Thermogravimetric Analysis of Groundnut Cake

Sachin Kumar, Ankit Agrawalla, and R. K. Singh

Abstract—**Biomass is increasingly considered as an important resource for alternative fuels whose use unlike fossil fuels (coal and fuel oil), does not increase atmospheric carbon dioxide content. Biomass may be utilized either by direct combustion or by transformation into fluid product. TGA has frequently been employed in the kinetic study of the thermal degradation of biomass materials. In this work, we have studied the thermo gravimetric analysis of the groundnut cake at 20^0C/min, 25^0C/min in the air and 25^0C/min in the N_2 atmosphere and determine the kinetic parameter (activation energy) by using thermogravimetric curves. The activation energy of the pyrolysis of groundnut de-oiled cake was found out to be in lower range thus enabling it to be used as a blend for easy pyrolysis of materials with higher activation energy.**

Index Terms—**Activation Energy, Groundnut Cake, Reaction Kinetics, Thermogravimetric Analysis.**

I. Introduction

In a growing economy like India, energy is an essential building block of its development. In the past decades, India's energy consumption has been increasing at one of the fastest rates in the world due to rapid population growth and economic development, with its primary commercial energy demand increasing by 6% from 1981 to 2001 as reported by Planning Commission, Government of India [1]. India accounted for 3.5% of the world commercial energy demand in the year 2003 making it fifth highest consumer in the world in terms of primary energy consumption [2]. However, per capita energy consumption in India is still very low compared to other developing/developed countries irrespective of its overall increase in energy demand.

In current scenario, where the consumption of fossil fuels, in both rural and urban sectors, have increased exponentially over the past decades and is expected to increases in the same manner for next couple of decades will lead to increase in not only its market price 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. In regard to this, a lot of research works are going on around the globe on various alternative sources of energy such as solar energy, wind energy, geothermal energy, hydrogen, nuclear energy, biofuel or biomass, etc. Material originated biologically, other than those which got embedded in geological formations and converted to fossils, are referred as biomass. Nowadays, a lot of modifications and pre-treatment of biomass have resulted into various efficient technologies. The advanced technologies are more focused on converting biomass into secondary energy forms such as electricity, gaseous and liquid fuels, hydrogen, etc. There are basically three principal methods of conversion of biomass: (a) Thermo-Chemical Conversion, (b) Physical-Chemical Conversion and, (c) Bio-Chemical Conversion.

Pyrolysis is a thermo-chemical process for conversion of biomass by heating the biomass feedstock at high temperature in absence of air which produces gaseous products which is then condensed to give liquid fuels consisting of pyrolytic oil or bio-oil and oily water (mixture of water and certain hydrocarbons).

Pyrolysis kinetics analysis is one important tool for the description of the effect of process parameters on the feedstock conversion process [3]. With kinetic analysis, the reaction system and mechanism during pyrolysis can be discussed, and some fundamental data of thermal chemical conversion can be provided. However, the investigation on the pyrolysis kinetics of biomass material is relatively scarce. Although the research on cellulose pyrolysis kinetics has prevailed for the past century, the kinetics research on whole biomass pyrolysis has its own characteristics that baffle the progress in this field, Michael (1995), Sharma & Rajeswara Rao (1999), Brigewater (1992) [4–6]. As the complicated polymer of cellulose, hemicellulose, lignin, and some extracts, biomass behaves differently from cellulose during the pyrolysis process. And also, the pyrolysis behaviour of different kinds of biomass varies with biochemical composition [4, 5]. Because of the different analysis apparatus and mathematics tools being applied, the result achieved from researchers around the world varies greatly and is even disputed sometimes, which weakens the foundation of the fundamental theory system of biomass thermal chemical conversion. According to World Market and Trade Analysis, Groundnut is the fourth largest oilseed produced in the world after Soybean, Rapeseed/Mustard and Cottonseed accounting for around 34.71 million metric tons produced in the fiscal year April 2010/11. Indian Oilseeds and Produce Exports Promotion Council [7] have analyzed that around 5.12 million tons of groundnut was produced during the year 2009-10 making it third largest produced oilseed of India after Soyabean and Rapeseed/Mustard. Thus, its abundance in quantity can make it a vital source for biomass in a developing country like India.

In this work, we have studied the thermo gravimetric analysis of the groundnut cake at 20^0C/min, 25^0C/min in the air and 25^0C/min in the N_2 atmosphere and determine the kinetic parameter (activation energy) by using thermogravimetric curves. The activation energy of the pyrolysis of groundnut de-oiled cake was found out to be in lower range thus enabling it to be used as a blend for easy pyrolysis of materials with higher activation energy.

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II. Kinetic Study of Reaction

Thermo gravimetric analysis (TGA) is one of the most commonly used methods to study the kinetics of thermal decomposition reactions. Kinetic analysis of a process can provide information on effect of process parameters on feedstock conversion. Researchers, Ahmaruzzaman & Sharma (2007), Hirata (1979), Parekh & Rotliwala (2009), Parikh & Rotliwala (2010), Ramiah (1970) [8-12] have investigated biomass pyrolysis and found that it can be modelled like a cellulose pyrolysis but since it contains polymers of cellulose, hemi cellulose and lignin so it may vary according to biochemical composition. It has also been stated that pyrolysis cracking can be modeled as 1st order rate equation as:

$$A_{Solids} \rightarrow B_{Solid} + C_{Volatiles} \quad (1)$$

For 1st order reaction, we have:

$$\frac{dx}{dt} = K(1-x) \quad (2)$$

where,

$$K = K_o * e^{\left(\frac{-E}{RT}\right)} \quad \& \quad x = \frac{(w_i - w)}{(w_i - w_f)} \quad (3)$$

So,

$$\frac{dx}{dt} = K_o * e^{\left(\frac{-E}{RT}\right)} * (1-x) \quad (4)$$

Taking heating rate (β) into account;

$$\frac{dx}{dT} * \beta = K_o * e^{\left(\frac{-E}{RT}\right)} * (1-x) \quad (5)$$

Now taking care of effect of variation of temperature on conversion (x), the following equation has been modelled to represent the pyrolysis reaction:

$$\ln(-\ln(1-x)) = \ln\left(\left(\frac{K_o R T^2}{\beta E}\right)\right) - \left(\frac{E}{RT}\right) \quad (6)$$

Activation energy (E) for the reaction is obtained by plotting ln(-ln(1-x)) versus 1/T using TGA data for each of the three runs as shown in Figure 3. As it can be observed that it is a linear plot thus the slope of this plot gives activation energy for each case as shown in Table 2.

III. Materials and Methods

A. Raw Material

The groundnut de-oiled cake used in the experiment was bought from a fodder shop from a local market of Rourkela, Orissa, India. The cake was in the form of flakes and was powdered, using a household grinder, before use so as to minimize voids inside the reactor as well as to fill maximum amount of cake into the reactor.

B. Characterization of Raw Material

The groundnut cake was analyzed in order to observe the change in the properties of the solid material as a result of pyrolysis.

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) Ultimate Analysis

Ultimate analysis is performed to determine the elemental composition of the material. It was carried out using a CHNSO elemental analyzer (Variael CUBE Germany) which provides carbon, hydrogen, nitrogen, sulphur percentage composition. And when sum of theses compositions is subtracted from 100, it gives oxygen percentage composition.

3) Calorific Value

Calorific value of a material is the amount of heat liberated when 1Kg of that material is burnt. It was determined for both cake and char using a bomb calorimeter (Model: AC-350, LECO Corporation, USA).

4) Oil Content

Oil content of the raw material was found out using Soxhlet apparatus.

C. Thermo-Gravimetric Analysis

Pyrolysis is heating of a substance in absence of air at a particular temperature. Therefore, the temperature for effective pyrolysis of the groundnut cake has to be determined. For this purpose, thermo-gravimetric analysis (TGA) of the sample cake was done using a DTG60 instrument. Around 20-30 milligrams of sample cake was taken and heated up to a final temperature of 800^0C and a residence time of 1 minute at 800^0C was allowed. TGA was performed both in air and nitrogen atmospheres at a heating rate of 25^0C/Min and one observation was taken at a heating rate of 20^0C/Min in air medium. Thermo-gravimetric weight loss curve was plotted against temperature. It provides a range of temperature in which maximum thermal degradation of groundnut de-oiled cake takes place.

IV. Results & Discussion

A. Characterization of Groundnut De-Oiled Cake

Proximate analysis is the quickest and simplest way of investigating the fuel quality of solid materials. High moisture content effects the conversion efficiency and heating value of biomass and have a potential to lose energy during storage as a result of decomposition. Higher value of ash content also affects heating value. High volatile content indicates that the material is more volatile than solid fuels whereas loss in fixed carbon content during pyrolysis should be less. As it can be observed in Table 1, the de-oiled cake has a very high volatile matter content of 83% which reduces drastically to 35.3% after pyrolysis. It indicates higher conversion of biomass to liquid fuels. As a result of decrease in volatile matter content, fixed carbon of material increased significantly which means there is less liberation of fixed carbon. Ultimate analysis listed in Table 1 showed significant variation in carbon and oxygen content whereas there were slight variations in hydrogen, nitrogen and sulphur content.

B. Thermo-Gravimetric Analysis and DTG analysis

The TGA curve Fig. 1 showed that the maximum thermal degradation of the cake took place in the temperature range of 160-500^0C in all the three observations. In nitrogen medium, a second temperature range of 500-650^0C is observed for thermal degradation of the cake but the vapours obtained during this phase are generally higher hydrocarbons and are non-condensable. Differential thermogravimetry (DTG) curve Fig. 2 for groundnut cake shows the normalized weight loss rates (-dx/dt) of the groundnut cake samples at the heating rates of 20^0C/min and

25^0C/min in the air atmosphere and 25^0C in the N_2 atmosphere. The weight loss started at 160-200^{0}C and terminated around 650^{0}C, the temperature range of 500-650^{0}C was neglected as it will not increase the yield of liquid product which is the main concern out here. Hence, the 160-500^{0}C range was selected for kinetic evaluation. The level of a considerable weight loss rate was achieved above 200^{0}C. The slow, flat tailing of the -dx/dt peak in the upper part of the T domain was considered less interesting than the main decomposition steps.

The pyrolysis temperature range for most of the de-oil cakes lies in the range of 400-800^{0}C, such as 400-700^{0}C for rapeseed Onay (2004) [13] similarly for the temperature range at which maximum thermal degradation took place was found out to be 250-500^{0}C Onay (2007) [14], for grape bagasse it was around 350-600^{0}C Ayan & Demiral (2011) [15], G. Duman (2011) reported 200-500^{0}C as pyrolysis range for cherry seeds [16] .

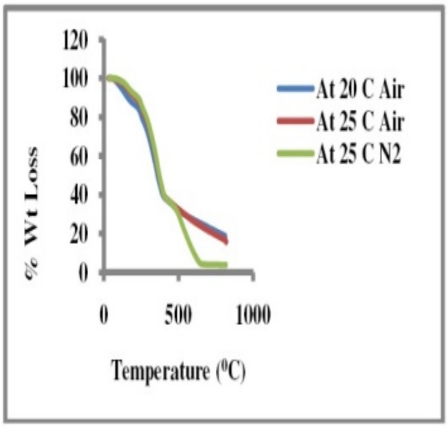

Fig. 1 TGA Curve at different heating rates

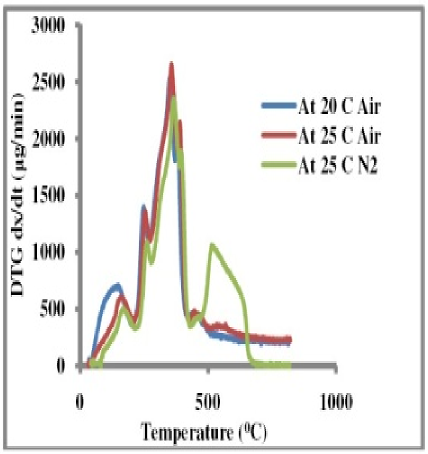

Fig. 2 DTG Curve at different heating rates

C. *Kinetic study by the thermo gravimetric analysis*

The reason behind kinetic study of pyrolysis reaction is to determine activation energy for the reaction which implicates the ease of occurrence of reaction. Fig. 3 shows the plot between ln(-ln(1-x)) and 1/T. Reactions having less activation energy take place much easily than reaction with high activation energy. Activation energy for groundnut pyrolysis is comparably low Table 2 shows the activation energies of three phases of degradation during thermal pyrolysis. Hence the low activation energy for ground pyrolysis can be used as a blend with biomass sources having high activation energy for their easier thermal degradation reaction.

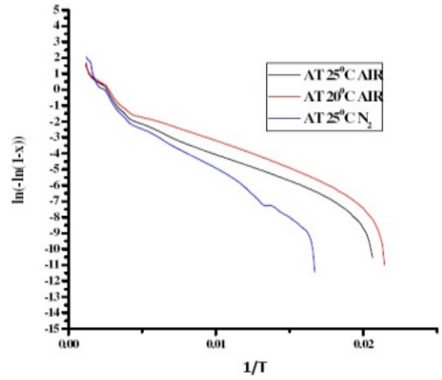

Fig.3 Kinetic analysis plot for determination of activation energy

TABLE 1 CHARACTERIZATION OF GROUNDNUT DE-OILED CAKE

Properties	Groundnut Cake
Moisture Content	5.6
Volatile Content	83
Ash Content	4.8
Fixed Carbon	6.6
C	46.37
H	7.015
N	6.89
S	0.287
O	39.438
C/H Molar Ratio	0.55
C/N Molar Ratio	7.851717465
% Oil Content	4.18
Empirical Formula	$C_{7.85}H_{14.25}O_{5.01}NS_{0.02}$
Gross Calorific Value(MJ/Kg)	15

TABLE 2 ACTIVATION ENERGY FOR PYROLYSIS OF GROUNDNUT DE-OILED CAKE

	Activation Energy (KJ/Mol)		
Sample	1st Phase	2nd Phase	3rd Phase
N_2 25^{o}C/min	45.12	4.55	11.58
Air25^{o}C /min	16.67	3.01	8.36
Air20^{o}C /min	15.01	2.73	7.83

V. CONCLUSIONS

The thermogravimetric study helps to interpret physical and chemical properties and the thermal behavior of the given type of biomass sample. Determining the kinetic parameters also provides information to design more effective conversion systems and optimum pyrolysis regimes. Activation energy of the pyrolysis of groundnut de-oiled cake was found out to be in lower range thus enabling it to be used as a blend for easy pyrolysis of materials with higher activation energy.

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