Flash pyrolysis of cotton shell in a fixed bed Reactor

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***Abstract*- Fixed bed pyrolysis experiments have been conducted on a sample of cotton shell to determine the effects of temperatures, particle sizes and heating rates on the pyrolysis products yield. The cotton shell was pyrolyzed at the temperatures of 400, 450, 500 and 550°C. The particle size of cotton shell was varied in the range of 0.425-1 mm. The heating rate of 16°C/min is used. Charcoal, liquid and gaseous fuel obtained from pyrolysis. Temperature is the most important factor, having a significant positive effect on yield of bio-oil. The maximum oil yield of 40 wt% was obtained at 500°C with heating rate of16°C/min at a particle size of 0.6 mm. Char production generally decreases as the Pyrolysis temperature was increased. Non condensable gases were analyzed with gas chromatography.**

***Index Terms*- Flash pyrolysis, fixed bed reactor, Cotton shell, bio oil, Gas chromatograph**

I. INTRODUCTION

Biomass in the form of agricultural residues is becoming popular among new renewable energy sources, especially given its wide potential and abundant usage. Pyrolysis is the most important process among the thermal conversion processes of biomass. The use of biomass as an energy source is an issue of great importance, as it constitutes part of an alternative solution for the replacement of fossil fuels. Biomass represents a renewable, inexpensive, and abundant resource, and also represents an important source of energy and chemicals. There are a number of technological options available to make use of a wide variety of biomass types as a renewable energy source. These technologies can be classified into two main groups; biochemical and thermo chemical conversion. Biochemical conversion is the use of the enzymes of bacteria and other microorganisms to convert biomass to fuels and chemicals. Biochemical conversion process includes anaerobic digestion, fermentation and mechanical extraction. Thermo chemical conversion can be performed using some processes which are gasification, pyrolysis (slow, fast, flash, and vacuum), hydrothermal upgrading (in water or solvent) and combustion. Pyrolysis is the technique of applying high heat to organic matter under the inert atmosphere which results in the converting organic materials into usable fuels and chemical feedstock. This process applied to lignocelluloses materials can produce charcoal, condensable organic liquids (pyrolytic bio fuel) and non-condensable gasses. It is the most effective process for biomass conversion. In general, pyrolysis of organic substances produces gas and liquid products and leaves a solid residue richer in carbon content, char. Extreme pyrolysis, which leaves mostly carbon as the residue, is called carbonization is used to a great extent in the chemical industry. Pyrolysis is also used in the creation of nanoparticles, zirconia and oxides utilizing an ultrasonic nozzle in a process called ultrasonic spray pyrolysis. Pyrolysis processes can be categorized as slow pyrolysis or fast pyrolysis. Fast pyrolysis is currently the most widely used pyrolysis system. Slow pyrolysis takes several hours to complete and results in biochar as the main product. On the other hand, fast pyrolysis yields 60% bio-oil and takes seconds for complete pyrolysis. In addition, it gives 20% biochar and 20% syngas. Compared to conventional fuels the main difference is storage, feeding system and burner. Biodiesel is a clean, non-toxic and biodegradable fuel. It does not contain aromatics and pollutant emissions of sulfur oxides, car- bon monoxide, unburned hydrocarbons, and the soot from the burning diesel engine is very low.

II. MATERIALS

Cotton shell is an agricultural waste. Cotton shells are crushed in ball mill. Cotton shell particles are the raw materials for the pyrolysis process. When cotton shell is used in solid form, energy value is low. By pyrolysis it can be converted to liquid and gaseous form. In liquid form handling and storage is easy. Pyrolysis oil can be used as furnace oil. Non condensable gases are directly used as gaseous fuel. Cotton shell for this study was obtained from local area nearer to Coimbatore. Samples were grinded and then screened to 1, 0.7, 0.6 and 0.425 mm particle sizes. Then the samples were dried for 48 h at 105 °C. Moisture, ash, fixed carbon, volatile matter contains were determined according to ASTD standards.

Table.1. Proximate analysis of cotton shell

Parameters	**Value (wt %)**
Moisture	3.05
Total ash	5.65
Fixed carbon	20.61
Volatile matter	70.69

III. METHODOLOGY

Cotton shell samples collected were grinded and screened to get desired fractions like 1, 0.7, 0.6 and 0.425 mm. Then the sample was dried to 48 hours in an electric oven. The pyrolysis experiment was performed by charging 100 g of cotton shell into the fixed bed reactor. An electric heater is used to heat the reactor. The experiments were conducted at the atmospheric pressure. Prepared 100g sample were put into the reactor and heated to the desired temperature. Thermal decomposition occurs and the solid and liquid phases separate. Char depositing on the bottom of the reactor and the hot pyrolysis gases passes through the water cooled condenser which quickly cools the condensable gases into liquid called bio-oil. The non condensable gases are collected in plastic bags. Gas chromatograph is used to find the composition of non condensable gases obtained from pyrolysis of cotton shell.

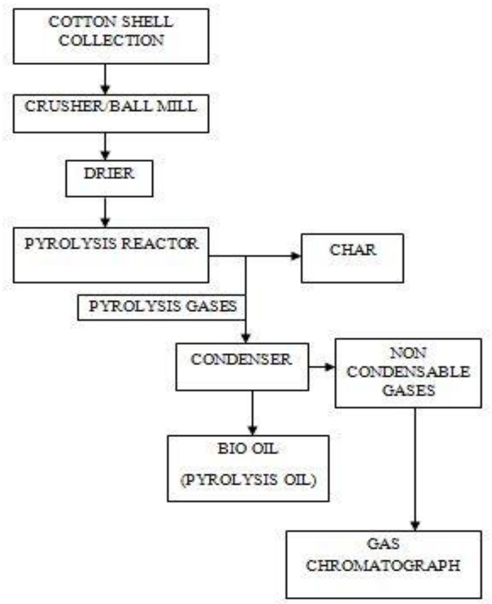

Fig.1 Experimental methodology

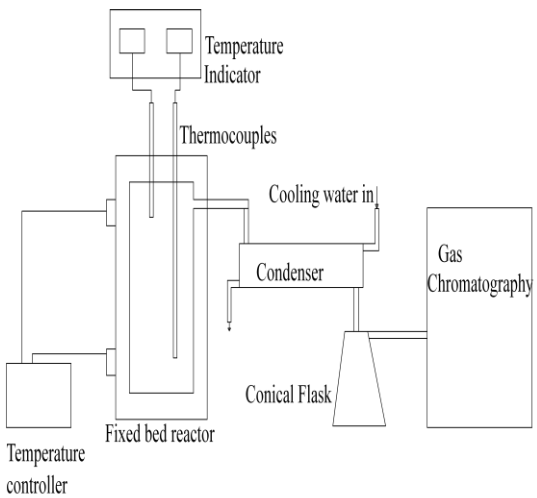

Fig.1 Experimental methodology

Fig.2 Fixed-bed pyrolysis reactor

Pyrolysis experiments were performed by charging 100 g of cotton shell in to a mild steel tubular reactor with a length of 120 mm and an internal diameter of 70 mm was heated externally by an electric heater of 750 watts. The reactor temperature being controlled by k-type (cromel-alumel) thermocouple placed inside the reactor which was heated from room temperature to the desired temperature. Reactor temperature was increased with suitable heating rate with the help of temperature controller. Water cooled condenser is used to cool the condensable gases into liquid called bio-oil and it is collected in a conical flask. The non condensable gases are collected in a plastic bag. Gas chromatograph is used to find the composition of non condensable gases obtained from pyrolysis of cotton shell. More detailed description of the pyrolysis set up is shown in figure.2.

The experiments were carried out in several series. The first series of experiments were carried out to determine the effect of the temperature on pyrolysis yields with a constant particle size of 1 mm with a heating rate of 16 °C/min and the temperature were maintained at 400, 450, 500 and 550 °C. The second series of experiments were carried out to determine the effect of the temperature on pyrolysis yields with a constant particle size of 0.7 mm with a heating rate of 16 °C/min and the temperature were maintained at 400, 450, 500 and 550 °C. The third series of experiments were carried out to determine the effect of the temperature on pyrolysis yields with a constant particle size of 0.6 mm with a heating rate of 16 °C/min and the temperature were maintained at 400, 450, 500 and 550 °C. The forth series of experiments were carried out to determine the effect of the temperature on pyrolysis yields with a constant particle size of 0.425 mm with a heating rate of 16 °C/min and the temperature were maintained at 400, 450, 500 and 550 °C. At the end of each experiment, the condensable product called bio-oil and the solid char were removed from the reactor and weighed.

The gas product was calculated by material balance. The product yields calculated as follows,

$$\text{Liquid yield, wt \%} = \frac{\text{Liquid yield out put (g)}}{\text{Cotton shell input(g)}} \times 100$$

$$\text{Char yield, wt \%} = \frac{\text{Char yield out put (g)}}{\text{Cotton shell input (g)}} \times 100$$

Non condensable gas yield, wt % = 100 wt %- (Liquid yield, wt % + Char yield, wt %).

The bio-oil obtained under the experimental conditions that gave maximum oil yield was used for characterization. The composition of the non condensable gases were determined by GC with Thermal Conductivity Detector (TCD), SHIMADZU Gas Chromatograph GC-2014 with Shin Carbon ST, 100/120 mesh, 2 m, 1/16 in. OD, 1.0 mm ID capillary column. Gas Chromatography–Thermal Conductivity Detector or GC-TCD is a technique used to analyze inorganic gases (Argon, Nitrogen, Hydrogen, Carbon Dioxide, etc) and small hydrocarbon molecules. The TCD compares the thermal conductivity of two gas flows – the pure carrier (reference) gas and the sample. Changes in the temperature of the electrically-heated wires in the detector are affected by the thermal conductivity of the gas which flows around this. The changes in this thermal conductivity are sensed as a change in electrical resistance and are measured.

Table.2. GC analyzer details

Instrument: THERMAL CONDUCTIVITY DETECTOR (TCD) SHIMADZU Gas Chromatograph GC-2014	
GC conditions	
Column oven temperature	120 °C (hold 52min).
Flow control mode	Linear velocity
Column flow rate	10 mL/min
Injection temperature	40 °C
Injection volume	5 µL packed on-column
Carrier gas	Helium 99.9995% purity (constant flow)

Column : Shin Carbon ST, 100/120 mesh, 2m, 1/16in. OD, 1.0mm ID(cat.#19808)	
Length of column	2 m
ID	1.0 mm
OD	1/16 in

Table.3. Capillary column condition of GC

Table.4. Analysis report of standard gases used for pyrolysis gas analysis.

Pyrolysis gas compositions	Wt %.
C_2H_2	5.150
N_2+O_2	5.130
CO	4.670
CH_4	4.880
CO_2	4.860
C_2H_4	4.850
IMPURITY	1.000

IV. RESULTS AND DISCUSSION

Effect of pyrolysis temperature on product yields

Fig.3 shows the liquid yield increased from 26% to 38% by weight, when the Pyrolysis temperature increased from 400 °C to 550 °C with a particle size of 1mm. While char and gaseous yield decreased. But at the temperature range between 550 °C and 600 °C liquid yield decreases to 37% by weight. While gas yield increases to 17% by weight. But char yield decreases to 46% by weight. At the temperature of 400 °C char yield was 51.5%, liquid yield was 26% and gas yield was 22.5%. At the temperature range between 400 °C to 450 °C char yield was 49%, liquid yield was 32% and gas yield was 19%. At the temperature range between 450 °C to 500 °C char yield was 47%, liquid yield was 38% and gas yield was 15%. At the temperature range between 500 °C to 550°C char yield was 46%, liquid yield was 37% and gaseous yield was 17%.

Table.5 Effect of temperature on pyrolysis products yield at particle size of 1 mm at a heating rate of 16 °C/min

Temperatures, °C	Char yield, wt %	Liquid yield, wt %	Non condensable gas yield, wt %
400	51.5	26	22.5
450	49	32	19
500	47	38	15
550	46	37	17

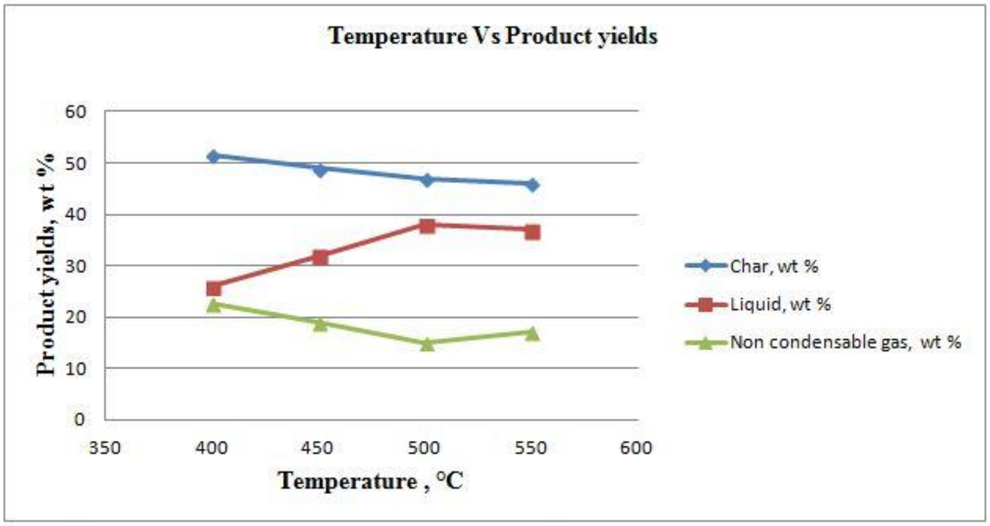

Fig.3. Effect of temperature on pyrolysis product yield at particle size1 mm at a heating rate of 16 °C/min.

Table.6 Effect of temperature on pyrolysis products yield at particle size of 0.7 mm at a heating rate of 16 °C/min

Temperatures, °C	Char yield, wt %	Liquid yield, wt %	Non condensable gas yield, wt %
400	45	33	22
450	44	37	19
500	42	39	19
550	41	37.5	21.5

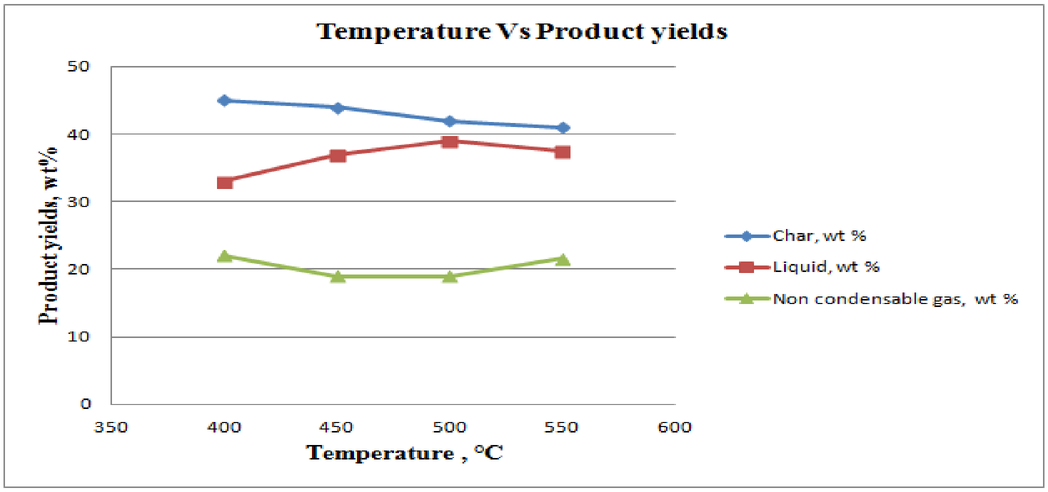

Fig.4. Effect of temperature on pyrolysis product yield at particle size 0.7 mm at a heating rate of 16 °C/min.

Fig.4 shows, at the temperature of 400 °C char yield was 45%, liquid yield was 33% and gas yield was 22%. At the temperature range between 400 °C to 450 °C char yield was 44%, liquid yield was 37% and gas yield was 19%. At the temperature range between 450 °C to 500 °C char yield was 42%, liquid yield was 39% and gas yield was 19%. At the temperature range between 500 °C to 550 °C char yield was 41%, liquid yield was 37.5% and gaseous yield was 21.5%.

Table.7 Effect of temperature on pyrolysis product yield at particle size 0.6 mm at a heating rate of 16 °C/min

Temperatures, °C	Char yield, wt %	Liquid yield, wt %	Non condensable gas yield, wt %
400	36.66	33.33	30
450	33.33	36.66	30
500	31.67	39	29.33
550	31.67	33.33	35

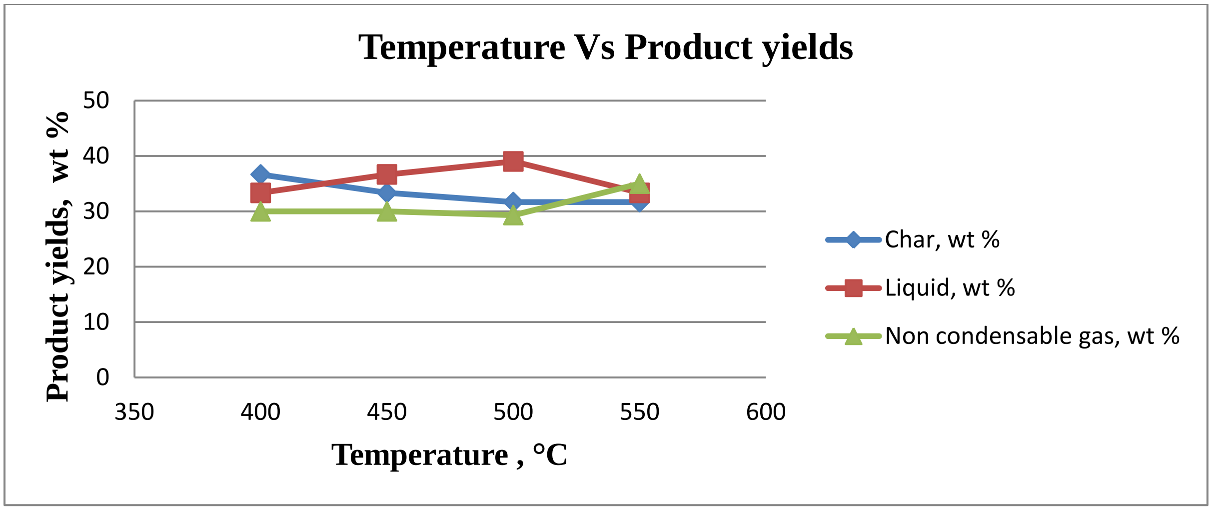

Fig.5 Effect of temperature on pyrolysis product yield at particle size 0.6 mm at a heating rate of 16 °C/min

Fig.5 shows, at the temperature of 400°C char yield was 36.66%, liquid yield was 33.33% and gas yield was 30%. At the temperature range between 400°C to 450°C char yield was 33.33%, liquid yield was 36.66% and gas yield was 30%. At the temperature range between 450°C to 500°C char yield was 31.6%, liquid yield was 39% and gas yield was 29.33%. At the temperature range between 500°C to550°C char yield was 31.67%, liquid yield was 33.33% and gaseous yield was 35%.

Table.8 Effect of temperature on pyrolysis product yield at particle size 0.425 mm at a heating rate of 16 °C/min

Temperatures, °C	Char yield, wt %	Liquid yield, wt %	Non condensable gas yield, wt %
400	39.33	28	32.67
450	39	29	32
500	33.33	36.67	25
550	33.33	32.5	34.17

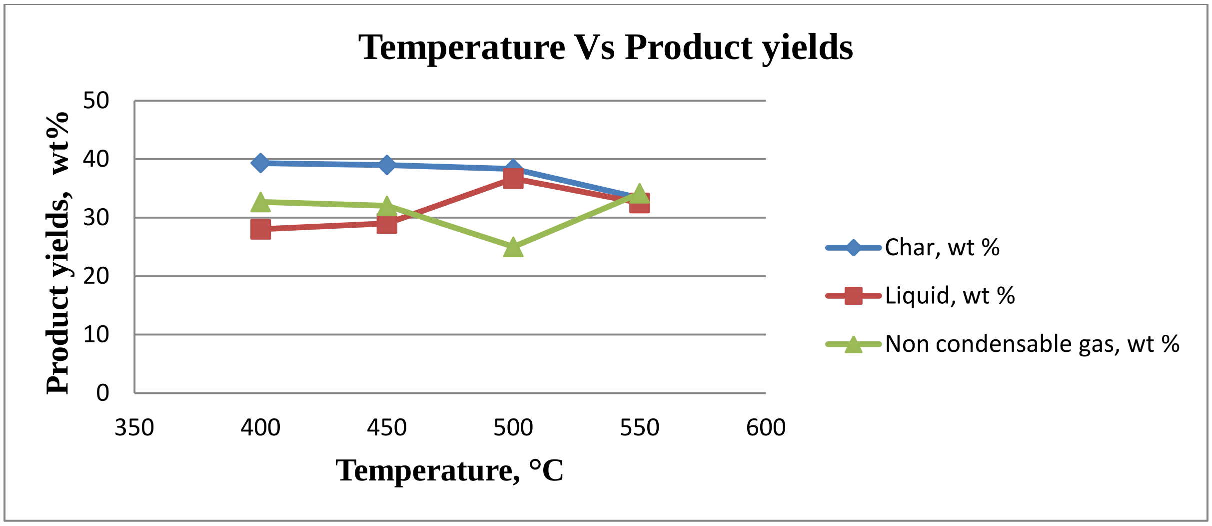

Fig.6 Effect of temperature on pyrolysis product yield at particle size 0.425 mm at a heating rate of 16 °C/min

Fig.6 shows, at the temperature of 400 °C char yield was 39.33%, liquid yield was 28% and gas yield was 32.67%. At the temperature range between 400 °C to 450 °C char yield was 39%, liquid yield was 29% and gas yield was 32%. At the temperature range between 450 °C to 500 °C char yield was 33.33%, liquid yield was 36.67% and gas yield was 25%. At the temperature range between 500 °C to 550 °C char yield was 33.33%, liquid yield was 32.5% and gaseous yield was 34.17%. The liquid yield increased from 28% to 36.67% by weight, when the Pyrolysis temperature increased from 400 °C to 550 °C with a particle size of 0.425 mm. While char and gaseous yield decreased. But at the temperature range between 550 °C and 600 °C liquid yield decreases to 32.5% by weight. While gas yield increases to 34.17% by weight. But char yield decreases to 33.33% by weight.

Figs. 3-6 show the influence of temperature on the product yields. Charcoal, liquid and gaseous fuel obtained from the pyrolysis of cotton shell. Particle sizes 1, 0.7, 0.6 and 0.425 mm examined at different temperatures of 400, 450, 500 and 550 °C in a fixed bed pyrolysis reactor of 100g capacity. For each run, the heater was started at ambient temperature and switched off when the desired temperature was reached. Fig.3-6 shows the effect of reaction temperature on the yields and the result indicated that at the temperature of 500 °C the bio-oil production became maximum (39 wt %). It was the optimum condition for production of bio-oil with temperature maintained at 500 °C. Then, from 500 °C to the final pyrolysis temperature 550 °C, the bio-oil yield was decreased. The reason why bio-oil product decreased at pyrolysis temperatures of 500 °C to 550 °C was the decreases of the organic and specific products and secondary cracking of volatiles at temperature above 550 °C. The cracking has led to more resulting in higher gas production. Charcoal consists of a small amount of volatile hydrocarbons, solid hydrocarbons and inorganic compounds. In higher temperature volatilize some of the solid hydrocarbons of the char and losses the weight of the char. The decrease in oil yield and increase in gas yield above the temperature of 550 °C is probably due to decomposition of some oil vapors into permanent gases and secondary carbonization reactions of oil hydrocarbon into char.

Effect of particle size on product yields

The oil yield increases as the particle size decreases from 1 mm to 0.6 mm and then decreases for the particle size of 0.425 mm. The gas yield decreases as the particle size decreases from 1 mm to 0.6 mm and then increase for the particle size of 0.425 mm. The particle size of 1 mm produced at optimum temperature of 500 °C, an oil yield of 38 wt % with a char yield of 47 wt % and gas yield 15 wt %. The particle size of 0.7 mm produced at optimum temperature of 500 °C, an oil yield of 39 wt % with a char yield of 42 w t% and gas yield 19 wt %. The particle size of 0.6 mm produced at optimum temperature of 500 °C, an oil yield of 39 wt % with a char yield of 31.67 wt % and gas yield 29.33 wt %. The particle size of 0.425mm produced at optimum temperature of 500 °C, an oil yield of 36.67 wt % with a char yield of 33.33 wt % and gas yield 25 wt %. These results suggested that mass and heat transfer restrictions had a profound influence at larger particle size resulting in minimum oil yield.

The gas yield obtained was found at the level of 15 wt % to 35 wt % for all particle sizes investigated. Particle size is known to influence pyrolysis product yield. Experimental result shows that particle size had significant effect on product yield. If the particle size is sufficiently small it can be heated uniformly results in high oil yield. The oil yield had an increasing trend as the particle size decreased from 1mm to 0.6 mm. Working at a particle size of 0.6 mm seems suitable for obtaining a high yield of oil, 39 wt % at a temperature of 500 °C. According to the study the maximum yield of oil (39 wt %) obtained at 0.6 mm particle size at a temperature of 500 °C with 16 °C/min heating rate.

Physical properties of bio-oil

Bio-oil from cotton shell is a dark brown organic liquid and free flowing with a strong acrid smell. Its carbon residue is 0.2%. The bio-oil obtained under the experimental conditions (500 °C with a heating rate of 16 °C/min and particle size of 0.6 mm) that gave maximum oil yield was used for characterization. Gross calorific value is the thermal energy contained in the bio-oil produced from the cotton shell.

Table.10 Comparison of properties of pyrolysis oil with diesel

Properties	**Diesel**	**Pyrolysis oil from cotton shell**
Calorific value	42.151 MJ/kg	6.43 MJ/kg
Viscosity @ 40 °C	5.5 mm²/s	2.9 mm²/s
Density @ 24°C	843 kg/m³	1010 kg/m³

The gross calorific value of bio-oil from cotton shell is nearly 6 times lower than diesel. The viscosity of bio oil obtained is 2.9 mm²/s at 40°C. For diesel, viscosity at 40 °C is about 5.5 mm²/s. The density of bio-oil at 24°C was 1010 kg/m³. It is denser than heavy fuel oil, which were typically about 843 kg/m³.

Pyrolysis gas composition using Gas chromatograph

Table.11 Pyrolysis gas compositions

Pyrolysis gas compositions	**Wt %.**
H_2	3.749
N_2+O_2	2.690
CO	11.002
CH_4	16.693
CO_2	17.877
C_2H_4	1.003
IMPURITY	1.440

Table 11 shows the gas composition of pyrolysis gases from cotton shell. Gas fractions were obtained using gas chromatography. The composition of non condensable gases was H_2, N_2, O_2, CO, CH_4, CO_2 and C_2H_4. The H_2, CO, CH_4, CO_2 and C_2H_4 content was 3.749 wt %, 11.002 wt %, 16.693 wt %, 17.877 wt % and 1.003 wt % respectively.

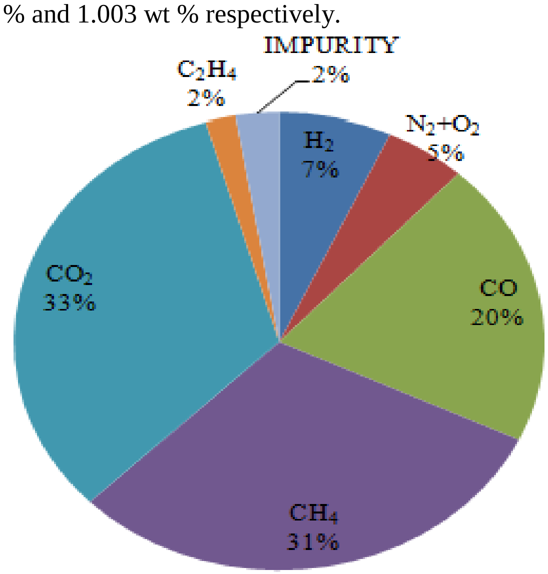

Fig.7 Pyrolysis gas composition

V. CONCLUSIONS

According to the study the maximum yield of oil obtained is 39 wt % at 0.6 mm particle size at a temperature of 500°C with a heating rate of 16°C/min. Bio-oil has been produced from cotton shell in a fixed bed reactor. The detailed characteristics of bio-oil were carried out. The gross calorific value of bio-oil was found to be 6.43MJ/kg. The density of bio-oil at 24°C was 1010 kg/m³. It is denser than heavy fuel oil, which were typically about 843 kg/m³. The viscosity bio oil obtained is 2.9 mm²/s at 40°C. The gross calorific value of bio-oil from cotton shell is nearly 6 times lower than diesel. This shows that the energy density of bio-oil is very less. This low quality oil cannot be used as fuel in engine directly. So that fuel up gradation is essential. We can use this low quality fuel as furnace oil. By transestrification process, we may improve the quality of bio-oil. Pyrolysis gas composition is obtained using gas chromatography. The composition of non condensable gases was H_2, CO, CH_4, CO_2 and C_2H_4. The H_2, CO, CH_4, CO_2 and C_2H_4 content was 3.749 wt %, 11.002 wt %, 16.693 wt %, 17.877 wt % and 1.003 wt % respectively. This non condensable gas can be used as source of heat for the pyrolysis reactor.

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