Evaluation of the Pyrolysis and Gasification Kinetics of Tropical Wood Biomass

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Two tropical biomass species, teak *(Tectona grandis)* and obobo (*Guarea thompsonii*), were obtained in the form of sawmill waste from Nigeria and evaluated to determine their potential for gasification. Pyrolysis and gasification kinetics of the samples were investigated using a thermogravimetric analyser (TGA) at temperatures of 900 ^{o}C and 1,000 ^{o}C. Four iso-conversional methods, one peak temperature method, and two model-fitting methods were employed to determine the kinetic parameters, *i.e.* the apparent activation energy E_a, and pre-exponential factor A. Values of the gasification kinetic rate constant K were determined using two gas-solid reaction models: the volumetric reaction model (VRM) and the shrinking core model (SCM). The values obtained for all three kinetic parameters showed good agreement with values derived for samples of non-tropical wood.

Keywords: Pyrolysis; Gasification; Kinetic parameters; Tropical biomass

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INTRODUCTION

Renewable energy has been gaining tremendous attention from many policy makers and scientists. The increasing cost of crude oil, coupled with the current financial crisis and overall downturn in world economy, has prompted governments and citizens everywhere to invest in improving technologies that enable faster breakthroughs. Among other renewable materials used as fuels for producing energy, biomass materials are proving to be more attractive due to their high availability, low cost, and recent development of technologies facilitating their use with low levels of emissions into the environment.

Materials such as sawdust, chips, pellets, off-cuts, wood barks, slabs, *etc*. are produced during wood processing activities. In third world countries, the management of these wastes tends to be grossly inadequate or simply non-existent. The most common methods of disposal include making stacks at the mills, open-air burning, and dumping close to waterways. These practices have undesirable and dangerous consequences that include: the aesthetic values of both the wood resources and the environment are reduced significantly; airborne particulates impair the air quality in the immediate vicinity and thereby constitute a health hazard; CO_2, NOx, and smoke are released, all of which are very dangerous to human health. Utilizing these biomass wastes as an energy source (*i.e.* fuel) puts these residues to good use in the form of energy materials. Past studies have been based on the thermal analysis of non-tropical wood biomass (such as the *poplar* used by Slopiecka *et al.* 2011). The assumed difference in the physical and chemical properties of the biomass samples as a result of different weather and soil conditions in the two regions makes it important to evaluate the thermal behavior of the tropical counterpart. The potential use of the tropical biomass for energy recovery can be enhanced by making use of the outcomes of such study. The set of wood samples considered in the present study is tropical. It is estimated that about 30,064,000 m^3 of wood waste is generated annually from different sawmills and other wood industries in Nigeria (Babayemi and Dauda 2010).

Basic technologies that convert biomass into bio-energy are bio-chemical, thermo-chemical, and physico-chemical, all of which involve a chemical transformation of biomass materials. Each kind of conversion has its own form of output (Huang *et al*. 2011). In this case, in which waste wood is to be used as the feedstock, the thermo-chemical method is preferred because it ensures that the entire biomass is converted into gases (Syngas) and then synthesized into the desired chemicals or used directly as fuels for the production of power. The different pathways involved in thermo-chemical conversion are (a) combustion, (b) pyrolysis, (c) gasification, and (d) liquefaction. The thermal option is chosen for fuel production from biomass based on the recalcitrant nature of the materials (Quaak *et al*. 1999) and also because, during energy conversions, biomass energy plants have a lesser degree of impact on the environment than fossil fuel plants.

The determination of the kinetic parameters, namely apparent activation energy E_a, pre-exponential factor A, and kinetic rate constant K, is very important for the design of the reactor, as it is vital that an optimal conversion is achieved. The data obtained from the thermal analysis is fed into kinetic models which employ a rate law that obeys the fundamental Arrhenius rate expression (White *et al*. 2011). The nucleation, geometrical contraction, diffusion, and reaction order are key aspects of different reaction mechanisms forming the basis for each kinetic approach. Model-free and model-fitting approaches are the two basic kinetic methods used to derive the kinetic parameters for both the isothermal and non-isothermal data. This study also employs an integral approach to the rate law obtained, as represented by the Coats-Redfern and Kissinger methods.

The objective of the present work is to evaluate the pyrolysis and gasification, employing a number of mathematically-derived models and methods with use of two types of samples from tropical biomass with differences in physical properties such as density and colour.

EXPERIMENTAL

Materials and Methodology

Samples of obobo (*Guarea thompsonii*) and teak (*Tectona grandis*) were collected from sawmills in Nigeria. A particle size of 0.20 mm was used in the experimental runs. The energy content of these materials depends greatly on their chemical compositions. The proximate and ultimate analyses of the two samples as performed by BELAB AB are shown in Table 1.

The thermographic experiments were performed using a TGA device developed by Rubotherm GmbH (Dyntherm HP). This consists of a magnetic suspension balance and automated gas-dosing system. The TGA instrument is provided with a wide range of operating conditions for temperature and pressure. The gas-dosing system is connected to the gas cylinders on one side and the magnetic-suspension balance on the other.

Table 1. Proximate and Ultimate Analyses for Samples of Obobo and Teak

Local name	Botanical name	Moisture % (105 °C)	Ash %ts (550 °C)	C %ts (dry)	H %ts (dry)	N %ts (dry)	S %ts (dry)
Teak	*Tectona grandis*	7.7	1.0	51.2	6.2	0.19	0.012
Obobo	*Guarea thompsonii*	6.6	5.3	48.3	5.7	0.34	0.035

Abbrev. ts=total solid, C=carbon, H=hydrogen, N=nitrogen, S=sulphur

The higher heating values (HHV) of the samples were measured with an IKA C 200 Bomb calorimeter according to ASTM D 240 and ASTM D 5865 standards.

Experimental Procedure

The calorific value was determined by weighing approximately 0.5 g of the material in a crucible, attaching it to the holder along with cotton thread (used to ignite the sample), and placing it inside the bomb vessel filled with pure oxygen at a pressure of approximately 30 bar. The vessel was then placed inside the calorimeter before being ignited. In this study, each experiment was repeated twice.

In the pyrolysis-gasification reaction runs, approximately 0.165 g of finely-ground sample was put in a ceramic crucible and, prior to pyrolysis, the already air-dried sample was dried further for an hour at a temperature of 105 °C in the TGA to a constant mass. The dried sample was subjected to pyrolysis at a temperature of 900 °C in an inert atmosphere of 100 mL/min nitrogen gas. A purge gas, composed of the N_2 gas and 100 mL/min of argon (Ar), was used to remove the volatiles that were generated. Once the pyrolysis temperature (900 °C) was attained, the sample was left in the same condition for an hour in order to ensure complete pyrolysis. The procedure was followed for all the heating rates (2, 5, 8, 12, 15, and 20 °C/min) and for both samples.

The char obtained from pyrolysis was subjected to isothermal gasification, where CO_2 was the gasifying agent at a temperature of 1,000 °C. The same 100 mL/min of Ar was used as the purge gas. The concentration of N_2 was varied with respect to the concentration of CO_2 so that a total of 100 mL/min of this combination was used, *e.g.* a combination of 70 mL/min of CO_2 and 30 mL/min of N_2 (totaling 100 mL/min) were used for both obobo and teak samples. The sample mass was kept in the gasification zone for about 2.5 h to ensure complete conversion of the char.

Procedure for Determining the Kinetic Parameters

The following expression can be derived by combining the solid-state reaction kinetic equation with the Arrhenius equation:

$$\frac{d\alpha}{dt} = A\,exp\left(-\frac{E_a}{RT}\right).f(\alpha) \qquad (1)$$

where $f(\alpha)$ is a conversion function that represents the reaction model used and also the controlling reaction mechanism, A is the exponential factor, E_a is the apparent activation energy, T is the temperature, and R is the molar gas constant.

For non-isothermal TGA experiments at linear heating rate $\beta = \frac{dT}{dt}$, Eq. 1 can be written as:

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right).exp\left(-\frac{E_a}{RT}\right).f(\alpha) \tag{2}$$

The fraction of materials consumed is as expressed in Eq. 2. Using a set of experimental tests at different heating rates to analyse the pyrolysis kinetics, E_a and A can be calculated. The various approaches employed include model-free and model-fitting methods, and a method based on peak temperatures.

Model-Free Methods

Model-free methods are also referred to as iso-conversional methods (Brown 2001). In iso-conversional methods, it is assumed that the reaction model $f(\alpha)$ in the rate Equation 1 is not dependent on either the temperature or heating rate (Vyazovkin and Wight 1999). In these methods, apparent activation energy can be calculated without any knowledge of the reaction model $f(\alpha)$ (Budrugeac and Segal 2004).

The Flynn-Wall-Ozawa (FWO) Method

In this method, it is assumed that the apparent activation energy is constant throughout the reaction (White *et al.* 2011). Plotting a graph of log β versus $\frac{1}{T_\alpha}$ at different heating rates gives a straight line with a slope equal to -0.4567 $\frac{E_a}{RT_\alpha}$, and a $\log A$ value can be calculated from its intercept. The governing equation is,

$$log\,\beta = log\left(\frac{AE_a}{R\,g(\alpha)}\right) - 2.315 - 0.4567\,\frac{E_a}{RT_\alpha} \tag{3}$$

where $g(\alpha)$ is constant at a given value of conversion.

The Kissinger–Akahira –Sunose Method (KAS)

Plotting a graph of $ln\left(\frac{\beta}{T_\alpha^2}\right)$ versus $\frac{1}{T_\alpha}$ gives a straight line, and the apparent activation energy can be calculated from its slope (White *et al*. 2011). The governing equation is:

$$ln\left(\frac{\beta}{T_\alpha^2}\right) = \ln\left(\frac{AR}{E_a g(\alpha)}\right) - \frac{E_a}{RT_\alpha} \tag{4}$$

The Friedman Method

Applying a logarithm to both sides of the non-isothermal rate equation gives a new Eq. (5):

$$ln\left[\beta\,\left(\frac{d\alpha}{dt}\right)\right] = ln\,A + n\,ln(1-\alpha) - \frac{E_a}{RT_\alpha} \tag{5}$$

A graph of $ln\left(\frac{d\alpha}{dt}\right)$ *versus* $\frac{1}{T_\alpha}$ yields a straight line, and the slope of which is equal to $\frac{-E_a}{R}$.

The Li – Tang Method

Initially, two different graphs are plotted: one is $\frac{1}{T}$ versus α and the other is $\frac{d\alpha}{dt}$ versus α. These two plots are then integrated numerically to fix the values of α. This process is carried out at different heating rates,

$$\int_0^\alpha ln\left(\frac{d\alpha}{dt}\right)\, d\alpha = -\frac{E}{R}\int_0^\alpha \frac{d\alpha}{T} + G(\alpha) \tag{6}$$

where $G(\alpha) = \alpha\, ln\, A + \int_0^\alpha ln\, f(\alpha) d\alpha$

The graph of $\int_0^\alpha ln\left(\frac{d\alpha}{dt}\right)\, d\alpha$ versus $\int_0^\alpha \left(\frac{1}{T}\right) d\alpha$ gives a straight line with a slope equal to $-\frac{E}{R}$.

Methods Based on Peak Temperature

The maximum reaction rate, according to Kissinger's assumption, coincides with the peak of the differential thermal analysis (DTA) curve (Brown and Gallagher 2003). Methods based upon this assumption are commonly known as "peak temperature methods".

The Kissinger Method

The general rate equation is transformed into:

$$ln\frac{\beta}{T_m^2} = ln\frac{AR}{E_a} + ln\left[n\,(1-\alpha)_m{}^{n-1}\right] - \frac{E}{RT_m} \tag{7}$$

where '*m'* is the maximum reaction rate. The apparent activation energy from the slope of a graph of $ln\frac{\beta}{T_m^2}$ versus $\frac{1}{T_m}$ at different heating rates can be obtained.

Model-Fitting Methods

Model fitting is the process of evaluating kinetic parameters by assuming a reaction mechanism that represents the decomposition rate. Based on the results of an ICTAC kinetic study, it can be inferred that, by fitting the data at different heating rates, reliable kinetic parameters can be obtained just as is the case in model-free iso-conversional methods (Vyazovkin *et al*. 2011). In both of the methods used below, $g(\alpha)$ represents the integral function of the reaction mechanism and is determined from an algebraic expression of $f(\alpha)$.

The Coats & Redfern Method

The Coats & Redfern method uses an integral form of equation to represent the non-isothermal rate equation (Khawam and Flanagan 2006). The equation for this method is of the form:

$$ln\left(\frac{g(\alpha)}{T^2}\right) = ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT} \tag{8}$$

Plotting a graph between $ln\left(\frac{g(\alpha)}{T^2}\right)$ and $\frac{1}{T}$ gives a straight line; the values of '-E_a' and 'A' can be determined by its slope and intercept, respectively (Ebrahimi-Kahrizsangi and Abbasi 2008).

The Kennedy and Clark Method

The governing equation is:

$$ln\left[\frac{\beta\, g(\alpha)}{(T-T_0)}\right] = ln\, A - \frac{E_a}{RT} \tag{9}$$

Plotting a graph between $ln\left[\frac{\beta\, g(\alpha)}{(T-T_0)}\right]$ and $\frac{1}{T}$ gives a straight line, the slope of which yields the values '-E_a' and 'A'.

Gas-Solid Reaction Models

The Shrinking Core Model (SCM)

The shrinking core model follows the general assumption that the reaction occurs initially at the external surface of the char and then gradually proceeds inwards (Karmakar and Datta 2011). In SCM, porosity is constant and the particle diameter decreases (Bell *et al*. 2010). Assuming that the particle is spherical in shape, the reaction rate can be expressed as:

$$dx/dt\ = k_{SCM}\,(1{-}\propto)^{2/3} \tag{10}$$

The Volume Reaction Model (VRM)

The VRM assumes that reactions are homogeneous throughout the particle and that the surface area of the reaction decreases with conversion (Karmakar and Datta, 2011). The rate equation can be described by:

$$dx/dt\ = k_{VRM}\,(1{-}\propto) \tag{11}$$

RESULTS AND DISCUSSION

Calorific Value

The higher heating values (HHV) found in the experiments were 18 kJ/kg for obobo and 19 kJ/kg for teak.

Thermogravimetric Analysis (TGA) Runs

TGA experimental data can be represented by different graphical methods. One way is to use weight loss curves, plotting weight loss on the ordinate and temperature (or time) on the abscissa. The TG curves show that the temperature interval for the maximum loss of material is different for both of the materials and for different heating rates. Only 2, 8, and 20 °C/min heating rates are represented in the relevant plots in order to ensure a clear view of the trend between the various heating rates used. The mass loss of the dried samples during pyrolysis at different heating rates can be observed in Figs. 1 and 2 for teak and obobo, respectively. The temperature intervals in the main pyrolysis zone are presented in Table 2 for both samples.

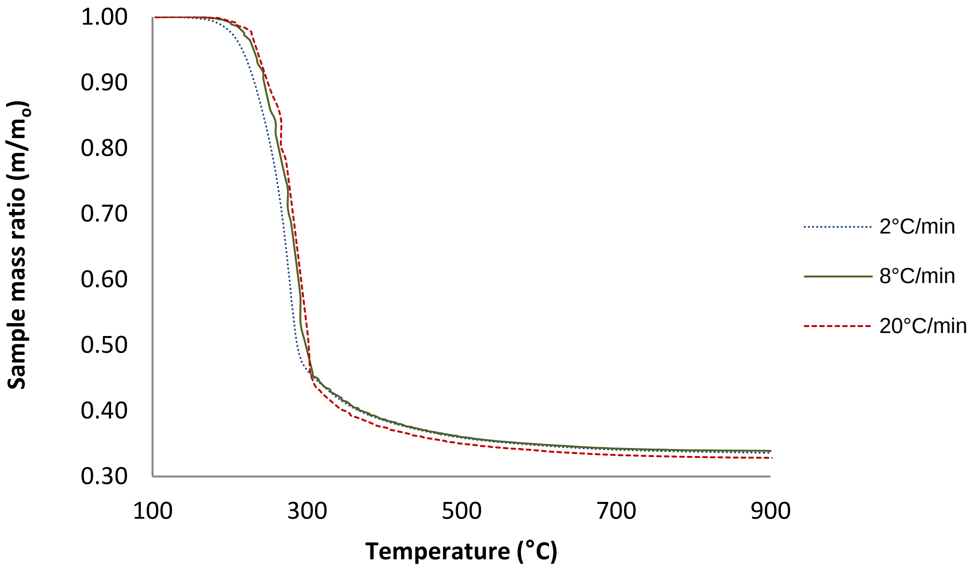

Fig. 1. Mass ratio of remaining material (teak) at different heating rates

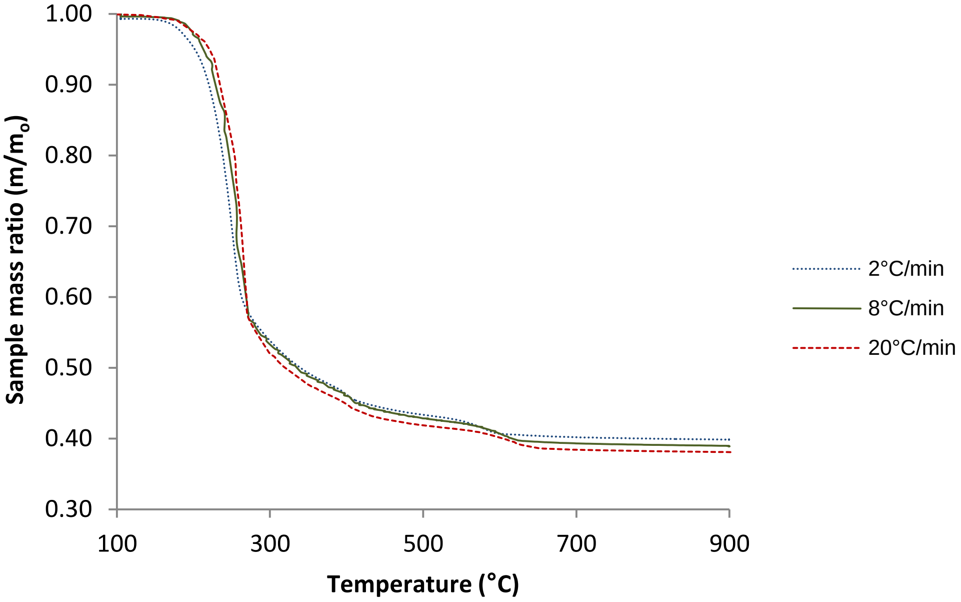

Fig. 2. Mass ratio of remaining material (obobo) at different heating rates

Differential thermogravimetry (DTG) curves, known as "derivative plots", represent the rate of weight loss as a function of time (or temperature). They are useful for resolving overlapping processes and evaluating kinetics. Moreover, it is possible to obtain the peak temperature for the decomposition process from these curves. Figures 3 and 4 represent the DTG curves for teak and obobo respectively, at different heating rates.

Table 2. Pyrolysis Temperature Range

Heating Rate (°C/min)	Main Pyrolysis Temperature Range (°C)	
	Teak	Obobo
2	192 - 301	165 - 279
5	190 - 312	180 - 286
8	201 - 314	186 - 288
12	195 - 327	197 - 288
15	217 - 331	198 - 295
20	209 - 355	178 - 298

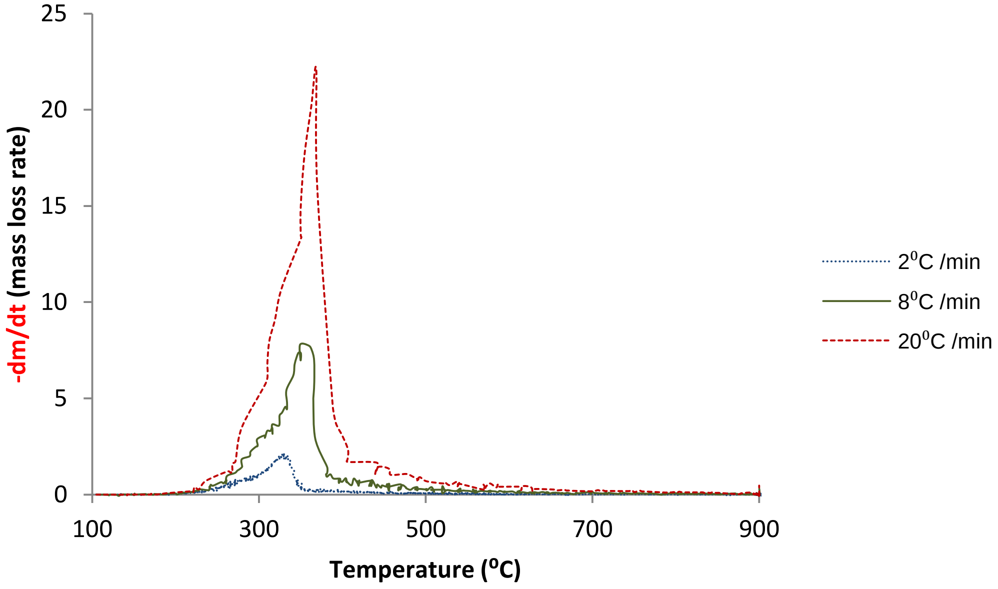

Fig. 3. DTG curve for teak

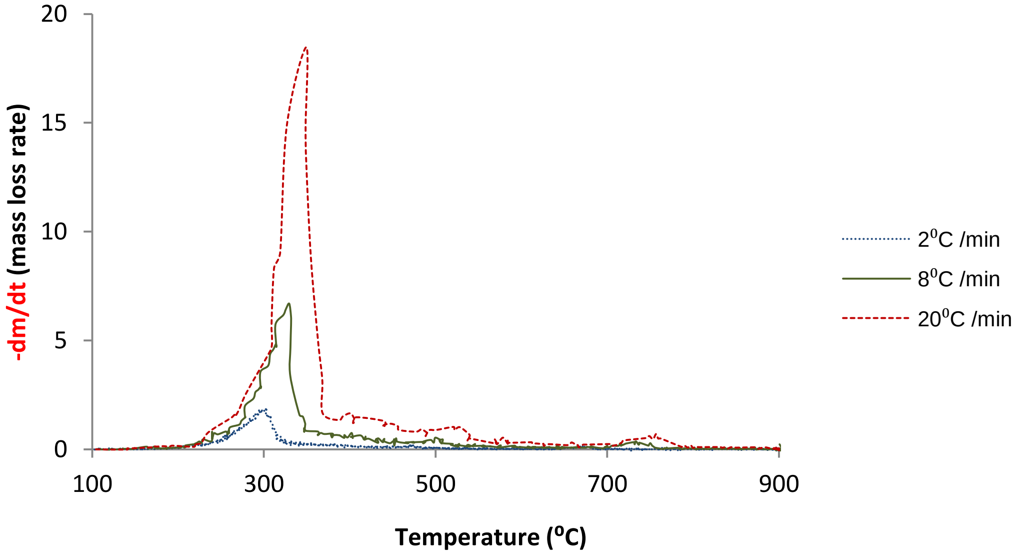

Fig. 4. DTG curve for obobo

The shoulders in the DTG curves represent the decomposition of hemicellulose, cellulose, and lignin according to different analyses of various biomass materials made by many researchers. The low temperature peak on the left hand side represents cellulose degradation and the flat tail on the right side represents the degradation of lignin material (White *et al*. 2011).

Determination of the Kinetic Parameters of Pyrolysis

A comprehensive graphical representation of various E_a values plotted against α derived for all the four iso-conversional (model-free) methods for the teak samples is shown in Fig. 5.

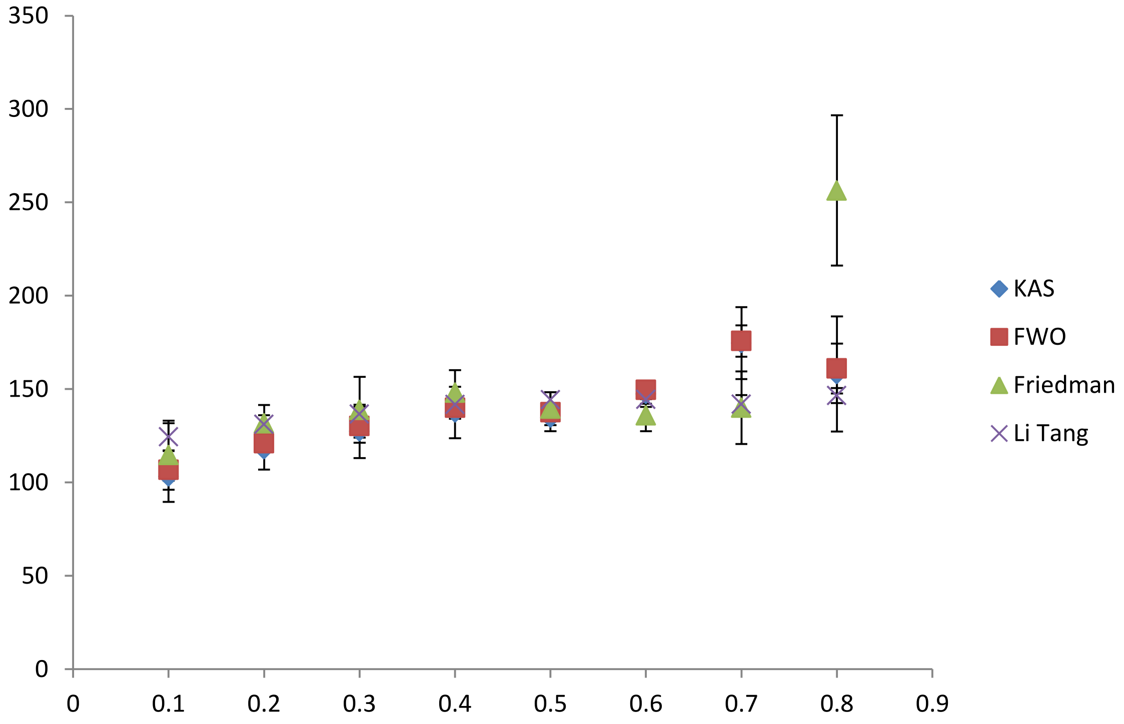

Fig. 5. Plot of E_a versus α for teak from model-free methods

At higher conversions above $\alpha = 0.6$, a comparison of the results obtained in the above iso-conversional methods for teak led to the conclusion that the Li-Tang approach gave a very low apparent activation energy, whereas the FWO and KAS methods yielded much higher values. The Friedman method gave high apparent activation energy values for the same teak material, which suggests that the materials have different kinds of reaction mechanisms at the end of the decomposition process. The results also showed E_a values in the range of 120 to 200 kJ/mol, 115-120 kJ/mol, 130-290 kJ/mol and 130-150 kJ/mol for the FWO, KAS, Friedman and Li-Tang methods, respectively. In contrast to the iso-conversional methods, the Kissinger method generated only one set of E_a values. The E_a values calculated based on the Kissinger were 147 and 179 kJ/mol for obobo and teak, respectively.

It is therefore evident from the model-free results that different activation energies at different conversions show that the apparent activation energy depends on the extent of conversion, α, and that the decomposition process is composed of multiple reactions with a complex reaction mechanism (Slopiecka *et al*. 2011).

Analysing the results of the model-fitting methods, it may generally be assumed that a suitable reaction mechanism can be identified and characterized based on the coefficient of determination (R^2) values (Cadenato *et al*. 2007). In this case, Cadenato *et al*. (2007) also suggested comparing the activation energies calculated from different models with the average apparent activation energy obtained from iso-conversional methods. Following these recommendation, both the Coats - Redfern and Kennedy-Clark methods could be modeled with a third-order reaction mechanism for both samples. Among the available reaction models, the results from different mechanisms including the Reaction order, Avrami-Erofeev, One-dimensional diffusion, and Contracting geometry are as shown in Table 3.

Table 3. Reaction Model Mechanism Results for Teak and Obobo (Model-fitting Methods)

Model	Teak			Obobo		
	Aver. E_a (kJ/mol)	Aver. A (min^{-1})	R^2	Aver. E_a (kJ/mol)	Aver. A (min^{-1})	R^2
Reaction order n=3	137.12	3.20E+12	0.9584	149.48	6.37E+16	0.9762
Avrami-Erofeev n=3	22.43	5.10E+00	0.9730	22.69	12.00E+00	0.9579
Diffusional 1D	142.87	7.86E+11	0.9880	149.99	7.82E+13	0.9682
Contracting geometry	79.23	7.03E+06	0.9874	79.77	1.60E+08	0.9779

From the results above, the activation energies for teak with third order (n=3) of reaction order model and 1D of diffusional model are 137 kJ/mol and 143 kJ/mol respectively, which is in close agreement with the average E_a value 155 kJ/mol obtained from iso-conversional methods. Similarly, the activation energies for obobo with third order (n=3) of reaction order model and 1D of diffusional model are 150 kJ/mol and 150 kJ/mol, respectively, which is almost the same as the average 'E_a' value 140 kJ/mol obtained from iso-conversional methods. On the other hand, the Avrami-Erofeev model is showing good coefficients of determination (R^2), but the activation energies are at very low range and not matching with the 'E_a' values from iso-conversional methods.

Gasification Kinetics

The gasification values of the kinetic rate constant K were determined using two gas-solid reaction models: the volumetric reaction model (VRM) and the shrinking core model (SCM). In the former, the calculated rate constant values were 0.1784 ± 0.009 and 0.2285 ± 0.0180 min^{-1} for teak and obobo, respectively; in the latter they were around 0.1333 ± 0.0236 and 0.1652 ± 0.0340 min^{-1} for teak and obobo, respectively.

CONCLUSIONS

1. The model-free methods gave results that showed good agreement with the values reported in the literature for non-tropical species that are already in use for energy conversions, thereby indicating that the tropical samples of obobo and teak are promising alternatives as fuel from which energy can be recovered.
2. The Kissinger method gave results very similar to those obtained using the model-free methods. It can be regarded as a faster approach for determining the kinetic parameters, as it generates only one set of E_a and A values.
3. Considering the results in general, it is clear that obobo has a level of higher reactivity than teak.
4. The overall study marks a step toward converting this abundant tropical wood waste into energy, since reactors meant for their conversion are designed and configured based on the typical values derived for the three kinetic parameters (E_a, A, and K) in question.

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