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Investigation on pyrolysis kinetics and thermodynamic parameters of soybean straw: a comparative study using model-free methods

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Abstract

Thermochemical conversion of surplus agro-residue for energy generation has gained renewed attention due to its abundant availability throughout the world. Although, it still needs the thermodynamic and pyrolysis kinetic background that plays an important role in the effectual design of thermochemical conversion reactors such as pyrolyzers and gasifiers. In the present study, the thermal profile (mass loss vs. temp) for soybean straw was examined at 20, 30, and 40 °C/min heating rates under a non-isothermal condition in an oxygen-limiting environment through a thermogravimetric analyzer (TGA). The pyrolysis kinetic parameters (activation energy and pre-exponential factor) were evaluated by applying isoconversional model-free methods such as Flynn–Wall–Ozawa (FWO), Kissinger–Akahira–Sunose (KAS), Starink, and Vyazkovin. The average values of activation energy for KAS, FWO, Starink, and Vyazkovin models were recorded to be around 150, 155, 147, and 153 kJ/mol, respectively. Thermodynamic variables (change of enthalpy, entropy, and Gibbs free energy) for soybean straw were also computed. The average values of enthalpy for FWO, KAS, and Starink were recorded to be 151, 147, and 142 kJ/mol, respectively. The obtained simulation findings of pyrolysis kinetic and thermodynamic variables are in good agreement.

Keywords Soybean straw · Thermal analysis · Pyrolysis · Model-free methods · Kinetic analysis · Enthalpy · Entropy · Gibbs free energy · Reaction mechanism

1 Introduction

The proper utilization of surplus agro-residue has gained significant attention owing to its potential for energy generation. The most common agro-residue disposal processes such as incineration, landfill, and other agricultural applications are becoming intolerable because of stringent rules and regulations. Therefore, the conversion of biomass into energy fuels via the thermochemical conversion process is recognized as an economically feasible and environmentally friendly option with many sustainable benefits. The agro-residue is recognized as organic renewable raw material for green fuel generation because of its salient features such as abundant availability, easy process, cleanness, lower sulfur, and nitrogen compositions as compared

to fossil resources. Among the thermochemical conversion techniques, the pyrolysis process is regarded as one of the important biomass conversion processes where precursor material is heated in an oxygen-free condition at a moderate temperature of 400–600 °C for getting energetic biofuels such as char, bio-oil, and syngases [1]. Biochar is referred to as organic carbon-rich material; and therefore, it is widely used as a soil conditioner or as a catalyst for biofuel generation, while liquid oil and syngases can be used as alternative fuel or for power generation because of their higher heating value. Biomass pyrolysis is a heterogeneous complex thermochemical conversion process where some physicochemical changes are occurred due to the occurrence of simultaneous competing reactions. Thus, investigation on pyrolysis kinetics of biomass is becoming very crucial to understand the reaction chemistry, thermal behavior, and for obtaining the desired products by optimizing different parameters.

Soybean (*Glycine max* (L.) Merr.) straw is a lignocellulosic fibrous residue of agricultural crop soybean which is taken worldwide. The annual production of soybean is about 315 million tons and an equivalent amount of by-products especially straw is produced throughout the world [2].

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Husk indicates 10% of the weight of the soybean crop and is mainly referred to as waste. A large quantity of surplus straw is not being managed properly but is mostly burnt in an open field by some peasants, which causes a serious environmental problem. Revalorization of soybean straw using thermochemical conversion route i.e. pyrolysis is projected to be an alternative promising option, at the time of minimizing the adverse effects of the current waste management problem.

However, pyrolysis of soybean straw on an extensive platform is becoming very crucial to understanding its pyrolysis kinetics. In addition, thermal analysis of biomass (mass loss vs. temp) and knowledge of thermodynamic parameters are very imperative for CFD modeling, design of reactors, process optimization, and energy balance. Kinetic analysis of biomass is comprised of a two-stage process, first contains decomposition of biomass through the pyrolysis process for getting the reaction progression data, and second involves obtaining kinetic triplet (pre-exponential factor, activation energy, and reaction model) by performing computational mathematics. The kinetic and thermodynamic analysis is very important in determining the complexity of the reaction system [3]. As lignocellulosic biomass used in the present study, i.e., soybean straw is subjected to pyrolysis to know its decomposition pattern relative to its operating temperature. Each constituent of soybean straw degrades at a different range of temperatures with a distinct range of complex reactions. The lignin constituent is considered more refractory compared to cellulose and hemicellulose, due to the availability of functional groups, it possesses wide dispersed thermal stability, and therefore it needs higher pyrolysis temperature (433–1173 K) for its thermal decomposition [4]. As a result, apparent kinetic parameters are varying in the reacting system during the whole reaction process. For this, a model-free or isoconversional method is regarded as well suited for performing the kinetic analysis. Model-free isoconversional methods such as Ozawa–Flynn–Wall, Kissenger–Akahira–Sunose, Starink, and Vyazkovin are widely accepted and promising methods to estimate the kinetic parameters. Non-isothermal condition for TG-DTG analysis is referred to as significant condition for computing the pyrolysis kinetics and thermodynamic variables. The International Confederation for Thermal Analysis and Calorimetry (ICTAC) recommended in 2011 [5] and 2014 [6] the main causes for getting improved attention on isoconversional methods.

In the present work, pyrolysis kinetics of soybean straw was performed at 20, 30, and 40 °C/min heating rates under a nitrogen atmosphere using the TGA technique. The kinetic parameters were estimated using isoconversional models like FWO, KAS, Starink, and Vyazkovin models. The advanced Vyazkovin nonlinear isoconversional model is rarely used in calculating the activation energy compared to FWO, KAS, and Starink models. Therefore, in the present study, the obtained values of activation energy using the FWO, KAS, and Starink models are compared with the nonlinear-based Vyazkovin isoconversional method. The obtained values of activation energy were also used for calculating the thermodynamic parameters such as enthalpy, entropy, and Gibbs free energy. In addition, the proximate, ultimate analysis, higher heating value, and thermal degradation analysis were also performed for soybean straw biomass using the different analytical techniques.

2 Material and methods

2.1 Raw material

Soybean straws were collected from the oilseed research station of Dr. Panjabrao Deshmukh Krishi Vidyapeeth, Akola. It was ground using a hammer mill to obtain a particle size of 200–400 µm and afterward oven-dried at 110 °C for 24 h. Then, the dried sample was placed in an airtight container to restrict the absorption of atmospheric moisture. Figure 1 indicates the images of raw soybean straw and its dried powder.

Fig. 1 Raw soybean straw and its dried powder

2.2 Methods

2.2.1 Proximate, ultimate analysis, and higher heating value

Proximate analysis of soybean straw was conducted by determining the moisture content, volatile matter, fixed carbon, and ash content as per the procedure suggested by Cai et al. [7]. The ultimate analysis of precursor viz., total carbon, nitrogen, oxygen, hydrogen, and sulfur composition was estimated by using an elemental analyzer. The calorific value of soybean straw was calculated using a microprocessor digital bomb calorimeter.

2.2.2 Thermo and differential thermogravimetric analysis

TG-DTG analysis of soybean straw was performed in a TG-DTG unit (model: STA 7300, make: Hitachi) for obtaining the thermal degradation curves or patterns. The weighed quantity of soybean powder was heated from 30 to 800 °C at 20, 30, and 40 °C/min heating rates under a nitrogen atmosphere by keeping a flow rate of 95 ml/min, nitrogen as an inert gas was used to move the air present into the pyrolysis chamber, thus averting the combustion of the sample. The obtained thermal degradation data were further used to estimate the kinetic parameters of biomass pyrolysis.

2.3 Kinetic analysis

Pyrolysis of lignocellulosic biomass is referred to as a complex method where multiple reactions are involved. A complete kinetic analysis is usually not practicable for a complex system, but some types of regular or efficient kinetic analysis are still needed. The pyrolysis kinetics of soybean straw was executed using the isoconversional method. A widely preferred global reaction is used to understand the kinetic description of the biomass pyrolysis process as represented in Eq. (1):

$$Biomass \rightarrow Char + Volatiles \tag{1}$$

From the Arrhenius equation, the rate of biomass conversion can be expressed as

$$\frac{d\alpha}{dt} = Ae^{-\frac{E}{RT}}f(\alpha) \tag{2}$$

where the main components in Eq. (2) are activation energy (E), reaction model [$F(\alpha)$], and pre-exponential factor (A), while the remaining elements are the degree of conversion (α), reaction temperature (t), and universal gas constant (R), respectively. The activation energy of biomass is the amount of energy required to stimulate the biomass

to an energetic state, where the reaction occurs. Activation energy is generally used for breaking the bonds within the structure and making a transition state complex, where further reactions occur on their own. The pre-exponential factor is also referred to as the "frequency factor," where several collisions took place with respect to time for maintaining a proper orientation during the reaction. The reaction model is a model-based function [$f(\alpha) = (1-\alpha)^n$], which shows the quantitative relationship between the extent of conversion and the degree of conversion. The mass loss data for soybean straw was converted into a degree of conversion (α) as

$$\alpha = \frac{m_o - m_t}{m_o - m_f} \tag{3}$$

where.

α degree of conversion,
m_o initial weight of biomass sample,
m_t weight of the sample after pyrolysis at a time t,
m_f weight of char after biomass pyrolysis

Generally, during thermal analysis, the reaction temperature (T) raises with time (t) at a constant heating rate under an anaerobic atmosphere and this heating rate, i.e., β (°C/min), can be described as in Eq. (4):

$$\beta = \frac{dT}{dt} \tag{4}$$

Merging Eqs. (2) and (4) offers an Eq. (5):

$$\beta\frac{d\alpha}{dt} = Ae^{-\left(\frac{E}{RT}\right)}f(1-\alpha)^n \tag{5}$$

Equation (5) integrated with respect to temperature from $T = T_0$ and $T = T$ gives

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta}\int_T^{T_0} e^{-\left(\frac{E}{RT}\right)}dT \tag{6}$$

Equation (6) is very useful while carrying out the kinetic calculations, whereas the difference between reference temperature and biomass pyrolysis temperature should be insignificant.

2.4 Isoconversional models

The obtained TG-DTG data at 20, 30, 40 °C/min of heating rate was further used for the estimation of activation energy values by adopting the isoconversional or model-free methods such as FWO, KAS, Starink, and Vyazkovin methods. As per the ICTAC report, FWO and KAS are the most effective and precise methods for the calculations of kinetic parameters [5]. These models can determine the activation

energy value on a model-free basis. The obtained activation energy values were used further for the evaluation of the pre-exponential factor and estimating the reaction model. Isoconversional methods are mainly categorized into integral and differential methods. FWO, KAS, Starink, and Vyazkovin models are mainly regarded as integral methods, while the Friedman model is coming under a differential method [8].

2.4.1 Flynn–Wall–Ozawa (FWO) method

FWO integral model is considered an extensively accepted method among the scientific community for calculating the thermal kinetic parameters. It undergoes a correlation of the activation energy, heating rate of the biomass, and inverse temperature that was initially adopted by Doyle [9]. The FWO model is represented by following Eq. (7) [10]:

$$\ln(\beta) = \ln\left(\frac{AE_\alpha}{RG(\alpha)}\right) - 5.331 - 1.052\left(\frac{E\alpha}{RT}\right) \tag{7}$$

Here, activation energy is calculated corresponding to each degree of conversion by putting an inverse plot between log (β) and $1/T$. At each degree of conversion, the values of activation energy are computed from the slope $-1.052\left(\frac{E\alpha}{R}\right)$.

2.4.2 Kissinger–Akahira–Sunose (KAS) method

The pyrolysis kinetics can be determined by the most widely assessed model-free method, i.e., KAS, which is represented by the following expression, Eq. (8) [11, 12]:

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

where,

β heating rate (K/min),
A pre-exponential factor (s^{-1})
a conversion rate (computed by diving the loss mass by total mass of soybean straw),
$G(a)$ decomposition mechanism
R gas constant (8.314 J/K.mol)

Here, the activation energy for each degree of conversion is calculated from the plot of the slope of an equation $\ln\left(\frac{\beta}{T^2}\right)$ vs. $\frac{1}{T}$.

2.4.3 Starink method

Activation energy can be computed in a Starink model by adopting the below expression Eq. (9) [13];

$$\ln\left(\frac{\beta}{T^{1.92}}\right) = \text{const.} - 1.0008\frac{E_\alpha}{RT} \tag{9}$$

Here, for each degree of conversion, a straight line is obtained due to the plotting of $\ln\left(\frac{\beta}{T^{1.92}}\right)$ vs. $1/T$. In addition, activation energy can be assessed from the slope -1.0008 $E\alpha/R$ for each degree of conversion.

2.4.4 Vyazkovin method

Activation energy is also calculated using the Vyazovkin method, which is considered a nonlinear flexible isoconversional model that mainly depends on operating temperature and degree of conversion as shown in Eqs. (10) and (11) [14]. The activation energy values at each degree of conversion can be calculated using the Vyazovkin model, which is mainly employed by using a Senum–Yang approximation and Microsoft Excel software tool.

$$I(E_\alpha, T_\alpha) = \int_0^{T_\alpha} \exp\left(\frac{-E_\alpha}{RT}\right)dT = p(x),\ x \cong \left(\frac{E_\alpha}{RT}\right) \tag{10}$$

Senum–Yang approximation:

$$p(x) = \frac{\exp(-x)}{x} \cdot \left(\frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120}\right) \tag{11}$$

where, $x = E/RT$.

2.5 Thermodynamic parameters

The FWO, KAS, and Starink models are adopted for obtaining the activation energy values for each degree of conversion, and these methods can be further implemented for calculating the different thermodynamic parameters such as change of enthalpy (ΔH), pre-exponential factor (A), entropy change (ΔS), and Gibbs free energy change (ΔG), etc. with the aid of mentioned expressions like Eqs. (12), (13), (14), and (15), respectively [15].

$$\Delta H = E_\alpha - RT \tag{12}$$

$$A = \beta E_\alpha \exp\frac{\left(\frac{E\alpha}{RT_m}\right)}{RT_m^2} \tag{13}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_m} \tag{14}$$

$$\Delta G = E_\alpha + RT_m \ln\left(\frac{T_m k_B}{hA}\right) \tag{15}$$

Here, *Tm* is addressed as a peak temperature in the DTG curve, while k_B and h are referred to as Boltzmann and plank constant, respectively.

3 Results and discussion

3.1 Characteristics of soybean straw biomass

The proximate, ultimate analysis, lignocellulosic composition, and higher heating value of soybean straw were investigated using different analytical methods are listed in Table 1. The proximate analysis of soybean straw indicated that the agro-residue has a more volatile matter of $74.05 \pm 1.5\%$, while lower moisture, ash, and fixed carbon content to be around 9.0 ± 1.1, 3.54 ± 0.8, and $8.41 \pm 1.3\%$, respectively. Here, higher volatile content in agro-residue showed its excellent thermal reactivity during the thermal decomposition process, easily devolatilize, and leads increase in bio-oil production. Lower moisture content in soybean straw facilitates uniform heat distribution during the pyrolysis process. If the available moisture percentage in the feedstock is ≥ 10, more amount of auxiliary energy is needed to complete the pyrolysis process. Interestingly, a lower percentage of fixed carbon is showing a lower lignin composition in the agro-residue. Soybean straw contains a low amount of ash, the proximate analysis of soybean straw well matches with another soybean straw feedstock as previously reported by Huang et al. [16]. The calorific value of soybean straw was

observed to be about 14.00 MJ/kg, which was found very closer to the other agricultural residues [17, 18].

Ultimate analysis results of soybean straw revealed that a percentage of oxygen to be around $47.53 \pm 0.02\%$, carbon $(44.64 \pm 0.02\%)$, hydrogen $(6.79 \pm 0.12\%)$, and a negligible percentage of nitrogen $(0.94 \pm 0.01\%)$, and sulfur content $(0.10 \pm 0.32\%)$. While hydrogen-to-carbon, oxygen-to-carbon, and nitrogen-to-carbon ratios were obtained using the empirical formula are 1.34 ± 0.01, 0.83 ± 0.01, and 52.98 ± 1.22, respectively. A higher oxygen-to-carbon ratio reduces the calorific value of the feedstock. However, a negligible percentage of sulfur and nitrogen in soybean straw results in lower emission of harmful gasses (NO*x*, SO*x*) [19]. As it can be observed from Table 1, biochemical analysis of soybean straw including cellulose, hemicellulose, and lignin composition was found to be 33.21, 18.40, and 5.12%, respectively. The lignocellulosic composition of soybean straw was found comparable with some other soybean straw biomass Huang et al. [16], whereas lower lignin composition in soybean straw (5–14%) was also reported by Reddy and Yang [20].

3.2 Thermal decomposition behavior of soybean straw

Soybean straw was thermally decomposed from ambient to 800 °C at 20, 30, and 40 °C/min heating rates in a TG furnace. The obtained TG and DTG curves for pyrolysis of soybean straw are shown in Fig. 2.

It can be seen that the thermal degradation (mass loss vs. temp) of soybean straw took place or might be categorized into three different stages; the first stage is attributed to the drying zone, the second stage indicates the devolatilization zone, and the third stage corresponded to the char formation zone. The first zone ranging from 30 to 200 °C, which

Table 1 Characteristics of soybean straw biomass (% wt.)

	Present study	Huang et al. [16]
Proximate analysis (% wt.)		
Moisture content	9.0 ± 1.1	1.8
Volatile matter	74.05 ± 1.5	75.5
Ash content	3.54 ± 0.8	4.7
Fixed carbon content	8.41 ± 1.3	19.8
Calorific value (MJ/kg)	17	19.71
Ultimate analysis (% wt.)		
C	44.64 ± 0.02	47.8
H	6.79 ± 0.12	6.9
O (by difference)	47.53 ± 0.02	44.3
N	0.94 ± 0.01	1.0
S	0.10 ± 0.32	0.1
H:C ratio	1.34 ± 0.01	1.73
O:C ratio	0.83 ± 0.01	–
C: N ratio	52.98 ± 1.22	–
Lignocellulosic composition (% wt.)		
Cellulose	33.21	–
Hemicelluloses	18.40	–
Lignin	5.12	–
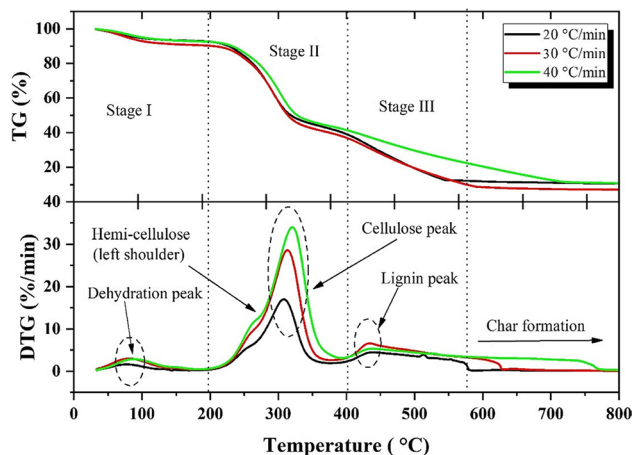
Fig. 2 TG and DTG behavior of soybean straw at 20, 30, and 40 °C/min

is mainly referred to as the dehydration stage is also known as the passive zone, where very light volatiles were present and that showed the hygroscopic nature of feedstock [21]. From 30 to 110 °C, some unbound moisture was liberated, whereas from 110 to 200 °C, bounded moisture, as well as small amount extractives, were released. The main decomposition of soybean straw took place between 200 and 400 °C, this zone is primarily known as the active pyrolysis zone where maximum mass loss (60–64%) was observed. The first peak in an active zone from 210 to 310 °C where hemicelluloses decompose, while the second peak from 310 to 400 °C revealed the decomposition of cellulose. However, a strong peak between 200 and 400 °C was obtained at 320 °C, which may be regarded for pyrolysis of hemicellulose and cellulose [22]. Taking after the second stage, a small shoulder between 400 and 550 °C was noticed, which should be corresponded to the degradation of lignin [23]. The DTG curve showed that the lignin content in soybean straw had greater thermal stability as compared to cellulose, and hemicellulose, a similar observation was also noticed by Hu et al. [24] for pyrolysis of chili straw waste (CSW) biomass. This stage is representing the passive zone of pyrolysis where minimum mass loss (1–4%) was observed. After 600 °C, the devolatilization curve was found almost constant, which was mainly considered.

an end of the pyrolysis process, i.e., char formation zone. A similar thermal decomposition behavior was also observed in a previous investigation on soybean straw by Huang et al. [16].

3.3 Kinetic analysis

The pyrolysis kinetics of soybean straw was performed to evaluate the relation between the activation energy and degree of conversion using model-free methods such as FWO, KAS, Starink, and Vyazovkin at 20, 30, and 40 °C/min heating rates, where a conversion ranged from 0.1 to 0.9, respectively. The obtained data were further used for calculating the thermodynamic variables, viz., change of enthalpy, entropy, and Gibbs free energy, respectively. The derivation of obtained activation energy values for three different models was found below 5%, justifying that the obtained activation energy values were reliable and might be supported by each other.

3.3.1 Evaluation of activation energy and pre-exponential factor

Here, linear Eq. (7) was used for the KAS model to calculate the activation energy values with the help of slope $(-E\alpha/R)$ at a different conversion. Likewise, the activation energy values for FWO, Starink, and Vyazovkin model were obtained using Eqs. (8), (9), (10), and (11), respectively. The

calculated activation energy values relative to the degree of conversion using FWO, KAS, Starink, and Vyazovkin models are listed in Table 2. The activation energy values for soybean straw were ranged between 88 and 178 kJ/mol, 78–175 kJ/mol, 74–172 kJ/mol, and 80–174 kJ/mol for a degree of conversion from 0.1 to 0.9 by adopting FWO, KAS, Starink, and Vyazovkin models. The average values of active energies derived from FWO, KAS, Starink, and Vyazovkin models were recorded to be around 155.34, 150.11, 147.17, and 153.21 kJ/mol, respectively. The deviation was found below 5% for all three models, indicating that obtained activation energy values are more reliable. Activation energy values for soybean straw obtained by nonlinear the Vyazovkin isoconversional model are found analogous with the results obtained by Emiola-Sadiq et al. [14]. A nearly similar result was also obtained by Islam et al. [25] for the pyrolysis of fruit hulls using FWO and KAS models.

The obtained values of activating energies from four different methods were found highly dependent on the degree of conversion, which signifies that pyrolysis of soybean straw is a complex process including multiple reactions. From Table 2, it was noticed that for all methods, the activation energy values were found to increase from the conversion of 0.1 to 0.5, which means that endothermicity rises relative to the degree of conversion. Then after the conversion of 0.5 to 0.9, the values of $E\alpha$ were found to drop, which justifies the occurrence of the exothermic reaction. For FWO conversion, activation energy values were increased from 158.31 to 178.63 kJ/mol for the conversion from 0.1 to 0.5, which might be because of the degradation of hemicellulose and cellulose present in the feedstock. While as the degree of conversion increased from 0.5 to 0.9, the activation energy values were significantly reduced from 160 to 88 kJ/mol, respectively. A similar trend was also noticed in $E\alpha$ values derived from KAS, Starink, and Vyazovkin models. For the KAS model, the values of activation energies increased from 153.66 to 175.36 kJ/mol for the conversion of 0.1 to 0.5, as the pyrolysis process proceeds, the activation energy found decreased from 168.23 to 68 kJ/mol with a conversion range of 0.6 to 0.9. Similarly, the values of $E\alpha$ were observed to rise from 150.32 to 172.32 kJ/mol corresponding to the conversion from 0.1 to 0.5, and then activation energy values significantly reduced from 170.33 to 54 kJ/mol for a degree of conversion ranging from 0.6 to 0.9, for Starink model, respectively. Vyazovkin model also showed a similar trend as the conversion rate increased from 0.1 to 0.5; the activation energy values were also increased from 157.41 to 174.12 kJ/mol, whereas the activation energy was found reduced from 158.21 to 80.12 kJ/mol for the degree of conversion from 0.6 to 0.9, respectively. Here, an increase in activation energy values for a conversion range of 0.1 to 0.5 shows the presence of endothermicity reactions, while decreased values of $E\alpha$ for conversion from 0.6 to 0.9 were

Table 2 Apparent activation energy and pre-exponential factor of soybean straw relevant to the degree of conversion (α) at 20 °C/min

Conversion factor	FWO			KAS			Starink			Vyazovkin		
α	E_α (kJ/mol)	R^2	A (s^{-1})	E_α (kJ/mol)	R^2	A (s^{-1})	E_α (kJ/mol)	R^2	A (s^{-1})	E_α (kJ/mol)	R^2	A (s^{-1})
0.10	158.31	0.9423	1.45×10^{17}	153.66	0.9521	1.45×10^{15}	150.32	0.9423	2.26×10^{10}	157.41	0.9514	1.13×10^{14}
0.20	169.32	0.9698	2.14×10^{15}	165.21	0.9569	2.47×10^{17}	156.32	0.9565	2.05×10^{11}	169.66	0.9647	1.47×10^{16}
0.30	172.32	0.9654	3.66×10^{17}	168.23	0.9674	1.54×10^{15}	163.23	0.9614	2.15×10^{11}	170.12	0.9588	1.44×10^{14}
0.40	175.63	0.9785	1.76×10^{15}	171.66	0.9632	2.26×10^{12}	169.36	0.9696	1.45×10^{12}	172.56	0.9698	1.46×10^{13}
0.50	178.63	0.9865	1.21×10^{16}	175.36	0.9698	2.68×10^{10}	172.32	0.9785	1.41×10^{11}	174.12	0.9784	2.58×10^{11}
0.60	160.32	0.9845	1.41×10^{14}	168.23	0.9879	3.11×10^{15}	170.33	0.9899	3.22×10^{08}	158.21	0.9584	2.22×10^{16}
0.70	155.36	0.9941	1.41×10^{15}	154.36	0.9785	2.12×10^{17}	165.36	0.9841	2.64×10^{10}	156.32	0.9914	1.12×10^{16}
0.80	140.23	0.9952	1.41×10^{17}	126.32	0.9894	2.09×10^{16}	123.33	0.9914	1.44×10^{09}	140.54	0.9941	2.12×10^{15}
0.90	88	0.9896	1.54×10^{16}	78	0.9925	2.71×10^{14}	74	0.9921	1.21×10^{08}	80.12	0.9825	1.71×10^{13}
Average	155.3467			150.1144			147.1744			153.2144		

mainly attributed to the occurrence of exothermic reactions during soybean straw pyrolysis. Here, the activation energy values decrease for all isoconversional models at a conversion range between 0.8 and 0.9, which was the final stage of pyrolysis, where lignin content in soybean straw has reached the temperature condition for biomass pyrolysis, thereby it causes a decrease in activation energy [26]. The degree of conversion from 0.6 to 0.9, where pyrolysis temperature varied from 500 to 800 °C, corresponded to the degradation of lignin and a small percentage of cellulose. As Vamvuka et al. [27] noticed that maximum activation energy (145–285 kJ/mol) was needed for thermal decomposition of cellulose and hemicellulose, whereas the lowest activation energy was needed for lignin (30–139 kJ/mol), which may be the main reason for decreasing the $E\alpha$ values for degree of conversion from 0.6 to 0.9. Based on the findings, it was observed that soybean straw requiring lower activation energy means a faster reaction rate because activation energy is simply defined as the smallest amount of energy needed to begin the reaction. Secondly, the soybean straw is considered an agricultural by-product, which was mainly composed of lignocellulosic constituents that indicate less aromaticity, easily react, and because of this, it shows minimum $E\alpha$ value. Similar observations for activation energy were also reported in previous literature for pyrolysis of agricultural residues such as soybean straw, peanut shell, and wheat straw [16, 28, 29]. In addition, for all three models, the values of R^2 were found maximum for all degrees of conversion signifies that obtained activation energy values are more accurate and reliable.

The $E\alpha$ values obtained from FWO, KAS, Starink, and Vyazovkin methods were further adopted to evaluate the pre-exponential factor, as the pre-exponential factor is considered one of the significant kinetic parameters to carry out a detailed kinetic study [30]. Here, the pre-exponential factor was evaluated using the Coats–Redfern method as represented in Eq. (6). Since, FWO, KAS, Starink, and Vyazovkin methods are referred to as reliable and therefore activation energy derived from these methods was well fitted to obtain the pre-exponential factor and reaction order. Calculated values of pre-exponential factors obtained from FWO, KAS, Starink, and Vyazovkin methods at 20, 30, and 40 °C/min heating rates using Eq. (6) are recorded in Table 2. From Table 2, it was observed that as pyrolysis temperature increased for all four models, the values of pre-exponential factor were also found to increase, which means that more complex reactions took place in a very short duration. Here, the values of pre-exponential factors obtained from FWO, KAS, Starink, and Vyazovkin were recorded between 10^9–10^{17}, which signifies that thermal degradation of soybean straw becomes spontaneous at maximum temperatures. The pre-exponential factor was estimated from intercept by using heating rate, activation energy, and gas

constant. Pawar et al. [31] reported that discrepancy in values of a pre-exponential factor for all models' links with the composition of biomass and due to a more complex reaction it undergoes during biomass pyrolysis. Whereas pre-exponential factor values as $A\alpha$ is $\leq 10^{9\,S-1}$, the reactor indicates less reactivity, that means a low value of $A\alpha$ links with a closed complex, whereas more the $A\alpha$ ($A\alpha \geq 10^{9\,S-1}$) specify that a system possesses a simple complex with an extremely reactive system. Similar observations are also conveyed in a previous study by Havilah et al. [32].

3.3.2 Analysis of thermodynamic parameters

Thermodynamic variables have received great importance because of their application in small- and large-scale pyrolysis reactor optimization. Here, thermodynamic parameters such as change of enthalpy: ΔH; Gibbs free energy: ΔG; change of entropy: ΔS with conversions were estimated from Eqs. (12), (14), and (15) corresponding to the values of $E\alpha$ calculated from FWO, KAS, and Starink models are shown in Table 3.

The change of enthalpy (ΔH) signifies the energy variance among the end products and reagents in a thermochemical reaction [33]. For the FWO model, the value of ΔH increased from 150.23 to 178.63 kJ/mol with a degree of conversion from 0.1 to 0.5 and then reduced after conversion of 0.5. A similar leaning was noticed for the KAS and Starink model, where enthalpy value hiked significantly, i.e., 140.23–170.23 kJ/mol and 140.21–165.69 kJ/mol with the function of conversion from 0.1 to 0.5 and then after 0.5 decreased. The average value of ΔH was recorded to be around 151, 147, and 143 kJ/mol for FWO, KAS, and Starink methods, respectively. Figure 3a indicates the progress of the ΔH relative to the degree of conversions. The rise in enthalpy values for all models corresponds to their degree of conversion up to 0.5, mainly due to the starting of an endothermic reaction. After 0.5 conversions, a significant drop in enthalpy values for all models indicates the moving of the reaction from endothermic to exothermic [28]. In the present study, from Tables 2 and 3, it was observed that there is a very small energy barrier among the average value of change in enthalpy and $E\alpha$ value (< 5 kJ/mol) for all FWO, KAS, and Starink methods. The same variation between activation energy and enthalpy was found in a previous study conveyed by Sahoo et al. [34]. In addition, Pawar et al. [31] also noticed a small variation between enthalpy and activation energy for coconut husk waste are 224 and 229 kJ/mol. A smaller alteration among the ΔH and $E\alpha$ is mainly attributed to the creation of activated complex, which is linked with the requirement of minimum additional energy for effective pyrolysis of soybean straw for energy fuel generation [35].

The Gibbs free energy (ΔG) indicates that the total energy rose in the reactor perspectives of the reactant and

Table 3 Thermodynamic parameters of soybean straw relevant to the degree of conversion (α) at 20 °C/min

	FWO			KAS			Starink		
α	ΔH^* (kJ/mol)	ΔG^* (kJ/mol)	ΔS^* (J/mol.K)	ΔH^* (kJ/mol)	ΔG^* (kJ/mol)	ΔS^* (J/mol.K)	ΔH^* (kJ/mol)	ΔG^* (kJ/mol)	ΔS^* (J/mol.K)
0.10	150.23	166.98	−226.71	140.23	172.95	−207.44	140.21	168.95	−233.71
0.20	160.22	166.52	−84.99	154.36	172.54	−66.98	145.18	168.21	−98.84
0.30	163.21	165.91	84.90	163.23	172.1	72.31	153.63	167.89	66.26
0.40	174.36	165.65	114.93	175.89	171.95	103.13	160.25	167.89	93.33
0.50	178.63	165.23	130.14	170.23	171.65	116.58	165.69	167.59	112.27
0.60	160.23	165.21	82.77	164.89	171.23	69.45	158.36	167.36	65.27
0.70	148.96	164.91	78.21	153.21	171.2	64.52	145.63	167.12	61.83
0.80	135.23	164.21	69.23	132.23	170.96	55.08	136.36	166.58	56.35
0.90	91	164	63.67	70	170.21	50.52	80	166.12	46.35
Averages	151.34	165.40		147.14	171.64		142.81	167.52	

Fig. 3 **a**, **b**, and **c** Change in ΔH, ΔG, and ΔS relative to the degree of conversion
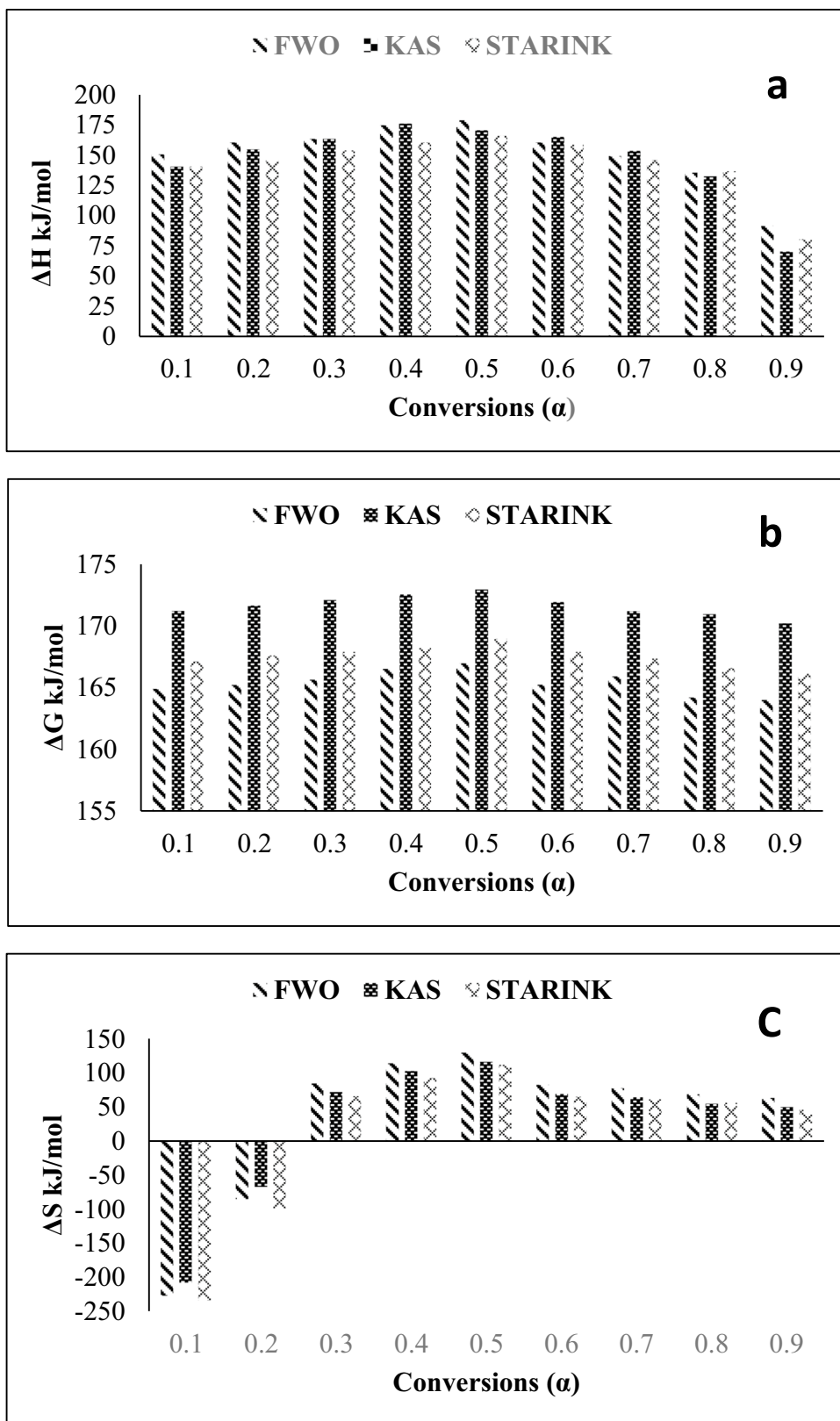
Table 4 Activation energies and thermodynamic parameters of soybean straw and other agro-waste

Agro-waste	Method	Activation energy, Ea (kJ/mol)	Thermodynamic variables			References
			ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/mol. k)	
Soybean straw	FWO, KAS, and Starink	155.34, 150.11, and 147.17	151.34, 147.14, and 142.81	165.40, 171.64, and 167.52	−233 to 130	Present study
Soybean straw	FWO and KAS	156.22 and 154.15	–	–	–	[16]
Maize cob	FWO, KAS, and Friedman	186.06, 185.39, and 197.63	192.83 and 180.58	176.49 and 176.66	−37 to 190	[36]
Peanut shell	KAS and Kissinger	144–295 and 172–218				[2]
Black gram straw	FWO, KAS, and Starink	172.96, 172.81, and 172.54	168.05, 167.90, and 167.64	166.99, 167.00, and 167.01	−20 to 69	[34]
Peanut shell	FWO and KAS	109.94 and 96.33	104.76	128.33	−0.040	[23]
Sugarcane leaves	KAS and FWO	226.75 and 226.97	–	–	–	[13]

the original state of the activated product [36]. In the present work, the average value of Gibbs free energy obtained for FWO, KAS, and Starink methods was found to be 165.40, 171.64, and 167.52 kJ/mol, respectively. The variation in Gibbs free energy values obtained for all three models showed that the formation of the activated complex and might be further used to solve the heat flow-related problems and disorders. For the FWO model, the values of Gibbs free energy were found to slightly decrease from 166.98 to 164 kJ/mol for conversion from 0.1 to 0.9. A similar observation was also noticed for KAS and Starink methods, where the Gibbs free energy slightly reduced from 172.95 to 170.21 kJ/mol and 168.95 to 166.12 kJ/mol, respectively. Figure 3b indicates the ΔG relative to the degree of conversions. Here, the increased value of Gibbs free energy corresponding to the degree of conversion discloses that overall energy supplied to the reactor at high pyrolysis temperature did not release rapidly from the system. In addition, from Table 2, it was observed that a higher value of ΔG was recorded at the beginning of conversion for all models, which means that auxiliary heat supplied to the reactor was found to be surplus. The positive value of ΔG obtained for all models justifies that the whole process is non-spontaneous and may be accomplished with the addition of some external energy.

Change in entropy represents the disorder in the degree of the reactant when it is exhibited for the reaction in any system. It means that the production of different end products and degree of randomness because of the thermal decomposition of soybean straw. From Table 2, it was observed that lower entropy was recorded at 0.1 conversions, and it rose to conversion 0.5. For the FWO model, the entropy value at 0.1 conversions was found to be −226.71 kJ/mol, and it increased up to 0.5 conversions to be around 130.14 kJ/mol, respectively. Likewise, for KAS and Starink models, the value of entropy changed from −207.44 to 116.58 kJ/mol and −233.71 to 112.27 kJ/

mol, respectively. Figure 3c indicates the ΔS relative to the degree of conversions. A smaller value of ΔS implies that selected biomass, i.e., soybean straw inclines toward the thermodynamic equilibrium, which means during the reaction process, it undergoes a small physicochemical change relevant to its operating conditions. The negative value of change in entropy at conversion 0.1 and 0.2 for all three models signifies that produced devolatilization products possess a lower degree of disorder as compared to raw biomass, i.e., soybean straw. Whereas the positive value of ΔS at different degrees of conversion indicates a higher degree of randomness for soybean straw than those end products [37]. A negative value of entropy at low conversion signifies that soybean straw possesses a lower chemical reactivity, while a positive value of entropy at higher conversion represents that the system was far from its equilibrium [38, 39]. Nevertheless, a negative value of entropy at low degree conversion and positive value of entropy at higher degree conversion for biomass pyrolysis was also reported in previous literature [40]. This matches very well with the previous study conveyed by Dhyani et al. [41] that enhancement in the reactivity at a specific degree of conversion and further dropped.

Similar results for change in enthalpy, entropy, and Gibbs free energy were also obtained in pyrolysis of agricultural residues such as wheat straw [29], black gram [42], rice bran, and rice straw [43], and peanut shell [28]. In addition, Table 4 compares the thermodynamic parameters and activation energy values obtained in the present experiment with other agricultural waste. From Table 4, it was noticed that soybean straw found a lower activation energy value than other agro-waste materials. The low activation energy for soybean straw means a requirement of minimum energy for efficient chemical reaction and because of this, it opens a new window to the researcher for appropriate utilization of soybean straw for bioenergy generation. In addition, knowledge of thermodynamic variables can play a significant role

in designing the different thermochemical conversion systems with a proper mass and energy balance.

4 Conclusion

In the present study, physicochemical characterization, calorific values, TG-DTG analysis, kinetic and thermodynamic analysis of soybean straw were explored. The maximum mass loss for soybean straw pyrolysis was observed in a temperature range of 200–400 °C, mainly referred to as the active pyrolysis stage. The average values of activation energy and change of enthalpy were recorded to be near to each other (< 5 kJ/mol). The obtained kinetic data from all models disclosed a good agreement with the experimental results. Taking into consideration of lower ash and moisture content, the thermochemical conversion system creates a new window for appropriate utilization of soybean straw for energy generation.

Abbreviations $A\alpha$: Pre-exponential factor, s^{-1}; α: Degree of conversion; ΔH: Enthalpy, kJ/mol; ΔG: Gibbs free energy, kJ/mol; ΔS: Entropy, J/mol.K; β: Heating rate, K/min; R: Universal gas constant (8.314 J/K.mol).; h: Planks constant, m2kg s^{-1}; $E\alpha$: Activation energy, kJ/mol; HHV: Higher heating value; TG: Thermogravimetric; R^2: Correlation coefficient; $F(\alpha)$: Model-based function or reaction model; m_o: Initial weight of sample, g; m_t: Weight of sample after pyrolysis at a time, t; m_f: Weight of biochar at the end of pyrolysis, g; t: Time, s; T: Process temperature, K; kB: Boltzmann constant, m2kg s^{-1} K^{-1}; KAS: Kissinger–Akahira–Sunose; FWO: Flynn–Wall–Ozawa (FWO); DTG: Differential thermogravimetric

Author contribution Abolee Jagtap (first author) has carried out the original experimental work and has written the original draft, and S. R. Kalbande (coauthor) reviewed and checked the manuscript.

Declarations

Competing interests The authors declare no competing interests.

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