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Fawzy, S., Osman Ahmed, A. O., Farrell, C., Al-Muhtaseb, A. H., Harrison, J., Sadeq Al-Fatesh, A., Fakeeha, A., & Rooney, D. (2022). Kinetic modelling for pyrolytic conversion of dedicated short rotation woody crop with predictions for isothermal, non-isothermal and stepwise heating regimes. *Applications in Energy and Combustion Science*, 9. <https://doi.org/10.1016/j.jaecs.2021.100048>

Published in:

Applications in Energy and Combustion Science

Document Version:

Publisher's PDF, also known as Version of record

Queen's University Belfast - Research Portal:

[Link to publication record in Queen's University Belfast Research Portal](#)

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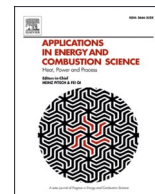
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Kinetic modelling for pyrolytic conversion of dedicated short rotation woody crop with predictions for isothermal, non-isothermal and stepwise heating regimes

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ARTICLE INFO

Keywords:

Thermo-chemical conversion

Biomass

Biochar

Computational modelling

Predictions

Kinetic modelling

ABSTRACT

Sesbania sesban, a promising short rotation woody crop, was first evaluated in order to assess its physicochemical attributes as a feedstock material in biochar manufacturing. Additionally, thermogravimetric analysis (TGA), performed at 0.5, 1, 4 and 8 °C.min⁻¹, was utilised to conduct thermal analysis, with the results being used to analyse the feedstock's kinetic behaviour during thermal degradation in an inert environment. For the first time, advanced kinetics and technology solutions (AKTS) software was used to analyse the kinetic parameters of sesbania pyrolysis and make kinetic predictions under various thermal conditions. The apparent activation energy (E_a) was determined using Friedman's differential iso-conversional model, which is the primary kinetic modelling method utilised. Other traditional models, such as the integral Flynn-Wall-Ozawa (FWO) and ASTM-E698 methods, were employed for comparison purposes. The activation energy of 124.53 kJ.mol⁻¹ was obtained using the ASTM-E698 technique, while the E_a value for the FWO method ranged from 50 to 200 kJ.mol⁻¹. As it accurately reflects the dynamic nature of lignocellulosic biomass degradation, the differential iso-conversional technique is the most reliable and precise approach, with E_a values ranging from 20 to 205 kJ.mol⁻¹. Predictions under isothermal, step-based and non-isothermal conditions were then constructed using the results computed through the differential iso-conversional model. This information can be used to improve production throughput in a variety of reactors. Additionally, the derived kinetic parameters can be used for process modelling.

1. Introduction

In an attempt to achieve energy security and climate change mitigation, short rotation plantations (SRPs), also referred to as short-rotation woody crops (SRWCs), have been developed to provide a stable source of woody biomass for the production of renewable energy [1]. Short rotation plantations of fast-growing woody biomass are generally harvested within 2–20 years, and the woody biomass is used in various energy-production related applications. Furthermore, SRPs provide an array of environmental benefits, those related to biodiversity, land

remediation, flood defence, etc. [2]. In addition to energy production, woody biomass can also be used for the pyrolytic production of biochar [3]. Biochar has recently emerged as a viable negative emissions technology, promoting atmospheric carbon removal while also providing several environmental and agronomic advantages [4].

Poplar (*Populus* sp.) and willow (*Salix* sp.) are amongst the most extensively cultivated woody crops in the EU [1], while short-rotation eucalyptus plantations are very popular in Brazil [5]. In addition to such common varieties, Md Noor et al. presented an extensive range of crops to cultivate SRPs for woody biomass production [6]. One of the

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<https://doi.org/10.1016/j.jaecs.2021.100048>

very interesting tree species mentioned is sesbania, a leguminous, nitrogen-fixing woody crop that is high yielding and very fast-growing, which can be harvested within 18–24 months after planting and can be managed as a short rotation coppice [7]. In Pakistan, Sesbania has been investigated as a feedstock for producing medium-density fibreboard (MDF) [7]. In Egypt, a specific variety, sesbania sesban, has gained much attention as a dedicated woody crop for MDF production; however, in general, it has not received much attention as a dedicated crop for bioenergy or biochar production.

The objective of this study is to carry out an investigation on the physicochemical characteristics and thermo-kinetic behaviour of sesbania sesban as a potential woody biomass feedstock for pyrolytic production of biochar. Kinetic modelling is conducted to obtain the kinetic triplet, namely, activation energy (E_a), pre-exponential factor (k_0), and reaction rate. This information can then be utilised to predict the pyrolytic reaction progress of sesbania under isothermal, step-based, and non-isothermal conditions. To compute the kinetic parameters, non-isothermal TGA is carried out, followed by various data analysis methodologies. The literature presents two main routes for data analysis, namely model fitting and model-free methods [8,9]. Model fitting methods have been criticised by the international confederation for thermal analysis and calorimetry (ICTAC) kinetics committee due to the computational uncertainties associated [9].

On the other hand, various model-free techniques are discussed within the literature, which includes Flynn-Wall and Ozawa (FWO), ASTM-E698, Kissinger-Akahira-Sunose (KAS) and Friedman's differential iso-conversional model [8–14]. In general, all methods may suffer drawbacks if mishandled [9,15]. For accurate analysis, kinetic modelling software can be utilised to compute the kinetic triplet, as well as construct solid predictions relating to the reaction progress of the feedstock under a variety of thermal profiles, representing various industrial biochar production systems that are based on continuous (isothermal) or batch (isothermal and non-isothermal) reactors.

Various kinetic investigations for pyrolysis of short-rotation woody crops have been carried out in the literature. Słopiecka et al. examined the kinetic behaviour of poplar wood (*populus* L.) pyrolysis using three models, Kissinger (ASTM-E698), FWO and KAS, obtaining activation energy values of 153.92, 107.86–209.49, and 104.95–209.90 kJ.mol⁻¹, respectively. For this investigation, four heating rates were used, 2, 5, 10 and 15 °C.min⁻¹ [16]. Rego et al. carried out a kinetic investigation on the pyrolysis of nine different poplar clones using the FWO and KAS methods by utilising TGA data obtained under five different heating rates of 10, 20, 30, 40 and 50 °C.min⁻¹. The results indicate activation energy values of 81–301 and 90–306 kJ.mol⁻¹ based on FWO and KAS methods, respectively [17]. In relation to Eucalyptus (*E. globulus*) wood pyrolysis, Sharma and Diwan carried out a kinetic investigation using FWO and modified Coats and Redfern methods. TGA results based on four heating rates of 5, 10, 15, and 20 °C.min⁻¹ were used in this study. The results indicate activation energy values of 156.63–182.46 and 146.54–173.37 kJ.mol⁻¹ within $\alpha = 0.05$ to 0.7, using the FWO and modified Coats and Redfern methods, respectively [18]. Chen et al., on the other hand, utilised the distributed activation energy model (DAEM), which is a model-fitting method, to examine the kinetic behaviour of eucalyptus residues. The authors computed activation energy using both, Gaussian and discrete DAEM for eucalyptus leaves, bark and sawdust. The Gaussian model revealed activation energy values of 141.15, 149.21 and 175.79 kJ.mol⁻¹, while the modified discrete model yielded activation energy values in the ranges of 122.67–308.64, 118.72–410.8 and 108.39–192.93 kJ.mol⁻¹ for leaves, bark and sawdust, respectively [19]. Based on an extensive review of the literature, a lack of kinetic studies on the pyrolysis of sesbania sesban has been identified, thus the motivation to carry out this study.

To the authors' knowledge, this research is the first to analyse the physicochemical properties of raw sesbania biomass as well as evaluate its thermo-kinetic behaviour via pyrolysis using Advanced Kinetics and Technology Solutions (AKTS) thermokinetics tool. Traditional thermo-

analytical data, such as that obtained using TGA, is used by AKTS to perform kinetic analysis, primarily using the differential iso-conversional method. Furthermore, for comparison purposes, the software computes activation energy using other model-free methods such as FWO and ASTM-E698. Because of the software's strong thermo-kinetic criteria, which establishes an average correlation coefficient R^2 of higher than 0.95, the results acquired using AKTS are highly robust. Model robustness is further enhanced by utilising high-resolution data covering 10,000 data points, where kinetic parameters such as activation energy and pre-exponential constant can be tracked from $\alpha=0$ to $\alpha=1$ in increments of 0.0001. Moreover, conversion progress predictions can be derived over a comprehensive range of temperature profiles using the computed kinetic parameters. This approach has been used effectively in various studies [10,11,13,20–22] and is regarded as a sophisticated tool due to its great accuracy in computing kinetic parameters and its reliable predictions (isothermal, non-isothermal and stepwise heating regimes).

2. Materials and methods

2.1. Materials

The sesbania sample used in this study was sourced from a short rotation sesbania plantation in southern Egypt. A two-year-old tree was cut down using a chainsaw and was left for two weeks to dry naturally. Furthermore, leaves and branches were removed, and the stem wood was de-barked manually, providing four different samples (a) leaves (SS-1), (b) branches (SS-2), (c) stem bark (SS-3), and (d) stem wood (SS-4). The stem wood, bark and branches were chipped manually, and a hammermill was then utilised for all four samples to achieve a size of less than 1 mm. The reason for selecting a two-year-old sample is that sesbania sesban is usually harvested in 1.5–2-year cycles. For characterization purposes, all four samples will be investigated; however, for kinetic analysis, only sample SS-2 is explored as it has been established to be a representative sample of the entire crop. From a practical and commercial perspective, the entire tree would be processed, and thus, a realistic sample would contain both wood and bark.

2.2. Sesbania sesban characterization

Proximate and ultimate analyses were employed to assess the composition of Sesbania sesban. Moisture content (British Standard EN 14775–3), volatile matter (British Standard EN 15148:2009), ash content (British Standard EN 14775:2009), and fixed carbon (by difference) were all determined concerning proximate analysis. Moreover, a Perkin Elmer PE2400 Series II CHNS/O Elemental analyser was used to perform an ultimate analysis to determine the content of carbon, hydrogen, nitrogen, sulfur, and oxygen content was determined by difference. To conduct heating value analysis, the calculation of HHV and LHV were based on Eq. (1) [23] and Eq. (2) [24], respectively.

$$\text{HHV} = 0.3443\text{Carbon\%} + 1.192\text{Hydrogen\%} - 0.113\text{Oxygen\%} \\ - 0.024\text{Nitrogen\%} + 0.093\text{Sulfur\%} \quad (1)$$

$$\text{LHV} = \text{HHV} - 0.212\text{Hydrogen\%} - 0.0245\text{Moisture\%} - 0.008\text{Oxygen\%} \quad (2)$$

Moreover, powder X-ray diffraction (XRD) analysis was carried out to investigate the physical and chemical structure of the samples, a PANalytical X'Pert Pro X-ray diffractometer was used to perform XRD. A CuK X-ray source with a wavelength of 1.5405 was used in this diffractometer. From $2\theta = 5$ – 90° , diffractograms were collected. The X-ray tube's voltage and current were set to 40 kV and 40 mA, respectively. Furthermore, Fourier transforms infrared (FT-IR) was carried out for functional group analysis. A Perkin Elmer Spectroscopy with a beam splitter in the wavenumber range of 400–4000 cm⁻¹ was used.

Table 1
Physicochemical characterization of sesbania sesban biomass.

		Sesbania Leaf (SS-1)	Sesbania Branches (SS-2)	Sesbania Bark (SS-3)	Sesbania Stemwood (SS-4)	Chen et al. [19] Eucalyptus Leaf	Chen et al. [19] Eucalyptus Bark	Chen et al. [19] Eucalyptus Sawdust	Slopiecka et al. [19] Poplar Wood
Proximate	Moisture	8.63	7.75	8.27	7.72	4.26	10.89	6.12	9.6
Analysis (wt% on a dry basis)	Volatile	76.13	82.6	73.55	82.62	81.19*	78.43*	79.14*	83.57*
	Fixed	9.95	15.64	17.93	16.25	12.66*	16.66*	19.99*	12.34*
	Carbon								
	Ash	13.92	1.76	8.52	1.13	6.15*	4.9*	0.86*	4.09*
Ultimate	C%	41.03	44.53	46.01	43.97	47.71	41.82	49.75	45.5
Analysis (wt% on a dry basis)	H%	5.99	6	5.59	6.44	4.85	5.01	5.77	6.26
	N%	3.72	0.48	1.95	0.44	3.49	0.28	0.17	1.04
	S%	< 0.3	< 0.3	< 0.3	< 0.3	0.45	0.07	0.03	–
	O%	35.04	46.93	37.64	47.72	43.37	52.76	44.26	47.2
Heating Value (in MJ.kg⁻¹ dry feedstock)	HHV	17.96	18.15	19	18.41	–	–	–	–
	LHV	16.2	16.32	17.31	16.48	14.98	15.04	17.64	–

* Calculated by the authors to dry basis for comparison.

2.3. Kinetic modelling

Kinetic parameters of sample SS-2 were investigated via TGA experiments from 25 to 900 °C under nitrogen flow at 40 cm³.min⁻¹, using a sample weight of 5 mg at four heating rates of 0.5, 1, 4 and 8 °C min⁻¹. The TGA experiments were conducted in accordance with the ICTAC's guidelines for acquiring experimental thermal analysis data for kinetic calculations with a ratio of 16 between the highest and lowest heating rates. This was done to ensure that the kinetic analysis results were accurate and that the data was well-resolved. The ICTAC Kinetics Committee released the challenges as well as the basic principles that should be followed in order to do effective kinetic computations using thermal analysis data. A Mettler Toledo Pyris TGA/DSC1 was utilised for this experiment. The apparatus was also calibrated for buoyancy effects so that weight variations could be quantified, and the standard error was determined to be ±1 °C. The results of the analyses were then utilised within AKTS software to compute the kinetic parameters. Various models were employed for the computation of kinetic parameters, primarily using Friedman's differential iso-conversional model, in addition to ASTM-E698 and FWO for comparison. Furthermore, isothermal, step-based, and non-isothermal predictions were presented based on the differential iso-conversional model.

The theory underlying the differential iso-conversional technique used by AKTS is described in full below:

As shown in Eq. (3), the rate of thermal decomposition of the sesbania sesban sample herein may be expressed in terms of the extent of conversion progress (α) and temperature (T).

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (3)$$

Where the sample's degraded mass fraction is represented in Eq. (4):

$$\alpha = \frac{m_i - m_a}{m_i - m_f} \quad (4)$$

Where the initial, actual, and final masses are denoted by m_i , m_a and m_f , respectively.

Furthermore, the Arrhenius equation (Eq. (5)) describes the temperature-dependent function in terms of activation energy and pre-

exponential factor.:

$$k(T) = k_0 \cdot e^{-E_a/RT} \quad (5)$$

Where k denotes the rate constant, T in Kelvin, k_0 is the pre-exponential constant, E_a denotes the activation energy, and R denotes the gas constant.

When Eqs. (3) and (5) are merged, the equation for sesbania sesban pyrolysis may be represented as Eq. (6) shown below.

$$\frac{d\alpha}{dt} = k_0 \cdot e^{-E_a/RT} f(\alpha) \quad (6)$$

In the non-isothermal isoconversional approach, the sample is subjected to a series of constant linear heating rates denoted as β . Furthermore, it is proportional to the temperature differential per unit time, as shown in Eq. (7) below:

$$\beta = \frac{dT}{dt} \quad (7)$$

β in Eq. (7) may then be employed in Eq. (6) as shown below in Eq. (8):

$$\frac{d\alpha}{dT} = \frac{k_0}{\beta} \cdot e^{-E_a/RT} f(\alpha) \quad (8)$$

Finally, the equation for Friedman's approach is constructed by applying the natural logarithm to both sides of Eq. (8), allowing for the determination of E_a and k_0 as the reaction progresses with α between 0 and 1.

$$\text{Friedman's differential iso-conversional method: } \ln \frac{d\alpha}{dT} = -\frac{E_a}{RT} + \ln[k_0 f(\alpha)] \quad (9)$$

In addition to the differential isoconversional approach, numerous non-isothermal non-isoconversional (ASTM-E698) and isoconversional (FWO) methods are described in the literature and will be employed for comparison in this work, as shown below [10].

$$\text{ASTM - E698 method: } \beta \frac{d\alpha}{dT} = k_0 \cdot e^{\left(\frac{-E_a}{RT}\right)} (1 - \alpha) \quad (10)$$

$$\text{Flynn - Wall - Ozawa (FWO) method: } \ln \beta = \ln \left(\frac{k_0}{R \cdot g(\alpha)} \right) - 5.331 - 1.052 \frac{E_a}{R \cdot T} \quad (11)$$

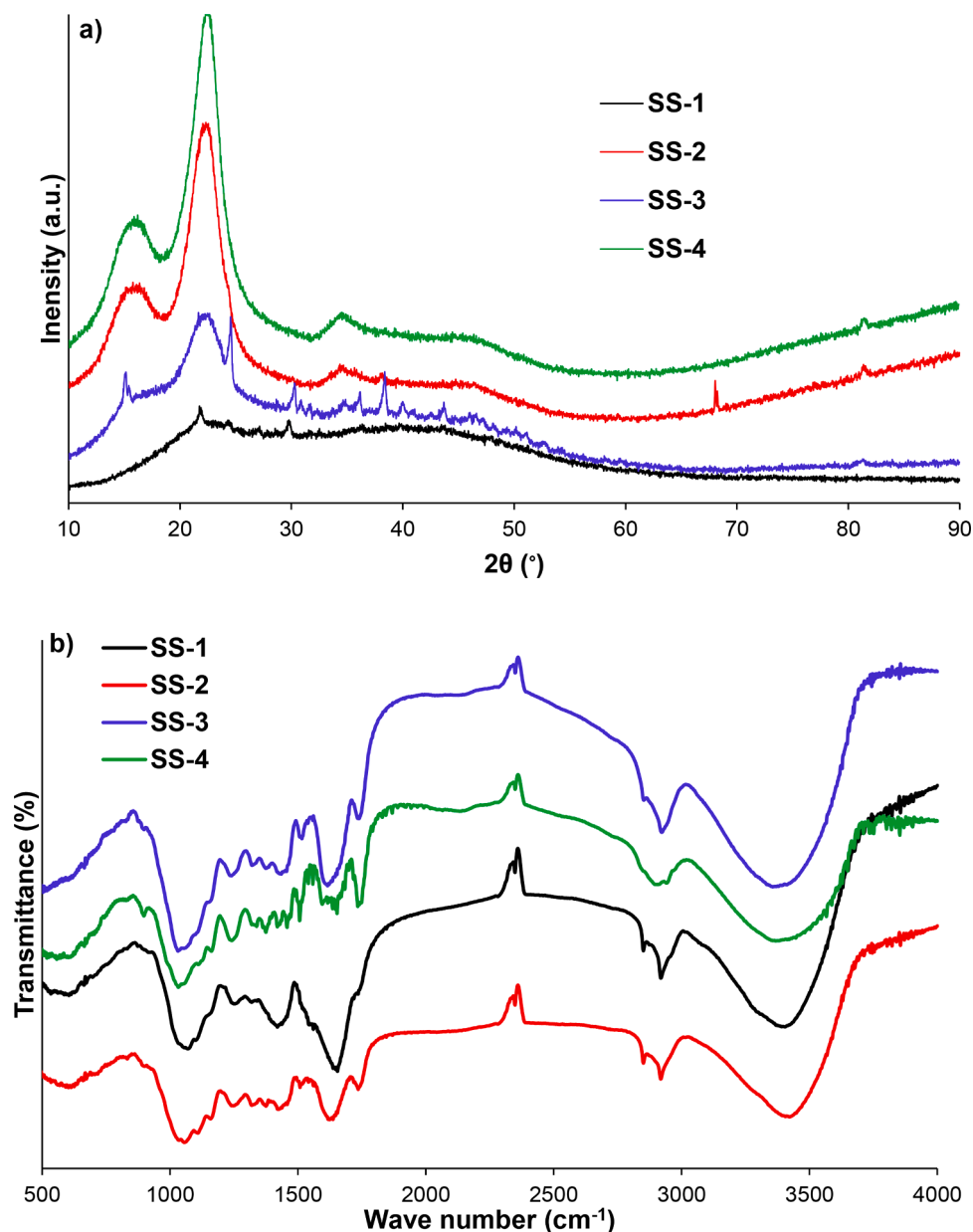


Fig. 1. (a) XRD patterns, and (b) FTIR spectra of sesbania sesban biomass components.

The reaction rate and reaction progress are determined by AKTS as shown below in Eqs. (12) and (13), respectively:

$$\frac{d\alpha}{dt} = \frac{(D(t) - B(t))}{\int_{t_{\text{initial}}}^{t_{\text{final}}} (D(t) - B(t)) dt} \quad (12)$$

$$\alpha(t) = \frac{\int_{t_{\text{initial}}}^t (D(t) - B(t)) dt}{\int_{t_{\text{initial}}}^{t_{\text{final}}} (D(t) - B(t)) dt} \quad (13)$$

To determine the E_a , k_0 , and reaction rate, the TGA weight loss curves were converted into DTG signals, and then a baseline was built to further integrate each curve and compute the kinetic triplet. AKTS offers various options for enhanced baseline construction, which is likely the most important aspect in the treatment of kinetic data. Furthermore, the created baselines can be quantitatively optimised. Following the

establishment of baselines for all heating rates, a baseline optimisation procedure was done with 100 iterations to ensure the R^2 value was maximised. Furthermore, the optimisation would ensure that the mass loss estimates provided for each heating rate were consistent and did not vary significantly due to manual baseline generation. The data was then utilised to generate a simulation, which was determined to be a good match with some minor differences, most likely due to instrument restrictions. Following that, 100 repetitions of the simulated calculations were done to ensure precision and repeatability.

3. Results and discussion

3.1. Characterization results

Table 1 displays the results of the proximate and ultimate analyses carried out on each of the four components of raw sesbania sesban biomass. In terms of proximate analysis, moisture content (MC) ranged from 7.72 to 8.63%, volatile matter (VM) 73.55–82.62%, fixed carbon (FC) 9.95–17.93% and ash content (AC) 1.13–13.92%. The values are

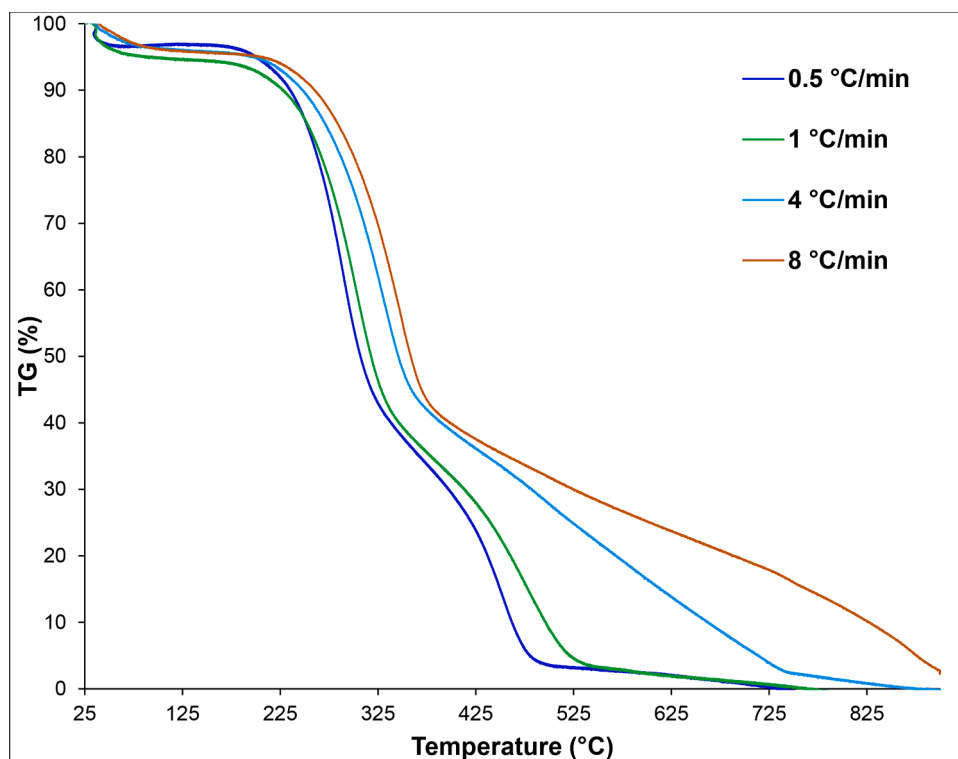


Fig. 2. TGA results for pyrolytic degradation of sesbania sesban (SS-2) biomass at heating rates of 0.5, 1, 4, and 8 °C min⁻¹.

reported on a dry basis. The results can be compared to other short-rotation woody crops such as those reported by Chen et al. for eucalyptus residues: leaves, bark and sawdust [19]. In comparison to eucalyptus leaves, it can be noted that sesbania leaves (SS-1) carry double the amount of moisture content at 8.63%, slightly lower volatile matter content at 76.13%, slightly lower fixed carbon at 9.95%, however more than double the ash content can be noted at 13.92%. Furthermore, sesbania bark (SS-3) shows a lower moisture content at 8.27%, slightly lower volatiles at 73.55%, slightly higher fixed carbon at 17.93% and higher ash content at 8.52% as compared to eucalyptus bark. The results associated with sesbania sesban branches (SS-2) and stem wood (SS-4) are comparable to those reported for eucalyptus sawdust, where moisture content is slightly higher at 7.72–7.75%, volatiles are higher at 82.6%, lower fixed carbon in the range of 15.64–16.25% and finally ash content for the SS-4 sample is almost similar to that of eucalyptus at 1.13%; however, the SS-2 sample carries double the amount of ash at 1.76% compared to the eucalyptus sawdust. Compared to the poplar wood results reported by Slopiecka et al. [16], the SS-2 and SS-4 samples carry similar volatile matter content, a higher fixed carbon and significantly less ash content.

In terms of ultimate analysis, the results for all sesbania components are comparable to those reported for the eucalyptus residues with slight deviations in some elements. For example, the carbon content for the SS-2 and SS-4 samples at 44.53% and 43.97%, respectively, are slightly lower than those reported for the eucalyptus sawdust at 49.75% [19]. Moreover, the results for these two samples are very similar to those reported for poplar wood. Furthermore, sesbania bark (SS-3) has shown a slightly higher carbon content at 46.01% as compared to eucalyptus bark at 41.82%. In terms of sesbania leaves (SS-1), the carbon content is slightly lower at 41.03% compared to those reported at 47.71% for eucalyptus leaves [19]. The remaining elements are very comparable, and the deviations in oxygen content for SS-1 and SS-3 are mainly attributed to the differences in ash content for such components compared to the eucalyptus samples. Based on the elemental analysis the higher and lower heating values were calculated at 17.96 / 16.2 MJ.kg⁻¹, 18.15 / 16.32 MJ.kg⁻¹, 19 / 17.31 MJ.kg⁻¹, and 18.41 / 16.48 MJ.

kg⁻¹ for the SS-1, SS-2, SS-3, and SS-4 samples, respectively. The LHV values calculated in this study are within range of those reported for the eucalyptus residues at 14.98 MJ.kg⁻¹, 15.04 MJ.kg⁻¹, and 17.64 MJ.kg⁻¹ for leaves, bark and sawdust, respectively [19].

The XRD patterns for the four sesbania components are presented in Fig. 1a. The analysis provides insight into the chemical composition of the biomass material. For SS-1 (leaves), diffraction lines are observed at $2\theta=21.7^\circ$ and 29.6° , which are attributed to cellulose and anhydrite, respectively [25]. The SS-2 sample (branches) shows peaks at $2\theta=15.7^\circ$, 22° , 34.8° , which are typical reflections for the (110), (002) and (004) planes of cellulose type I, respectively [26,27]. Furthermore, the peak observed at $2\theta=67.9^\circ$ suggests the presence of calcite [25]. The SS-3 sample (bark) presented significant diffraction lines at $2\theta=15^\circ$, 22.5° , 24.5° , 30.8° and 38.3° attributed to the presence of lignin, (002) plane of cellulose type I, inorganic minerals (Na_2SO_4 (74–2036)), $\text{K}_4\text{H}_2(\text{CO}_3)_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ and SiO_2 phase (83–2465), respectively [24,28]. Furthermore, less significant peaks were observed at $2\theta=34.8^\circ$ and 43.6° , representing (004) plane of cellulose type I [26,27] and Fe_3O_4 [29], respectively. The presence of minerals on bark is expected due to the natural exposure of such samples. Finally, the SS-4 sample (stem wood) presents the typical pattern for the presence of cellulose with diffraction peaks at $2\theta=15.7^\circ$, 22.6° , and 34.8° attributed to the reflections for (110), (002) and (004) planes of cellulose type I, respectively [26,27].

Fig. 1b presents the FTIR results of the four components of sesbania biomass. In general, the four samples almost exhibit the same absorbance bands. Prominent bands are observed at ~ 1635 , 2920, and 3400 cm^{-1} which are attributed to a conjugated C=C stretch, C-H stretch and O-H stretch, respectively. The conjugated C=C stretching observed at 1635 cm^{-1} relates to the presence of lignin [30,31], while the two absorption bands at 2920 and 3400 cm^{-1} are related to the three ligno-cellulosic components (cellulose, hemicellulose and lignin) since all components have C-H and O-H bond structures [32]. Another prominent absorption band is observed at 1055 cm^{-1} , which may represent several organic compounds. This band may be attributed to the C-O stretch associated with cellulose [33], in-plane C-H bending vibrations related to aromatic compounds in lignin [31], as well as C-O, C-C stretching and

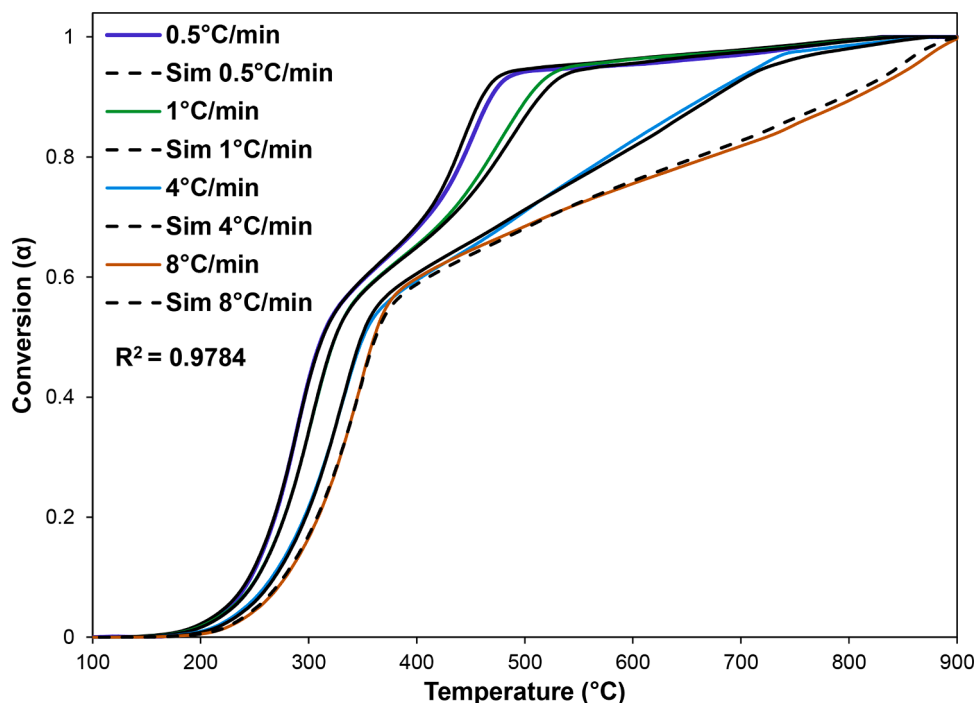


Fig. 3. Sesbania sesban (SS-2) pyrolysis reaction progress, demonstrating conversion (α) vs temperature ($^{\circ}\text{C}$) at various heating rates, with actual and simulated data.

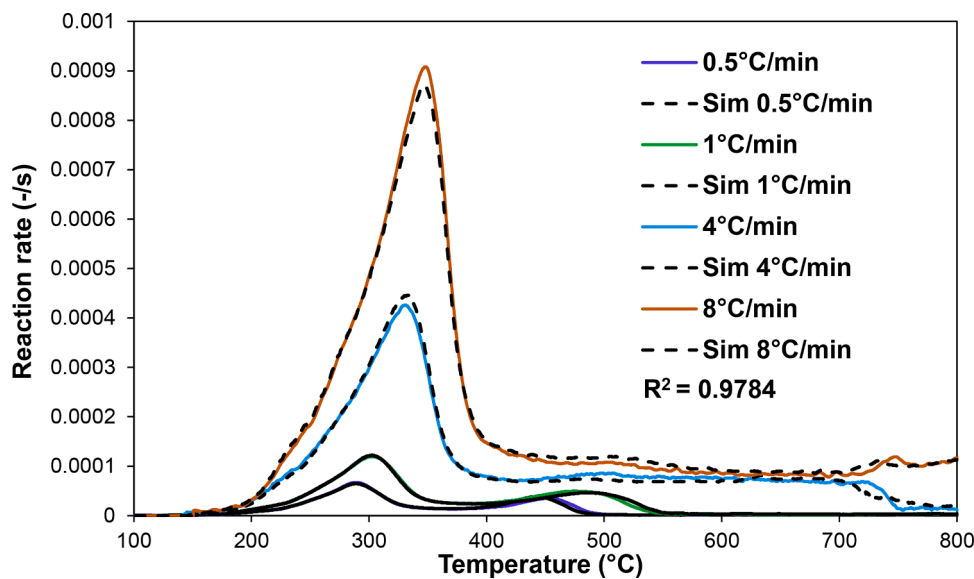


Fig. 4. Sesbania sesban (SS-2) pyrolysis reaction rate (S^{-1}) vs temperature ($^{\circ}\text{C}$), with actual and simulated data.

C-OH bending related to hemicellulose [33]. Furthermore, less significant bands are observed at $\sim 1160, 1250, 1375, 1420, 1740 \text{ cm}^{-1}$, which correspond to in-plane C-H bending (lignin), =C-H stretch in aromatic ether group (lignin), O-H bending (cellulose), CH_2 bending (cellulose), and C-O stretching of unconjugated carbonyl compounds (hemicellulose), respectively [25,30,31,33,34]. Furthermore, an inverted band is observed at $\sim 2360 \text{ cm}^{-1}$; this absorption band corresponds to the presence of CO_2 in the air [35]. Vibration modes corresponding to the presence of cellulose, hemicellulose and lignin are explicitly noted in this analysis.

3.2. Kinetic modelling results

To simulate pyrolysis, a non-isothermal thermogravimetric analysis

(TGA) for sample SS-2 was carried out in an inert environment under nitrogen flow. As indicated in Fig. 2, the analysis was carried out at four different heating rates of 0.5, 1, 4 and 8 C min^{-1} . As the reaction progresses, the analysis is based on detecting mass loss as a function of temperature and time. It can be noted that the reaction proceeds through three stages of mass loss. The initial stage, caused by dehydration, can be observed between 50 and 200 $^{\circ}\text{C}$. The second stage is primarily due to cellulose and hemicellulose degradation, taking place between 200 and 390 $^{\circ}\text{C}$. This is where a significant proportion of pyrolytic degradation took place. The last stage is shown at temperatures above 390 $^{\circ}\text{C}$. Although lignin decomposition occurs across the entire temperature range, it is mainly responsible for most of the mass loss in the final stage [36,37]. The results are consistent with published thermal degradation characteristics of common lignocellulosic materials [8,21,38–40].

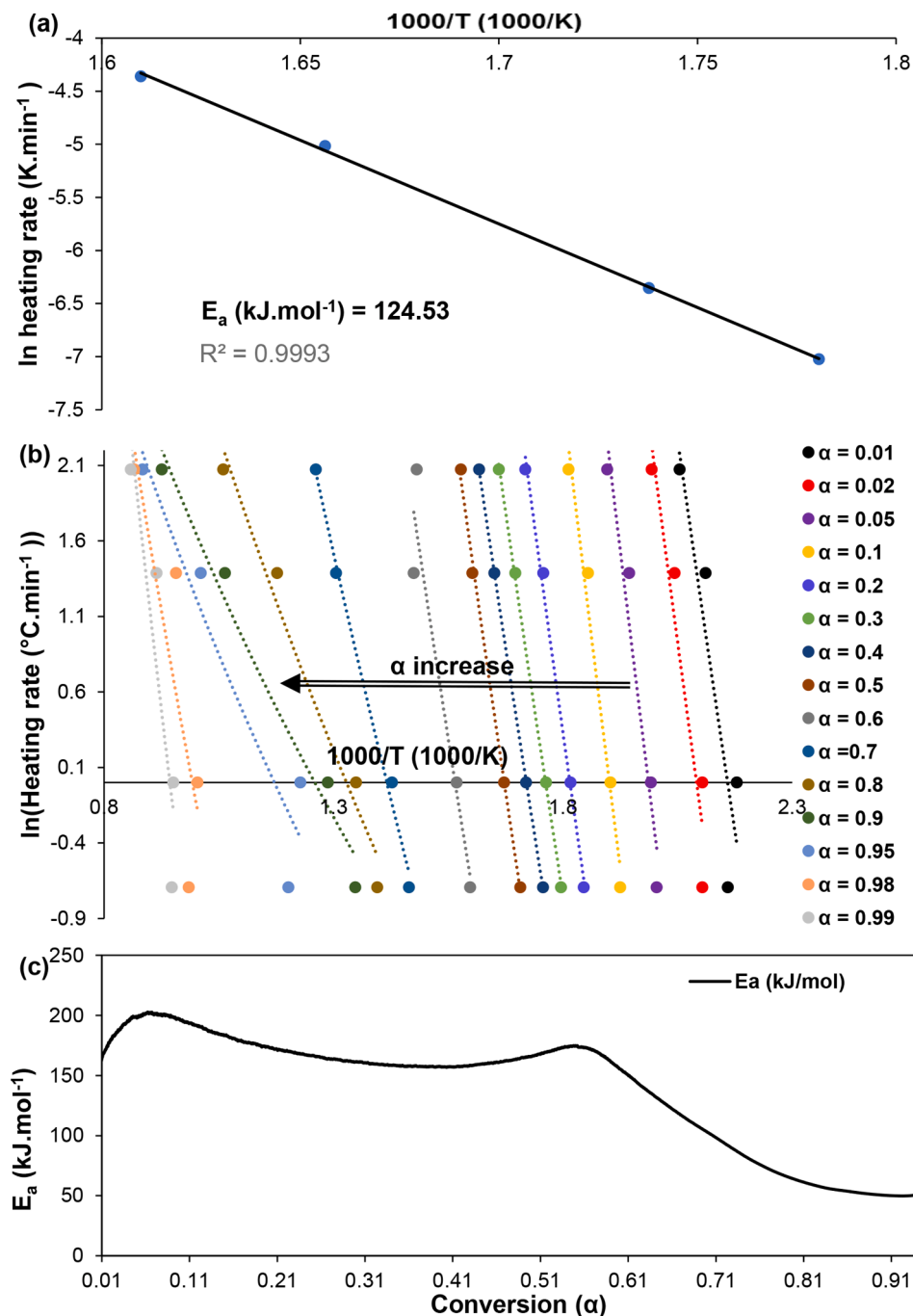


Fig. 5. The apparent activation energy (E_a) as determined by (a) the ASTM-E698 and (b, c) Flynn-Wall and Ozawa (FWO) for sesbania sesban (SS-2) pyrolysis.

The kinetic parameters were then investigated using three methods in the AKTS software: Friedman's differential iso-conversional model, in addition to FWO and ASTM-E698. Fig. 3 shows the progression of sesbania conversion at four different heating rates (0.5, 1, 4, and 8 $^{\circ}\text{C} \cdot \text{min}^{-1}$). It is worth noting that the actual and AKTS-simulated results are extremely similar, with an R^2 of 0.9784. It is also important to note that the reaction starts at around 190–200 $^{\circ}\text{C}$ for all four heating rates. Furthermore, as the heating rate is increased, a shift in reaction temperature is seen. This delay in decomposition can be attributable to a combined effect involving mass and heat transfer limitations and degradation kinetics of the feedstock [13]. Furthermore, the occurrence of a temperature gradient caused by a thermal lag due to the biomass's poor conductivity may result in the emergence of multiple phases of devolatilization [13,36].

Fig. 4 shows the reaction rate as a function of temperature for sesbania pyrolysis under various heating rates. Both actual and AKTS-simulated results demonstrate a strong correlation with an R^2 of 0.9784. Maximum reaction rates of 0.000065, 0.000123, 0.00042, and 0.00098 s^{-1} were obtained at temperatures of 287, 302, 334 and 347 $^{\circ}\text{C}$, respectively, at heating rates of 0.5, 1, 4, and 8 $^{\circ}\text{C} \cdot \text{min}^{-1}$. By raising the heating rate from 0.5 to 8 $^{\circ}\text{C} \cdot \text{min}^{-1}$, the reaction rate increased by 15 times.

Fig. 5a shows a single value for activation energy determined using the ASTM-E698 method: 124.53 $\text{kJ} \cdot \text{mol}^{-1}$. Biomass decomposition is a complicated process involving many reactions occurring at the same time. A single activation value is insufficient to accurately describe the complexity of biomass decomposition; thus, the ASTM-E698 approach is insufficient and may result in unreliable conversion predictions. Any

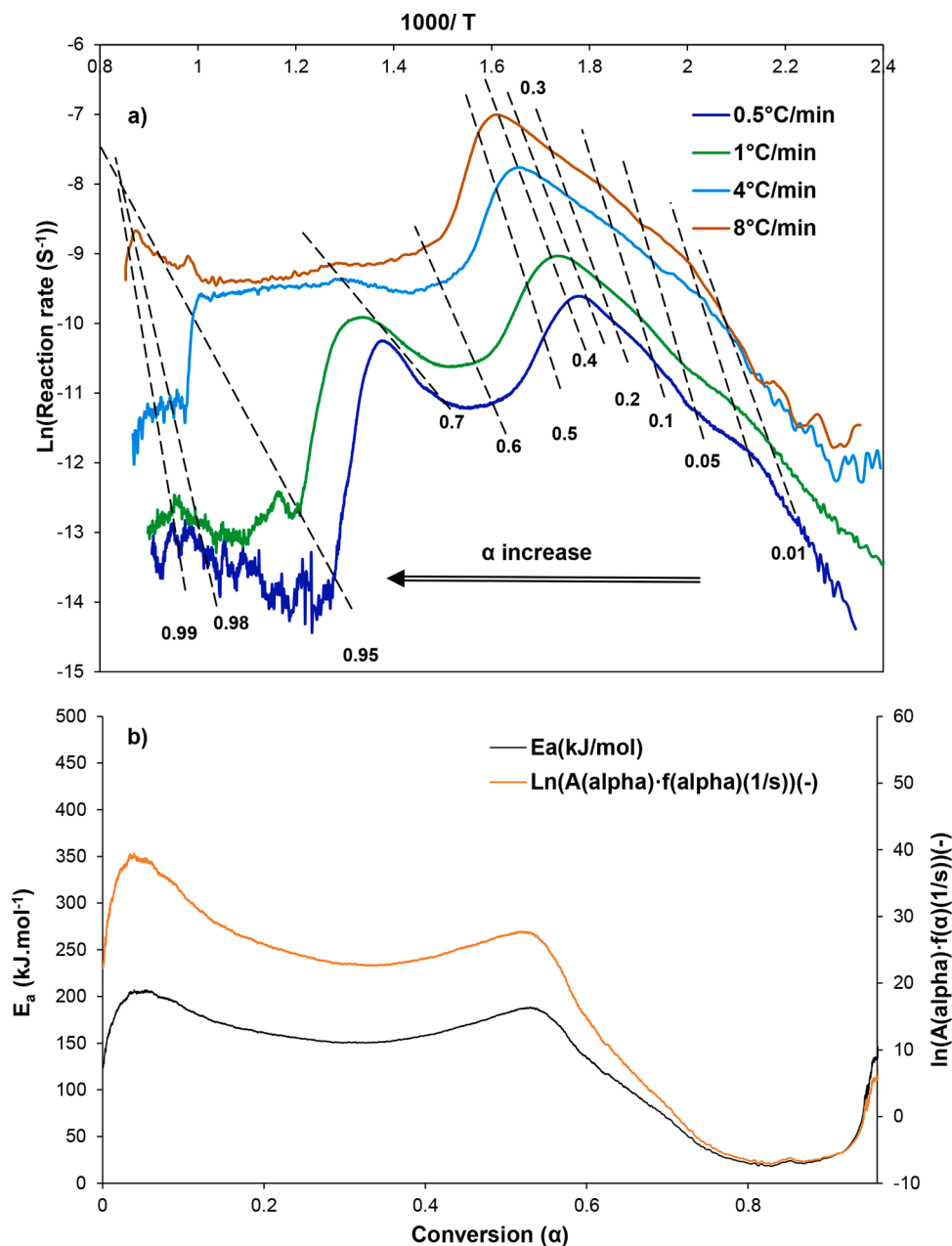


Fig. 6. Apparent activation energy for sesbania sesban (SS-2) pyrolysis based on the differential iso-conversional method.

method that computes a single activation energy value carries the same drawback. The integral iso-conversional approach, FWO, would be more appropriate as it considers the kinetic behaviour of the material as the conversion process advances. Fig. 5b depicts a plot of FWO natural logarithm (heating rate) versus inverse temperature at various stages of reaction progression. The graph shows that the results are quite well matched, with the only occurrences slightly outside the trend lines appearing after $\alpha=0.95$. Fig. 5c depicts the apparent activation energy for sesbania pyrolysis as a function of reaction progress.

The data shows that the reaction starts with an activation energy of $\sim 165 \text{ kJ.mol}^{-1}$, peaks at $\sim 200 \text{ kJ.mol}^{-1}$ at 5% ($\alpha=0.05$), and then gradually decreases as the conversion advances. At conversion rates of 20 ($\alpha=0.2$), 40, 60, and 80%, E_a values of 173.62, 157.03, 155.59, and 63.61 kJ.mol^{-1} are obtained, respectively. To a certain extent, the results are in line with E_a values of other SRC crops reported in the literature. Slopicka et al. reported an E_a range of 107–210 kJ.mol^{-1} for the pyrolytic conversion of poplar wood (populus L.), using the FWO

method [16]. Moreover, Sharma & Diwan reported an E_a range of 156–182 kJ.mol^{-1} for eucalyptus wood (*E. globulus*), also using the FWO method [18]. The ranges reported only cover the conversion progress until 70%. In this study, the E_a range covering the conversion progress until 70% is 103–200 kJ.mol^{-1} , which is comparable to the results reported for poplar wood.

Friedman's differential iso-conversional model, a very reliable technique, was used to compute the kinetic parameters within AKTS. Fig. 6a and b present the results associated with this model, showing the natural logarithm of the reaction rate (S^{-1}) versus inverse temperature (T^{-1}) and E_a and K_0 as a function of the reaction progress (α), respectively. As presented, the activation energy rises sharply during the initial 5% ($\alpha=0.05$) of the conversion process to $\sim 205 \text{ kJ.mol}^{-1}$ and then gradually decreases as the process advances. A second peak is observed at a conversion rate $\sim 54\%$ ($\alpha=0.54$) with an associated E_a value of 187 kJ.mol^{-1} . At conversion rates of 20 ($\alpha=0.2$), 40, 60, and 80%, E_a values of 161.12, 157.98, 134.21, and 21.42 kJ.mol^{-1} are obtained,

Table 2

Apparent activation energy of sesbania sesban (SS-2) pyrolysis using the differential iso-conversional and FWO methods.

α %	This Study <i>Sesbania Sesban</i> Differential Iso- Conversional kJ.mol^{-1}	This Study FWO	Sharma and Diwan [18] <i>Eucalyptus</i> FWO	Slopiecka et al. [18] <i>Poplar</i> FWO
5	203.72	197.96	161.5	107.86
10	188.3	195.94	156.63	124.4
15	170.68	183.44	158.45	129.27
20	161.12	173.62	160.02	130.08
25	154.78	166.67	162.13	137.88
30	150.7	161.46	162.51	150.77
35	151.5	158.16	165.12	171.88
40	157.98	157.03	168.55	181.54
45	169.43	160.35	172.99	–
50	182.26	166.19	176.49	198.53
55	181.62	174.7	178.72	–
60	134.21	155.59	180.69	202.73
65	101.22	127.55	182.46	–
70	69.7	103	179.89	209.49
75	36.01	79.85	–	–
80	21.42	63.61	–	–
85	23.8	54.68	–	–
90	27.41	50.48	–	–
95	107.5	58.32	–	–

respectively. The results determined through this model are very similar to those obtained by FWO. However, it is important to note that the differential iso-conversional method is more robust and precise. Table 2 displays the kinetic results utilising Friedman's differential iso-conversional and FWO methods at various stages of the conversion process. The findings of this research are compared to those found in the literature.

3.3. Thermal predictions of sesbania pyrolysis

Based on the results obtained using the differential iso-conversional

methodology, isothermal, step-based, and non-isothermal predictions are devised. The predictions offer useful insights to biochar project developers and technology providers in terms of process optimisation for continuous and batch type reactors based on this particular feedstock. Additionally, the results can be useful for small scale operators and academics interested in understanding the behaviour of sesbania under a variety of thermal profiles. It is worth noting that the predictions herein are based on thermogravimetric experiments that utilise a particle size of <1 mm. Therefore, predictions for larger particle sizes may slightly differ due to heat and mass transfer limitations.

3.3.1. Isothermal prediction of sesbania pyrolysis

In evaluating kinetic behaviour in reactors running under isothermal conditions, such as those used in large scale biochar production, isothermal predictions are of great value. Fig. 7 presents sesbania kinetic predictions for isothermal pyrolytic conditions between 300 and 800 °C. According to the findings, the reaction takes about 60 min to complete at 800 °C. In this timeframe, lower temperatures are unable to achieve complete conversion. It is, however, also important to note that approximately 96% conversion is achieved in 30 min at 800 °C. In the case of biochar production, however, a 100% conversion may not be required. The desired specifications can be reached at lower conversion rates depending on the intended biochar application. Residence time is a critical aspect in defining the productivity and profitability of industrial biochar systems and thus requires optimisation. Isothermal predictions offer the opportunity to identify processing temperatures that can achieve the desired conversion targets at reduced residence times. For instance, to reach 90% conversion, this can be achieved within 21–2408 min depending on the processing temperature (300–800 °C). It would be unprofitable and unrealistic to operate at such long residence times. The results suggest that an adequate reaction residence time of 21–54 min can be achieved by operating at a temperature range of 550–800 °C. Understanding the effect of this temperature range on the properties of the biochar is fundamental. Other factors influencing the overall viability of the production system, such as desired biochar properties, energy efficiency, and yield must be considered for process optimisation.

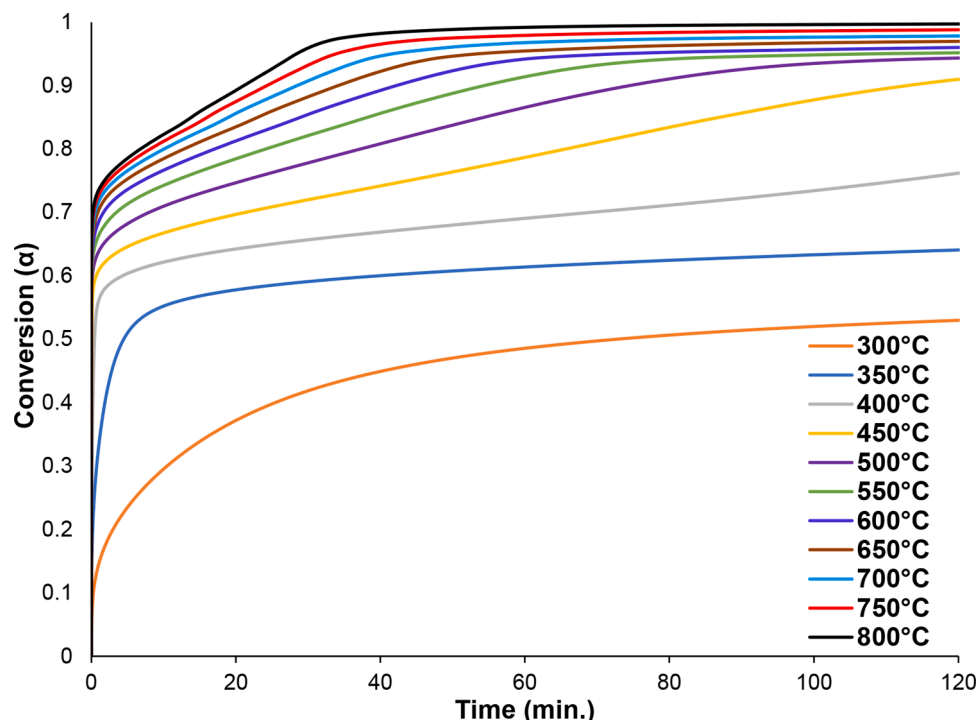


Fig. 7. Isothermal prediction of sesbania sesban (SS-2) pyrolysis in the temperature range of 300–800 °C.

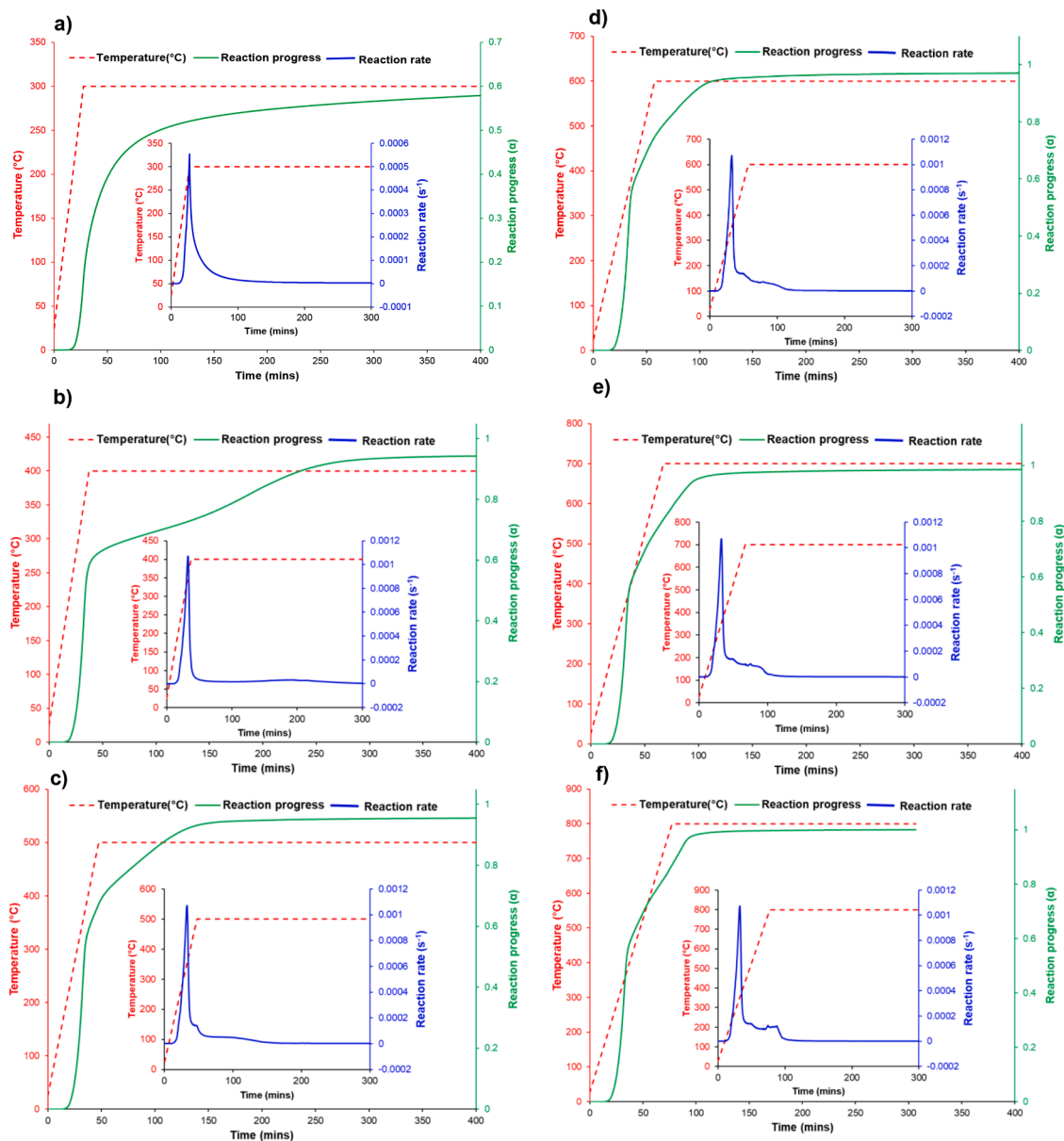


Fig. 8. Step-based predictions of sesbania sesban (SS-2) pyrolysis at a temperature ramp of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ and holding temperatures of 300–800 $^{\circ}\text{C}$ (a–f).

3.3.2. Step-based prediction of sesbania pyrolysis

Step-based predictions are particularly useful to small-scale biochar system operators as well as researchers using batch reactors that rely on a temperature ramp before reaching a specified holding temperature. Fig. 8a–f presents step-based predictions for six scenarios where a temperature ramp of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ is used, and a holding temperature of 300–800 $^{\circ}\text{C}$ is specified. The results clearly indicated a point of diminishing returns for each of the temperature profiles. These are points where further processing would yield very little benefit. This is observed at $\sim 300, 250, 150, 111, 105, 95$ min, at which a conversion rate of $\sim 56.6, 91, 93.8, 94.2, 95.9, 97.4\%$ is achieved at a temperature of 300, 400, 500, 600, 700, 800 $^{\circ}\text{C}$, respectively. Based on the results, temperatures above 500 $^{\circ}\text{C}$ are highly recommended under such reactor operating conditions. Depending on the conversion target, which is based on the required physicochemical properties, estimated reaction times can be obtained from the curves presented. For example, a 90% conversion would require 240, 118, 93, 85, and 82 min using holding temperatures of 400, 500, 600, 700, 800 $^{\circ}\text{C}$, respectively. Other aspects to consider include yield and process energy efficiency when selecting

conversion targets. It is important to note that conversion is achieved much slower as compared to isothermal conditions. This can be explained by the fact that the material is exposed to the highest heating temperature quicker and for a longer period under isothermal conditions. Fig. 9a–d presents step-based predictions under various temperature ramps while the holding temperature is kept at a constant 600 $^{\circ}\text{C}$. The results clearly demonstrate the impact of heating rate on reaction time for achieving a conversion target of 94.2%, the point after which the reaction yields diminishing returns at such temperature. A total reaction time of $\sim 295, 111, 85$ and 71 min is required at heating rates of 5, 10, 20 and 50 $^{\circ}\text{C}\cdot\text{min}^{-1}$.

3.3.3. Non-isothermal prediction of sesbania pyrolysis

Non-isothermal predictions can be useful for academics using lab-scale batch reactors. Fig. 10 presents the prediction results using 10, 20, 30, 40 and 50 $^{\circ}\text{C}\cdot\text{min}^{-1}$ heating rates. As noted, up to a conversion rate of 60%, all heating rates yield similar results where a temperature of 400–450 $^{\circ}\text{C}$ is required to reach such a target. However, at higher conversion rates, a gap in temperature requirement is clearly noted. For

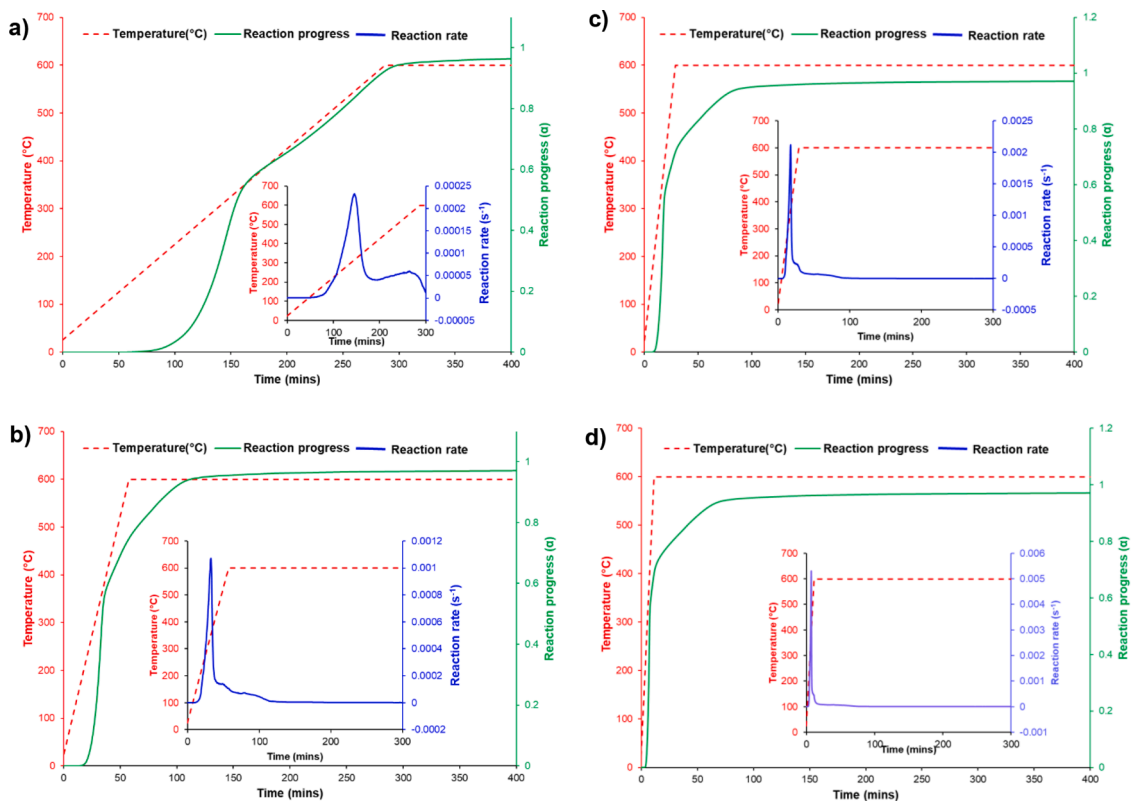


Fig. 9. Step-based predictions of sesbania sesban (SS-2) pyrolysis at temperature ramps of 5–50 °C.min⁻¹ and a holding temperature of 600 °C (a–d).

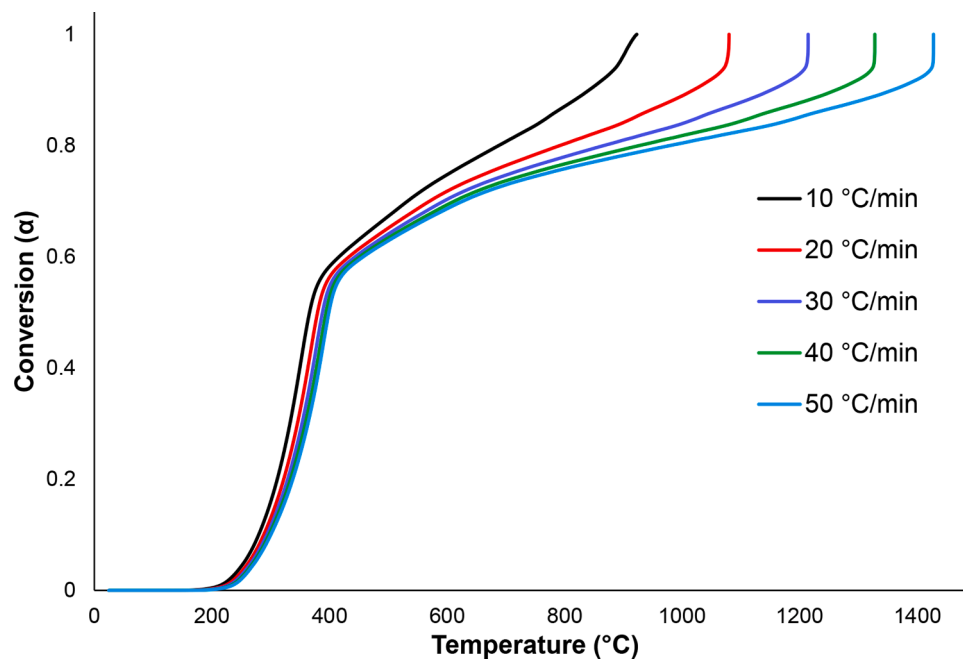


Fig. 10. Non-isothermal prediction of SS-2 pyrolysis at heating rates of 10, 20, 30, 40 and 50 °C.min⁻¹.

instance, an 80% conversion requires 688, 792, 867, 927, and 978 °C, while a complete conversion will require temperatures of 922, 1080, 1214, 1328 and 1428 °C using heating rates of 10, 20, 30, 40 and 50 °C.min⁻¹, respectively.

4. Conclusion

The physicochemical attributes of sesbania sesban biomass as a feedstock for biochar production were first characterised in this work. Furthermore, AKTS software was used to calculate the kinetic parameters and provide predictions under various thermal conditions. The E_a value was calculated using three methods: Friedman's differential iso-

conversional model, FWO and ASTM-E-698. The differential iso-conversional method yielded results that were comparable to those obtained with FWO, however, at a higher degree of reliability with an E_a range of ~ 20 – 205 kJ.mol^{-1} . On the basis of these findings, isothermal, step-based, and non-isothermal kinetic predictions were made. The predictions provide useful information for biochar project developers and operators, as production throughput optimisation can be examined further.

Additionally, the predictions provide insight to academics investigating such feedstock. Moreover, the acquired kinetic parameters can be used for process modelling [10]. According to the study's thermal predictions, a processing temperature of 550°C or higher will be necessary to convert sesbania into biochar efficiently using isothermal reactors, while a minimum temperature of 500 – 600°C is recommended for small-scale batch reactors that rely on an initial heat ramp followed by a holding period. Under non-isothermal conditions, the predictions suggest that irrespective of heating rate, a 60% conversion rate can be achieved between 400 and 450°C , however, to achieve higher degrees of conversion, heating rate becomes more critical. Overall, the results suggest that isothermal processing conditions are more efficient in terms of productivity where conversion can be achieved in shorter periods. More experimental research is necessary to validate the predictions made in this study, as well as investigate the impact of various production parameters on yield and biochar physicochemical attributes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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