



# Article Kinetic Parameters Estimation of Thermal and Co-Pyrolysis of Groundnut De-oiled Cake and Polyethylene Terephthalate (PET) Waste

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**Abstract:** The physicochemical characterization and kinetic evaluation of the thermal and co-pyrolysis of groundnut de-oiled cake (GDC) and PET plastic is examined in this present study. A bomb calorimeter, proximate/CHNS analysis, and a thermogravimetric analyzer were used to study the physicochemical characteristics of the biomass and plastic. By using a FTIR analysis, it was found that both samples had distinct functional groups. Iso-conversional models, such as Friedman's, the Kissinger–Akhaira–Sunose, the Ozawa–Flynn–Wall, Starink's, and the distributed activation energy models were employed in the calculation of the kinetic parameters. The physicochemical characterization provided valuable insights into the pyrolysis characteristics. The rate at which the feedstock was heated were 10, 20, and 30 °C min<sup>-1</sup>, and were used to study the thermal breakdown behavior of the GDC and PET by the TGA. The following temperatures are the active pyrolysis zones for the thermal pyrolysis and the co-pyrolysis: for the groundnut de-oiled cake, T = 150–650 °C; for the PET, T = 375–600 °C; and for the co-pyrolysis, T = 175–550 °C. For the thermal pyrolysis (for GDC, E = 127.49 kJ mol<sup>-1</sup>; PET, E = 201.45 kJ mol<sup>-1</sup>); and the co-pyrolysis (E = 175.86 kJ mol<sup>-1</sup>), Kissinger–Akhaira–Sunose revealed low activation energy.

Keywords: groundnut de-oiled cake; PET plastic; TGA; kinetics

# 1. Introduction

The continuous decline of availability of fossil reserves and the rising population opened up the path for using natural resources. Therefore, cutting-edge, sustainable and environmentally friendly technologies are required to meet energy and ecological demands without harming the environment [1]. The best help in this regard is those abundantly available naturally, such as biomass, which has a 2 billion tons higher energy content than regular coal. The primary renewable source for developing biofuels and value-added chemicals is the biomass resources, as the other clean energy sources have significant limitations. Thus, the replacement of fossil fuels might greatly benefit from the use of a lignocellulosic biomass. Numerous lignocellulose feedstocks are used to produce a widerange of value-added compounds in addition to serving as an alternative to transportation based-fuels [2].

The conversion of a biomass into energy-intensive end products can be accomplished using a variety of approaches. Chemical, biological, mechanical, and thermochemical are a few of them. But a thermochemical conversion is significantly effective compared to other conversion techniques, particularly in biomass valorization. Pyrolysis is one of the existing thermochemical conversion methods that effectively transforms waste materials into usable materials, including bioenergy based fuels and value-added chemicals. The simplest methods for effectively and efficiently utilizing many types of feedstock with the energy consumption needed from the individual feedstock, is considered to be co-pyrolysis. A large quantity of waste might be substantially used as raw material during the co-pyrolysis



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). process, ensuring an efficient waste management as well. Additionally, co-pyrolysis has the potential to significantly minimize energy usage, production costs, and processing times. In order to generate biofuels while managing waste with minimal negative environmental effects, biomass and plastic materials are co-pyrolyzed [3]. Polymers have the potential to serve as a source of hydrogen and carbon in thermal co-processing alongside organic natural materials containing less hydrogen and carbon, such as biomass. The co-pyrolysis of plastic and biomass increases the heating value and pyrolytic liquid yield. Using biomass and plastic waste to make liquid fuel through a co-pyrolysis process is a key way to solve the environment problems that come from throwing the waste away [4].

Alternative fuels like those made from waste materials, known as biofuels, are attracting a lot of interest because of their many benefits and the abundance of feedstocks, such as organic solid waste. Non-edible oil seeds (vegetable oil), wheat husk, sawdust, wheat straw, bagasse, algal biomass, de oiled cake, oil seed outer shells, waste products, etc., are some of the raw materials utilized in the generation of biofuels. Numerous experiments have been done using agricultural waste, including non-edible oil crops, to generate biofuels. In addition to the biodiesel revenue generation from non-edible oil seeds, pyrolysis and co-pyrolysis technologies can be employed to create value-added chemicals from the shell waste and de oiled cake of the seed. High levels of protein can be found in groundnut seeds. Around 30–35 kg of oil and 50 kg of meal can be extracted from a quintal of groundnuts on average [5–7]. The cake, which is full of protein, was traditionally fed to cattle or used as manure. Due to the excess availability of de-oiled cakes as a by-product from the oil extraction process, this can be a potential feedstock for production of biofuel and value-added chemicals [8]. Polystyrene (WPS), polyethylene terephthalate (PET), low density polyethylene (LDPE), and polyvinyl chloride (PVC) types of wastes are only a few examples of the common plastics whose volume is rising. The global scenario says that about 150 million tons of plastic are discarded and end up in landfills. Additionally, despite recycling garbage equivalent to almost 100 million barrels of oil, an estimate of 8 million tons of landfill space still exists, according to research by European nations. The Indian scenario accounts for the majority of plastic waste (PET) generated by the packaging sector. It is estimated that 42% of all plastics are used in this industry, making it one of the most important ones. Roughly 100 million tons of garbage are dumped annually, including garbage from households. In this way, this PET plastic might be viewed as a source of fuel [9]. The de oiled groundnut cake and PET plastic waste are co-pyrolyzed to generate biofuels while managing waste with a minimal adverse environmental impact. This study was carried out to examine the detailed kinetic variables in the desired reaction utilizing TGA in the context of emphasizing the development of the reaction mechanism of the co-pyrolysis process.

There are two main approaches to evaluate the kinetics of solid-state materials for both isothermal and non-isothermal processes, which can be used to determine the pyrolysis kinetics. These are called model-fitting and model-free methods, and both have advantages and limitations. In general, the differential Friedman (DFM), the Kissinger– Akhaira-Sunose(KAS), the Ozawa-Flynn-Wall (OFW), Starink's (STR), and the distributed activation energy method (DAEM) are a few effective non-isothermal model-free methods [10]. Model-free techniques were utilized more frequently than model-fitting methods since they do not assume anything about the particular reaction model. The data obtained from the experiments are usually considered with numerous heating rates, leading to a reduction in error in the fluctuating kinetic results when the coefficient of the correlation is strong. In addition, these techniques enable the extraction of kinetic parameters from biomass waste by using constant-temperature or increasing temperature TG and DTG data. A non-isothermal thermogram and differential thermogram data are more reliable in assessing multi compound thermal degradation kinetics than isothermal TG data, since it is challenging to achieve the exact isothermal conditions throughout the TGA experiment, especially during the reaction initialization [4].

A study on estimating the kinetic parameters by the Coats–Redfern method for the different de oiled cakes, i.e., Neem, sesame, mustard, and mahua seed, indicated that the reaction followed the first-order mechanism with the apparent activation energies ranging from 11–28 kJ mol<sup>-1</sup>. The study also found that mustard de oiled cake requires the highest activation energy compared to the rest of the biomass [8]. Furthermore, an investigation of the non-isothermal kinetic analysis of PET plastic indicated that the activation energy of 166–180 kJ mol<sup>-1</sup> when the Ozawa–Flynn–Wall method was used [11]. Additionally, a recent study on the determination of the kinetics of co-pyrolysis of pinewood with a variety of polymer wastes such as PP, PET, and PC yielded the highest synergistic effect of biomass with PET plastic. A DAEM kinetic model was employed to estimate the average activation energy, which was found to be 250–290 kJ mol<sup>-1</sup> [12].

The aim and scope of this study is to analyze the feasibility of the co-pyrolysis of groundnut de oiled cake (GDC) and PET plastic at a ratio of 1:1. The co-feed (1:1) ratio was explicitly chosen because the maximum yields of pyrolytic products are generally reported to produce bio-oil with a maximum yield of 30–40 wt% via co-pyrolysis, as reported in the earlier literature. [13,14]. Additionally, to determine the thermal decomposition behavior and to estimate the kinetic parameters, we used TGA equipment under non-isothermal conditions in a nitrogen atmosphere at three different heating rates of 10, 20, 30 °C min<sup>-1</sup>. Furthermore, the GDC: PET mixture thermal degradation behavior is compared with that of the GDC and PET components, individually. The study of the chemical kinetics is extremely important since it is predicated on the rate of reaction, which gives crucial background information regarding the working mechanisms of the chemical processes that are being considered. So, it's important to get accurate experimental data in order to make reliable and useful kinetic models that can be used to make a full-size industrial reactor, for this process that uses this feedstock.

#### 2. Materials and Methods

#### 2.1. Feedstock Collection and Preparation

The groundnut de oiled cake was collected from Rajasthan, India. The obtained biomass was dried for 24 h under ambient conditions and ground to reduce the size to <1 mm. The moisture present in powdered biomass was analyzed by placing the sample in an oven for 1 h at 105  $^{\circ}$ C and the sample was stored to avoid any moisture absorption [13].

The PET plastic was collected in the form of flakes from Central Institute of Petrochemical Engineering and Technology (CIPET), Guwahati. The sample was sieved for 300 microns and analyzed for the moisture content using the same procedure as the biomass. The moisture-free sample was stored in an air-tight container [13].

#### 2.2. Characterization of the Raw Material

#### 2.2.1. Proximate and CHNS Analyses

The proximate analysis of the GDC and PET was conducted using ASTM standards (E-871, D1102-84). 1.0 g of a sun-dried sample in a crucible was kept in a hot air oven at 105 °C for 60 min. Then, the oven-dried sample was weighed to measure the moisture removed during the process. Further, a similar amount of an oven-dried sample was taken in a ceramic sample holder and placed in a muffle furnace operated at 950 °C, 925 °C for 7 min for the biomass and plastic, respectively. Then, the sample from the furnace was placed in a desiccator to reduce the temperature. The variation in the weights of the samples provided the volatile matter in the samples. Additionally, 1.0 g of an oven-dried sample was kept in the same furnace at 550 °C for 4 h. Once cooled, the weight difference was noted, which provided the ash content of both the GDC and PET [14]. The fixed carbon was calculated using the following formula:

An elemental analyzer was used for the CHNS content of the samples (Euro EA3000, Euro Vector, Italy). With the aid of an oxygen bomb calorimeter, the calorific value was measured (Parr, Model: 1341 Plain Jacket Calorimeter). The experiments were all carried out three times, and the results presented here are the averages. Hexane was utilized as solvent in a Soxhlet unit to measure the extractive content of the biomass.

## 2.2.2. FTIR Analysis

A Fourier transform infrared spectrophotometer (FTIR, PerkinElmer, Spectrum Two) was used to investigate the functional groups present in the biomass. The dynamic range of scanning chosen was  $400 \text{ cm}^{-1}$  to  $4000 \text{ cm}^{-1}$  at a scanning rate of 40 with 4 cm<sup>-1</sup> as a step size [10].

## 2.2.3. TGA Analysis

The thermal decomposition behavior of the GDC, PET and the co-pyrolysis mixture were performed in PerkinElmer TGA 4000 instruments in an inert environment (N<sub>2</sub>). Around 5–9 mg of the sample was taken in a ceramic sample holder and heated from 30 °C to 900 °C and the rate of N<sub>2</sub> gas was maintained at 20 mL min<sup>-1</sup>. The heating rates of 10, 20 and 30 °C min<sup>-1</sup> were used to understand the kinetic behavior.

#### 2.3. Kinetic Modelling

The thermochemical conversion of the biomass is a very complex reaction due to the compositional variations within the biomass itself. The pyrolysis of the biomass is represented by the proposed mechanism, as follows:

$$Biomass \rightarrow Volatiles (gases + tar) + Solid residues (char)$$
(2)

The fraction of the biomass which is pyrolyzed (conversion factor),  $\alpha$  is defined, as follows:

$$\mathbf{y} = \left[\frac{\alpha_0 - \alpha_t}{\alpha_0 - \alpha_\infty}\right] \tag{3}$$

where  $\alpha_0$ ,  $\alpha_t$  and  $\alpha_\infty$  represents the initial mass, mass at a certain time (*t*) and mass at the completion of the process [5].

The kinetic equation can be written as:

$$\frac{dy}{dT} = a f(y) \tag{4}$$

where  $\frac{dx}{dT}$  represents the degradation rate and the rate constant (a) is given by the Arrhenius equation:

$$a = a_0 e^{-E* (R^{-1}*T^{-1})}$$
(5)

where  $a_0$  represents the pre-exponential factor, *E* is the activation energy of the reaction [2]. According to the n<sup>th</sup> order kinetics, f(x) can be represented, as follows:

$$f(y) = (1 - y)^n$$
(6)

Combining the Equations. (4)–(6), we get

$$\frac{dy}{dT} = a_0 e^{-E*(R^{-1}*T^{-1})} (1 - y)^n$$
(7)

Heating rate ( $\beta$ ) can be defined, as follows:

$$\beta = \frac{dT}{dt} = \frac{dT}{dy} \times \frac{dy}{dt}$$
(8)

Combination of Equations (7) and (8), we get

$$\frac{dy}{dT} = \frac{a_0}{\beta} \times e^{-E* (R^{-1}*T^{-1})} \times (1 - y)^n$$
(9)

Re-arrangement of Equation (9) results in the following equation:

$$\frac{dy}{(1-y)^n} = \frac{a}{\beta} \times e^{-E* (R^{-1}*T^{-1})} \times dT$$
(10)

Equation (10) represents the conversion of the biomass as a function of the temperature. Integrating Equation (10), we get

$$g(y) = \int_0^x \frac{dy}{f(y)} = \int_0^T \frac{a_0}{\beta} \times e^{-E* (R^{-1}*T^{-1})} \times dT$$
(11)

$$g(\mathbf{y}) = \frac{a_0 E}{\beta R} \int_0^x u^{-2} \times e^{-u} du = \frac{a_0 E}{\delta R} \times \mathbf{p}(\mathbf{y})$$
(12)

where, g(y) is the integral conversion and  $u = \frac{E}{RT}$ . Nevertheless, p(y) has no exact solution, henceforth the numerical approximations can be used to solve this Equation (7).

The different iso-conversional model-free methods adopted in this study are the differential Friedman (DFM), the Kissinger–Akhaira–Sunose(KAS), the Ozawa–Flynn–Wall (OFW), the Starink method (STR), and the simplified distributed activation energy model (DAEM). The kinetic modelling of these methods are discussed in Table 1 [10].

**Table 1.** Kinetic modelling equations for the iso-conversional model-free methods. Reprinted with permission from [10].

S.No.	Model	Equation	Plot	Determination of the Kinetic Parameter
1.	Differential Friedman Method	$\ln\left(\frac{dx}{dt}\right) = -\frac{E}{RT} + \ln(Af(x))$	$\ln\left(\frac{dx}{dt}\right)$ vs. $\frac{1}{T}$	The activation energy is obtained from the slope of the plot. The frequency factor is calculated from the intercept.
2.	Kissinger–Akahira– Sunose (KAS)	$\ln\left(\frac{\beta}{T^2}\right) = \\ \ln\left(\frac{AE}{Rg(x)}\right) - \frac{E}{RT}$	$\ln\left(\frac{\beta}{T^2}\right)$ vs. $\frac{1}{T}$	The activation energy is obtained from the slope of the plot. The frequency factor is calculated from the intercept.
3.	Ozawa-Flynn-Wall (OFW)	$\ln(\beta) = \ln\left(\frac{AE}{Rg(x)}\right) - 2.315 - 0.457 * \frac{E}{RT}$	$\ln(\beta)$ vs. $\frac{1}{T}$	This method uses Doyle's approximation. E can be calculated from the slope. The frequency factor can be calculated from the intercept.
4.	Starink Method (STR)	$\ln\left(rac{eta_{i}}{T_{lpha,i}^{1.92}} ight) = Constant - 1.0008 * \left(rac{E_{lpha}}{RT_{lpha,i}} ight)$	$\ln\left(rac{eta_i}{T^{1.92}_{lpha,i}} ight)$ vs. $\left(rac{1}{T^{1.92}_{lpha,i}} ight)$	A temperature approximation integral is used in this model for the simplification of the kinetic model. Activation energy is determined from the slope of the plot. The frequency factor is calculated from the intercept.
5.	Simplified Distributed activation energy model (DAEM)	$\ln\left(\frac{\beta}{T^2}\right) = \\ \ln\left(\frac{AR}{E}\right) + 0.6075 - \frac{E}{RT}$	$\ln\left(\frac{\beta}{T^2}\right)$ vs. $\frac{1}{T}$	The activation energy is determined from the slope of the plot while the intercept provides the information of the pre-exponential factor.

# 3. Results and Discussion

3.1. Physico-Chemical Analysis

The physicochemical characterization of the GDC, palm kernel cake, Karanja seed, and the Mesua ferrea L de oiled cake along with the PET is represented in Table 2, which shows that all of the de-oiled cake biomass and plastics contain no more than 10% moisture. The biomass, along with the plastics has a low amount of moisture and is considered to be

a suitable feedstock for the thermochemical conversion to liquid fuels. The literature on the pyrolysis processes indicates that the faster heat transmission to the particles occurs when the feedstock has a lower moisture content (<10%) [13]. Furthermore, it is observed that the groundnut de-oiled cake and the PET had a higher content of volatile matter (83%) and (94.3%), respectively, and a low ash content (4.8%) and (0.058%), respectively. Furthermore, compared to the biomass with the low volatile matter, the biomass with a higher volatile content contained more reactive chemicals that quickly degraded to produce more gaseous compounds (both condensable and non-condensable). Moreover, the lower ash content is an essential pyrolysis property that biomass must possess. Higher combustion rates and less slag formation at higher temperatures are the advantages of less ash content. This dramatically improves the biomass thermochemical conversion and decreases the operational costs. The feedstock having a high volatile matter and less ash content signifies the instant ignition of fuel [10]. The fixed carbon present in the biomass is used as a heat generator during the combustion due to its high energy value. An inadequate sample combustion and difficulties with waste disposal are additional issues associated with a high ash level. The energy value of feedstock is significantly influenced by its fixed carbon content [4]. The elemental analysis of the GDC and PET confirm a higher percentage of carbon (46.36%) and (62.888%), respectively, and a low nitrogen and sulfur content which lowers the SO<sub>x</sub> and NO<sub>x</sub> emissions during the co-pyrolysis [14]. The high calorific value of the co-feedstock of the GDC and PET confirms the ease of the biofuel production.

**Table 2.** Comparison of the Proximate/Ultimate characteristics of the present study with the existing literature.

Properties	Groundnut De-oiled Cake (Present Study)	Palm Kernel Cake [15]	Karanja Seed Cake [16]	Mesua Ferrea L De-oiled Cake [17]	Polyethylene Terephthalate Plastic (PET) (Present Study)	Polyethylene Terephthalate (PET) [12]
Moisture Content	5.6	7.92	7.27	4.08	0.61	0.0
Volatile Matter	83	71.84	89.23	82.63	94.3	99.99
Ash Content	4.8	4.28	1.5	8.46	0.059	0.08
Fixed Carbon	6.6	16.00	2.0	4.82	5.00	0.02
С	44.8	52.53	53.04	48.63	62.88	85.4
Н	11.24	5.65	7.32	8.46	4.73	13.1
Ν	7.23	2.86	3.94	48.63	0.37	-
S	0.31	0.03	35.53	7.38	0.0	0.41
0	36.42	38.93	0.17	3.36	32.018	1.09
Extractive Content	7.136	-	-	-	-	-
Gross Value (MJ kg <sup>-1</sup> )	15.5	18.67	37.65	-	23.0	-

## 3.2. Fourier Transform Infrared Spectroscopy Analysis

The Fourier transform infrared spectroscopy (FTIR) analysis of the GDC and the PET were presented in Figure 1. In the case of the groundnut de-oiled cake peak at 3275 cm<sup>-1</sup>, is mainly due to the presence of the O-H in the hydroxyl group of samples. The peak at 2962 cm<sup>-1</sup> signifies the presence of the C-H symmetrical stretching of an alkyl and alkene components. The presence of the carbonyl group (C = O) was observed at peak 1740 cm<sup>-1</sup> which signifies the presence of a hemicellulose in the biomass. The C-O was bound and seen at 1237 and 1035 cm<sup>-1</sup>. This is due to the presence of the callulose and hemicellulose, and the lignin components of the biomass. The peak at 550 cm<sup>-1</sup> indicates the presence of alkyl halide C-I, C-Br, or C-Cl. In the case of the PET, the FTIR peak at 871 cm<sup>-1</sup> is of the H vibration to the phenyl rings. The stretching at 1248 cm<sup>-1</sup> is due to the C-O stretch present in terephthalate group. The peak at 1343, 1411, and 1452 cm<sup>-1</sup> was observed, due to the C-O vibration of ethylene glycol. The peak at 1721 cm<sup>-1</sup> is mainly attributed to the C = O bond in the carboxylic acid group present in the compounds. The peak at 2962 cm<sup>-1</sup>



Figure 1. FTIR analysis of (a) Groundnut de-oiled cake (b) PET plastic.

#### 3.3. Thermal Decomposition Behavior of the Feedstock

The thermogravimetric analysis of the individual feedstock and the co-pyrolyzed feedstock was performed at various heating rates ranging from 10–30 °C min<sup>-1</sup> and within the temperature range of 30–900 °C. Figure 2 shows the thermogravimetric (TG) and the differential thermogravimetric (DTG) analysis of the feedstocks. From the figure, it is evident that the TGA analysis of the biomass and the mixture (co-feed) occurred in three stages, namely, the dehydration stage (30–175 °C); the active pyrolysis stage (175–550 °C); the last step is also known as the formation of char, and this stage occurs in the temperature range of 550–900 °C. Whereas, the plastic has shown a higher initial stability and the three zones occurred in the temperature ranges of 30–375 °C; 375–600 °C; 600–900 °C. The decomposition of biomass generally occurs due to the presence of three significant compounds: hemicellulose, cellulose, and lignin [18]. In contrast, plastic degradation occurs due to additive fillers, diethylene glycol, and terephthalate monomers [11].



**Figure 2.** Thermal decomposition behavior of (**a**) Groundnut de-oiled cake (GDC) (**b**) PET plastic and (**c**) Co-feedstock of the GDC and PET (1:1).

For the GDC biomass, in the first stage (30–175  $^{\circ}$ C), there was loss of water and lighter volatile components, but only a 2.5–4 wt%. Whereas, the weight loss for the PET plastic was infinitesimal i.e., 0.2–0.8 wt% in the temperature range of 30–375 °C. The mass loss for the co-pyrolysis of the DR and TW were, respectively, 5–6.5 wt%. The active pyrolysis zone for the GDC (175–550 °C) noted a maximum decomposition of 47, 48, and 57.5 wt% at 10, 20, and 30  $^{\circ}$ C min<sup>-1</sup>. However, the active pyrolysis zone of the PET plastic occurred at 375–600 °C with a significant degradation of 78.8, 71.6, 83.8 wt% of the above specified heating rates. However, the addition of the PET to the GDC feedstock facilitated an increase of degradation of the mixture in the active pyrolysis zone (175–550 °C). The maximum weight loss in this region is noted to be 62, 66.5, and 60.7 wt%. The primary constituents of the co-pyrolysis mixture of the GDC and PET, hemicellulose, cellulose, lignin, diethylene glycol, and terephthalate, undergo decomposition in the presence of heat to evolve numerous volatile species. In the presence of a continual source of heat energy, heavier molecular weight compounds fragment into smaller molecular weight components in the second zone [19]. Thermogravimetric (TG) and differential thermogravimetric (DTG) thermograms shown in Figure 1 revealed that the thermal degradation of all of the feedstock shifted to a higher temperature region with the increasing heating rate without influencing the decomposition behavior [20]. The increased heating rate shifted the DTG peak towards a higher temperature for all of the feedstocks. The temperature shift for the GDC is 350, 375, and 390 °C, whereas, for the PET, it is noted to be 440, 460, and 458 °C. Further, the DTG shift for the co-pyrolysis mixture was found to be 420, 435, and 440 °C. A similar trend was observed in a recent study on Samanea saman seeds and PET plastic, where the DTG peak shifted from 165–195 °C as the heating rate varied from 10–50 °C min<sup>-1</sup> [17,21]. Similar observations in the DTG curves were found in [4,6,12].

The behavior was accompanied by faster heating rates and a less efficient mass transfer among the particles. As the heating rate increases, the peak temperatures rise, indicating that the feedstock has reached the required degradation temperature in lesser time [21]. According to [22], such a trend demonstrated that the overall reaction pathway was unaltered by the rate of heating. The degradation of biomass happens in numerous stages at lower heating rates and temperatures. Insufficient heat transport to biomass particles slows decomposition. At reduced heating rates, there is a considerable transfer of heat through the biomass [22].

## 3.4. Estimation of the Activation Energy from the Different Models

The activation energy and the pre-exponential factor, also known as the kinetic variables, were estimated using five model-free iso-conversional methods: DFM, KAS, OFW, STR, and DAEM. The kinetic parameters were calculated for the active pyrolysis zone mentioned in Section 3.3 for the different feedstocks. The kinetic analysis showed that the data fitted well in the conversion range of 0.1–0.8 for the GDC and 0.2–0.9 for both the PET and the co-feedstock, respectively. Figure 3 represents the variation of the activation energy with conversion ( $\alpha$ ). The reason for such a trend can probably be attributed to the simultaneous degradation of various components present in the feedstock [20]. The experimental data in Tables 3–5 are consistent with all of the models, as shown by a high coefficient of determination values ( $\mathbb{R}^2$ ). The  $\mathbb{R}^2$  values of all of the models for the different feedstocks were greater than 0.9, indicating a good fit of the data with the models.



Figure 3. Activation energy vs the conversion plot of (A) PET (B) GDC + PET (C) GDC.

Table 3. Activation Energy and the pre-exponential factors for the groundnut residue.

	Model Free Iso-Conversional Methods														
Conversion Differential Friedman			Kissinger	-Akahira-Sunose	e (KAS)	Ozawa–Flynn–Wall (OFW)			Star	rink Method (STR	1)	Distributed Activation Energy Model (DAEM)			
α	E (kJ mol <sup>-1</sup> )	A (min <sup>-1</sup> )	R <sup>2</sup>	E (kJ mol <sup>-1</sup> )	A (min <sup>-1</sup> )	R <sup>2</sup>	E (kJ mol <sup>-1</sup> )	A (min <sup>-1</sup> )	R <sup>2</sup>	E (kJ mol <sup>-1</sup> )	A (min <sup>-1</sup> )	R <sup>2</sup>	E (kJ mol <sup>-1</sup> )	A (min <sup>-1</sup> )	R <sup>2</sup>
0.1	92.32	2.18x10 <sup>7</sup>	0.995	90.89	$1.68 \times 10^7$	0.999	95.34	$3.14 \times 10^5$	0.99	91.20	$1.44 \times 10^7$	0.99	90.89	$1.59 \times 10^{8}$	0.99
0.2	80.87	$1.70 \times 10^{6}$	0.978	91.45	$1.68 \times 10^{7}$	0.997	96.22	$3.33 \times 10^{5}$	0.99	91.77	$1.44 \times 10^{7}$	0.99	91.45	$7.42 \times 10^{7}$	0.99
0.3	124.52	$8.56 \times 10^{9}$	0.999	96.21	$4.03 \times 10^{7}$	0.997	101.05	$7.76 \times 10^{5}$	0.99	96.53	$3.46 \times 10^{7}$	0.99	96.21	$1.13 \times 10^8$	0.99
0.4	112.38	$6.80 \times 10^8$	0.999	98.52	$5.58 \times 10^{7}$	0.998	103.37	$1.05 \times 10^{6}$	0.99	98.85	$4.79 \times 10^{7}$	0.99	98.52	$1.08 \times 10^8$	0.99
0.5	120.13	$2.98 \times 10^{9}$	0.993	104.19	$1.59 \times 10^{8}$	0.997	109.06	$2.85 \times 10^{6}$	0.99	104.53	$1.36 \times 10^{8}$	0.99	104.19	$2.29 \times 10^{8}$	0.99
0.6	136.48	$5.63 \times 10^{10}$	0.997	108.39	$3.42 \times 10^{8}$	0.995	113.11	$5.74 \times 10^{6}$	0.99	108.74	$2.92 \times 10^{8}$	0.99	108.39	$3.71 \times 10^{8}$	0.99
0.7	142.53	$1.01 \times 10^{11}$	0.998	124.82	$7.21 \times 10^{9}$	0.994	129.02	$9.75 \times 10^{7}$	0.99	125.15	$6.09 \times 10^{9}$	0.99	124.82	$5.98 \times 10^{9}$	0.99
0.8	321.96	$6.83 \times 10^{23}$	0.984	305.49	$4.18 \times 10^{23}$	0.995	301.07	$1.04 \times 10^{21}$	0.99	305.69	$3.29 \times 10^{23}$	0.99	305.49	$2.59 \times 10^{23}$	0.99
Average	141.39	$8.54\times 10^{22}$		127.49	$5.23\times 10^{22}$		131.03	$1.30\times 10^{22}$		127.80	$4.12\times10^{22}$		127.49	$3.24\times 10^{22}$	

	Model Free Iso-Conversional Methods														
Conversion Differential Friedman			Kissinger	-Akahira-Sunose	(KAS)	Ozawa–Flynn–Wall (OFW)			Sta	rink Method (STF	2)	Distributed Activation Energy Model (DAEM)			
α	E kJ mol <sup>-1</sup> )	A (min <sup>-1</sup> )	R <sup>2</sup>	E (kJ mol <sup>-1</sup> )	A (min <sup>-1</sup> )	R <sup>2</sup>	E (kJ mol <sup>-1</sup> )	A (min <sup>-1</sup> )	R <sup>2</sup>	E (kJ mol <sup>-1</sup> )	A (min <sup>-1</sup> )	R <sup>2</sup>	E (kJ mol <sup>-1</sup> )	A (min <sup>-1</sup> )	R <sup>2</sup>
0.1	247.58	$6.01 \times 10^{17}$	0.75	190.05	$1.39 \times 10^{13}$	0.9	191.85	$9.59 \times 10^{10}$	0.9	190.36	$1.1  imes 10^{13}$	0.9	190.05	$1.15 \times 10^{14}$	0.9
0.2	31.34	$4.62 \times 10^{1}$	0.029	192.92	$2.98 \times 10^{13}$	0.96	194.64	$2.03 \times 10^{11}$	0.96	193.24	$2.45 \times 10^{13}$	0.96	192.92	$1.29 \times 10^{14}$	0.96
0.3	211.08	$1.30 \times 10^{15}$	0.96	192.17	$3.13 \times 10^{13}$	0.93	194.03	$2.18 \times 10^{11}$	0.94	192.49	$2.57 \times 10^{13}$	0.93	192.17	$8.39 \times 10^{13}$	0.93
0.4	213.40	$2.00 \times 10^{15}$	0.97	198.12	$1.00 \times 10^{14}$	0.91	199.76	$6.69 \times 10^{11}$	0.92	198.44	$8.23 \times 10^{13}$	0.91	198.12	$1.85 \times 10^{14}$	0.91
0.5	222.46	$9.13 \times 10^{15}$	0.97	205.08	$3.61 \times 10^{14}$	0.94	206.44	$2.27 \times 10^{12}$	0.95	205.40	$2.95 \times 10^{14}$	0.94	205.08	$4.98 \times 10^{14}$	0.94
0.6	224.47	$1.18 \times 10^{16}$	0.93	201.54	$2.06 \times 10^{14}$	0.92	203.15	$1.36 \times 10^{12}$	0.93	201.86	$1.69 \times 10^{14}$	0.92	201.54	$2.18 \times 10^{14}$	0.92
0.7	271.72	$2.51 \times 10^{19}$	0.94	218.87	$4.08 \times 10^{15}$	0.96	219.70	$2.32 \times 10^{13}$	0.96	219.18	$3.32 \times 10^{15}$	0.96	218.87	$3.27 \times 10^{15}$	0.96
0.8	328.17	$1.48 \times 10^{23}$	0.76	231.6	$3.23 \times 10^{16}$	0.923	231.91	$1.67 \times 10^{14}$	0.93	231.91	$2.62 \times 10^{16}$	0.923	231.6	$3.03 \times 10^{15}$	0.93
Average	240.83	$1.15 \times 10^{21}$		201.45	$8.01 \times 10^{14}$		202.95	$4.66 \times 10^{12}$		201.77	$6.53 \times 10^{14}$		201.45	$7.30 \times 10^{14}$	

Table 4. Activation Energy and the pre-exponential factors for PET plastic.

**Table 5.** Activation Energy and the pre-exponential factors for the co-pyrolysis of the groundnut de-oiled cake and plastic (PET).

	Model Free Iso-Conversional Methods														
Conversion Differential Friedman			Kissinger	-Akahira-Sunose	(KAS)	Ozawa–Flynn–Wall (OFW)			Sta	rink Method (STR	)	Distributed Activation Energy Model (DAEM)			
α	E (kJ mol <sup>-1</sup> )	A (min <sup>-1</sup> )	R <sup>2</sup>	E (kJ mol <sup>-1</sup> )	A (min <sup>-1</sup> )	R <sup>2</sup>	E (kJ mol <sup>-1</sup> )	A (min <sup>-1</sup> )	R <sup>2</sup>	E (kJ mol <sup>-1</sup> )	A (min <sup>-1</sup> )	R <sup>2</sup>	E (kJ mol <sup>-1</sup> )	A (min <sup>-1</sup> )	R <sup>2</sup>
0.1	97.85	$4.08 \times 10^7$	0.98	100.28	$9.97 \times 10^7$	0.91	104.11	$1.50 \times 10^{6}$	0.93	100.23	$7.89 \times 10^7$	0.91	100.28	$9.31  imes 10^8$	0.91
0.2	151.13	$8.51 \times 10^{11}$	1.00	112.29	$6.83 \times 10^{8}$	0.97	116.41	$9.88 \times 10^{6}$	0.97	112.61	$5.79 \times 10^{8}$	0.97	112.29	$2.95 \times 10^{9}$	0.97
0.3	99.96	$2.01 \times 10^{7}$	1.00	125.91	$7.47 \times 10^{9}$	0.99	129.65	$9.19 \times 10^{7}$	1	126.23	$6.2 \times 10^{9}$	0.99	125.91	$2.04 \times 10^{10}$	1
0.4	174.14	$6.59 \times 10^{12}$	0.99	121.46	$1.24 \times 10^{9}$	0.99	125.91	$1.80 \times 10^{7}$	1	121.80	$1.05 \times 10^{9}$	0.99	121.46	$2.41 \times 10^{9}$	0.99
0.5	181.00	$2.17 \times 10^{13}$	0.99	165.05	$2.51 \times 10^{12}$	0.99	167.68	$2.14 \times 10^{10}$	1	165.37	$2.08 \times 10^{12}$	0.99	165.05	$3.59 \times 10^{12}$	0.99
0.6	226.65	$5.67 \times 10^{16}$	0.99	186.99	$9.91 \times 10^{12}$	0.99	188.74	$6.85 \times 10^{11}$	0.99	187.31	$8.14 \times 10^{13}$	0.99	186.99	$1.07 \times 10^{14}$	0.99
0.7	224.19	$3.33 \times 10^{12}$	0.99	203.34	$1.48 \times 10^{15}$	0.99	204.43	$8.84 \times 10^{12}$	1	203.64	$1.19 \times 10^{15}$	0.99	203.34	$1.21 \times 10^{15}$	0.99
0.8	259.56	$9.89\times 10^{18}$	0.99	221.49	$2.85\times 10^{16}$	0.99	221.85	$^{1.499}_{10^{14}} \times$	1	221.79	$2.31\times 10^{16}$	0.99	221.49	$1.75\times 10^{16}$	1
0.9	560.52	$9.58 \times 10^{33}$	0.99	345.96	$2.23 \times 10^{23}$	0.99	340.48	$5.12 \times 10^{22}$	1	346.16	$1.75 \times 10^{19}$	0.99	345.96	$9.59 \times 10^{24}$	1
Average	219.45	$1.06\times 10^{39}$		175.86	$2.48\times10^{24}$		177.70	$5.68\times10^{21}$		176.13	$1.94\times 10^{24}$		175.83	$1.07\times 10^{24}$	

The apparent activation energy of the groundnut de-oiled cake (GDC) for the differential Friedman (DFM) was 141.39 kJ mol<sup>-1</sup>. At the same time, the integral methods, such as KAS, OFW, STR, and DAEM were found to be 127.49, 131.02, 127.80, and 127.49 kJ mol<sup>-1</sup>, respectively. The variation in the E values for each model is due to the simultaneous decomposition of the biomass components, paving the way for a multi-step reaction [13]. It was also observed that the activation energy increases as the reaction nears completion, i.e., an increase in the conversion value of up to 0.9. It is evident that when the conversion values increase, the apparent activation energy correspondingly increased. The emission of lighter volatiles at low temperatures (200 °C) resulted in a low activation energy value at a lower conversion ( $\alpha = 0.1$ ). Low to high molecular weight compounds were released as the process' temperature increased, requiring more energy (often provided by an external source), which raised the activation energy. This suggested that the process was predominantly endothermic [23].

An analysis revealed that the average activation energies obtained from the OFW method of the Mesua ferrea L de-oiled cake in two zones, of T = 130–260 °C and T = 260–380 °C, were 94 kJ mol<sup>-1</sup> and 147 kJ mol<sup>-1</sup>, respectively [17]. In the present investigation, however, the average activation energy determined by the same kinetic analysis in the pyrolysis zone of 150–550 °C was 131.02 kJ mol<sup>-1</sup>. Consequently, the reported activation energy suggests that the thermochemical conversion of the GDC could be more energy efficient than the Mesua ferret L de-oiled cake. Another study on the determination of the kinetic parameters by the KAS and OFW methods for the Karanja seed cake was in agreement with the present study. The E values were obtained to be 110–127 kJ mol<sup>-1</sup> [16].

The kinetics variable estimation for the PET plastic performed by the different methods found that the KAS method yielded the lowest activation energy with a good  $R^2$  correlation for all of the conversion values. The detailed values are provided in Table 4. The average apparent activation energy for the methods, such as the DFM, KAS, OFW, STR and DAEM are 240.83, 201.45, 202.95, 201.77 and 201.45 kJ mol<sup>-1</sup>.

A study on the kinetic parameters estimation of PVC plastic waste by the OFW model provided that the plastic decomposition is a two stage process with average activation energy values of 141 kJ mol<sup>-1</sup> and 266 kJ mol<sup>-1</sup> [24]. The literature also reported that the pyrolysis kinetics of the fire retardant polyolefins cables have an activation energy of 155 and 239 kJ mol<sup>-1</sup> in two distinct conversion ranges [25].

Lastly, the kinetic parameters estimation of the co-pyrolysis for the GDC and PET plastic provided the activation energy and the pre-exponential factor for the DFM was around 219.45 kJ mol<sup>-1</sup>. While that in the range of 175.86–177 kJ mol<sup>-1</sup> for the KAS, OFW, STR and DAEM methods. The detailed values are provided in Table 5. The obtained E and A values were higher than those of the biomass alone and lower than the PET plastic itself. The addition of the biomass waste to the plastic significantly reduced the activation energy of the plastic waste. The activation energy increased with the increase in the conversion stating a possible interaction of both feedstocks. The obtained results are well in agreement with some of the literature available [4,21].

The iso-conversional methods of Friedman's, the KAS, the OFW, Starink's, and the simplified DAEM are used to calculate the pre-exponential factor. The average values of A obtained were, for the KAS method, were  $5.2 \times 10^{22}$ ,  $5.29 \times 10^{24}$ ,  $5.29 \times 10^{15}$ , for the biomass, co-feed and plastic, respectively. The pre-exponential factor is thought to be a temperature-dependent variable, in accordance with the hypothesis of the molecular collision of the reactants. According to the findings shown in Tables 2–4, the A values ranged from  $10^7$  to  $10^{25}$ . This suggested that the different feedstocks have a complex composition that includes a number of different molecules ranging from a lower to a higher mass [26]. It is believed that the majority of the surface reactions occur at lower exponential values (A >  $10^9$ ). Hemicellulose, cellulose, and diethylene glycol typically decompose at high A values (about  $10^9$  to  $10^{12}$ ) and at a lesser conversion ( $\alpha < 0.5$ ), while lignin and terephthalate decay at greater A values ( $\alpha > 10^{14}$ ) and at a higher conversion ( $\alpha > 0.5$ ). The increased pre-exponential factor suggested a high rate of molecules' collision. As a result, the reaction needed greater energy, which was consistent with the obtained apparent activation energy [10].

## 4. Conclusions

The physicochemical characterization and thermal analysis of the groundnut de-oiled cake and PET plastic confirms the bioenergy potential of fuel. The apparent activation energy and pre-exponential factor was determined by different iso-conversional methods which include the DFM, KAS, OFW, STR and DAEM methods. The useful functional groups present in the material were confirmed by the FTIR analysis. Among all of the methods, the KAS method provided the lowest activation energy (for the GDC, E= 127.49 kJ mol<sup>-1</sup>; PET, E = 201.45 kJ mol<sup>-1</sup>; and co-pyrolysis (E = 175.86 kJ mol<sup>-1</sup>). From the analysis, it is also known that the biomass blending with plastic can significantly reduce the activation energy to effectively design the pyrolyzer.

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