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Thermal Behavior and Pyrolytic Kinetics of De-Oiled Jatropha Seed Cake

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ABSTRACT

The disposal of cake residues after the oil extraction from *Jatropha curcas* (jatropha) seed as a waste raises serious environmental concerns due to oily and toxic nature. The aim of the present work is to study the effects of heating rate on thermochemical conversion of de-oiled jatropha seed cake (DJSC). Initial physicochemical characterization of DJSC was carried out by proximate and ultimate analysis. The kinetics of the slow pyrolysis behavior was investigated using thermogravimetric analysis (TGA) at various heating rates of 10, 20 and 30°C/min. The results of TGA revealed that onset and offset temperature of the devolatilization step were shifted and the activation energy increased with increasing heating rates. The activation energies of DJSC were found in the range of 14.14 to 24.74 kJ/mol by applying iso-conversional methods to pyrolysis data. The outcome of the study could assist in proposing the appropriate blending of DJSC for efficient pyrolysis by varying blending ratios with higher activation energy materials.

Keywords – Bioenergy, Biomass kinetics, Jatropha, Seed cake, Pyrolysis, Waste to energy

1. INTRODUCTION

The prime concern over the effects of using fossil fuel as major energy sources in depleting nature and greenhouse emissions has emerged the search for new and renewable energies. Energy is the key building block of economic growth of any nation that plays a vital role in sustainable development and advocating biomass-based energy sources is essential for rural livelihood in India [1-3]. The lignocellulosic biomass derived from either energy crops or agro residues promotes as a natural energy resource for the production of gaseous, liquid fuels and chemicals without increase of carbon dioxide into the atmosphere [4]. The thermochemical energy conversion of non-edible de-oiled seed cakes has received attention in recent decades as 65 to 70% of solid residues is being discarded in the form of solid cakes containing cellulosic components on varying proportion [5]. Rather, it could be promoted as a sustainable renewable energy source for power generation by comprehending the combustion and pyrolytic characteristics. However, the fundamental combustion and pyrolysis study on de-oiled seed cakes have not been widely explicated.

Thermogravimetric analysis is the essential tool widely used for studying the pyrolysis kinetics due to its ease and recovery of valuable information from a thermogram [6, 7]. Many methods of differential, integral and special types are reported in the literature for finding out the kinetic parameters activation energy (E), pre-exponential factor (A), and reaction order (n) [8, 9]. Differential methods necessitate both mass loss data as well as the rate while the integral type depends on mass loss data alone. The special category methods need a couple of experimental data from different heating rates or the evaluated data from graphical plots.

In this work, we have studied the thermogravimetric analysis of de-oiled jatropha (*Jatropha curcas*) seed cakes (DJSC) at a various heating rate of 10, 20 and 30°C/min to find the kinetic parameters such as *E and A* by using Arrhenius model. The outcome of the study could assist in proposing the proper blending for efficient pyrolysis of these non-edible seed cakes in varying ratios with higher activation energy materials.

2. MATERIALS AND METHODS

2.1 Materials

The raw biomass of DJSC was utilized from Energy lab of Department of Mechanical Engineering, Periyar Maniammai University, India. The collected de-oiled seed cake residues were powdered using the household grinder for size reduction to minimize the heat transfer effects during pyrolysis study. The powdered samples were air-dried and desiccated before it subjected to characterization and further analysis.

2.2 Thermogravimetric analysis

The thermogravimetric analysis of DSJC was measured by conducting non-isothermal experiments using Shimadzu TGA 50 H analyzer at three different heating rates of 10, 20, and 30°C/min in a high purity nitrogen gas atmosphere with a flow rate of 20ml/min. The experiments were conducted at ambient temperature to 1000°C by taking sample weight of 5 to 6 mg approximately.

2.3 Kinetic studies

The biomass conversion could be denoted in pyrolysis process as the reaction products of biochar and volatiles. Moreover, the kinetic expression is given by Arrhenius equation as

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \qquad (1)$$

$$k(T) = Aexp\left(\frac{-E}{RT}\right) \qquad (2)$$

Where, *f(α)* is the reaction model that depends on the reaction mechanism; *k(T)* is the rate constant; *A* is the frequency factor; *E* is the activation energy (J/mol); *T* is the absolute temperature (°C); *t* is the time (min); and α is the universal constant (8.314 J/mol/K)

$$Heating\ rate(\beta) = \frac{dT}{dt} = constant \qquad (3)$$

$$dt = \frac{dT}{\beta} \qquad (4)$$

Substituting *k(T)* from equation (2) and *dt* from equation (4) in equation (1) and after rearrangement, the integration of equation (1) is given as

$$\int_0^{\propto} \frac{d\alpha}{f(\alpha)} \int_0^T \mathrm{Aexp}\left(\frac{-\mathrm{E}}{\mathrm{RT}}\right)\frac{\mathrm{dT}}{\beta} = g(\alpha) \qquad (5)$$

2.4 Model fitting methods

The thermal kinetics of a reaction could be evaluated using a few model-fitting methods by utilizing thermogravimetric data to determine the mass or heat exchange as a function of temperature and time. By solving the equation (5) based on approximation analysis, the resulted Coats-Redfern (CR) equation form could be further used to evaluate the non-isothermal data for computing kinetic parameters as in equation (6) and (7):

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left(\frac{\mathrm{AR}}{\beta\mathrm{E}}\right)\left(1 - \frac{2\mathrm{RT}}{\mathrm{E}}\right) - \frac{\mathrm{E}}{\mathrm{RT}} \qquad (6)$$

$$\alpha = \frac{m_{i-}\ m_{\alpha}}{m_{i\,-}\,m_f} \qquad (7)$$

Where $m_{i,}$ $m_{\alpha,}$ and m_f are the values, refer at the initial, instantaneous and final time respectively. The best mechanism for the chemical reaction was analyzed by using CR equation on various kinetic models (as in Table 1) after resulting in straight line fit with a high regression coefficient for $\ln[g(\alpha)/T^2]$ versus 1/T data for comprehending the experimental observations.

Table 1 Kinetic models used in pyrolytic reaction mechanisms

Model	Mechanism	*f(α)*	*g(α)*
1	I order	$(1-\alpha)$	$[-\ln(1-\alpha)]$
2	II order	$(1-\alpha)^2$	$[(1-\alpha)^{-1}-1]$
3	III order	$(1-\alpha)^3$	$[(1-\alpha)^{-2}-1]/2$

2.5 Iso-conversational methods

The iso-conversional methods mainly differ in an approximation of the temperature integral in equation (5), and many of them give rise to a linear equation. After the substitution of *E/RT* as p in equation (5) and rearrangement would result as follows:

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\frac{E}{R}\int_p^{\alpha} \mathrm{p}^{-2}\exp(-\mathrm{p})\mathrm{dp} \qquad (8)$$

KAS method takes the following approximation for the integral on the right side term of the equation (8):

$$\int_{\mathrm{p}}^{\alpha} \mathrm{p}^{-2}\,\mathrm{EXP}\,(-\mathrm{p})dp = p^{-2}\ exp\ (-p) \qquad (9)$$

The solution of equation (9) based on the approximation and substitute modification given as equation (10) was used to determine the activation energy and frequency factor.

$$\ln\frac{\beta}{T^2} = \ln\left(\frac{AE}{Rg(\alpha} - \frac{E}{RT}\right) \qquad (10)$$

OFW method applies Doyle's approximation for integral term of the right-hand side of the equation (8) which becomes,

$$log\left[\int_p^{\alpha} p^{-2}\exp(-p)dp\right] = -2.315 + 0.457\,p \ (11)$$

By substituting equation (11) in equation (8) and on rearrangement, equation (12) was obtained and used for calculating the Arrhenius parameters.

$$\log(\beta) = log\left[\frac{AE}{Rg(\alpha)} - 2.315 - 0.457\frac{E}{RT}\right] \qquad (12)$$

The plot of ln[β/T^2] versus 1/T by KAS method provides the slope of –E/R. On the contrary, the plot of log β versus 1/T in the case of OFW method allows the activation energy to be calculated from the slope (-0.457 E/RT) of a straight line.

3. RESULTS AND DISCUSSION

3.1 Physicochemical characterization of DJSC

The characterization of DJSC as a bioenergy feedstock is taken into consideration in the present investigation. The processed DJSC were subjected to thorough physicochemical characterization for comprehending the properties of cake residues. The proximate analysis unveils the characterization of any material in view of the volatile matter, fixed carbon, ash and moisture content that aids in comprehending the fuel quality of the biomass residues. The proximate analysis of DSJC revealed that the biomass had been predominated with the volatile matter of 65% could strongly influence its decomposition behavior of the biomass material. The moisture content of DJSC is around 7.70% which could further influence the thermal properties of the biomass. Moisture content is the prime property of biomass that influences physical, mechanical and thermal properties of biomass fuels and hence utmost importance has been given while selecting for biomass conversion technology. The gross calorific value (GCV) and net calorific value (NCV) for DJSC was 16.95 and 14.37 MJ/kg, respectively. The fixed carbon and ash content of the DJSC were above 12%, and less than 3% suggests the potentiality of these cake residues as the appropriate biomass feedstocks for pyrolysis process. The overall physicochemical characterization of DJSC was summarized in Table 2.

3.2 Thermogravimetric analysis of DJSC

The thermal behavior of DJSC in the temperature range of ambient to 1000°C was studied at three different heating rates of 10, 20 and 30°C/min. The thermogravimetric data of DJSC revealed that the removal of moisture was found to be between a temperature of 165-185^{o}C. It has been observed that the temperature characteristics towards pyrolysis and devolatilization shifted towards higher temperature with the increase of heating rate. However, the peak mass loss rate in all the three heating rates observed at 325± 10^{o}C. The heating rate showed an effect on the overall conversion of biomass, and by comparing the conversion of biomass at three different heating rates, the minimum residue was found at 30^{o}C/min. Reduction in the mass of the sample with the temperature at the various heating rates were shown in Fig. 1.

Table 2 Physicochemical characteristics of DJSC

Properties (%)	***DJSC***
Moisture content	7.70
Volatile content	64.99
Fixed carbon	12.58
Ash content	2.30
Carbon content (C)	44.02
Hydrogen content (H)	6.00
Nitrogen content (N)	6.67
Sulphur content (S)	0.00
Oxygen content (O)	43.02
C/H Molar Ratio	0.61
C/N Molar Ratio	7.70
Gross calorific value (MJ/Kg)	16.95
Net calorific value (MJ/Kg)	14.37
Empirical formula	$CH_{1.69}O_{0.75}$

3.3 Kinetic study of thermogravimetric analysis for DJSC

The kinetic study of pyrolysis supports the examination of activation energy required for the reaction and dictates the nature of reactions in thermal degradation. The degradation of cellulose and hemicellulose components were observed to happen between 280-380^{o}C and 200-320^{o}C.

The first stage of pyrolysis starts at ambient temperature and finishes at 180^{o}C. The weight loss occurred at this stage for three different heating rates was around 10, 8 and 6%. It could be attributed to the elimination of physically absorbed water in the biomass and external water. However, there is also the possibility of removal of some light volatile compounds. The second stage starts at 180^{o}C and finishes at 320 ^{o}C with a mass loss of 38, 42 and 48% at three different heating rates. It is observed that the rate of maximum mass loss occurred at around 330°C. This stage could be referred to as active pyrolysis stage since weight loss rate was quite high.

The third stage varies at 353-507, 388-584 and 395-621^{o}C for three different heating rates of 10, 20 and 30°C/min. This stage shows a mass loss of 16.12, 10.46

and 24.16%. This stage can also be referred to as the stage of active pyrolysis based on the high mass loss rate. The fourth stage starts around 700°C and continues up to 1000°C. Weight loss occurred at this stage was less than 25%, and so it could be referred as a zone of passive pyrolysis since mass loss rate is much lower compared to other pyrolytic regimes.

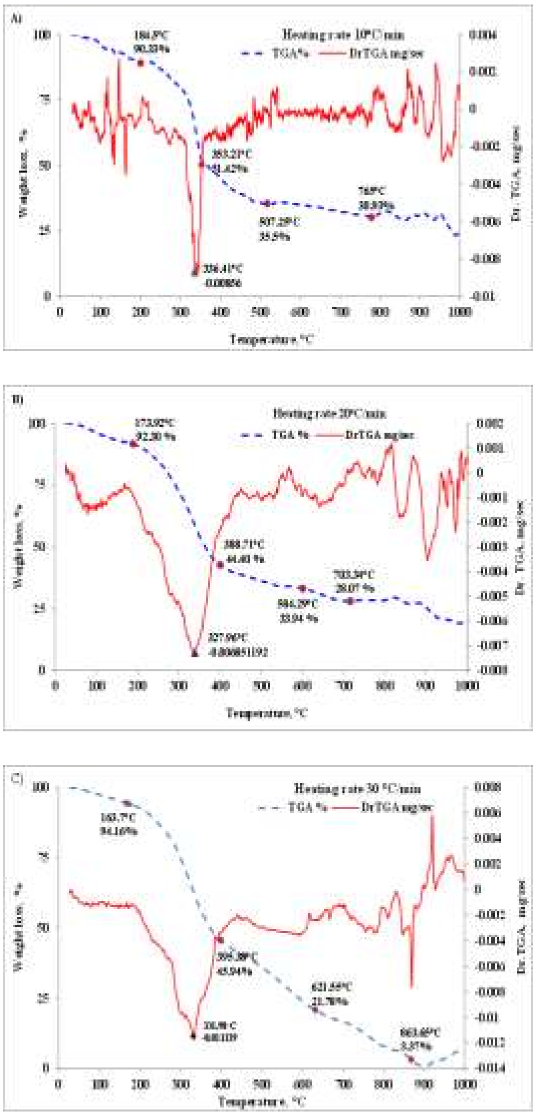

Fig. 1 Thermogravimetric analysis of de-oiled jatropha seed cakes at a heating rate of a) 10 deg C/min; b) 20 deg C/min; and c) 30 deg C/min

Since the oil has been extracted from the non-edible seed cakes, the activation energy for thermal decomposition of DJSC is varied depending on their biochemical composition of cellulose, hemicellulose and lignin content. The reported activation energies for cellulose, hemicellulose and lignin were 145-285, 90-125 and 30-39 kJ/mol respectively [12]. The research and development activities in pyrolysis and the contributions from Indian scientific community were exhaustively reviewed by Murugan and Sai Gu [13].

3.4 Pyrolytic kinetic models for DJSC

By using reaction models given in Table 1 and TGA data, the best correlation was obtained with the first order reaction model [f(α) =1-α] at three different heating rates. Then CR method has been applied to derive the regression plots (Fig. 2). The activation energies were calculated (Table 3) and are ranged from 14.14 to 24.74 kJ/mol. It is evident from the tabulated values that heating rate has a significant influence on activation energy in the decomposition process.

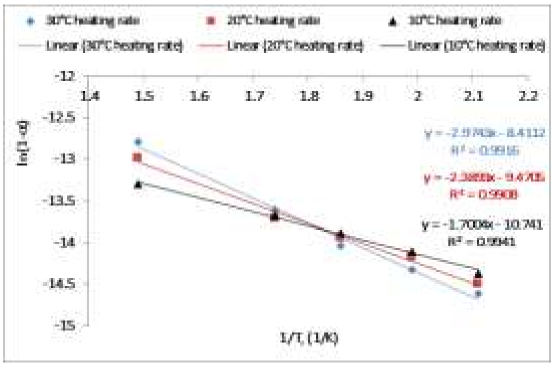

Fig. 2 First order reaction model fitted to thermogravimetric data by Coats-Redfern method

The increase in heating rates to 30°C/min resulted in an increase of activation energies for DJSC especially during the active zone of the pyrolytic reactions. The smaller activation energy shows that the reaction rates are faster. The model-free KAS and OFW method yielded 15.15 and 4.83 kJ/mol in the 0.2–0.9 conversion interval (Fig. 3). However, it would be suitable to compare the results on average basis (i.e.) average of the results at different heating rates. Very few studies have evaluated the activation energy on individual stages of DJSC at various heating rates [14, 15].

Table 3 Activation energies of de-oiled jatropha seed cake at various heating rates

Heating Rate, °C/min	***Reaction model, f(α)***	***Activation energy (E), kJ/mol***	***Frequency factor (A), min^{-1}***	***Correlation Coefficient (R^2), Dimensionless***
10	(1-α)	14.14	0.0004	0.9941
20	(1-α)	19.86	0.0037	0.9908
30	(1-α)	24.74	0.0178	0.9916

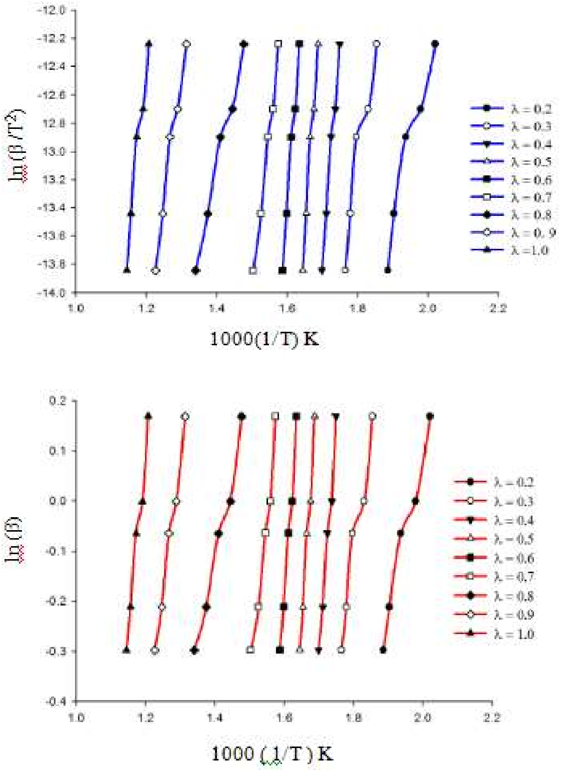

Fig. 3 Regression lines for finding the activation energy by (A) KAS method (B) OFW method

4. CONCLUSION

The physicochemical characteristics and the thermal behavior of the de-oiled jatropha seed cakes (DJSC) have been studied at three different heating rates of 10, 20 and 30°C/min. The activation energies of DJSC at these heating rates were found to be as 14.14 kJ/mol, 19.86 kJ/mol and 24.74 kJ/mol respectively. The low moisture (7.70%), ash content (2.30%) and high volatile matter (65%) suggest DJSC as a promising biomass candidate for pyrolysis to produce liquid biofuels. The kinetic analysis provides information on activation energy and explains the thermal degradation nature of thermochemical conversion of energy could assist in optimizing the pyrolysis regimes in the design of conversion systems and contributes to the advancement in co-gasification technology.

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