



Original Research Article

A Slow Pyrolysis of Cotton Stalk (*Gossypium arboreum*) Waste for Bio-Oil Production

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ABSTRACT

Cotton stalk (*Gossypium arboreum*) collected from local region of Indore, Central India for the study of pyrolysis due to the high volatile matter, carbon content and easily availability. Pyrolysis is destructive distillation of organic materials at higher temperature in absence of oxygen, pyrolysis can be converted cotton stalk biomass into bio-oil, charcoal and pyro gases. This work presents pyrolysis of cotton stalk waste at controlled temperature 600°C in electrical based heating reactor and in this process nitrogen flow rate used at 20 ml/min. and produced bio-oil (17.12%). Cotton stalk waste has good fuel properties it has calorific value 4386 Kcal/Kg and higher volatile matter 67% and less moisture content 9.7%. 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 Coats and Redfern method namely activation energy (E) 14.93 Kcal/mol, frequency factor (A) $2.93 \times 10^{-8} \text{ s}^{-1}$ and kinetic rate constant (K) $6.08 \times 10^{-8} \text{ min}^{-1}$. This article is a novel study for the pyrolysis of cotton stalk and determination of the kinetic parameters with using TGA analyzer.

Keyword: Biomass, pyrolysis, kinetic parameters, bio-oil, activation energy

INTRODUCTION

The consumption of natural sources has been increased day by day due to the increasing population and depletion of the natural

sources. The main consumer of petroleum products are commercial sector, agriculture sector and industrial sectors. The dependency of these sectors increased day by day and it

continuously emitted the toxic emission and increased the pollution rate in environment [1-3]. Biomass has an attractive nature due to its low cost, biodegradable and eco-friendly nature, and energy demand increased day by day due to the fast depleting of the natural sources coal and petroleum products [4-5]. Thermochemical conversion process also subdivided into pyrolysis, combustion, gasification and liquefaction.

Liquids from biomass obtained through thermochemical 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 [1, 6-9]. 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 [10-11].

This article focused on designing of the pyrolysis reactor and production of bio-oil and evaluation of kinetic parameters by using Coats and Redfern method.

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 [12]. 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 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 biomass material were analyzed by Spectrum flame photometer (Model no. 335, Systronics). Cellulose, hemicellulose and lignin contents were determined by using biological method.

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 set up

The experimental set up consists of tubular fixed bed pyrolysis reactor, mesh, and condenser arrangement for supply and control of sweep gas as well as pyrogas condensing train etc. (Figure 1). The outer dimensions of the tubular fixed bed pyrolysis reactor was (78 x 8 cm) and the inner dimensions of 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 (before Pyrolysis) and charcoal (after pyrolysis). Reactor was made using SS-304 having 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 [8], To reduce the heat losses, the reactor was insulated with ceramic

respectively. It was used for storing biomass 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 Fig 1.



Fig.1: Experimental set up of pyrolysis reactor

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 certain quantity of ice to cool the pyro gases Fig.1.

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 condenser. The condenser (Fig. 1) was fabricated using stainless steel tube of 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.

Kinetics study of bio-oil production:

Thermo-gravimetric analysis of biomass 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 following formula:

Bio-oil yield = weight of bio-oil produced/weight of biomass material used in the reactor

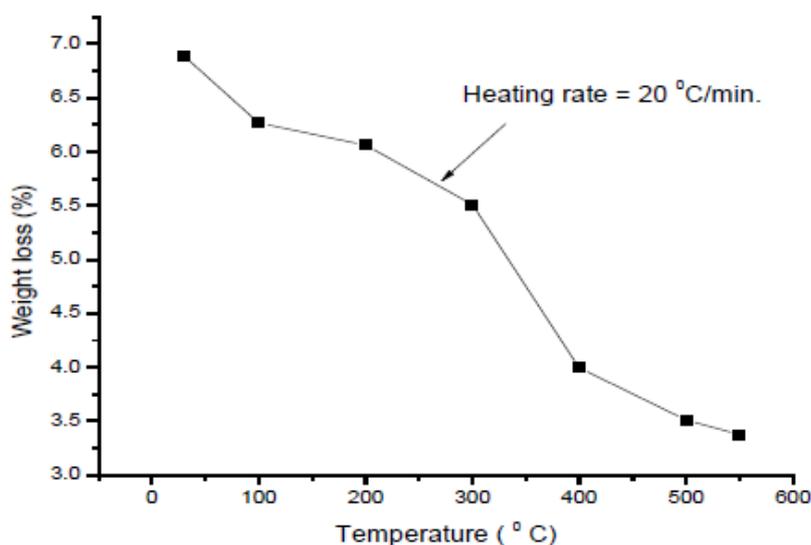
% of bio-oil = bio-oil yield × 100

RESULTS**Pyrolysis experiment****Table 1: Characterization of cotton stalks biomass**

Sl. No.	Components of cotton stalk	Units	Cotton stalk
1	Cellulose	%	38
2	Hemi-cellulose	%	32
3	Lignin	%	20.88
4	Extractive matter	%	9.12
5	Moisture content	%	9.7
6	Volatile matter	%	67
7	Fixed carbon	%	7.1
8	Ash content	%	16.8
9	Na	mg/L	13.7
10	K	mg/L	11.7
11	C	%	41.21
12	H	%	4.92
13	N	%	1.98
14	O	%	51.89
15	Calorific value	Kcal/kg	4386
16	Density	gm/cc	2.83

Table 2: Bio-oil production:

Sl.No.	Sample name	Temperature	Heating rate	Bio-oil	Charcoal	Pyro-gas
1	Cotton stalk	600 °C	20 °C/min.	17.14	38	44.86

Kinetics study of cotton stalk:**Fig.2 Thermo-gram of cotton stalk**

The TGA experiments were conducted in nitrogen environment at 20 °C/min. above Fig.[1] presented the thermo gram of cotton stalk.

Table 3: Kinetics parameters of cotton stalk

Biomass sample	Temperature	Heating rate °C/min.	Activation energy (Kcal/mol)	Frequency factor (s-1)	Kinetic rate (min. ⁻¹)	R ² value
Cotton stalk	30-550 °C	20	14.93	2.93 x 10 ⁻⁸	6.08x10 ⁻⁸	0.98

DISCUSSION

Closed look of Table 1 indicated that higher holo-cellulose (cellulose + hemicellulose) and less lignin content, it has low moisture content 9.7, high volatile matter and high calorific value increased fuel quality to use for pyrolysis, it has (13.7) % Na content and 11.7% K content , it created problems during combustion due to the increased amount of ash %. These results are very similar to [12,17]. Pretreatment of biomass with Hcl, NaOH or KOH also increased the amount of volatile matter, and decreased the amount of ash contents [12-13].

Pyrolysis of cotton stalk at 600C temperature with 20 C/min. heating rate and 20 ml/min mass flow rate of nitrogen produced 17.14 % bio-oil, 38 % charcoal and 44.86 % pyro gases. Less bio-oil produced by this method indicated that Na and K contents are increased the charcoal and pyro-gases[12].

Kinetic study of cotton stalk biomass was analyzed by using Coats and Redferen method, Above figure 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 cotton stalk completely pyrolysed. The measure contents into cotton stalk are cellulose, hemicellulose contents and these contents degraded at 200-300 °C temperature and volatiles emitted due to the presence of

hemicellulose and charcoal found due to the presence of lignin content into cotton stalk [14]. Coats and Redferen method Vovelle Technical report , [12,15-16] was used for kinetic calculation of biomass. It is an integral method used for non – isothermal kinetic analysis. This method eliminated the rate constant and gave activation energy and frequency factor directly. It can be also written in the equation form as:

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

For n=1 , the above equation modifies as

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

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.

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

Where, W₀ = 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

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

The moisture (W0) and residue (Wf) (char + ash) are obtained from the individual TGA experimental data [15].

CONCLUSION

This work presents pyrolysis of cotton stalk waste at 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 20C/min. heating rate and 20 ml/min. nitrogen flow rate into the reactor. Condensing train used for the condensation of the emitted vapors.

Cotton stalk selected for this study due to the good calorific value 4386 Kcal/Kg and higher volatile matter 67% and less moisture content 9.7% and after the pyrolysis experiment carried out 17.14 % bio-oil, 38 % charcoal and 44.86 % 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 Coats and Redfern method namely activation energy (E) 14.93 Kcal/mol, frequency factor (A) $2.93 \times 10^{-8} \text{ S}^{-1}$ and kinetic rate constant (K) $6.08 \times 10^{-8} \text{ min}^{-1}$.

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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CONFLICT OF INTEREST STATEMENT

None Declared

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