

# Overriding investigation on strengthening of thermal stability of torrefied pigeon pea stalk and kinetic compensation

## Abstract

This article diagnoses the kinetic compensation due to the torrefaction effect on the Pigeon pea stalk. In order to that, the thermal treatment of the raw pigeon pea stalk was done up to 250 °C in a reactor in an inert environment. The obtained solid biomaterial was subjected to the thermogravimetric analysis for four various heating rates (10, 20, 30, and 40 °C/min) to investigate the changes occurring in thermal behaviour and kinetic parameters over the raw material. The deconvolution analysis of the thermogravimetric signals leads the study to an overriding investigation on thermal stability of the intrinsic bioconstituent. In addition, the kinetic triplet and thermodynamic parameters were estimated by employing the ICTAC recommended Ozawa-Flynn-Wall isoconversional method. The computed average activation energy level of the torrefied biomaterial (229 kJ/mol) was registered significantly higher than the raw pigeon pea stalk (139 kJ/mol). Also, the changes registered in thermodynamic parameters such as  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  give a beneficial sign on the thermal stability of the existing bioconstituents. Torrefaction of the pigeon pea stalk enhances the kinetics and thermodynamic balancing of the biomaterial. The thermally established biomaterial can be stored for a longer period and it can utilize as the bioenergy generating feedstock during idle periods.

**Keywords:** Activation energy; Thermodynamic parameters; Pigeon pea stalk; Torrefaction; deconvolution analysis.

## 1. Introduction

Environmental pollution and the rapid depletion of fossil fuels became a global issue, that forces us to replace hazardous energy sources with green and clean energy sources [1]. Biomass, especially agricultural crop residues has the advantage to renew and generate environmentally friendly energy [2]. In India, approximately 611 million tons of biomass produces annually. A surplus amount of about 25% is available for energy generation [3]. Agricultural biomass has enough energy potential that can mitigate the dependency on fossil fuels and also reduces the risk of climatic change which is one of the most concerning issues globally [4]. The main bioconstituents of biomass are hemicellulose, cellulose, and lignin [5].

Many researchers have found the technology and methods of energy harnessing from biomass such as biological, thermochemical, and physiological methods [6][7]. Some of these technologies are pyrolysis, gasification, briquetting, and microbial decomposition. Even though the availability of these technologies, the utilization of biomass is limited due to high moisture content, transportation, and logistics issues. These limitations can be removed by pre-treatment of raw biomass [8][9]. The biomass pre-treatment process enhances the physiochemical properties and optimizes pyrolysis product yields and composition and also reduces the formation of undesired products [10]. One of the methods to improve the physical and chemical properties of biomass is torrefaction.

Torrefaction is a thermochemical process also known as mild pyrolysis. In the torrefaction process, raw biomass is heated at a temperature range of 200–300 °C for a definite time under ambient pressure, in the absence of oxygen or limited oxygen concentration [11]. Due to the torrefaction process, the reduction in surface moisture, the devolatilization of lighter volatile materials, and changes in the value of the O/C and H/C ratio can be noticed [12]. Torrefaction product shows superior quality as compared to native biomass by means of water resistance, calorific value, grindability, and biodegradability [13].

Although there is enough information available on the torrefaction of biomass which highlighted the properties changes due to the torrefaction effect. Still, there is no literature available that deals with the reaction kinetics changes in torrefied pigeon pea stalk biomaterial. The in-depth prior knowledge about the thermal behaviour of biomass improves the yield and better control of the pyrolysis process parameters [14]. For better designing of the system to generate energy from biomaterials, it must precisely analyze the initial energy input needed to start the thermal decomposition of biomaterial [15].

To diagnose the thermal behaviour of biomass, thermogravimetric analysis (TGA) is the prominent method. TGA experiment shows the weight loss of the biomass per unit of time or temperature. An in-depth study explores the thermal decomposition of the intrinsic bioconstituents of pigeon pea stalks by employing the mathematical deconvolution process [16]. The overriding knowledge of kinetic and thermodynamic parameters enhances the system efficiency and production of a better-quality product. The estimation of the pyrolytic kinetic triplet is very challenging because a series of chemical reactions proceed simultaneously while the conversion of volatile material into a different value-added product. ICTAC has recommended various methods for the computation of kinetic parameters, nowadays which are being used commonly [17]. The suggested methods are classified into model-free and model-fitting approaches. The isoconversional model-free method is more accurate and time-saving as compared to model fitting methods available for the estimation of the kinetic parameter [18][19]. The popular methods are the Friedman method, Coats-Redfern (CR), Kissinger-Akahira-Sunose (KAS), Starink, Tang, and Flynn-Wall-Ozawa (FWO) [18]. Mathematically, CR, KAS, and OFW are integral isoconversional methods, whereas the Friedman method is a differential isoconversional method [20].

This paper aims to investigate the changes that occurred in biopolymeric components of PPS and their activation energy levels due to the torrefaction effect. To investigate the torrefaction effect on pyrolysis behaviour, thermogravimetric analysis of raw and torrefied biomass was performed. To evaluate the kinetic parameters Ozawa-Flynn-Wall (FWO) isoconversional method was employed and discussed critically.

## **2. Material and Methods**

### **2.1 Materials and torrefaction experiment**

The experimental biomass raw pigeon pea stalk (RPS) was amazed from the research field of the ICAR-CIAE, Bhopal (MP). Before the experiment, the raw material was dried in sunlight at desired moisture level. In order to that, carried out the torrefaction of RPS material, about 1 kg of dried biomass was subjected to thermal treatment in a horizontal type fixed bed reactor up to an intermediate temperature range of torrefaction (250°C) and holding time (30 min), respectively. To stabilize the inert environment in the reactor, the nitrogen gas with the highest purity level of 99.99% was supplied as a carrier gas at a flow rate of 250 ml/min. The heating rate of 10°C/min was maintained while doing the torrefaction. The reactor cooled down slowly with the continuous supply of carrier gas (N<sub>2</sub>). The obtained product is named torrefied pigeon pea stalk (TPS). The characterization and other analyses were conducted by combining the TPS and RPS biomaterial.

## **2.2 Characterization of experimental material**

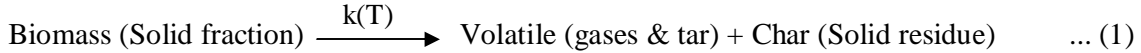
The characterization of both the experimental biomass RPS and TPS includes the proximate and ultimate analysis to diagnose the physical and chemical properties. The proximate analysis explores the percentage of moisture, volatile material, ash and fixed carbon content existence in the biomaterial, whereas the elemental compound (C, H, N, and O) and their relative proportion are represented by the ultimate analysis. The proximate analysis was conducted in the institute (ICAR-CIAE, Bhopal) by following the ASTM standard and the ultimate analysis was done at the Indian Institute of Technology, Mumbai. In addition, the structural component analysis was conducted to assess the percentage changes that occurred in the major biomass compositions (hemicellulose, cellulose and lignin) due to the torrefaction effect.

## **2.3 Thermal behaviour and kinetic study**

To investigate the thermal behaviour of the RPS and TPS biomaterial, TGA analysis was done by using a thermogravimetric analyzer (TA, TGA55, Discovery series) under nitrogen atmosphere @ 60 ml/min at four different heating rates ( $\beta = 10, 20, 30$  and  $40^\circ\text{C}/\text{min}$ ) from room temperature to  $1000^\circ\text{C}$ . TGA experiment generated data about the weight loss of biomaterials concerning temperature or time (thermogram) and also the first order derivative of thermogram (DTG) against the same parameters. The Gaussian deconvolution analysis was employed to explore the various stages of the thermal degradation of PPS. While thermal degradation of PPS, TG-signals reflect the thermal loosening causing the breakdown of internal bio-compound molecules.

The kinetic study includes the computation of activation energy, pre-exponential factor and order of reaction which are the parameters that ultimately affected the process rate. Thermal analysis is concerned with thermally stimulated processes, i.e., the processes that can be initiated by a change in temperature. It is very challenging to precisely explain the reaction mechanism that occurred while doing pyrolysis of biomass due to the large variability in the biomass compositions (hemicelluloses, cellulose, lignin and other complex material) and their devolatilization process overlaying to the elevated temperate range [21]. The literature available on the kinetic approach attempted by the researchers explains the different

parameters involved in the reaction. Generally in the pyrolysis process, the conversion of raw biomass into the final product is described as [22].



Where  $k$  is the rate constant which is defined by the Arrhenius equation

$$k = Ae^{\left(\frac{-E_a}{RT}\right)} \quad \dots (2)$$

Where  $E_a$  is activation energy ( $\text{kJ}\cdot\text{mol}^{-1}$ );  $T$  is the absolute temperature (K);  $A$  is the Pre-exponential factor ( $\text{s}^{-1}$ ) and  $R$  is the universal gas constant ( $8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ).

The majority of kinetic methods used in the area of thermal analysis consider the rate to be a function of only two variables,  $T$  and  $\alpha$ . The rate of conversion from solid state to volatile state can be written as:

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

Where  $\alpha$  represents the degree of conversion of the pyrolysis process in a fraction of time ( $t$ ) and reaction model  $f(\alpha)$ .

If a process is accompanied by mass loss, the extent of conversion ( $\alpha$ ) is evaluated as a fraction of the total mass loss in the process. It increases from 0 to 1 as the process progresses from initiation to completion and can be calculated by using equation no. (4),

$$\alpha = \frac{m_i - m_t}{m_i - m_e} \quad \dots (4)$$

Where  $m_i$  is the initial weight of the biomass sample,  $m_t$  is the mass of the sample at a time ( $t$ ) and  $m_e$  is the mass residue left after the ending of the process.

Resultant of equations (2) and (3) can be written as;

$$\frac{d\alpha}{dt} = A \cdot e^{\left(\frac{-E_a}{RT}\right)} f(\alpha) \quad \dots (5)$$

Equation (5) represents the fundamental equation useful for the estimation of kinetic parameters.

Generally, effective kinetic parameters are functions of the intrinsic kinetic parameters of the individual steps. In this study, to investigate the activation energy level of RPS and TPS biomaterial, ICTAC recommended Flynn-Wall-Ozawa (FWO) isoconversional method [23] was used, which is mathematically formulated in Eq.6. The isoconversional levels were selected at  $\alpha$ -value from 0.1 to 0.9.

$$\ln\beta = \ln\left(\frac{A \cdot E_a}{Rg(\alpha)}\right) - 5.331 - 1.052\left(\frac{E_a}{RT}\right) \quad \dots (6)$$

Where  $\beta$  is the heating rate ( $^{\circ}\text{C}/\text{min}$ ).

The above mentioned mathematical equations are being used for drawing linear plots between  $\ln\beta$  and  $\left(\frac{1}{T}\right)$ . The activation energy at the various conversion level (0.1-0.9) was computed concerning the slope value  $-1.052\left(\frac{E_a}{RT}\right)$  for linear plotting.

The thermodynamic parameters such as a change in Gibbs free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ) entropy ( $\Delta S$ ), and also a pre-exponential factor ( $A$ ) were calculated. The value of  $A$  ( $\text{s}^{-1}$ ) indicates how quickly the reaction will take place under the variable temperature range, whereas the value of  $\Delta G$  and  $\Delta S$  indicates the reaction process is spontaneous or non-

spontaneous. The value of  $\Delta H$  shows that the particular reaction is endothermic or exothermic. The computational method was adopted by the equations given by Kim et al. [24] and the obtained result is discussed critically.

### 3. Result and discussion

#### 3.1 Characterization of experimental biomass

Table 1 elucidates the characteristics of the RPS and TPS biomaterial by making an impactful assessment of the property changes in a TPS biomaterial over the RPS. The moisture content (MC) of the TPS was reduced by 5.56% from 9.12% (RPS), which indicated that the torrefaction removes the moisture presented in raw biomass. Literature available on the torrefaction of agricultural biomass is suggesting that up to 250°C escaping of surface moisture happens with a higher rate of dehydration whereas a lesser amount of bounded moisture is removed [25].

Table 1 Characterization of experimental biomass

Particulars	Biomass	Parameters						Literature
Proximate analysis		MC	VM	AC	FC			
	RPS	9.12	79.19	1.86	9.83		Present study	
	TPS	5.56	74.76	2.18	17.50		Present study	
	RPS	5.43	82.12	1.49	10.96		[26]	
	TPS-250°C	2.34	68.43	2.93	26.30		[26]	
Elemental analysis		C	H	N	O	O/C	H/C	
	RPS	43.60	7.25	0.25	48.90	0.84	1.98	Present study
	TPS	46.30	7.65	0.75	45.30	0.73	1.96	Present study
	RPS	46.10	6.73	0.73	46.42	1.00	0.15	[26]
	TPS-250°C	51.85	7.02	0.82	40.31	0.78	0.14	[26]
Fiber analysis		HC	CL	LN				
	RPS	29.50	43.20	15.10			Present study	
	TPS	27.80	37.90	14.20			Present study	

The volatile matters are supposed to be released partially due to the torrefaction process. Therefore, a significant reduction in the volatile matter was noticed in table 1. These reductions in volatile matter promote the increment of ash content as well as the fixed carbon content in treated biomaterial as compared to raw biomass. The present study showed the reduction of volatile matters from 79.19% (RPS) to 74.76% (TPS) and its resultant increment of ash content as 2.18% (TPS) from 1.86% (RPS) and also in fixed carbon as 17.50% (TPS) from 9.83% (RPS).

Elemental analysis of biomass revealed the compositions as carbon (C), hydrogen (H), nitrogen (N), and oxygen (O). It can be observed from the table that the torrefaction process affected the oxygen and carbon content significantly as compared to hydrogen and nitrogen content. Carbon and hydrogen content presented in biomass is considered a major energy source during the combustion process. In this study oxygen content reduced from 48.90% (RPS) to 45.30% (TPS). At the same time, O/C and H/C ratio reduction was estimated which

is caused by an increment in carbon element. The thermal process of raw biomass also devolatilise the lighter volatile material that reduces the percentage composition of the structural fibers hemicellulosic, cellulosic, and lignin as shown in table 1.

It is concluded that the torrefaction of PPS is beneficial by escaping moisture and significant reduction in oxygen content. It is the backing of lesser favourability for the biological decomposition while logistic for a longer time as it can be used for bioenergy generating feedstock.

### 3.2 Thermal behaviour and Gaussian deconvolution analysis

The result of the typical thermogravimetric analysis is discussed in the earlier published article [21]. An in-depth analysis is presented here by comparative action between RPS and TPS. To understand the insights into the thermal degradation of RPS and TPS biomaterial, a Gaussian deconvolution analysis was performed. Figure 1 shows the typical deconvolution of RPS and TPS biomaterial at 10 °C/min, the peaks that appeared into TG-signals were selected and a large number of iterations of the concerning peak data has been done to fit the cumulative curve with the higher level of accuracy ( $R^2 = >99\%$ ). The obtained peak temperature range and Full Width at Half Maximum (FWHM) values of major bioconstituents such as hemicellulose (HC), cellulose (CL), and lignin (LN) at each heating rate (10 to 40 °C/min) are presented in table 2. A measure of sharpness or flatness of the peak is represented by the FWHM value. A lower value shows a higher degree of sharpness whereas a higher value shows flatness [27]. The flatness of the peak shows the difficulty level to degrade the biomaterial [2].

Table 2 Gaussian deconvoluted data of RPS and TPS

$\beta$	Biomaterial	HC		CL		LN	
		$T_p$	FWHM	$T_p$	FWHM	$T_p$	FWHM
10	RPS	305	113	337	55	450	147
	TPS	295	105	341	57	495	353
20	RPS	320	121	355	58	540	60
	TPS	306	105	362	60	481	90
30	RPS	330	116	360	72	558	116
	TPS	310	110	373	75	448	364
40	RPS	333	116	367	76	568	251
	TPS	314	108	376	78	436	371

$\beta$  - Heating rate (°C/min),  $T_p$  - Peak temperature (°C), FWHM- Full-Width at Half-Maximum

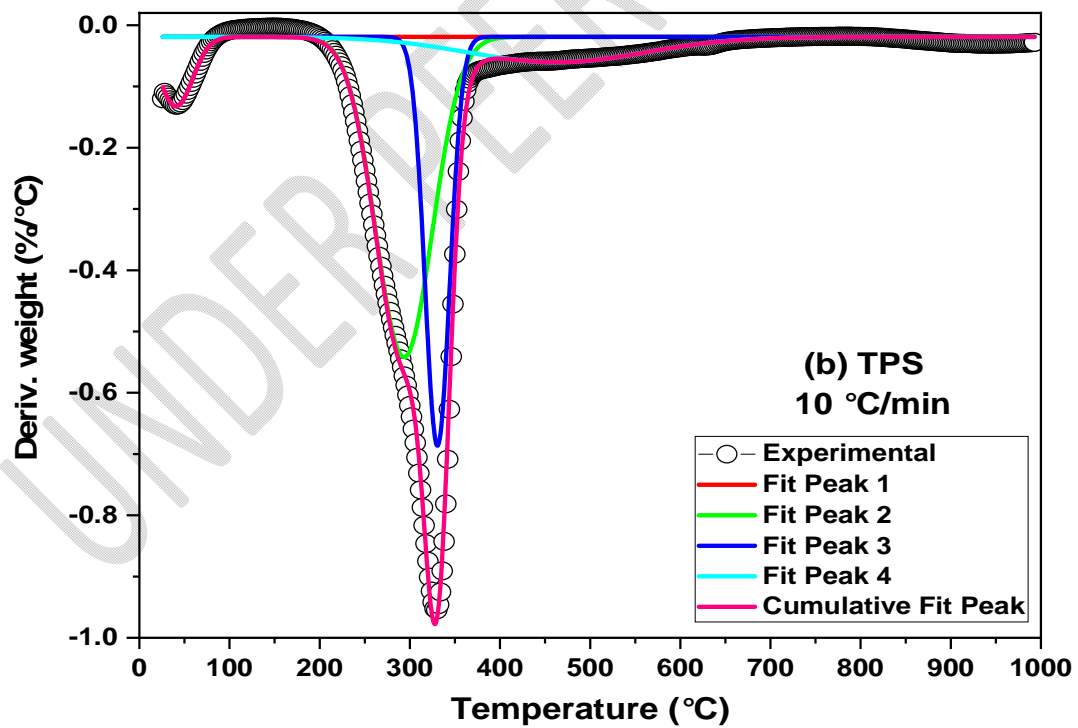
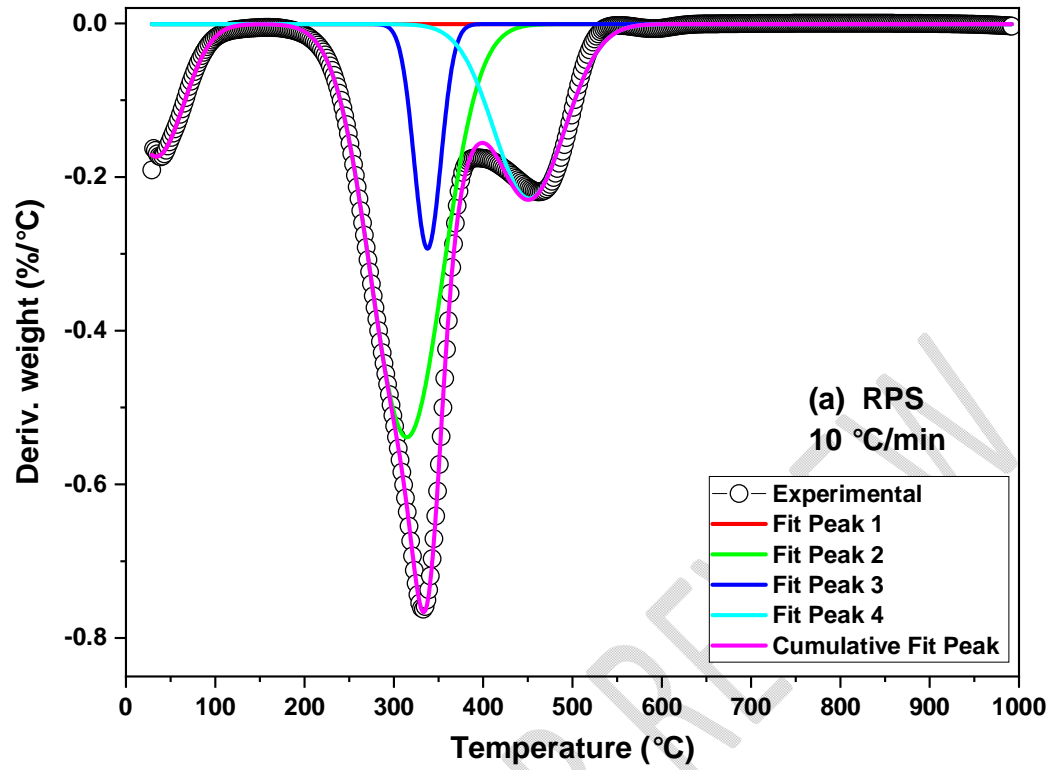


Fig. 1 Gaussian deconvolution of TG-signal (a) RPS and (b)TPS

Table 2 disclosed that the peak temperature and FWHM value of the hemicellulose insight of the TPS tend to a little shrink as compared to RPS from  $T_p = 305$  to  $295$  °C and  $\text{FWHM} = 113$  to  $105$  at  $\beta = 10$  °C/min, and similar for all other heating rates (20, 30 and 40 °C/min). Whereas cellulose and lignin it is registered with a little increase in TPS than the RPS biomaterial. All the obtained results show that the hemicellulosic structure is affected due to the torrefaction process. The lower torrefaction temperature (250°C) influences the dehydration of the hydroxyl group and side chain of the structure [28]. Also, the devolatilization of lighter molecules of the cellulosic and lignin material stabilized the rigidity in a higher temperature range by making it strong enough to the interlinked chain. This rigidity property of the intrinsic bioconstituents refuses the logistic problem of biomass by enhancing thermal stability.

### 3.3 Kinetic analysis of raw and torrefied pigeon pea straw

This study includes the evaluation of pyrolytic kinetics of the RPS and TPS biomaterial to ensure the compensation made in the values of the relevant parameters. In order to that, the kinetic parameters such as activation energy ( $E_a$ ) and pre-exponential factor ( $A$ ) were computed by employing the ICTAC recommended isoconversional model at selected conversion values (0.1-0.9). The computation of the kinetic parameters is a very challenging and complicated process, to make it a simpler one the linear fitted plots between the model exponential and their concerning temperature (K) are shown in figure 2. The coefficient of determination values was found to be higher level ( $R^2 = >90\%$ ), which reflected the correctness of the estimation. The resultant values are appended in table 3, which shows the significant increase in the activation energy level of the TPS as compared to the RPS biomaterial. The activation energy ( $E_a$ ) is the concerning parameter that correlates with the initiation or promotion of the thermal degradation process of particular bioconstituents by breaking down the chemically bounded biopolymers. The higher activation energy level indicates the thermal stability of biomaterials [29].

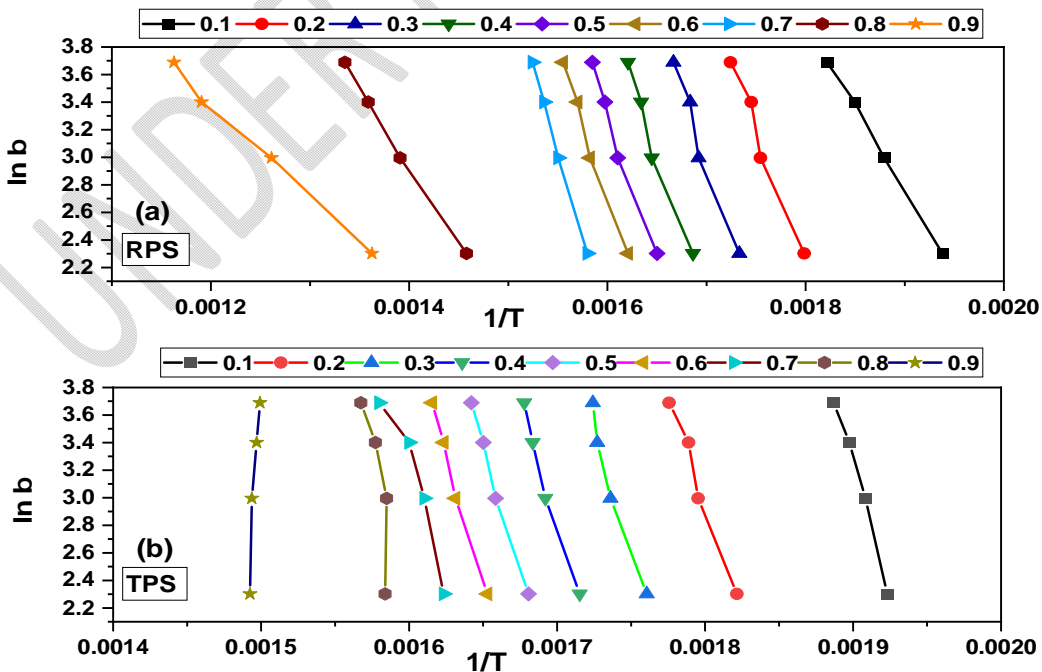


Fig. 2 Linear fitting of FWO isoconversional methods (a) RPS and (b) TPS

The average activation energy for TPS was computed 229 kJ/mol which is comparatively higher than the RPS (139 kJ/mol). It is clear from the table that at the initial stage of conversion ( $\alpha = 0.1$ ) of RPS biomaterial, the estimated activation energy was significantly lower  $E_a = 93$  kJ/mol. Breakdown of weaker bonds, moisture removal and devolatilization of lighter volatile materials required lower energy [30]. Whereas; TPS biomaterial had much higher activation energy as  $E_a = 304$  kJ/mol at the initial conversion level ( $\alpha = 0.1$ ). Fig. 3 shows the activation energy trend, which revealed the differences in activation energy level at the initial stage to ending of the conversion (from  $\alpha = 0.1$  to 0.9). TPS biomaterial required more energy to activate the particles as compared to the RPS. A similar result was reported by the researchers in the study conducted for other biomaterials having the same compositions (HC, CL and LN) [28].

Table 3 Activation energy and Pre exponential factor of RPS and TPS

Model	Conversion ( $\alpha$ )	RPS			TPS		
		$E_a$ (kJ/mol)	$R^2$	A ( $s^{-1}$ )	$E_a$ (kJ/mol)	$R^2$	A ( $s^{-1}$ )
FWO	0.1	91	0.976	9.6E+01	304	0.985	9.96E+35
	0.2	149	0.975	6.3E+04	283	0.941	2.66E+33
	0.3	166	0.974	4.5E+05	282	0.961	1.83E+33
	0.4	165	0.977	4.2E+05	286	0.983	5.55E+33
	0.5	166	0.985	4.7E+05	284	0.991	3.49E+33
	0.6	168	0.988	5.7E+05	293	0.991	5.40E+34
	0.7	198	0.998	2.1E+07	245	0.905	4.97E+28
	0.8	89	0.997	3.9E+01	62	0.676	3.09E+05
	0.9	53	0.995	4.0E-01	25	0.854	3.74E+00
	Avg.	139	-	-	229	-	-

The pre-exponential (A) factor is an important kinetic parameter for a comprehensive kinetic study [31]. The activation energy level of the specific conversion affected the pre-exponential factor. Values of the pre-exponential factor estimated are shown in Table 3. The lower value of pre-exponential factors ( $<10^9 s^{-1}$ ) reflects a surface reaction, but if the reaction is not related to the surface area, the lower factor indicates a closed complex. Whereas the higher value of pre-exponential factors ( $\geq 10^9 s^{-1}$ ) reflects a simple complex [32].

The pre-exponential factor calculated for RPS was found in the range of  $A = 3.9E+01 s^{-1}$  to  $A = 1.7E+12 s^{-1}$  and also observed somewhat negative power values ( $10^{-1}$ ,  $10^{-2}$ ,  $10^{-3}$ ), which indicates that degradation of RPS is easier and faster. The lower value of A and  $E_a$  reveals a faster and easier degradation effect of biomass for the respective degrees of conversion [33]. The presence of significant porous carbon in biomass leads to easy degrading and reduces the thermal stability of biomaterial [32]. Whereas the value of A for TPS was observed in the range of  $A = 3.74E+00 s^{-1}$  to  $A = 9.96E+35 s^{-1}$ . The higher values of A for TPS reflected that the torrefaction of biomass influenced the activated complex formation.

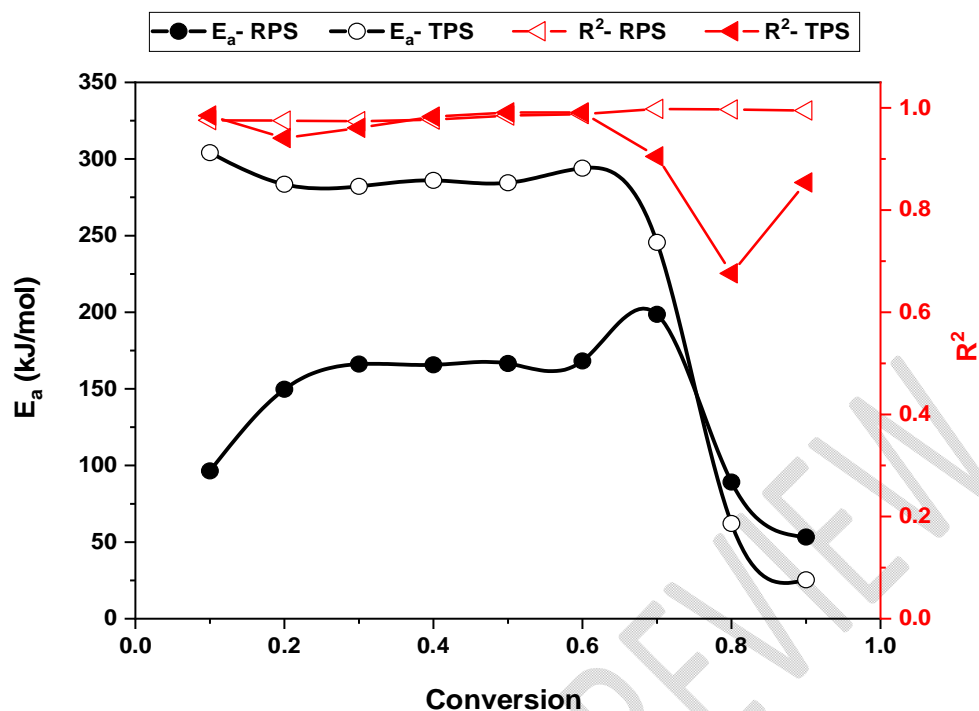


Fig. 3 Trend of activation energy of RPS and TPS at various conversion levels

### 3.4 Thermodynamic evaluation

Thermodynamic parameters namely change in enthalpy ( $\Delta H$ ), change in Gibbs free energy ( $\Delta G$ ), and change in Entropy ( $\Delta S$ ) were estimated by using the computed activation energy and pre-exponential factor. Figure 4 revealed the significant variation registered in thermodynamic parameters at conversion fraction (0.1-0.9).

It is notable that all values of  $\Delta H$  obtained positive for all conversion fractions (0.1-0.9). The average value of  $\Delta H = 134$  kJ/mol and 230 kJ/mol for RPS and TPS biomaterial respectively. In general, the average value of  $\Delta H$  significantly increased after the torrefaction of biomass, which indicates that the torrefied biomaterial required more energy to activate than the raw biomass. Mishra and Mohanti also concluded for agricultural waste that biomass having a higher average enthalpy value needs more energy for activation [34].

The Gibbs free energy value shows an increase in the total energy of the system at the point of the reagent and formation of complex activated [35]. The average value of  $\Delta G$  was calculated as  $\Delta G = 327$  kJ/mol for RPS and  $\Delta G = 119$  kJ/mol for TPS biomaterial. In general, it can be analyzed that the torrefaction lowering the Gibbs free energy in biomaterial is desirable for the thermal stability of biomaterial, the higher value of  $\Delta G$  indicates the less favourability of the biomass for reaction as extreme heat flow and randomness occurred [36].

The change in entropy value ( $\Delta S$ ) reflected the degree of randomness of the system/process, it may be a negative and positive value. The average value was estimated, at  $\Delta S = -179$  J/mol.K for RPS, whereas for TPS it was found  $\Delta S = 261$  J/mol.K. The negative value indicates that the randomness (degree of disorder) of the product that occurred during the

dissociation of complex chemical bonds was low as compared to the actual reactant. In order to bring biomass into its thermodynamic equilibrium, it passes through a certain physiochemical process. At this condition, more time is needed to start the formation of the activated complex. In case of a higher  $\Delta S$  value, it is considered as the biomass is far from its thermodynamic equilibrium, at this condition quick reaction takes place to form an activated complex [37]. In the presented study RPS biomaterial had a negative value at all conversion fractions (0.1-0.9) that stipulate the raw biomass needed more time as compared to torrefied biomass for activation.

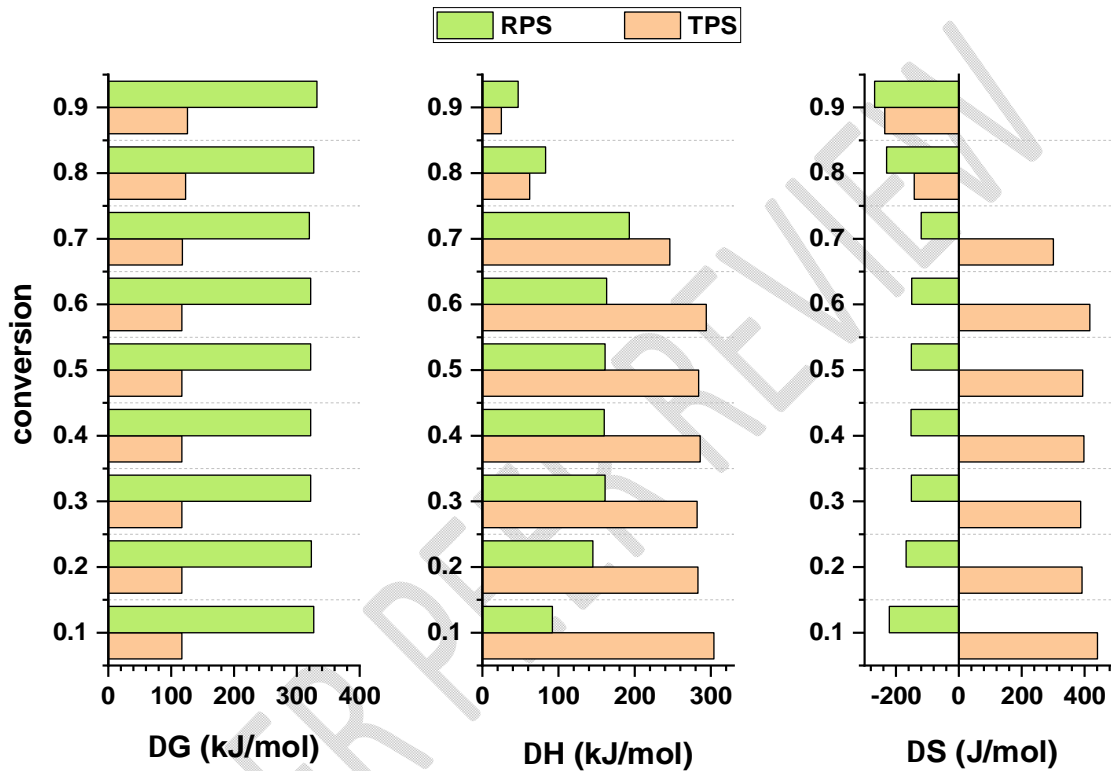


Fig. 4 Thermodynamic evaluation ( $\Delta G$ ,  $\Delta H$ ,  $\Delta S$ ) with conversion fraction ( $\alpha$ ) for RPS and TPS biomaterial

#### 4. Conclusion

The present article found that the escaping of moisture and lighter volatile materials of the intrinsic hemicellulosic and cellulosic bioconstituents of the pigeon pea stalk contributed positively to enhancing of thermal stability of the biomaterial. TPS biomaterial has assured the higher level of  $E_a = 229$  kJ/mol,  $\Delta H = 230$  kJ/mol and  $\Delta S = 261$  J/mol.K and the lower level of  $\Delta G = 119$  kJ/mol as compared to the RPS. The present paper shows that the torrefaction process enhances the degradation kinetic compensation and produces a thermodynamically balanced biomaterial that is sustainable for a longer period and can be utilized in the idle period as an energy generating feedstock.

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