

# Influence of Temperature on Yield, Composition and Properties of The Sub-Fractions Derived from Slow Pyrolysis of *Grevillea Robusta*

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**Abstract-** Slow pyrolysis of *Grevillea Robusta* has been conducted in a fixed bed reactor to determine the effect of temperature on the by-product yield. The characterization of the *Grevillea Robusta* has been carried out using Thermogravimetric Analysis (TGA) to optimize the reactor temperatures. Pyrolysis experiments were performed at temperature between 300- 450 °C, and particle sizes of 2-3 mm with constant fixed nitrogen flow rate of 100 cm<sup>3</sup>min<sup>-1</sup> and heating rate of 20 °C min<sup>-1</sup> (slow mode). The highest liquid oil yield obtained was 58.5 % at temperature 400 °C. The obtained yield of liquid, solid and gas from pyrolysis were found in the range of 35.6-54.3 %, 30.6-46.2 % and 10.4-18.1 % respectively at different pyrolysis conditions. Liquid bio-oil produced from the pyrolysis of *Grevillea Robusta* shows high water content in the range of 58.09-72.74 % which was checked using Karl Fisher Titration. From Gas Chromatography, the chemical components present in the pyrolytic gas from pyrolysis of *Grevillea Robusta* include H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>3</sub>H<sub>6</sub> and some other species of hydrocarbons were found.

**Keywords-** *Grevillea Robusta*, TGA, heating rate, nitrogen flow, Gas Chromatography.

## I. INTRODUCTION

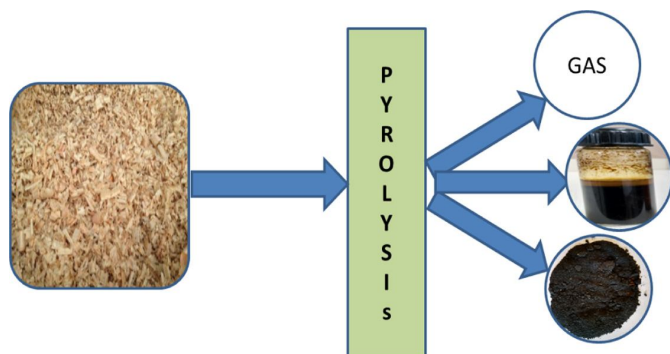


Fig 1: Pyrolysis reaction matrix with by products

Nowadays, energy has become a status symbol for economic growth and human development. It has been observed that energy consumption shows a two way relationship with economic development: the first being the fact that economy growth which relies on availability of cost effective and environmental friendly energy resources whereas on the other hand, the level of economic development is observed to be reliant on energy demand, specifically in developing countries like India. Since this increase in energy demand has been compensated mainly by fossil fuels, it accounted for overall increase in India's CO<sub>2</sub> emissions [1]. In current scenario, where the consumption of fossil fuels, in both rural and urban sectors, have increased exponentially over the past decades, is leading to increase in not only its market value but also in the greenhouse gas emissions. Thus, a dire need to put a control over its consumption has been felt by environmentalists and economists as well. Current technologies available to convert biomass into fuels can be classified into three categories based on their methodologies namely biochemical, thermal, and thermochemical conversion. Thermochemical conversion of biomass includes a number of processes such as liquefaction, gasification, and pyrolysis [2]. Among these, pyrolysis is the main spotlight of thermochemical conversion of biomass that produces solid and liquid fuels, both are easy to handle and transport. The liquid fuel (bio-oil) contains various added-value chemicals in economical recoverable concentrations and can be upgraded into refined fuels for transportation purpose [3].

The pyrolysis of biomass is produced by the thermal degradation of the raw material at high temperature in the absence of oxygen, yielding between 30 to 70 wt.% of a liquid product composed by a large number of compounds, mostly oxygenated, which can be easily separated into two fractions according to their water solubility [4]. The water insoluble fraction (tar) is viscous, and denser than the water soluble, organic fraction, usually named bio-oil.

Utilization of seed shell/cover from different kinds of fruits by pyrolysis have been reported in various literatures.

Das and Ganesh (2003) reported the studies on pyrolysis of cashew nut shell in a packed bed vacuum pyrolysis unit for pyrolytic liquid production and its potential use as a fuel. The properties of oil have been found to be near to that of petroleum fuels with calorific value of 40 MJ/kg [5]. Tsai et al. (2006) performed pyrolysis of coconut shell in a fixed-bed reactor to investigate the effect of pyrolysis temperature, heating rate and holding time on the yields of pyrolysis products and their chemical compositions [6]. It was observed that the maximum pyrolysis liquid yield of 50 wt.% was achieved by employing higher pyrolysis temperature of  $>500$  °C, faster heating rate of  $>200$  °C/min<sup>-1</sup>, and longer holding time of  $> 2$  min. Zabaniotou et al. (2008) reported the pyrolysis of sunflower shells in a captive sample batch reactor. The maximum oil yield of about 21 wt.%, was obtained at 400 °C [7]. Manurung et al. (2009) reported the fast pyrolysis of *Jatropha curcas* L. nut shells to pyrolytic oil. The experiments were carried out in a continuous bench scale rotating cone fast pyrolysis at 470–490 °C and atmospheric pressure. The non-optimized pyrolysis liquid yield of 50 wt.% was obtained along with char and gas yield of 23 and 17 wt.% respectively [8].

This work focuses on characterization of by-products obtained from thermal pyrolysis of *Grevillea Robusta* at different temperature range. Thermal pyrolysis of saw dust of *Grevillea Robusta* was done in a semi-batch reactor at a temperature range of 300 – 450 °C and at a heating rate of 20 °C/min. The effect of pyrolytic temperature on reaction time, liquid yield, and volatiles were also studied. The obtained by-products were characterized for different physical and chemical properties using Thermo Gravimetric analysis, Differential Thermo Gravimetric analysis, Derivative Thermal Analysis along with GC-MS, and FTIR

## II. MATERIALS AND METHODOLOGY

### 2.1. Raw material

The saw dust of *Grevillea Robusta* used in the experiment was obtained at the carpentry shop from Government College of Technology, Coimbatore, Tamilnadu, India. The raw saw dust were dried in the atmospheric temperature for a week and then crushed, grained and meshed to a particle size of 2-3 mm so as to minimize voids inside the reactor as well as to fill maximum amount of cake into the reactor.

### 2.2. Characterization of raw material

#### 2.2.1. Proximate analysis

It provides information on moisture content, ash content, volatile matter content and fixed carbon content of the material. It was carried out using ASTM D3172-07a method.

#### 2.2.2. Ultimate analysis

Ultimate analysis is performed to determine the elemental composition of the material. It was carried out using a CHNSO elemental analyser (Varioel CUBE, Germany) which provides carbon, hydrogen, nitrogen, sulphur percentage. When sum of these components is subtracted from 100, it gives oxygen percentage.

#### 2.3. Thermo-gravimetric analysis

Pyrolysis is heating of a substance in absence of oxygen (inert atmosphere) at a particular temperature. Therefore, the temperature for effective pyrolysis of the *Grevillea Robusta* saw dust had to be determined. For this purpose, thermo-gravimetric analysis (TGA) of the sample cake was done using a DTG60 instrument. Around 20–30 mg of sample cake was taken and heated up to a final temperature of 500 °C and a residence time of 1 min at 500 °C was allowed. TGA was performed both in air and nitrogen atmospheres at a heating rate of 25 °C/min and one observation was taken at a heating rate of 20 °C/min in air. Thermo-gravimetric weight loss curve was plotted against temperature. It provides a range of temperature in which maximum thermal degradation of *Grevillea Robusta* saw dust takes place.

#### 2.4. Experimental procedure

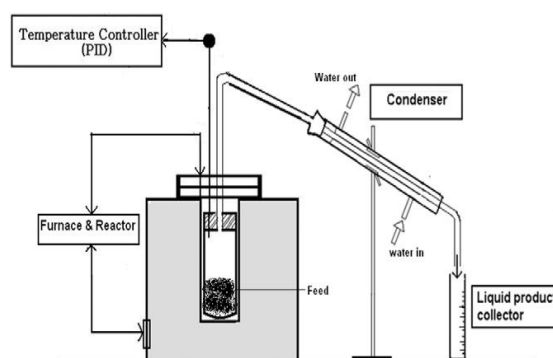


Fig 2: Experimental pyrolysis reactor setup

The experiment was conducted in a reactor-furnace system in which the furnace temperature was maintained constant using a PID controller. At the outlet of reactor, a condenser was attached to condense the vapours coming out of it. The condensed liquid was collected in a collecting jar at the end of condenser. The powdered saw dust is filled in a reactor of 1.5 kg and the reactor is kept in the furnace for heating at

constant temperature. When the reaction starts, vapours coming out of reactor through the provided outlet are condensed in a condenser as shown in Fig 2. Water is circulated as cooling medium in the condenser via a pump. The condensed vapours are collected in a container as the liquid product whereas there is some amount of non-condensable gases which are simply left out. The liquid product collected contains oily water and bio-oil. Oily water is basically water with some dissolved hydrocarbons. Oily-water and bio-oil is further separated by difference in their density.

### 2.5. Physical characterization of bio-oil

Physical properties such as density, specific gravity, viscosity, flash point, fire point, pour point, cloud point, calorific value and sulphur content of the bio-oil were determined using the standard methods.

### 2.6. Characterization of bio char

Char obtained after pyrolysis was analysed in order to observe the change in the properties of the solid material as a result of pyrolysis. Proximate analysis, ultimate analysis and calorific value of the obtained char were determined by using the same methods as for the raw material.

### 2.7 Characterization of pyrolysis gas

Pyrolytic gas evolved during the thermal decomposition was analysed using Shimadzu GC-2014 gas analyser equipped with Thermal conductivity detector TCD-2014 incorporated with an automatic filament shielding circuit. A micro pack shin carbon column of inner diameter 1mm and length 2 m was used in this analysis. A split less injection unit SPL-2014 with Helium as the carrier gas was employed in this analysis purpose. The calibration gas standard mixture consisted of N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>, CO and C<sub>2</sub>H<sub>6</sub> (Praxair Speciality Gases, Austin) with an analytical accuracy of  $\pm 5\%$ . The initial column temperature was set at 65°C for 10 minutes before ramping at the rate of 16 °C/min to a final temperature of 250°C.

## III. RESULT AND DISCUSSION

### 3.1 Thermogravimetric Analysis (TGA)

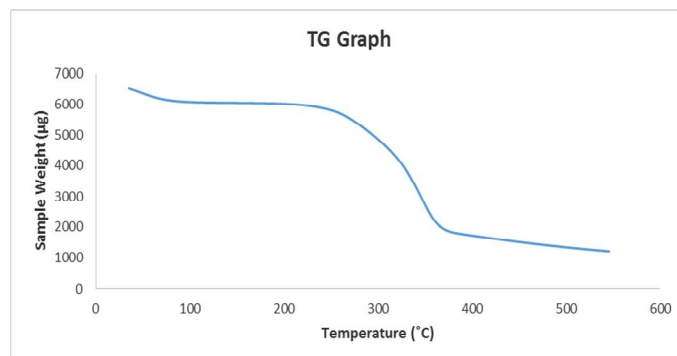


Fig 3: Thermo Gravimetric analysis of Grevillea Robusta bio mass

TGA is used to determine the thermal stability of Grevillea Robusta during the heating process. Weight reduction caused by the release of volatile compounds was observed as a function of temperature. Fig 3 shows the TGA curve of Grevillea Robusta saw dust. In the TGA curve at temperatures below 200°C, weight reduction of saw dust is dominantly caused by the evaporation of the water of the solid structure. Saw dust weight decreased significantly at temperatures 200-400°C. This is caused by the decomposition of cellulose and hemicellulose in Grevillea Robusta saw dust. At temperatures above 400°C, weight reduction is caused by the decomposition of lignin [9].

### 3.2 Variation of by product yield with Temperature

Table 1: Variation of by product yield with temperature

	350 °C	400 °C	450 °C
Liquid Product (%)	35.6	58.5	52.3
Char (%)	46.2	30.6	33
Gas (%)	18.1	10.4	14.4

Table 1 shows the product yield distribution for the pyrolysis of Grevillea Robusta in relation to final temperature at heating rate of 25 °C min<sup>-1</sup>. The liquid product obtained was reddish-brown in colour with an irritant odour and has a clear phase separation when stored in bottles. The liquid product yield was 35.6% at the pyrolysis temperature of 350 °C and it increased to a maximum of 58.5% at a temperature of 400 °C and again decreased to 52.3% by weight at a temperature of 450 °C. The yield of char varies from 46.2 %, 30.6 % to 33.0 % by weight when the pyrolysis temperature was increased. The decrease in char yield with increasing temperature could be either due to greater primary decomposition or de-polymerization of de-oiled cake to primary volatiles at higher temperatures or may be due to secondary decomposition of the char residue. The gaseous yield decreased initially then increased with increase in temperature. This may be due to secondary cracking of the

pyrolysis vapours or the formation of some non-condensable gaseous products during secondary decomposition of the char at higher temperatures.

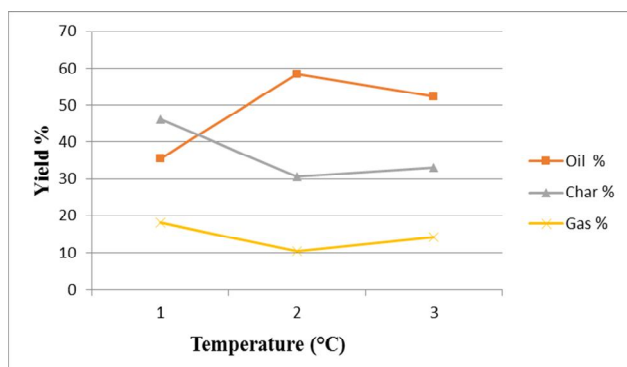


Fig 4: Effect of pyrolysis temperature on product yields

### 3.3 Characterization of biomass and biochar

Table 2 shows the proximate and ultimate analysis of *Grevillea Robusta* bio mass and bio char obtained at the three different temperatures. Moisture content and Volatile matter of bio char shows a decreasing trend with respect to the increase in temperature. It has been observed that at 450°C moisture content and volatile content in bio char is 69% and 83% respectively lesser than that of bio mass sample. This is because when the temperature increases the water content substances present in the sample gets reduced. Whereas ash content and fixed carbon shows an increasing trend with respect to the increase in temperature. The experimental results shows there has been 273% and 296% higher amount of ash content and fixed carbon content respectively present in the bio char at 450°C than that of the original biomass sample.

Table 2: Characterisation of bio mass and bio char

(%)	Bio Mass	Bio Char		
		350 °C	400 °C	450 °C
Moisture content	4.25	2.37	1.94	1.31
Ash content	3.42	10.61	12.12	12.78
Volatile content	73.83	18.4	13.69	12.34
Fixed content	18.5	68.61	72.15	73.37
C	45.3	62.3	66.3	71.8
H	3.28	3.82	2.83	1.48
N	2.84	2.18	1.46	1.12
O	48.3	30.91	28.67	24.64
H/C molar ratio	0.87	0.74	0.53	0.25
O/C molar ratio	0.81	0.37	0.32	0.27
Calorific value (MJ/kg)	14.62	23.06	23.67	24.2

It has been reported that feedstock containing high percentage of volatile matter and less percentage of ash content strongly influences its combustion behaviour and thermal decomposition. These characteristics also suggest good potentiality of the feedstock for energy production by

pyrolysis and gasification [10]. The C, H, N and O content of biochar for 350°C, 400°C and 450 °C compared with the raw bio mass sample. Biomass at different temperatures are shown in Table 2. The H/C and O/C atomic ratios decrease with the increase in terminal temperatures, which may be due to increase in carbonization of bio-chars [11]. Kim et al. (2011) and Tang and Bacon (1964) suggested that with increasing temperature, the O/C ratio in biochar decreases due to the fact that oxygen functionalities are decomposed by decarbonylation and decarboxylation [12,13]. Yuan et al. (2011) explained that the increase in the pH may be due to separation of alkali salts from organic materials. Biochar with high pH may correct the soil acidity problem and therefore, may be used as a liming agent [14].

### 3.4 Characterisation of bio-oil

The effect of pyrolysis temperature on the quality of bio-oil was studied by analysing the physicochemical properties of bio-oil. The property testing was performed to analyse the feasibility of utilizing bio-oil in engines as a transportation fuel. The results of the tests are summarized in Table 3. It can be seen that the physical appearance and characteristic odour were same for pyrolytic oils obtained at different temperatures. The experimental results clearly showed that there was an increase in water content of bio-oil with respect to temperature. An increase in water content of 14.3 % was observed when the pyrolysis temperature raised from 300°C to 450°C. This augmentation of water content with temperature can be attributed to the decomposition of lignin structure at higher temperatures, especially the cracking of –OH bond of the lignin structure [15]. Kinematic viscosity is one of the most important key property of fuel which determines the spray pattern, atomization and responsible for the performance of the engine. Moreover high viscous oil adversely affects the operation of the fuel injector on start-up due to poor fuel atomization. Kinematic viscosity showed an inverse trend as compared to water content such that viscosity of bio-oil decreased by 23.8% as the temperature raised from 300°C to 450°C. This decreasing trend in viscosity was due to the fact that higher pyrolysis temperature disintegrates complex molecules and forms smaller molecules with lower molecular weight. The lowest density for pyrolysis oil was observed at the pyrolytic temperature of 450 °C.

Table 3: Characterisation of Bio-oil

	Grevillea Robusta – Bio Oil		
	350 °C	400 °C	450 °C
Physical Appearance	Dark Brown	Dark Brown	Dark Brown
Odour	Smoky Smell	Smoky Smell	Smoky Smell
Flash Point (°C)	85	89	93
Fire Point (°C)	101	103	110
Water Content (wt%)	23.2	24.7	27.1
Kinematic Viscosity at 40°C (Cst)	14.6	13.4	11.2
Cetane Number	39	41	38
pH	3.4	4.1	4.7
Calorific Value (MJ/kg)	33.16	34.49	36.18
Density at 30°C (g/cc)	1.31	1.21	1.13

The bio-oil at all temperatures showed lower pH rating that indicates its acidic character which was a great barrier to its usage as a fuel. Minor increase in pH value was observed with raise in temperature which may be due to the increase in water content of bio oil at higher temperatures. The observed kinematic viscosity, density and pH values in this research work are similar to the results obtained by researchers in previous studies.

### 3.5 Characterisation of pyrolysis gases

Table 4: Components obtained from Gas Chromatography

	H <sub>2</sub>	CO	CH <sub>4</sub>	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>	N <sub>2</sub>
350° C	4.9	9.5	16.5	31.4	3.7	1.1	1.14	0.22
400° C	6.3	8.1	18.3	27.2	4.4	1.5	1.82	0.46
450° C	7.3	7.2	21.4	21.7	5.5	2.32	2.81	1.4

The gaseous products compositions during the pyrolysis 300–450 °C range | are shown in Table 4. The main compounds were carbon dioxide (between 20 and 30 wt.%), hydrogen (between 4 and 7 wt.%), hydrocarbons with up to 3 carbon atoms per molecule (between 1 and 5 wt.%) and Nitrogen (between 0.2 and 1.5 wt.%).

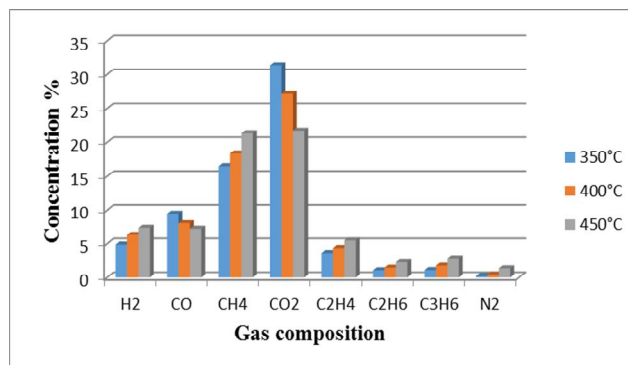


Fig 5: Gas Composition in pyrolysis oil

Most important hydrocarbons were methane, ethylene and propylene. These results are consistent with reports from other authors for various biomasses such as pine sawdust, corncob and oregano stalks [16]. Typically, the heating value of pyrolysis gases is relatively low and they are used as fluidizing agents in the reactors and as fuels to provide part of the energy needed to carry out the pyrolysis.

## IV. CONCLUSION

Pyrolysis studies of Grevillea Robusta saw dust in a fixed bed reactor indicated that operating temperature not only influenced product yield but also affects the properties of the products. As the pyrolysis temperature increased from 300 °C to 450 °C, significant improvement in gas yield was observed with declination in bio-oil and char yield. The physicochemical properties of bio oil suggest that it can be used as a potential fuel additive after upgradation. Meanwhile, GC results of pyrolytic gas revealed the presence of combustible gases which can be utilized as fuel in IC engines. On the other hand, Lower moisture content with a higher carbon content of biochar increased its calorific value which showed that it can be used as solid fuel in furnaces. Also increased nitrogen and ash content in biochar indicated its potential usage as bio fertilizer as well as an adsorbent.

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