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THERMAL BEHAVIOUR KINETIC MODELING OF CAPSICUM ANNUUM WASTE BIOMASS USING AN ISO-CONVERSION METHOD

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ABSTRACT

In the present study, the pyrolysis behaviour of Capsicum Annuum stem Waste (CAW) was studied applying thermogravimetric analysis to evaluate the intrinsic kinetic parameters to develop a pyrolysis reactor for utilizing CAW. The thermal decomposition of CAW was achieved between 373 – 1173 K under inert conditions at different heating rates of 10, 20, and 30 K min^{-1}. Model-free kinetic methods like Kissinger-Akahira-Sunose (KAS), Ozawa Flynn Wall (OFW) and Coats Redfern methods were applied to work out the kinetic parameters. To identify the utility of CAW and its biochar, physio-chemical characteristics such as proximate and ultimate analysis, scanning electron microscopy, and Fourier Transform Infrared analysis are reported.

Keywords: *Capsicum Annuum, Thermogravimetric Analysis, Kissinger-Akahira-Sunose (KAS), Ozawa Flynn Wall (OFW), Coats Redfern Method.*

INTRODUCTION

Biomass is exemplified as bio-debris coming from all kinds of vegetation or plantation. Various biomass resources are available in India in different forms. The biomass derivatives (e.g., methane, ethanol, char, and bio-oil) and the biomass itself releases CO_2 when applied as a fuel but during its growth while photosynthetic process it absorbs back [1,7]. Nevertheless, biomass shared up to 14% of global primary energy need, it is not unconditionally utilized under its minor adaptation to energy [6,28]. In India, Capsicum Annuum (CA) is widely cultivated with an annual production of around 1.2 million tonnes, which contributes to about 27.24 % of the total spice cultivation area and 25.65% of spice production in India [13,24]. According to Ministry of Agriculture (Department of Agriculture & Cooperation), capsicum annuum production in India is 7.5 lakhs hectares, which leads to the generation of 52.5 lakhs tonnes of waste.

Pyrolysis is an assuring technology for biochar and bio-oil production. Bio-oil can be enhanced to light hydrocarbons with fewer aromatics and sulfur correlated to petroleum-based fuels. Biochar is a carbon-immense product obtained from the pyrolysis of sustainable raw materials and is widely used as a soil amendment in agriculture [22]. By the thermal decomposition of biomass wastes, biochar is produced [10]. Expertise on the kinetics of lignocellulosic decomposition is necessary to design various pyrolysis units. Even at high temperatures during pyrolysis there is no reaction with, water, oxygen and other reagents. Pyrolysis is the harbinger for all thermochemical methods (11,7). The main constituents of biomass are cellulose, hemicelluloses, and lignin by weight percent and these proportions may vary depending on the type of biomass [5, 21]. Previous studies have explored the thermal behavior of various biomass materials and their degradation temperatures [16, 19]. Before the conversion of biomass to fuel, its kinetic analysis should be performed which provides the information related to the optimization of process parameters and pyrolysis reactors designing [26,4,7]. Due to differing composition, Individual feedstocks exhibit distinct thermal behavior profiles. Previous studies[2,23,16,27] have reported the thermal behaviour of coir pith, bagasse, casuarinas leaves and groundnut shell which shows contrasting individual deterioration temperatures. Besides, it caters to solving mathematical modeling. Kinetic behavioral variables include an order of reaction (n), frequency factor (A) and activation energy (Ea) which can be regulated by using thermogravimetric (TGA) analysis. The first attempt to analyze the kinetic behavior of Capsicum Annuum Waste (CAW) was made in this study, in spite of many other reports on

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other materials. The present study aims to know about the physicochemical characteristics and heat deterioration behavior (kinetic analysis) of CAW at heating rates of 10, 20 and 30 K min^{-1} whose data is not available in the past to validate it as a source for thermo-chemical method.

TGA studies can be accomplished in both isothermal and non-isothermal conditions. Non-isothermal experiments are preferred over the isothermal experiments due to its less error. Non-isothermal data is widely used for determining kinetic parameters as they can be fitted to different methods. These methods are more predictable and rapid. There are definite methods accessible for interpreting the TGA report. Three model-free methods such as Kissinger-Akahira-Sunose (KAS), Ozawa Flynn Wall (OFW) and Coats Redfern method was applied to work out the kinetic parameters. Since this method doesn’t require any assumption, they provide accurate values for activation energy. The data obtained from TGA analysis can be interpreted to calculate kinetic parameters of CAW.

MATERIALS AND METHODS

Materials

CAW were gathered from the nearby fields in the Guntur region of Andhra Pradesh. CAW was thoroughly washed with distilled water, sun-dried, crushed into the desired size of less than 1 mm pieces and sealed in an airtight container to avoid moisture absorption.

Methods

Proximate and ultimate analysis

Proximate analysis for CAW was determined according to ASTM D 1762-84 standard method. Moisture content, volatile matter, ash content and fixed carbon of both biomass and Biochar were investigated. The ultimate analysis was done using Elemental (C, H, N, S) Analyser (True spec micro CHNS 209-190, LECO Corporation, USA.

TG/DTG/DSC Analysis

The thermal stability of CAW of pyrolysis reaction was analysed in triplicate using a simultaneous thermal analyser (STA 7200, Hitachi HTG, Japan) under an inert atmosphere. CAW sample of 8 mg was taken in an aluminum crucible with a nitrogen flow rate at 30 mL min^{-1} within 375 to 1170 K. Loss in the weight of biomass with temperature and time were noted. Differential Scanning Calorimetry (DSC) of CAW biomass was carried out using EX STAR DSC 7020, Hitachi HTG, Japan at three distinct heating rates of 10, 20 and 30 K min^{-1}. In this study, the energy flow of CAW was reported against temperature.

SEM Analysis

The structural surface of the CAW was examined using a scanning electron microscopy (HITACHI S-3000 N made in Germany) by placing the CAW and CAW Biochar samples on the aluminum holder using carbon tape whose image is scanned with an electron beam. Discharged electrons from the sample were gathered and rearranged at various amplifications to obtain the image of the sample.

FTIR Analysis

Spectra of all the CAW and CAW Biochar samples was captured using Fourier Transform Infrared Spectroscopy (Cary 630 FTIR with diamond ATR, Agilent Technologies, USA) which contains a detector, beam source, a ceramic source, and a beam splitter. The ATR sampling device applies a Dura Sample IR internal reflection accessory coated with diamond (Smiths Detection, Danbury, CT), and through the stainless steel rod, continuous pressure was employed along with an electronic load display.

Kinetic methods

Coats Redfern method ,Kissinger–Akahira–Sunose (KAS) and Ozawa–Flynn–Wall (OFW) methods (Ceylan and Topçu) were used to calculate reaction model $f(\alpha)$, frequency factor (A) and activation energy (E). Isoconversional methods are preferred by researches for two reasons (a) model-free kinetics are sufficiently flexible to allow for a change in mechanism during a reaction, and (b) mass loss transfer limitations are reduced by the use of multiple heating rates.

Method 1:
Coats Redfern method:
In the pyrolysis reactor, the overall reaction mechanism of CAW is given by (Harrison)

$$Biomass\ (Solid) = Volatile(Gases + Tar) + Char(Solid\ residue) \tag{1}$$

In the present work, it was assumed that the conversion of CAW into CAW biochar is a single step process (Kumar et al.) and the rate of reaction (K) is given by the following equation

$$k = Ae^{-\left(\frac{E}{RT}\right)} \tag{2}$$

Where A=pre-exponential factor, k= Reaction rate constant, E =Activation energy (J mol^{-1} K^{-1}), R = Gas constant (8.314 J mol^{-1} K^{-1}) and T= Absolute temperature (K).

The rate equation for modifying CAW to volatile state is given as

$$\frac{d\alpha}{dt} = k\,f(\alpha) \tag{3}$$

Where α = rate of conversion
t= time
$f(\alpha)$ is the reaction model

Conversion (α) is defined as

$$\alpha = \frac{w_0 - w_t}{w_0 - w_f} \tag{4}$$

Where w_0 = Initial weight of CAW
w_t = Weight of CAW at a particular time
w_f = Final weight of the CAW

By combining equations (3) and (4), we get

$$\frac{d\alpha}{dt} = Ae^{-\left(\frac{E}{RT}\right)} f(\alpha) \tag{5}$$

heating rate is defined as

$$\text{Heating rate, } \beta = \frac{dT}{dt} = constant \tag{6}$$

$$dt = \frac{dT}{\beta} \tag{7}$$

Substituting dt from eq 7 in eq 5 and after integration, we get

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \int_0^{T} A\ \exp\left(\frac{-E}{RT}\right)\frac{dT}{\beta} = g(\alpha) \tag{8}$$

$$\frac{d\alpha}{dt} = \frac{A}{\beta}\exp^{\left(\frac{-E}{RT}\right)} f(\alpha) \tag{9}$$

Up on integration,

$$g(\alpha) = \frac{A}{\beta}\int_0^T \exp^{\left(\frac{E_a}{RT}\right)} dT \tag{10}$$

$$g(\alpha) = \frac{AE_a}{RT}\int_x^\infty \frac{\exp(-x)}{x^2} dx = \frac{AE_a}{RT} p(x) \tag{11}$$

Coats redfern method is the best approximation for the p(x) and utilizes the asymptotic series expansion for approximating the exponential integral in eq 11,giving

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E}\right)\left(1 - \frac{2RT}{E} - \frac{E}{RT}\right) \tag{12}$$

Individual kinetic models symbolizing reaction between the phases, random nucleation, Nuclei growth, chemical reaction, and diffusion models are used to examine TGA data [3, 20, 25]. The data obtained from the TGA analysis during the pyrolysis of CAW stalk was analyzed using fourteen kinetic models (Table 1) using coats- Redfern equation. The reaction model best suited is the one which has the highest regression coefficient for the graph between $\ln(g(\alpha)/T^2)$versus 1/T.

Table 1: Various kinetic models for solid-state reactions

Model	**Mechanism**	$f(\alpha)$	$g(\alpha)$
Chemical Reaction			
1	First-order	$1-\alpha$	$[-ln\,(1-\alpha)]$
2	Second-order	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
3	Third-order	$(1-\alpha)^3$	$[(1-\alpha)^{-2}-1]/2$
4	Nth order	$(1-\alpha)^n$	$[(1-\alpha)^{1-n}-1]/n-1$
Random nucleation and nuclei growth			
5	Two-dimensional	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-ln\,(1-\alpha)]^{1/2}$
6	Three-dimensional	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-ln\,(1-\alpha)]^{1/3}$
Limiting surface reaction between both phases			
7	One dimension	1	α
8	Two dimensions	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
9	Three dimensions	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
Diffusion			
10	One way transport	$1/2\alpha$	α^2
11	Two-way transport	$[-ln\,(1-\alpha)]^{-1}$	$\alpha+(1-\alpha)\ln(1-\alpha)$
12	Three-way transport	$(2/3)(1-\alpha)^{2/3}/[1-(1-\alpha)^{1/3}]$	$[1-(1-\alpha)^{1/3}]^2$
13	Ginstling-Brounshtein equation	$(2/3)(1-\alpha)^{1/3}/[1-(1-\alpha)^{1/3}]$	$1-2\alpha/3-(1-\alpha)^{2/3}$
14	Zhuravlev equation	$(2/3)(1-\alpha)^{5/3}/[1-(1-\alpha)^{1/3}]$	$[(1-\alpha)\text{^}((-1)\,/\,3)-1]^2$

Method 2:

Kissinger–Akahira–Sunose (KAS) method: The kinetic energy of the CAW stalk can be calculated by using the model-free iso-conversion method named Kissinger–Akahira–Sunose (*KAS*).

$$\frac{E}{RT} = C \tag{13}$$

$$dC = \frac{-E}{R} T^{-2}\, dT$$

As $T \to 0; C \to \infty \; and \; T \to T; C \to C$

On rearrangement eq 9 is transformed to

$$\ln \frac{\beta}{T^2} = \ln \frac{AR}{Eg(\alpha)} - \frac{E}{RT} \tag{14}$$

Thus a plot of $\ln \frac{\beta}{T^2} \frac{1}{T}$vs gives Activation energy and pre-exponential factor values.

Method 3:

*The Flynn-Wall-Ozawa (FWO) Method***:** This is one of the integral methods that can determine the activation energy which does not require the knowledge of reaction order.

Ozawa Flynn wall method is based on Doyle's approximation for eq 9

$$\log(\beta) = \log\left[\frac{(AE)}{Rg(\alpha)}\right] - 2.315 - 0.457\frac{E}{RT} \tag{15}$$

Thus a plot of $\ln \beta \frac{1}{T}$ vs gives activation energy and pre-exponential factor values.

Enthalpy (ΔH) values are calculated using Flynn-Wall-Ozawa (FWO) method by using the following equation

$$\Delta H = E - RT \tag{16}$$

RESULTS AND DISCUSSION

Proximate and ultimate analysis

Pyrolysis of CAW was performed using the TG-DTG analyzer and the product CAW Biochar was obtained at 1173 K. Proximate and ultimate analysis was done for CAW and CAW Biochar obtained through pyrolysis and the results were tabulated in Table 2.

From Table 2 it was clear that CAW has 3 % moisture ensuring to be the best feedstock for the pyrolysis process moreover it has a volatile matter of 80.23% and less ash content of 0.82% indicating higher ignition of the fuel. Ultimate analysis of CAW confirmed the higher amounts of carbon (40.53%) illustrating the feasibility of CAW as fuel and energy production. The release of S-N compounds all along the pyrolysis of CAW will be limited due to the existence of reduced amounts of nitrogen and sulfur.

Table 2: Proximate and Ultimate analysis of CAW and CAW Biochar

Component	**CAW**	**CAW Biochar 10 K min^{-1}**
Ultimate Analysis (wt. %)		
C	40.53	78.6
H	5.02	2.67
N	0.77	1.29
S	0.14	0.41
O	53.54	17.03
Proximate Analysis (wt. %)		
Ash	0.82	12.12
Volatile Matter	80.23	25.32
Fixed carbon	18.95	62.56
Moisture	3	-
Other Properties		
H/C	0.123	0.033
C/O	0.757	4.615

TG/DTG and DSC Analysis

The results of Wt Loss of the sample was reported against time (Figure 1). Heat disintegration behavior of CAW was studied at 10, 20 and 30 K min^{-1} heating rates. During the pyrolysis of CAW, initially, dehydration occurs for about 10 minutes up to 523 K where moisture and volatile matter were taken off thereby decomposition of cellulose, hemicellulose and lignin content takes place. The vigorous mass loss appears within 473 to 673 K from 10 to 20 minutes where cellulose and hemicellulose decompose.

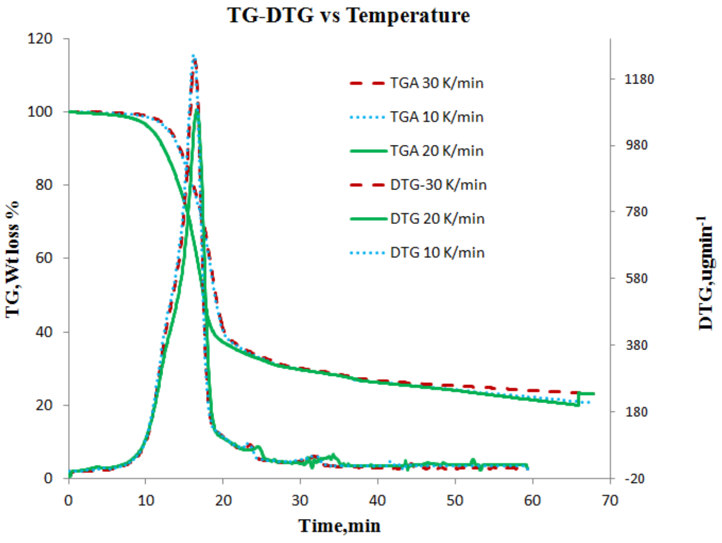

Figure 1. Thermogram of CAW at 10, 20 and 30 K min^{-1} heating rates

During 473 to 673 K of primary pyrolysis stage the aromatic compounds decomposed are only 2-methoxy phenols and 2,6 -dimethoxy phenols since aromatic methoxy groups are stable during this stage . But when the pyrolysis temperature increased above 673 K, secondary pyrolysis reactions takes place and guaiacols/syringols rapidly transition to catechols or pyrogallols and O - cresols along with phenols. Lignin content may not be completely degraded at 1173K. Similar trend was observed for all the heating rates employed.

Differential Scanning Calorimetric analysis:

Heat flow property of the CAW was studied using Differential Scanning Calorimetric analysis at individual heating rates of 10, 20 and 30 K min^{-1} (Figure 2). DSC curve depicts that the reaction pathway of CAW went from endothermic to the exothermic stage and also the appearance of the first peak below 373 K indicates endothermic evaporation of water molecules.

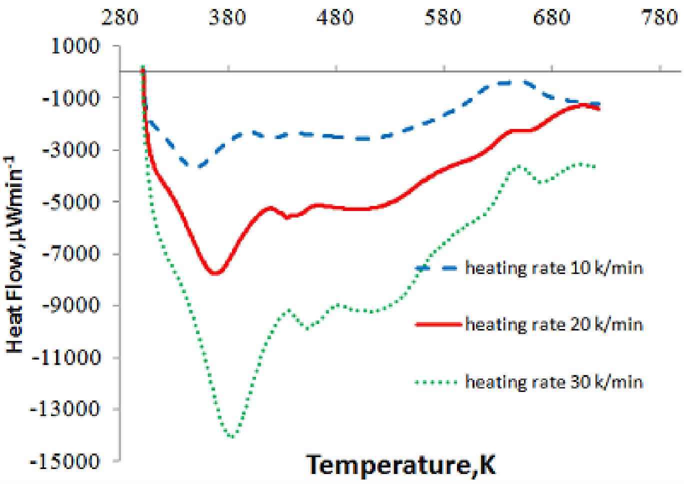

Figure 2: DSC analysis of CAW at heating rates of 10, 20 and 30 K min-1

The peaks observed above 423 K indicates decomposition of cellulose and hemicellulose compounds and a comparable trend was marked in the previous works [25].

Scanning Electron Microscope Analysis

The surface morphology changes from CAW to CAW Biochar were analyzed using a scanning electron microscope (SEM) and are presented in Figure 3 for CAW and CAW Biochar obtained through pyrolysis. It was observed that a good number of pore volumes are available in the case of CAW Biochar as compared to that of CAW resembling high surface areas for carbofuran adsorption.

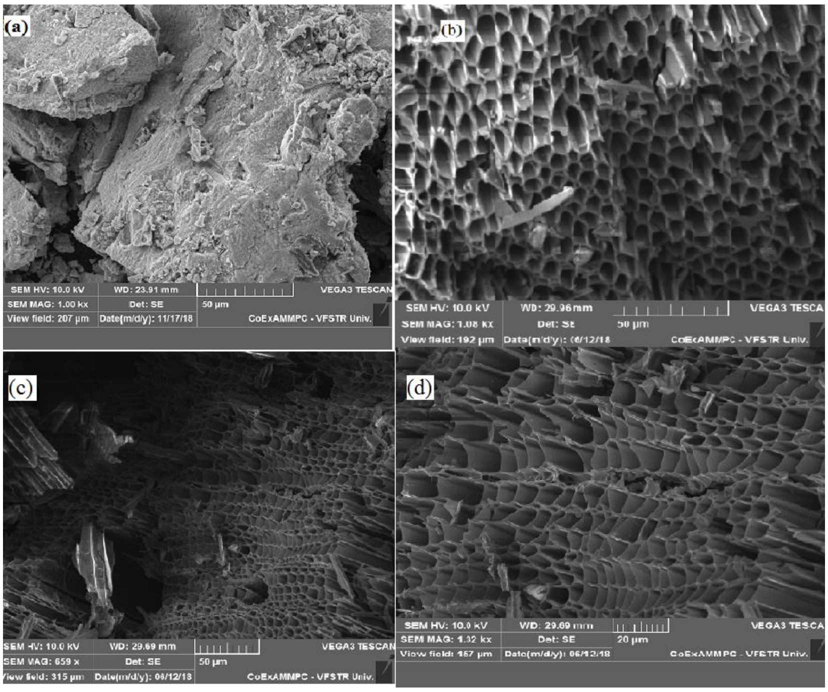

Figure 3: Surface morphology images of (a) CAW (b) CAW Biochar (300 °C) (c) CAW Biochar (700 °) (d)Carbofuran adsorbed biochar

FTIR analysis

FTIR analyses of the raw CAW and CAW Biochar have been investigated to identify the variation in the functional groups through spectral changes, which is displayed in Figure 4.

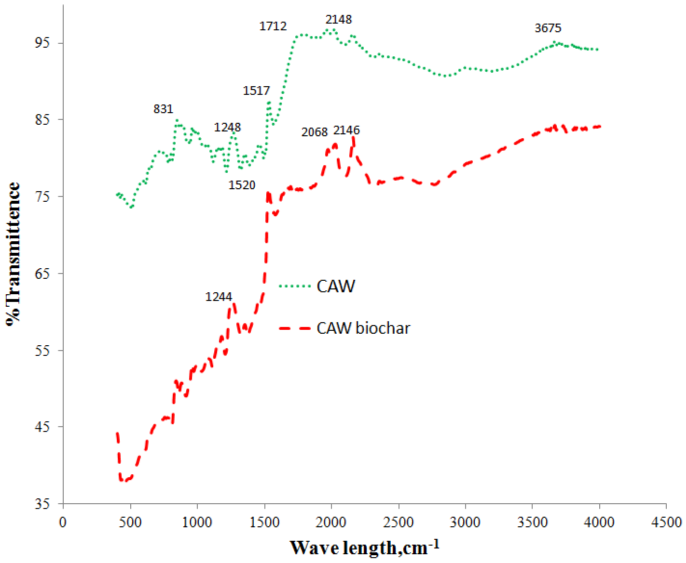

Figure 4: FTIR spectrum of (a) CAW (b) CAW Biochar

In CAW, the wavenumber observed between 800–1000 cm^{-1} indicates the medium C-O stretching vibration of carboxyl groups in the cell wall and there is a sudden drop in the transmittance from 87.04 to 82.86 cm^{-1} which represents the strong C-H bending. A peak around 1200 cm^{-1} indicates the presence of symmetrical stretch nitro compounds. The peaks close to 1500 cm^{-1} are accredited to C=C stretching vibration of aromatic rings [14]. A peak at 1200 cm^{-1} signifies the presence of aliphatic C-O-C and secondary alcohol, C-O stretch at around 1000 cm^{-1} group indicate the presence of hemicelluloses and cellulose in CAW and CAW Biochar. Broad peaks observed between 3500 – 3800 cm^{-1} for CAW decreased in the case of CAW Biochar, which indicates the desiccation of cellulose and ligneous constituents.

Kinetic parameter estimation:

Pyrolysis of CAW involves both heat and mass transfer phenomenon and the obtained data were analyzed using fourteen distinctive models (Table 1). From the results third –order reaction model with $(\alpha)=(1-\alpha)$^3 was observed to be the best correlation at three individual heating rates of 10, 20, 30 K min^{-1} (Figure 5).

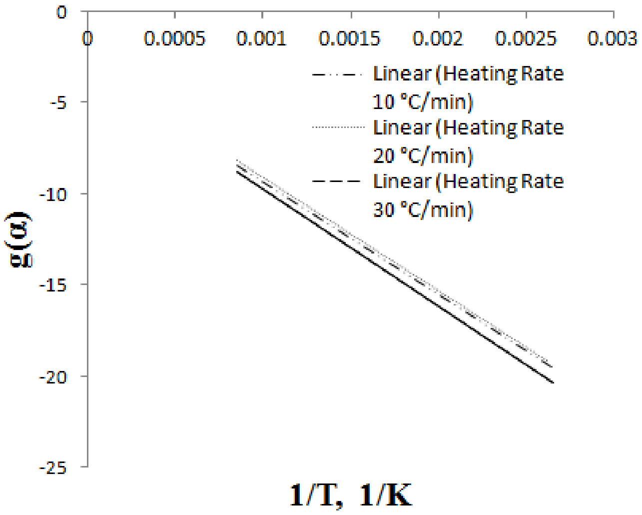

Figure 5: Coats Redfern method- Third-order reaction model

Kinetic triplet for CAW pyrolysis reaction from the Coats-Redfern method was given in Table: 3. Activation energy values are found to be 51.26, 51.63 and 53.60 KJ/mol and frequency factor values are found to be 2650, 7070 and 7480 min^{-1} at three heating rates of 10, 20 and 30 K min^{-1} respectively. Both the kinetic parameters, Activation energy, and frequency factor were increased with heating rate and the same trend is observed in the literature [15].

Table 3: Kinetic triplet for CAW pyrolysis using coats -Redfern method

Heating rate, K min^{-1}	**Reaction model, $f(\alpha)$**	**Activation energy, E, KJ mol^{-1}**	**Frequency factor, A, min^{-1}**	**Correlation coefficient, R^2**
10	$(1-\alpha)^3$	51.26	2.65x10^3	0.9639
20	$(1-\alpha)^3$	51.63	7.07x10^3	0.9511
30	$(1-\alpha)^3$	53.60	7.48x10^3	0.9465

The obtained TGA data were also analyzed using iso-conversion methods such as Kissinger–Akahira–Sunose (KAS) method and Flynn-Wall-Ozawa (FWO) method and the regression lines for different conversion values at three individual heating rates of 10, 20, 30 K min^{-1} are displayed in Figure 6a and 6b respectively. Activation energy and regression coefficient values obtained by both the methods are presented in table 4. Activation energy values from the KAS method range from 32.49 to 15.28 KJ/mol as the conversion values vary from 0.1 to 0.9 and that of Flynn-Wall-Ozawa (FWO) method varies from 69.76 to 45.07 KJ/mol. Enthalpy (ΔH) values are calculated using Flynn-Wall-Ozawa (FWO) method. Since there is a small difference between activation energies of the CAW at different conversion percentages, less amount of energy is sufficient for the thermal conversion of this CAW [18].

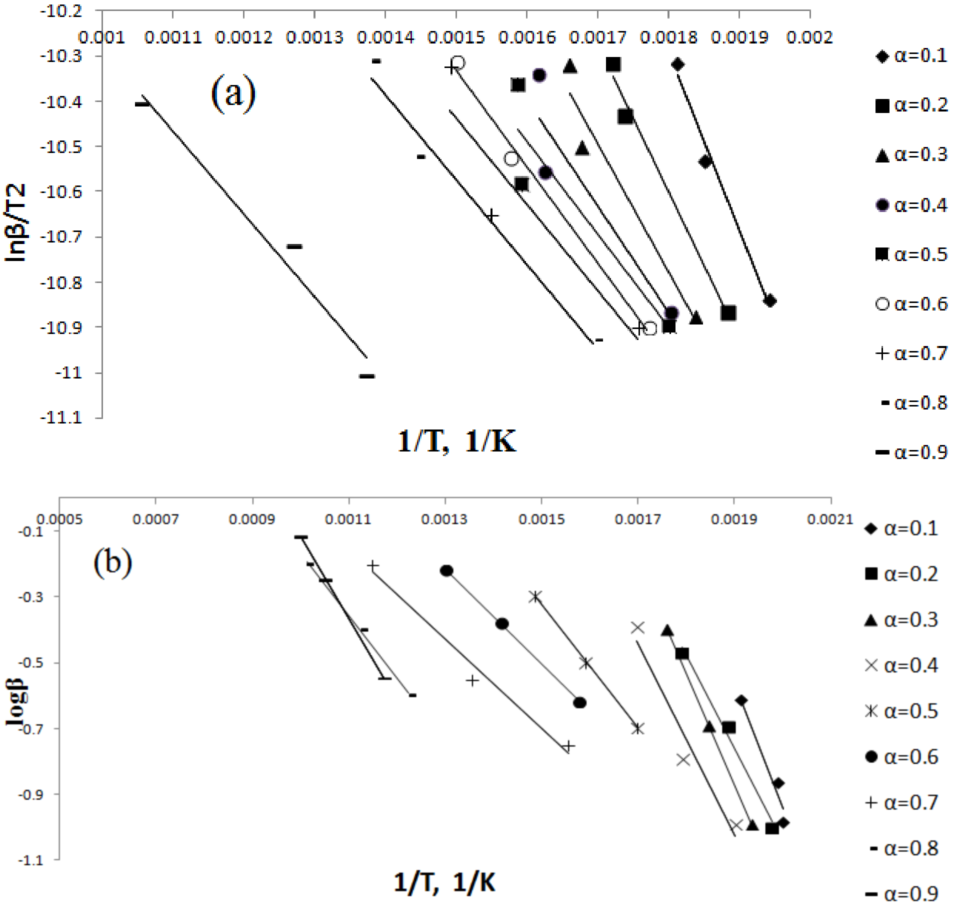

Figure 6: (a) Kissinger-Akahira-Sunose (KAS) method and (b) Flynn-Wall-Ozawa

Table 4: Arrhenius parameters and regression values from KAS and OFW methods

Conversion	**KAS method**		**OFW method**		
α	**E, KJ/mol**	R^2	**E, KJ/mol**	R^2	**ΔH, KJ/mol**
0.1	32.49	0.9836	69.76	0.9519	65.1678
0.2	26.89	0.9891	51.19	0.9886	46.3629
0.3	23.46	0.9424	61.04	0.9999	56.0348
0.4	19.32	0.8599	52.40	0.9468	47.2570
0.5	17.61	0.8511	33.86	0.9999	28.6160
0.6	16.90	0.9927	26.16	0.9997	20.8314
0.7	15.75	0.8453	24.66	0.9778	19.2242
0.8	15.48	0.9761	34.39	0.999	28.5156
0.9	15.28	0.9714	45.07	0.9998	37.2007

There is a decreasing trend in the activation energies using KAS method but in OFW method even though there is a small discrepancy in the decreasing trend, the activation energy decreased from 69.76 to 45.07 when the conversion increases from 0.1 to 0.9.With increasing conversions since at high temperatures, high conversions are attained and there is a need for fewer activation energies at these high temperatures. For large-scale design and operation of pyrolysis processes, the kinetic parameter values obtained from these model-free methods are favorable and these values tie technical parameters at predefined conditions, which in turn give the complete picture of the pyrolysis products.

CONCLUSION

This article is the first of its kind to study the thermogravimetric analysis for CAW at 10, 20 and 30 K min $^{-1}$ heating rates under inert N_2 atmosphere to examine the solid-state reaction kinetics of CAW pyrolysis and kinetic parameters. The methods Kissinger–Akahira–Sunose (KAS), Flynn-Wall-Ozawa (FWO) and Coats-Redfern were used and the experimental information acquired was well correlated for CAW pyrolysis reaction with third-order reaction model. Characteristic studies also depict that the CAW biochar has the number of pores that can have more applications as a soil conditioner, biosorbent, etc. Activation energy from Coats Redfern method was found to be 51.26, 51.63 and 53.60 kJ mol^{-1} and Arrhenius frequency factor was found to be 2650, 7070 and 7480 min^{-1} at three heating rates of 10, 20 and 30 K min^{-1} respectively. Average values of activation energies computed from KAS and OFW were found to be 20.35 and 44.28 kJ mol^{-1} respectively. The obtained kinetic report can be useful to the design and development of pyrolyzers. From the present study, it was also clear that CAW can be effectively used for energy generation.

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