher temperatures and as it possesses make) for elemental analysis. The analyzer works on the principle of the Dumas method, which involves the instantaneous oxidation of the sample by flash combustion. Calorific value of biomass was analyzed using automatic bomb calorimeter (Toshniwal make) 300 g providing uniform heat transfer throughout the ASTM E870-82 (2006) (E711) test method. Na and K content in the biomass material were analyzed by a Spectrum flame photometer (Model no. 335, Systronics). Cellulose, hemicellulose and lignin contents were determined by using biological methods.

Design of pyrolysis reactor

The stainless steel sheet was selected to construct the reactor, which is excellent for working in temperature range of 500-600 °C with heating rate of 20 °C/min. The highest value of flow rate of sweep gas (Nitrogen) was selected maximum up to 20- 50 ml/min.

Experimental

The experimental setup consists of tubular fixed bed pyrolysis reactor, mesh, and condenser arrangement for supply and control of sweep gas as well as progress condensing train etc. (Fig. 1). The outer dimensions of the tubular fixed bed pyrolysis reactor were (78 x 8 cm) and the inner dimensions of the pyrolysis reactor were chosen to be 74 x 6 cm (length x diameter) considering holding capacity as 300 gm and

to have uniform heat transfer throughout the biomass. Mesh (sample holder) was fitted inside the reactor, which was made using 1 mm thick stainless steel sheet, welded in the form of a cylindrical pipe. The mesh height was maintained at 74 cm, inner and outer diameter of the pipe was 5 and 6 cm respectively. It was used for storing biomass (before Pyrolysis) and charcoal (after pyrolysis). The reactor was made using SS-304 having a thickness of 2 mm. Stainless steel was chosen, because it can sustain higher temperatures and it has anti-corrosion properties. The height was maintained longer as compared to width, keeping in mind rapid and easy heat transfer among the particles of biomass samples used horizontal tube reactor (height 127 mm x diameter 17 mm) by [11]. To reduce the heat losses, the reactor was insulated with ceramic blanket of 50 mm dia. The reactor was heated externally through five electrical heaters (400 x 5 watts). In the center of the reactor provision had been made to fix the thermocouple. K-Type thermocouple along with PID controller and auto switch was used to measure and control the reactor temperature. The PID controller and thermocouple were calibrated before use. Photograph of the complete experimental set up has been shown in following **Fig 1.**

To supply sweep gas (nitrogen) to the reactor, copper capillary tube (2 mm inner dia) was fixed at the bottom. Fig.1. The supply of N_2 gas to the reactor removes oxygen from biomass. To ensure the flow of sweep gas, soap bubble flow meter was used and it was maintained at 20 ml/min throughout the experiment. Condensing train is also an important part of the experimental set up. It consists of 5 boxes (1L capacity each) connected in series and made of stainless steel. The number of boxes to be used was decided based upon the quantity of pyro-gas to be produced. All the boxes were kept in a rectangular enclosure. The dimension of the enclosure was chosen in such a way that, it could accommodate all the 5 boxes along with a certain quantity of ice to cool the Pyro gases Fig.1.



Figure 1: Experimental set up of pyrolysis reactor

The condenser is cooled by circulating cold water and by keeping sufficient amount of ice in the rectangular enclosure. For circulating cold-water 0.25 hp water pump was used (Fig. 1, which was connected to the inlet of the condenser. The condenser (Fig. 1) was fabricated using stainless steel tube about 1.2 cm inner diameter and 120 cm long; this small tube was covered with another tube of larger diameter (6 cm inner diameter) for circulation of water. It also had provision for inlet (cold water) and outlet of water.

Thermogravimetric analysis of bagasse:

Thermo-gravimetric analysis of bagasse waste was carried out using Diamond thermogravimetric/Differential Thermal Analyzer (TG/DTA) equipment (made of Perkin Elmer, USA) maintaining temperature range 300 °C (ambient) to 1500 °C, heating rate 0.01 – 100 °C/min and inert gas flow rate 0-1000 ml/min at the vacuum of 10 –12 Torr.

Bio-oil yield calculated by using the following formula:

$$\text{Bio-oil yield} = \frac{\text{weight of bio-oil produced}}{\text{weight of biomass material used in the reactor}} \times 100$$

RESULTS AND DISCUSSION

Biomass characterization:

Results of bagasse biomass characterization and bio-oil production presented below in **Table 1** and **Table 2** respectively.

Table 1: Characterization of bagasse biomass

Sl.No.	Components of cotton stalk	Units	Bagasse
1	Cellulose	%	44
2	Hemi-cellulose	%	30
3	Lignin	%	19
4	Extractive matter	%	7.0
5	Moisture content	%	19
6	Volatile matter	%	75.7
8	Ash content	%	3.1
9	Extractive	%	7.0
9	Na	mg/L	30
10	K	mg/L	38
11	C	%	42.39
12	H	%	6.15
13	N	%	0.0
14	O (calculated by difference)	%	51.46
15	Calorific value	Kcal/kg	3186
16	Density	gm/cc	2.43

Table 2: Bio-oil production:

Sample name	Bio-oil yield gm of bio-oil produced/gm of biomass material used	Bio-oil %	Charcoal %	Pyro-gas %
Bagasse	0.122	12.2	31	56.81

Mass balance equation used for the calculation of pyro gas , mass balance equation is given below:

Mass balance of materials:

Using the following equation performed Mass balance.

Input weight = weight of biomass (gm)

Output weight = weight of bio-oil + weight of charcoal + weight of pyro gas

Where, weight of Gas = weight of Biomass – (weight of Biomass + weight of Charcoal)

Kinetics study of agricultural wastes:

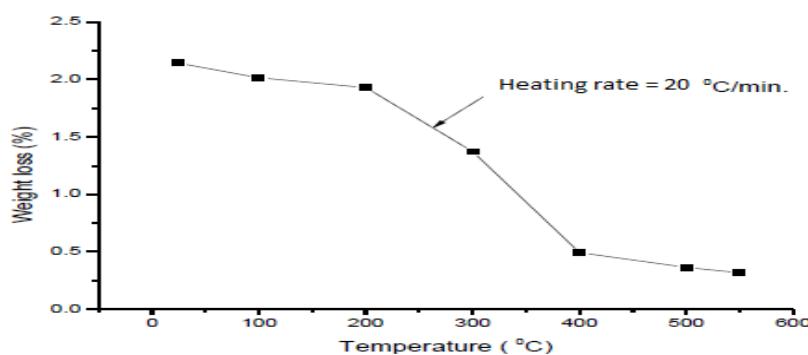


Figure 2 Thermo-gram of bagasse waste

Kinetics analysis performed with using thermogram of bagasse degradation at 550 °C with heating rate of 20 °C/min. It is illustrated in following **Fig.2**.

The TGA experiments were conducted in nitrogen environment at 20 °C/min. above Fig.[2] presented the thermo gram of bagasse waste. Kinetics parameter analyzed with using Coats and Redfern method, activation energy curve presented in **Fig.3**.

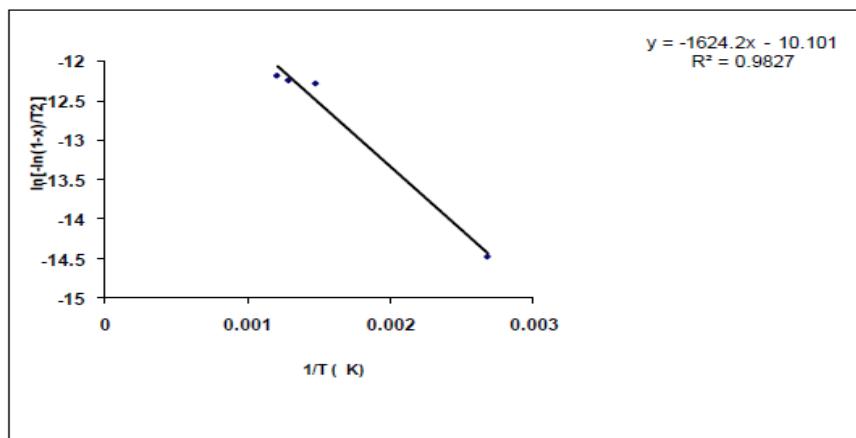


Figure 3: Activation energy plot of bagasse waste

Coats and Redferen method was used for kinetic calculation of biomass, it is an integral method used for non – isothermal kinetic analysis [12-13]. This method eliminated the rate constant and gave activation energy and frequency factor directly.

It can be also written in the equation form as:

$$\ln[1 - (1 - x)^{(1-n)}] / T^2 (1 - n) = \ln(AR/\beta E)(1 - 2RT/E) - E/RT \text{ for } (n \neq 1) \quad \dots \dots \dots (1)$$

For $n=1$, the above equation modifies as

$$\ln[-\ln(1 - x)] / T^2 = \ln(AR/\beta E)(1 - 2RT/E) - E/RT \text{ for } (n=1) \quad \dots \dots \dots (2)$$

Where, x is fractional weight loss, In equation (2) except fractional weight loss (x) and TGA temperature T , other parameter are constant, thus plotting a graph between and the value of $-E/R$ could be obtained, from which activation energy (E) could be calculated. For calculating the fractional weight of the biomass sample following equation has been used.

$$\text{Fractional weight of the biomass sample } x = (W_0 - W_t) / (W_0 - W_f)$$

Where, W_0 = initial weight of sample (weight of sample recorded at a temperature from where the data is to be considered for analysis).

W_t = weight recorded at any time t . and

W_f = final weight of sample (weight of sample recorded at a temperature up to where the data is to be considered for analysis).

Table 3: Kinetics parameters of bagasse waste

Biomass sample	Temperature	Heating rate °C/min.	Activation energy (Kcal/mol)	Frequency factor (s-1)	Kinetic rate (min. ⁻¹)	R ² value
Bagasse waste	24-550 °C	20 °C/min.	13.49	0.25×10^{-8}	0.018×10^{-8}	0.98

The moisture (W_0) and residue (W_f) (char + ash) are obtained from the individual TGA experimental data [14]. Calculated activation energy, frequency factor and kinetic rate constant presented below in **Table 3**.

Table 1 indicated that higher holo-cellulose (cellulose + hemicellulose) and less lignin content (19 %), it has high volatile matter (75.7%) and high calorific value 3186 increased fuel quality to use for pyrolysis, it has (30) % Na content and 38 % K content, it created problems during combustion due to the increased amount of ash % and it can increased the gas yield due to the unburned hydrocarbons. These results are very similar to published work [5, 12]. Pretreatment of biomass with HCl, NaOH or KOH also increased the amount of volatile matter, and decreased the amount of ash contents [9].

Pyrolysis of bagasse at 600 °C temperature with 20 °C/min. heating rate and 20 ml/min mass flow rate of nitrogen produced 12.12 % bio-oil, 31 % charcoal and 51.81 % pyro gases. Less bio-oil produced by this method indicated that Na and K contents are increased the pyro-gases[11,13].

Analysis of kinetics also performed by using Fig.2 and Fig.3 thermogram of bagasse and pyrolysis activation curve respectively with using Coats and Redfern method for determination of kinetic parameters. Fig. 2 depicted the weight losses of cotton stalk waste with increasing temperature, at 100 °C moisture start to decrease and at 100-150 °C temperature moisture decreased abruptly and measure weight losses occurred at 200 °C to 500 °C and more than 500 °C temperature bagasse completely pyrolysed. The measure contents into bagasse are cellulose, hemicellulose contents and these contents degraded at 200-300 °C of temperature and volatiles emitted due to the presence of hemicellulose and charcoal found due to the presence of lignin content into [14-16].

CONCLUSION

This work presents pyrolysis of bagasse waste at the controlled temperature 600 °C in electrical heating based tubular reactor; Stainless steel tubular reactor is an electrical based heating system. It constructed with using SS-316 , five heaters used for the heating of the reactor. N₂ gas used for the removal of the air from reactor. Pyrolysis performed at 600 °C temperatures with using heating rate at 20 °C/min. and nitrogen flow rate at 20 ml/min. into the reactor. Condensing train used for the condensation of the emitted vapors.

Bagasse selected for this study due to the easy availability and it is a rich source of carbon content 42.39 % contents higher volatile matter 75.7 % , less ash contents 3.1% and higher hello-cellulose (cellulose 44 % , hemicellulose 30 %) Cellulose and hemicellulose percentage increased the volatiles during pyrolysis and less lignin content (19 %) minimized the ash contents (3.1%) into the bagasse as a input product. After the pyrolysis experiment carried out 12.12 % bio-oil , 31 % charcoal and 51.81 % pyro gases.

Thermogravimetric analysis also performed for the analysis of kinetic parameters by using Coats and Redfern method. Coats and Redfern method is a non-isothermal kinetics method. Kinetic parameters determined by using Coast and Redfern method namely activation energy (E), 13.49 Kcal/mol, frequency factor (A), $0.25 \times 10^{-8} S^{-1}$ and kinetic rate constant (K), $0.08 \times 10^{-8} min^{-1}$.

This study focused to convert the cotton stalk waste into bio-oil which is the main product during the pyrolysis and charcoal, pyro gases are byproducts.

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