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PYROLYSIS BEHAVIOR AND KINETIC STUDY ON SANDING WASTE WOOD FINE PARTICLES DURING PARTICLE BOARD PROCESSING USING THERMOGRAVIMETRIC ANALYSIS

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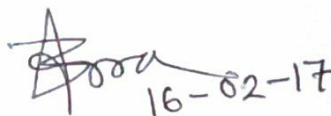
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DEDICATED
TO
MY BELOVED PARENTS

Declaration

I, Mahfuz Ara, declare that this thesis is a result of my own works and that it has not been submitted or accepted for a degree in any other University

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Date ....16-02-17........

Abstract

In the present study, sanding waste wood fine particle (SWFP) of the particle board industries was pyrolysed by a thermogravimetric analyzer from room temperature to 650°C in a highly purified N_2 atmosphere at 5°, 10° and 15°C/min heating rates. The physicochemical properties were determined by bomb calorimeter, elemental analysis. The results revealed the three stages of thermal degradation process. Increasing the heating rate, peak temperature was also increased and it turned to a higher value. The increased heating rate was also increased the volatile matter. The kinetic analysis of the main pyrolysis process was followed a mixed path involving the Coats Redfern and Flynn–Wall–Ozawa (FWO) Methods. The iso- conversional method showed that the pyrolysis reaction should conform to a single reaction model with activation energy of was 103.95 kj/mol. From the physicochemical characteristics, this waste wood particle sample has mid calorific value compared to solid wood and the amount of sulfur was zero. The results of this study express useful information for designing a pyrolytic processing system using that wastage as useful source of energy or chemicals.

ACKNOWLEDGEMENTS

LIST OF ABBREVIATIONS

SWFP = Sanding Waste Wood Fine Particle

TGA = Thermogravimetric Analysis

DTA = Deferential Thermogravimetric Analysis

BCSRI = Bangladesh Council of Scientific and Industrial research

IFRD = Institute of Fuel Research and Development

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CAHPTER ONE

INTRODUCTION

1.1 Introduction

The continuous decrease in amount of accessible fossil fuels, concerning about environmental pollution and demand for a well secured supply of fuel, chemical and energy have increased the interest in renewable and sustainable sources (Lopez-Velazquez et al., 2013). Biomass is one of the promising options as an alternative to fossil fuels because it is clean, renewable and sustainable (Kim et al., 2013). The proper utilization of biomass will reduce dependency on limited amount fossil fuels and it seems to have positive environmental effects such as reduced releases of carbon dioxides and sulfur oxides (Mythili et al., 2013). In Bangladesh as well as in the world the alternative sources of wood based materials are used to decline the pressure on solid wood and forest. Considering these, technologies are developed day by day. Now particle board manufacturing industries are captured lion part of the alternate of wood based materials. Because of this huge amount of particle board manufacturing industries are established. During the manufacturing process of Akij Particle Board about 8410 kg amount of waste produced every day. These huge amounts of residues have no usage area accept as a fuel in the boiler.

Pyrolysis is one of the most applied methods in converting waste biomass into valuable chemicals of fuels. It is a thermochemical process that conducted in the absence of oxygen. End products are carbon-rich char, condensable and non-condensable gases. Through pyrolysis, the molecules of biomass are broken down to low molecular weight gases (volatiles), liquids (tars) and solid char. The combustible gases, as well as the liquid products, can be used as fuel due to their high calorific value (Damartzis et al., 2011). In addition, this process can be source of various chemicals (Mythili et al., 2013). Therefore research on the pyrolysis process of a ligno-cellulosic waste would be beneficial for a better understanding of the pyrolytic-cracking mechanism and to improve its transformation and application as bio-fuels, chemical products and bio-materials (Lopez-Velazquez et al., 2013). Pyrolysis technologies represents an excellent way of utilizing lignocellulosic biomass such which makes them highly attractive especially when concerning environmental issues during energy production. There are various studies on pyrolysis analysis of different biomasses but biomass properties can significantly influence both

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heat transfer and reaction rates such that the optimal operating conditions are highly variable (Lopez-Velazquez et al., 2013; Sait et al., 2012). Kinetic analysis is essential to design and establish efficient, safe and reasonable processes. Determination of thermo-kinetic behavior of biomass allows control of decomposition mechanism of biomass as a function of pressure, temperature and combustion. Kinetic parameters of reaction are necessary for accurately prediction of reactions' behavior and optimization of the process towards products during the pyrolytic degradation (Lopez-Velazquez et al., 2013; Damartzis et al., 2011). Furthermore information about biomass pyrolysis kinetics is important to evaluate biomass as a feedstock for fuel or chemical production and efficient design and control of thermochemical processes.

From literature it is showed that the pyrolysis of agricultural biomass consist four individual conversion stages, i.e., moisture evolution, decomposition of hemicellulose, cellulose, and then lignin (Raveendran K et al., 1996). Hemicellulose, which is a branched polymer with a low degree of polymerization, is normally decomposed at 493–588 K, where cellulose maintains highly ordered and stable crystalline structures. As a result this, the cellulose undergoes decomposition at 588–673 K (Islam et al., 2015; Yang et al., 2007). Lignin is a three-dimensional polymer consisting of hydroxyl phenylpropane monomers, and bound adjacent to the cellulose fibers to form a lignocellulose. The lignin is more refractory than the other two components, while having functional groups with widely distributed thermal stability, and this result in a board temperature range of decomposition from 433 to 1173 K (Yang H et al., 2007; Yaman, 2004).

1.2 Objective of the study

The aim of the present research works is to determine the physicochemical Characteristics, kinetics parameter and pyrolysis behavior of the sanding waste fine particle of the particle board manufacturing industries.

CHAPTER TWO
LITERATURE REVIEW

2.1 Thermogravimetric analysis

Thermogravimetric analysis or thermal gravim analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss). TGA can provide information about physical phenomena, such as second-order phase transitions, including vaporization, sublimation, absorption, adsorption, and desorption. Likewise, TGA can provide information about chemical phenomena including chemisorptions, desolvation (especially dehydration), decomposition, and solid-gas reactions (e.g., oxidation or reduction).

TGA is commonly used to determine selected characteristics of materials that exhibit either mass loss or gain due to decomposition, oxidation, or loss of volatiles (such as moisture). Common applications of TGA are (1) materials characterization through analysis of characteristic decomposition patterns, (2) studies of degradation mechanisms and reaction kinetics, (3) determination of organic content in a sample, and (4) determination of inorganic (e.g. ash) content in a sample, which may be useful for corroborating predicted material structures or simply used as a chemical analysis. It is an especially useful technique for the study of polymeric materials, including thermoplastics, thermosets, elastomers, composites, plastic films, fibers, coatings and paints. Discussion of the TGA apparatus, methods, and trace analysis will be elaborated upon below. Thermal stability, oxidation, and combustion, all of which are possible interpretations of TGA traces, will also be discussed.

2.1.1 Instrumental apparatus

Thermogravimetric analysis (TGA) relies on a high degree of precision in three measurements: mass change, temperature, and temperature change. Therefore, the basic instrumental requirements for TGA are a precision balance with a pan loaded with the sample, and a programmable furnace. The furnace can be programmed either for a constant heating rate, or for heating to acquire a constant mass loss with time.

Though a constant heating rate is more common, a constant mass loss rate can illuminate specific reaction kinetics. For example, the kinetic parameters of the carbonization of polyvinyl butyral were found using a constant mass loss rate of 0.2 wt %/min. Regardless of the furnace programming, the sample is placed in a small, electrically heated furnace equipped with a thermocouple to monitor accurate measurements of the temperature by comparing its voltage output with that of the voltage-versus-temperature table stored in the computer's memory. A reference sample may be placed on another balance in a separate chamber. The atmosphere in the sample chamber may be purged with an inert gas to prevent oxidation or other undesired reactions. A different process using a quartz crystal microbalance has been devised for measuring smaller samples on the order of a microgram (versus milligram with conventional TGA).

2.1.2 Methods

The TGA instrument continuously weighs a sample as it is heated to temperatures of up to 2000°C for coupling with FTIR and Mass spectrometry gas analysis. As the temperature increases, various components of the sample are decomposed and the weight percentage of each resulting mass change can be measured. Results are plotted with temperature on the X-axis and mass loss on the Y-axis. The data can be adjusted using curve smoothing and first derivatives are often also plotted to determine points of inflection for more in-depth interpretations. TGA instruments can be temperature calibrated with melting point standards or Curie point of ferromagnetic materials such as Fe or Ni. A ferromagnetic material is placed in the sample pan which is placed in a magnetic field. The standard is heated and at the Curie point the material becomes paramagnetic which nullifies the apparent weight change effect of the magnetic field.

2.1.3 Trace analysis

If the identity of the product after heating is known, then the ceramic yield can be found from analysis of the ash content. By taking the weight of the known product and dividing it by the initial mass of the starting material, the mass percentage of all inclusions can be found. Knowing the mass of the starting material and the total mass of inclusions, such as ligands, structural defects, or side-products of reaction, which are liberated upon heating, the stoichiometric ratio can be used to calculate the percent mass of the substance in a sample. The results from

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thermogravimetric analysis may be presented by (1) mass versus temperature (or time) curve, referred to as the thermogravimetric curve, or (2) rate of mass loss versus temperature curve, referred to as the differential thermogravimetric curve. Though this is by no means an exhaustive list, simple thermogravimetric curves may contain the following features:

- A horizontal portion, or plateau that indicates constant sample weight
- A curved portion; the steepness of the curve indicates the rate of mass loss
- An inflection (at which $\frac{dw}{dt}$ is a minimum, but not zero)

Certain features in the TGA curve that are not readily seen can be more clearly discerned in the first derivative TGA curve. For example, any change in the rate of weight loss can immediately be seen in the first derivative TGA curve as a trough, or as a shoulder or tail to the peak, indicating two consecutive or overlapping reactions. Differential TGA curves also can show considerable similarity to differential thermal analysis (DTA) curves, which can permit easy comparisons to be made.

2.2 Pyrolysis

Pyrolysis is thermal degradation either in the complete absence of oxidizing agent, or with such a limited supply that gasification does not occur to an appreciable extent or may be described as partial gasification. Relatively low temperature is employed of 500 to 800 °C, compared to 800 to 1000 °C in gasification. Three products are usually produced: gas, pyrolysis oil and charcoal, the relative proportions of which depend very much on the pyrolysis method, the characteristics of the biomass and the reaction parameters. Fast or flash pyrolysis is used to maximize either gas or liquid products according to the temperature employed.

2.2.1 History of Biomass Pyrolysis

Charcoal is a smokeless fuel which is still used for heating purposes. It first technological use can be dated back to the Iron Age when charcoal was used in ore melting to produce iron. Production of wood vapor was usually related to the smocking which is one of the oldest food preservation methods, probably applied since the development of cooking with fire. These vapors, which contain nature preservatives like formaldehyde and alcohol, were used as feedstock. The main attraction is small and very simple plants could be made at a very low investment cost. The disadvantage is rather low energy yield and the air pollution.

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2.2.2 Why is pyrolysis getting interesting now?

There are several ways to make use of the energy contained in the biomass from old direct burning to gasification, pyrolysis. The selection of the most profitable technique to recover the energy from a particular type biomass is and most important step towards a profitable investment. Direct Combustion is the old way of using biomass. The biomass is completely transformed into heat, but the efficiency is just about 10 percent. The gasification pushes to the maximum level the cracking of biomass by completely transforming it into a combustible gas before burning it. The charcoal production, the slow pyrolysis of wood at temperature 500 °C is a process that charcoal makers have exploited for thousands years.

The biomass pyrolysis is attractive because solid biomass and wastes which are very difficult and costly to manage which can be readily converted into liquid products. These liquids, as crude bio-oil or slurry of charcoal of water or oil, have advantages in transport, storage, combustion, retrofitting and flexibility in production and marketing.

2.2.3 Current Status of the Technologies

In European, a demonstration plant of 500 kg/h is currently operating in Italy for liquid production. There are plans for small commercial units to be derived from this technology in Italy, Spain and Greece as LEBEN projects. A 250 kg/h pilot plant based on the Waterloo processes has been constructed in Spain. Several plants are in operation at a demonstration level for sewage sludge and refuse/WSW in West Germany at capacities up to 2 t/h, based on slow temperature pyrolysis. Elsewhere, a number of demonstration plants for flash pyrolysis are operation in North America at a scale of up to 25 kg/h with plans for several commercial developments ranging up to 40 kg/h, including a commercial installation planned for California based on the SERI ablative pyrolysis and sewage sludge pyrolysis in Canada and Australia.

2.2.4 Products and their characteristics

The primary products can be gas, liquid and solid depending on the process employed. Most of the projects interest in the liquid products due to their high energy density and potential for oil substitution.

The liquid, when formed, approximates to biomass in elemental composition with a slight higher heating value of 20-25 MJ/Kg, and is composed of a very complex mixture of oxygenated

hydrocarbons. The complexity arises from the degradation of lignin, and the broad spectrum of phenolic compounds. The liquid is often called oil, but is more like tar. This also can be degraded to liquid hydrocarbon fuels. The crude pyrolysis liquid is a thick black tarry fluid with up to 20 % wt water and viscosity as heavy oil.

The solid products from pyrolysis process is char, which has limited application in developed countries for metallurgical and leisure use. An alternative approach to liquid products lies in grinding the car and slurry it with water with a stabilizer. Stable and mobile concentration of up to 60 % wt has been reported. The slurry can also be made from the bio-oil and char, but the maximum solid concentration appears to be 30 %. The gas products from pyrolysis usually a MHV fuel gas around 15-22 MJ/NM^3 or a LHV fuel gas of around 4-8 MJ/Nm^3 from partial gasification depending on feed and processing parameters.

2.2.5 Pyrolysis Production Related to the Biomass Composition

The pyrolysis of wood results in the production of gas, tar and char (solid). Of course, the yields of these products are directly related to the composition of the biomass. Biomass consists of three major components: cellulose, hemicellulose and lignin. Cellulose is a straight and stiff molecule with a polymerization degree of approximately 10.000 glucose unite (C6 sugar) Hemicellulose are polymers built C5, C6 sugars with a polymerisation degree of about 200 sugar units. Both cellulose and hemicellulose can be vapored with negligible char formation at temperatures above 500°C. Lignin is a three dimensional branched polymer composed phenolic units. Due to the aromatic content of lignin, it degrades slowly on heating and contributes to a major fraction of the char formation. In addition to the major cell wall composition like cellulose, hemicellulose and lignin, biomass often contains varying amounts of species called "extractives". These extractives, which are soluble in polar or no polar solvents, consists of terpenes, fatty acids, aromatic compounds and volatile oil.

2.2.6 Industrial sources

Many sources of organic matter can be used as feedstock for pyrolysis. Suitable plant material includes green waste, sawdust, waste wood, woody weeds; and agricultural sources including nut shells, straw, cotton trash, rice hulls, switch grass; and animal waste including poultry litter, dairy manure, and potentially other manures. Pyrolysis is used as a form of thermal treatment to

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reduce waste volumes of domestic refuse. Some industrial byproducts are also suitable feedstock including paper sludge and distillers grain. There is also the possibility of integrating with other processes such as mechanical biological treatment and anaerobic digestion

2.2.7 Industrial products

- Syngas (flammable mixture of carbon monoxide and hydrogen): can be produced in sufficient quantities to provide both the energy needed for pyrolysis and some excess production.
- Solid char that can either be burned for energy or be recycled as a fertilizer (biochar)

2.2.8 Fire protection

Destructive fires in buildings will often burn with limited oxygen supply, resulting in pyrolysis reactions. Thus, pyrolysis reaction mechanisms and the pyrolysis properties of materials are important in fire protection engineering for passive fire protection. Pyrolytic carbon is also important to fire investigators as a tool for discovering origin and cause of fires.

2.2.9 Chemistry

Current research examines the multiple reaction pathways of pyrolysis to understand how to manipulate the formation of pyrolysis multiple products (oil, gas, char, and miscellaneous chemicals) to enhance the economic value of pyrolysis; identifying catalysts to manipulate pyrolysis reactions is also a goal of some pyrolysis research. Published research suggests that pyrolysis reactions have some dependence upon the structural composition of feedstocks (e.g. lignocellulosic biomass), with contributions from some minerals present in the feedstocks; some minerals present in feedstock are thought to increase the cost of operation of pyrolysis or decrease the value of oil produced from pyrolysis, through corrosive reactions. The low quality of oils produced through pyrolysis can be improved by subjecting the oils to one or many physical and chemical processes, which might drive production costs, but may make sense economically as circumstances change.

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2.2.10 Gasification vs. Pyrolysis

Pyrolysis is the thermal decomposition of the volatile components of an organic substance, in the temperature range of 400-1,400°F (200-760°C), and in the absence of air or oxygen, forming syngas and/or liquids. An indirect source of heat is used. A mixture of un-reacted carbon char (the non-volatile components) and ash remains as a residual.

Gasification takes this to the next step. It occurs in a higher temperature range of 900-3,000°F (480-1,650°C) with very little air or oxygen. In addition to the thermal decomposition of the volatile components of the substance, the non-volatile carbon char that would remain from pyrolysis is converted to additional syngas. Steam may also be added to the gasifier to convert the carbon to syngas. Gasification uses only a fraction of the oxygen that would be needed to burn the material. Heat is supplied directly by partial oxidation of the carbon in the feedstock. Ash remains as a residual.

CHAPTER THREE
EXPERIMENTAL

3.1 Materials

Sanding waste fine particles were collected from the Akij Particle board. These particles were produced in the particle board industry during sanding operation of particle board. These were very fine powder form wood waste and very light in color. It had no odor. The size of the particles was <200μm. After collecting from the industry it was stored in an airtight container before use.

3.2 Methods

To characterize the sanding waste fine particle ultimate and proximate analysis were conducted. Proximate analysis was conducted in the lab of IFRD (Institute of Fuel Research and Development) by using Seiko Instruments EXSTAR 6000 thermogravimetric analyzer. Moisture content, ash content, volatile matter and fixed carbon were tested through this proximate analysis. The sample weight was 1g and the N_2 flow rate was 20 mL/min. The temperature was used for proximate analysis was 900°c. This condition was held for 7.5minutes.

Ultimate analysis was also conducted in the same lab. CHNS were conducted on an elemental analyzer flash 2000. The heating values of the samples were determined with a bomb calorimeter.

3.3 Thermogravimetric Analysis.

The TGA experiments were carried out in a Seiko Instruments EXSTAR 6000 thermogravimetric analyzer. In each experiment, approximately 5 mg sample was spread uniformly on the bottom of the alumina crucible of the thermal analyzer. The pyrolysis experiments were performed at three heating rates of 5, 10, 15° C/min in a dynamic high purity nitrogen flow of 80 ml/min. The temperature of the analyzer was programmed to rise from 25 to 700°C and the temperature increase from 30°C to 110° C was maintained for 10 min to completely remove the moisture content. Subsequently, the temperature continued to increase up to 700°C.

3.4 Background of Kinetic modeling

Pyrolysis of biomass can be described by a general expression:-

Biomass (solid) →Char (solid) + Volatiles

Where volatiles contain gases and tar. To describe the reaction rate from solid state to volatile product is given here in equation 1.

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad \text{...} \quad (1)$$

Where α is the conversion during combustion, whereas $d\alpha/dt$ represents the rate of conversion over time t. α can be calculated with Eq. (2).

$$\alpha = \frac{m_0 - m_t}{m_0 - m_e} \quad \text{...} \quad (2)$$

Where m_o, m_t, and m_e refer to the sample mass at the initial period, time t, and the end, respectively. k(T) is the reaction rate constant that may be explained by the Arrhenius law as

$$k(T) = A\exp\left(-\frac{E_a}{RT}\right) \quad \text{...} \quad (3)$$

Where E_a is the activation energy of the reaction, A is the pre-exponential factor, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature in Kelvin.

Now, Eq. (1) can be written as

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E_a}{RT}\right)f(\alpha) \quad \text{...} \quad (4)$$

If the temperature increases with the constant heating rate β, then $\beta = \frac{dT}{dt} = \frac{dT}{d\alpha} \times \frac{d\alpha}{dt}$. Therefore, Eq. (4) can be re written as follows:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{A}{\beta}\int_0^T exp^{-E/RT} dT \quad \text{...........................} \quad (5)$$

Where g(α) is the integral function of conversion.

Therefore, Eq. (5) is the fundamental equation that is followed by all kinetic methods to determine the kinetic parameters during the pyrolysis process (Islam MA et al., 2015).

3.4.1 Flynn–Wall–Ozawa method

The FWO method is an isoconversional method (Ozawa, 1965; Flynn and Wall, 1966) derived from Doyle's approximation (Doyle, 1961). The method is referred to as a "model-free" method. Therefore, the FWO method calculates the activation energy (Ea) without prior knowledge of the reaction mechanism.

With Eq.(5), the reaction rate in logarithmic form can be expressed as follow:

$$ln(\beta) = ln\left(\frac{AE_a}{Rg(\alpha)}\right) - 5.331 - 1.052\frac{E_a}{R}\frac{1}{T} \quad\text{......................} (6)$$

The slope of plot $ln(\beta)$ against $1/T$ at different heating rates determines the value of apparent activation energy E_a when α is constant.

3.4.2 Coats–Redfern method

Coats and Redfern (1964) described the thermal decomposition mechanisms for mass loss. This method is a common integral kinetic method used to describe the reaction process during pyrolysis. The Coats–Redfern method is also based on Eq. (5), that is, if $2RT/E_a \rightarrow 0$, then Eq. (5) can be expressed in the following logarithmic way:

$$ln\frac{g(\alpha)}{T^2} = ln\frac{AR}{\beta E} - \frac{E_a}{RT} \quad\text{............................} (7)$$

A plot of $ln[g(\alpha)/T^2]$ against $1/T$ provides a straight line. The activation energy E_a is calculated from the slope, whereas the pre exponential factor A is intercepted from the plot. The theoretical explanation for the three kinetic mechanisms to calculate the $g(\alpha)$ values is presented in Table 1. The selection of appropriate mechanisms is based on the high determination of the regression coefficient (R^2) value.

3.4.4 Calculation Formula of thermal Kinetics.

Mechanism	$g(\alpha)$	Symbol
Chemical Reaction		
First Order	$-ln(1-\alpha)$	F1
Second Order	$(1-\alpha)^{-1}-1$	F2
Third Order	$[(1-\alpha)^{-2}-1]/2$	F3
Diffusion Model		
One-way Transport	α^2	D1
Two-way Transport	$\alpha+(1-\alpha)ln(1-\alpha)$	D2
Three-way Transport	$1-((1-\alpha)^{1/3})^2$	D3
Ginstling-Brounshtein Eq	$1-2\alpha/3-(1-\alpha)^{2/3}$	D4

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1. Physical and chemical characteristics

The characteristic features of sanding waste wood fine particle are given in **Table 1**. A comparison of the proximate and ultimate analysis results of sanding waste wood particle with common biomass is made in **Table 2** and **Table 3** respectively.

The result of the Physicochemical Characteristics of the sanding waste is showed in **Table 1**.

Table 1. Physicochemical Characteristics of the Sanding waste fine particle.

Sample	Proximate analysis (wt.%)				Ultimate analysis					HHV(Kcal/kg)
	Moisture	Volatile	Fixed Carbon	Ash	C	H	O	N	S	
SWFP	2.97	69.84	21.59	5.60	48.82	6.28	38.09	6.81	0	3475

According to **Table 1**, proximate analysis results for sanding waste wood particle are similar to other common biomass that studied. Sanding waste wood particle has a high amount of volatile matter content, 69.84% that could be considered suitable for combustion or gasification processes. Another important feature, ash content, which is 5.60%, seems moderate in waste wood particle. High ash content is disadvantage because it can affect burning rate and can cause fouling or aggregation. Higher processing costs, worse combustion quality, disposal problems and reduction of energy conversion are the other results of high ash content (McKendry, 2002; Sarenbo, 2009; Sait et al., 2012). The moisture content is 2.97% and its very low in amount which is the another indicator of good fuel material. If a material has higher moisture content then it will take more temperature to evaporate the moisture in the first stage of combustion. This characteristics is consume more energy during ignition. On the other hand the fixed carbon is 21.59% is found in this study. In ultimate analysis C is 48.82%, 6.28% H, 6.81% N and 38.09% O is found. The result is also presented by **Table 1**.

Ultimate analysis comparison of sanding waste wood particle with other biomass can be seen in **Table 2**. Low nitrogen content is important because higher N percentages may cause toxic NO_x emissions during combustion (Damartzis et al., 2011). Additionally, sanding waste particle has

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also the lowest S content and its 0% as shown in **Table 1** which implies fewer emissions or corrosion during utilization. **Table 1** depicts another important characteristics of the sample, the calorific values which is 3475kcal/kg.

Sanding waste wood particle has a mid-calorific value which is also favorable for a good fuel quality. Thus waste wood particle can be considered as an attractive biomass to be used as an alternative fuel.

Table 2. Comparative Proximate analysis of sanding waste wood fine particle and other biomass (% wt).

Biomass	Volatile Matter	Fixed Carbon	Ash	Moisture	References
Sanding Waste	**69.84**	**21.59**	**5.60**	**2.97**	**This study**
Orange waste	74.60	16.68	3.02	5.70	Lopez-Velazquez et al. (2013)
Saw dust	73.00	14.04	5.95	7.01	Mythili et al. (2013)
Rice husk	73.80	15.80	4.57	5.83	Mythili et al. (2013)
Wheat Husk	68.10	16.40	1.60	13.90	Mythili et al. (2013)
Pinewood waste	73.40	16.70	0.50	9.40	Amutio et al. (2012)
Hazel nut Husk	73.86	20.87	5.27	7.21	Ceylan et al (2014)

Table 3. Comparative Ultimate analysis of sanding waste wood fine particle and other biomass (% wt).

Biomass	C	H	N	O	References
Sanding Waste	**48.82**	**6.28**	**6.81**	**38.09**	**This study**
Orange waste	47.00	6.90	1.30	44.71	Lopez-Velazquez et al. (2013)
Saw dust	46.81	5.96	3.44	43.79	Mythili et al. (2013)
Rice husk	47.79	6.04	2.02	44.16	Mythili et al. (2013)
Wheat Husk	48.29	6.22	0.62	44.87	Mythili et al. (2013)
Pinewood waste	49.33	6.06	0.04	44.54	Amutio et al. (2012)
Hazel nut Husk	47.610	5.509	1.129	45.615	Ceylan et al (2014)

4.2 Thermogravemetric experiment

4.2.1 Weight loss characteristics

Thermal behavior of the sanding waste wood fine particle was studied by the weight loss and derivative weight in the temperature range 25–650°C under a nitrogen environment. In **Fig. 1** change in conversion with temperature for 5°, 10°, 15° C/min heating rate in a nitrogen environment can be seen. Pyrolysis of biomass consists of three stages. These stages can be outlined as; (i) dehydration process for temperatures below 250°C, (ii) Pyrolytic cracking from 250 to 350°C, stage consist of two exothermic simultaneous processes where the main components, hemicelluloses, cellulose and lignin are decomposed and a high amount of volatile matter formation occur, and (iii) the last endothermic decomposition of the lignin at temperatures above 350°C.

Table 4. Temperature interval of different region.

| Heating rate (°C/min)	Temperature intervals (°C)		
	First region	Second region	Third region
5	31.41-254.8	254.8-339.9	339.9-626.35
10	40.62-253.2	253.2-349.9	349.9-616.2
15	35.12-262.4	262.4-359.5	359.5-617.6

In first stage, as seen in **Fig. 1** moisture removal stills up to 250 C. The lignocellulosic part of the sanding waste was stable until 200°C with minor losses of moisture and low molecular weight volatile matter (d'Almeida et al., 2008; Cepeliog˘ulları and Putun, 2013). In the first stage the weight loss percentage were 3.6%, 5.48% and 7.72% for the 5°, 10°, 15°c/min heating rate respectively which are reported in the table 5. In the second stage, main components of waste wood particle hemicelluloses and cellulose, start degradation within the temperature range of 250–350°C. The weight losses were 64.5%, 55.3% and 69.99% for the predefined heating rate respectively. It was due to break down of hemicelluloses and cellulose and volatile matter removal. White et al. (2011) stated that decomposition of cellulosic part of biomass occurs in two ways. In the first way which occurs at low temperatures up to 350°C in this study break down of bounds in polymers and formation of CO, CO2 and carbonaceous are formed. In the second way, at high temperatures 350–620°C in this study integration of bonds which leads liquid formation takes place (Cepeliog˘ulları and Putun, 2013). Lignin volatilization occurs in a

wide temperature range which results a high char yield that maximizes at 460°C (Bilbao et al., 1997; Jauhiainen et al., 2004; Barneto et al., 2010). Weight loss between 400 and 700°C can be attributed to decomposition of tars. After 700°C only a small change in weight loss has observed.

Table 5. Weight loss of the sample of the different region at different heating rate

Heating rate (°C/min)	Weight loss of samples, % by weight		
	First region	Second region	Third region
5	3.6	64.5	31.9
10	5.48	55.3	39.22
15	7.72	69.99	22.29
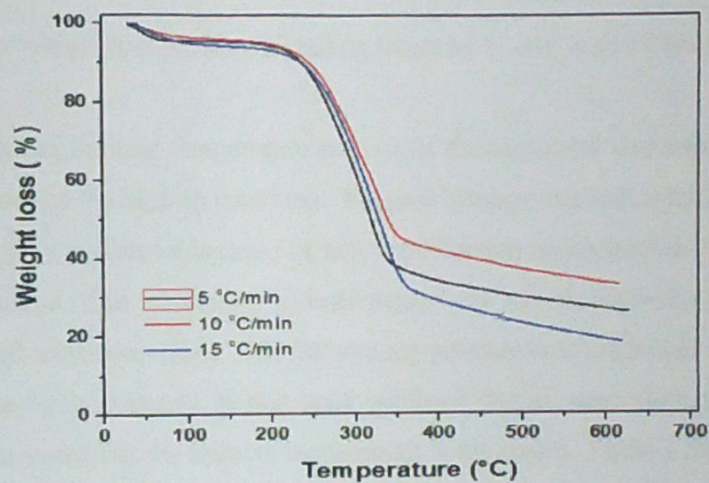
Fig. 1. Weight loss profile of sanding waste wood particle by 5°, 10° and 15°C/min heating rate.

The derivative weight loss, which is related to the weight loss percentage, is shown in **Fig. 2** for the waste wood fine particle. A large peak and a high peak temperature is observed in case of 15°c/min heating rate, here the temperature range is 200-350°c and the derivative weight loss is ~0.59mg/min. For the 5°c/min heating rate with same temperature range, the derivative weight loss is ~0.19mg/min. and the another is between these two.
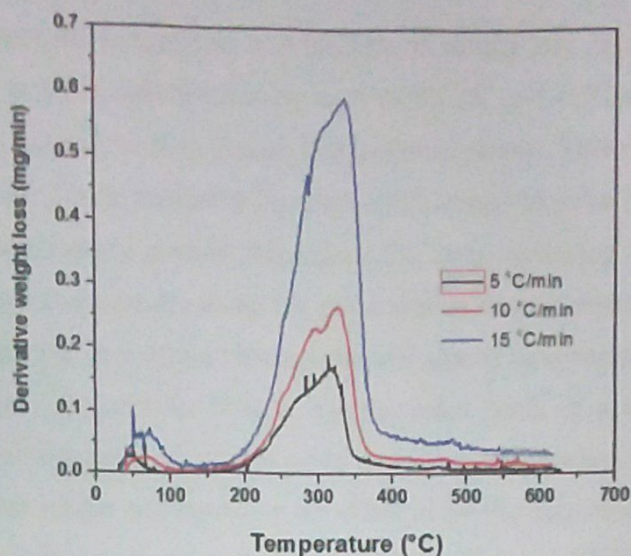
Fig. 2. Derivative Weight loss profile of Sanding waste by 5°, 10° and15°c/min heating rate.

Peak temperature and burnout temperature are one of the important characteristics of the DTG curve. They depend on the heating condition. The peak temperature indicates the point where the rate of weight loss is maximum because of fast volatilization accompanied by the formation of carbonaceous residue. This parameter is used mainly for the assessment of the point where highest amount of conversion occur. The burnout temperature is the indicator of the point where the sample are burned completely. In this study we found that increase the heating rate, the peak temperature is increased but the burnout temperature is decreased. **Table 6** showed the result of the peak and burnout temperature.

Table 6: Peak temperature and burnout temperature in °C

Heating rate	Peak temperature (°C)		Burn out temperature (°C)
	Second region	Third region	
5	313.60	548.10	626.35
10	326.83	542.44	616.20
15	335.68	485.34	617.60

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4.2.2. Effect of heating Rate

Fig. 1 and Fig. 2 show the weight loss and the rate of weight loss curves obtained from the pyrolysis of sanding waste at different heating rates of 5°, 10° and 15°C/min. When the heating rate is increased the general shift to higher temperatures occurs. This is typical for all non-isothermal experiments. The main reason for these shifts is that biomass is a poor conductor of heat, there exists a temperature gradient throughout the cross-section of the biomass. At lower heating rate, the temperature profile along the cross-section can be assumed linear as both the outer surface and the inner core of the biomass material attains same temperature at a particular time as sufficient time is given for heating. On the other hand, at a higher heating rate, a substantial difference in temperature profile exists along the cross-section of the biomass (Maiti et al., 2007). The other reason may be due to the effect of heating rate on secondary reactions of the primary pyrolysis products that may be tar and high-molecular- weight compounds, as some authors have reported (Juntgen, 1984). On the other hand, Table 5 shows the total % mass losses in the second stage were 64.5%, 55.3% and 69.99% on original basis at the heating rates of 5^0, 10^0 and 15^0C/min, respectively. It is evident from the results that the increased heating rate resulted in increases in the total volatile matter. Lower heating rates results in longer residence times inside the reactor and favor secondary reactions such as cracking, re-polymerization and re-condensation, which ultimately lead to the formation of the solid char (Maiti et al., 2007). The other reason may be due to some resistances to mass or heat transfer in the complex matrix of sample at low heating rates, however, an increase in heating rate may overcome these resistances by means of strengthened driving forces of mass and heat transfer inside the particles of biomass, and lead to a higher conversion

4.3. Kinetics

Iso-conversional method

The corresponding kinetic parameters of the main degradation stages of samples' thermal degradation under inert atmospheres were determined by using Coats–Redfern method. The first region corresponding to moisture, thermal kinetics was not calculated. The mechanisms which were the best suited for the different regions for describing conversion condition of that region were selected according to their R^2 value.

These mechanisms of the Coats Redfern Method was aslo used to calculate the activation energy and pre-exponential factor of the sample. According to Eq (7) a plot of ln $[g(\alpha)/T^2]$ against $1/T$ provides a straight line. From the slop of line, we can estimate apparent activation energy of the dynamic degradation at various conversion α. The activation energies calculated using Coats Redfern Method are listed in **Table 7**. As shown in **Table 7**, all plots had fairly high linear correlation coefficients greater than 0.99. The activation energies hardly varied with the degree of conversion, indicating that there exists a high probability for the presence of a single-step reaction (Vyazovkin, 2000). Thermal kinetics results of the sample are analyzed and showed in **Table 7**.

Table 7. Thermal Kinetics result of the Sanding Waste according to Coats Redfern method.

Heating Rate	Region	Method	R^2	E(kj/mol)	A(min^{-1})
5^{0}C/min	2nd	F1	0.9994	55.22	4.42E+02
	3rd	D3	0.992	7.21	1.12E-04
10^{0}C/min	2nd	F1	0.9997	51.61	1.61E+02
	3rd	D3	0.9962	6.22	1.14E-04
15^{0}C/min	2nd	F1	0.9997	51.01	1.26E+02
	3rd	D3	0.9965	6.30	1.16E-04

The variation in reaction mechanism causes change in Ea values with progressing conversion. Since activation energy is minimum energy requirement to start a reaction, higher Ea values mean slower reactions. Ea can also be used for determination of reactivity of a fuel (Gai et al., 2013).

The Coats–Redfern method for thermogravimetric data was used for the calculation that involved a heating rate of 10°C/min. Only the best-fitted mechanisms in different zones of the decomposition on the basis of the R^2 value are presented in **Table 7**.

The first-order (F1) mechanism in the second zone and the three way transport (D3) in the third zone were identified as effective solid state mechanisms for the sanding waste wood particle. The activation energy value for the sanding waste wood particle sample in the second zone was 51.61kj/mol which was higher than in the third zone. There were another 2 heating rate and their activation energy which were showed in **Table 7**. Al the three heating rate results of activation energy indicate that the second zone was the main critical zone during pyrolysis, whereas the third zone was the easiest zone for the degradation of biomass because of physical and mechanical changes that promote high combustibility. Gai et al. (2013) studied kinetic

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mechanism of rice husk and calculated Ea values 79. Amutio et al. (2012) examined pinewood waste pyrolysis kinetics and reported that E_a starts from 62 kJ/mol. This study is the first report on sanding waste wood fine particle pyrolysis kinetics and calculated mid-activation energy values for SWFP makes it considerable as potential biomass fuel.

In order to validate kinetic parameters, the pre-exponential factors as a function of conversion were determined using Coats– Redfern method. Calculated pre-exponential factor vales are shown in **Table 7**. For the 10^0C/min heating rate the pre exponential factor of the first order reaction was 161.00753 A(min⁻¹).

Table 8. Activation energy and pre-exponential values obtained by FWO method.

(α)	E_{FWO}, kJ/mol	R^2	A(min⁻¹)
0.1	129.065	0.8855	1.64E+11
0.2	115.384	0.8692	5.84E+09
0.3	110.990	0.8986	1.78E+09
0.4	101.064	0.8675	1.88E+08
0.5	96.710	0.9017	6.84E+07
0.6	70.492	0.8521	3.69E+05
Average	103.95		2.87E+10

Fig. 3, and their corresponding values calculated from the slopes and intercepts at different degrees of conversion (α) are presented in **Table 8**. The average activation energy values for SWFP with the use of the FWO method was 103.95 kJ/mol. From the literature it is established that a high activation energy value is considered good for the potential biomass energy. In FWO method the activation energy is decreased with the increment of α value. This may be done due to the degradation of the cellulose and hemicellulose structure in extreme temperature and pressure during the particle board production. The activation energy differs according to the changes in conversional value α and the methods used. On the other hand, the decomposition reaction mechanism was not the same and a multi-step mechanism was involved during the entire process. The complex and heterogeneous nature of the biomass with highly cross-linked cell wall components of cellulose, hemicellulose, and lignin contributed to this outcome. Here lignin content is the main indicating factor. Therefore, identifying the appropriate heat and mass transfer mechanisms at different reaction stages is necessary to achieve complete degradation. (Islam et al., 2015).

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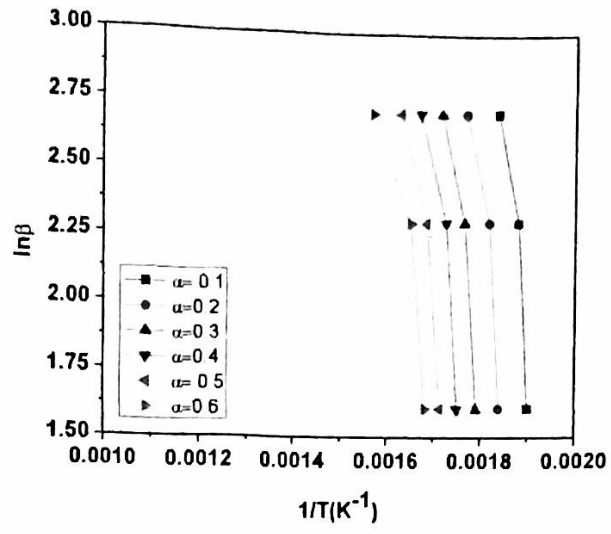
Fig. 3. Plots for determination of activation energy of the sanding waste at different α by FWO method.

CHAPTER FIVE
CONCLUSION

5. Conclusion

The thermogravimetric pyrolysis process of sanding waste wood fine particle was investigated under a N_2 environment at different heating rates. The heating rates were $5^\circ, 10^\circ$ and 15° C/min. The result of thermogravimetric analysis showed that three stages can be distinguished during the heating process. The moisture is removed in the first stage; the second stage is the main pyrolysis reaction zone and most of the organic materials are decomposed in this stage. And the solid residual slowly decomposed in the third stage. The initial temperature of pyrolysis and the temperature at which the pyrolysis rate reaches the peak value shift to the higher temperature as the heating rate increasing. The increased heating rate also resulted in small increases in the total volatiles release. To model the main stage of weight loss that is 2nd stage, the isoconversional method was applied to estimate the apparent activation energy Ea. The most probable mechanism function f(α) was determined by using the Coats Redfern method. The result showed that the most probable mechanism is the First order chemical reaction and Diffusion Mechanism. The activation energy was 51.61kj/mol and the pre exponential factor was 161 A(min⁻¹). But FWO method also uses for the determination of the activation energy and that was 103.95kJ/mol. This sample had a good amount of calorific value and other related characteristics which are the indicator of a better energy source. At the last, it can be enclosed that this waste wood fine particle can be used as a source of fuel or any other thermal energy.

Appendix

Sanding waste fine particle sample

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