

Thermo-kinetic Study of Genetically Different Carbon-Source Materials

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Cite This: *ACS Omega* 2023, 8, 38704–38714

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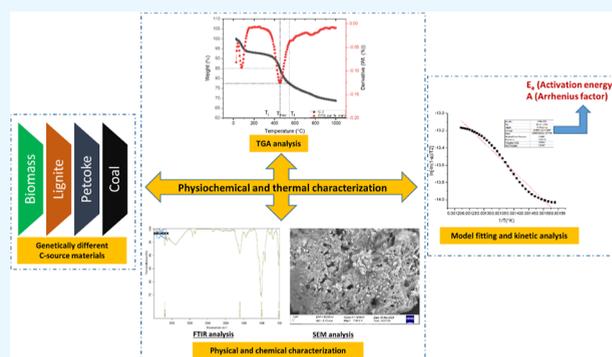
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ABSTRACT: A nonisothermal thermogravimetric analysis (TGA) technique was applied to determine the devolatilization kinetic parameters of completely different genesis samples of four groups: coal, biomass, lignite, and petcoke. The physical and chemical characteristics were determined using the proximate and ultimate analysis and the ash composition profile using the X-ray fluorescence method. Heating rates of 10, 15, and 20 °C/min were used in the temperature range of 25–1000 °C during the slow pyrolysis under an inert gas atmosphere. A widely used and proposed first-order Coats–Redfern kinetic model was applied, which showed the highest values of activation energies (E_a) for the petcoke sample from 57.17 to 67.58 kJ/mol at three different heating rates, while the lignite sample represented the lowest E_a values between 12.84 and 16.03 kJ/mol. The thermo-kinetic behavior was explained based on the catalytic effect of the ash composition profile, morphology, and structure of the substances determined using different analytical techniques. For the TGA process, the application of scanning electron microscopy, Fourier-transform infrared spectroscopy, etc., for the physiochemical analysis of the four genetically different carbon-source materials represented the novelty of the present work.



The thermo-kinetic behavior was explained based on the catalytic effect of the ash composition profile, morphology, and structure of the substances determined using different analytical techniques. For the TGA process, the application of scanning electron microscopy, Fourier-transform infrared spectroscopy, etc., for the physiochemical analysis of the four genetically different carbon-source materials represented the novelty of the present work.

1. INTRODUCTION

Coal is the most dominant and prevalent energy generation resource in the current global scenario. However, to utilize this resource sustainably for power generation, we need to develop technologies such as gasification with integrated carbon capture, utilization, and storage (CCUS) in place of existing combustion-based power plants. Along with coal, lignite, biomass, and petcoke can also play a significant role in gasification-based technologies to mitigate the global warming issues the world faces now, which have arisen due to human-borne CO₂ emissions.¹ Therefore, determining these carbonaceous materials' physical, chemical, and other compositional characteristics, along with those of biomass, is vital in predicting their performance during gasification, combustion, pyrolysis, and other utilization techniques. The pyrolysis process of a carbonaceous substance is assumed to be a complex prestep of application processes like gasification. A complete understanding of pyrolysis can be further applied to the design of a gasification reactor, highlighting the importance of the pyrolysis process. However, obtaining reliable and accurate kinetic parameters is challenging for the pyrolysis process of different materials. Usually, techniques such as thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and differential thermal analysis (DTA) are utilized and applied in isothermal or nonisothermal modes to identify the reaction mechanism of the pyrolysis process. Out of these, nonisothermal TGA is considered a more

reliable, productive, and simplified method to investigate the pyrolysis profile of a solid substance.^{2,3}

Much research has been performed to investigate the pyrolysis process involving mass loss with time and temperature by using a TGA tool. TGA of carbonaceous and biomass materials has been applied quite often to determine the reactivity of the char product and devolatilization kinetics, where this complex process is explained using several models: the single reaction model, distributed activation energy model (DAEM), kinetic evolution model, etc. Li et al.⁴ performed the high temperature and high heating rate fast pyrolysis experiments with the land and sea waste biomass by the TGA method. They determined the kinetic parameters by applying isoconversion and other methods. The volatile product stream also observed different hydrocarbons, oxygen heterocycle compounds, and phenols. Polat and Sayan⁵ performed the thermogravimetric and mass-spectrometric (TG–MS) study of spent coffee waste and analyzed the product gases evolved at different heating rates of 5 to 40 °C/

Received: August 15, 2023

Accepted: September 21, 2023

Published: October 5, 2023



Table 1. Proximate and Ultimate Analysis of Different Solid Substances

sample name	code	proximate analysis (air-dry basis)				ultimate analysis (dry, mineral matter free basis)						GCV (kcal/kg)
		ash, A (%)	volatiles, VM (%)	moisture, M (%)	fixed C, FC (%)	C (%)	H (%)	N (%)	S (%)	O (%)		
coal-1	C-1	29.96	30.89	10.74	28.42	77.12	8.06	1.78	0.69	12.36	3867	
coal-2	C-2	36.34	26.98	9.33	27.34	69.85	7.23	1.63	0.71	20.57	3594	
coal-3	C-3	37.55	27.15	8.64	26.66	68.65	6.59	1.57	0.65	22.55	3612	
comm. coal-1	C-4	31.36	29.80	6.43	32.41	85.38	7.39	1.94	1.23	4.07	4626	
comm. coal-2	C-5	40.35	25.34	5.59	28.72	73.25	6.38	1.45	0.95	17.99	3895	
petcoke	RPC-1	0.50	9.35	0.94	89.21	87.25	3.70	1.90	5.82	1.33	8436	
lignite-1	LG-1	22.86	31.43	23.18	22.54	65.39	9.93	0.99	8.26	15.43	3639	
lignite-2	LG-2	27.47	28.15	24.62	19.75	55.13	9.63	0.91	8.21	26.13	3224	
biomass-1	BM-1	16.97	69.81	8.48	4.74	63.74	9.59	1.77	0.23	24.66	3386	
biomass-2	BM-2	12.52	72.87	8.83	5.78	71.50	10.50	3.59	0.22	14.19	4178	

min. Along with nonisothermal, isothermal pyrolysis studies have also been conducted at different heating rates over a wide temperature range for other lignocellulosic biomass waste materials⁶ and banana stem.⁷ Materials such as agriculture and forestry residue,⁸ Egyptian biomasses,⁹ olive kernels,¹⁰ torrefied biomass residues,¹¹ and even municipal solid waste¹² have been investigated using thermogravimetric techniques to identify their potential for different applications. Zhang et al.¹³ studied thermochemical processes of combustion, pyrolysis, and gasification in the atmosphere of air, Ar, and CO₂, respectively, for bituminous coal of China origin in a fixed bed reactor. Nonisothermal thermogravimetric studies have also been conducted by Oner et al.¹⁴ for two petroleum pitches to determine the first- and second-order kinetic parameters of the pyrolysis process at different heating rates from 5 °C/min to 30 °C/min due to the dissimilarities in the structure and complex nature of the materials. Polymer materials such as polystyrene particles have also been studied for evaluating the kinetic parameters of the pyrolysis process with the effect of different particle sizes.¹⁵ Different reaction models are applied to identify the pyrolysis controlling reaction steps with varying particle sizes, and based on that, a modified model was also developed. Lignite feed has also been part of the pyrolysis experiments at different heating rates and kinetic parameters discussed using the Coats–Redfern (CR) method.¹⁶ The effect of the ash content on the pyrolysis characteristics was also analyzed, which showed the decreasing activation energy values with increasing lignite sample ash content.

During the pyrolysis process, the externally added compounds^{17–19} and the inherent substances of different samples exhibit catalytic effects, as explained in various studies.^{20,21} Alkali and alkaline elements significantly affect the thermal degradation profile.²² Zarnegar²³ reviewed the effect of different catalysts, such as activated char, supported metals, and alkali/alkaline metals, on the pyrolysis product yield and quality performance improvement. Although there have been extensive studies on the catalytic effects of different substances during the pyrolysis process, all of these catalytic studies were limited to one or two genetically distinct substances. In comparison, a detailed novel investigation has been carried out in the present research for four genetically different samples. More details about the research work associated with the recent TGA–DSC analysis work carried out by multiple groups worldwide are available in the [Supporting Information](#) related to this article. It is evident

from the detailed literature investigation that the CR kinetic model has been the most widely adopted and applied method to model the pyrolysis process of different substances.

There are highly scarce comparative nonisothermal degradation kinetic data for carbonaceous materials of different genetic types and groups with energy potential to sustainably meet the growing energy demand. Most of the work was conducted for individual feeds or comparisons between the two groups of materials. Therefore, in the present work, first, we perform repeated TGA–DSC-based pyrolysis experiments on materials like coal, biomass, lignite, and petcoke collected from different parts of the Indian subcontinent. We determine the intrinsic mass loss kinetics and perform the kinetic parameter estimation to determine the relevant parameters—activation energy and the pre-exponential factor of the pyrolysis process. For the selected materials of different groups, the TGA–DSC study is carried out at three different heating rates to determine the comparative kinetic parameters. Later on, the effect of catalytic properties of the inherent substance of the different materials is correlated with their kinetic and thermodynamic parameters obtained from the model fitting analysis with good agreement and repeatability. FTIR-based detailed functional group analysis of all four types of samples also depicts the novelty associated with this work. Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM–EDX) and field emission scanning electron microscopy (FE–SEM) analysis of the petcoke and lignite samples with extreme kinetic behavior was performed to strengthen the findings further. This investigation highlights a detailed comparative analysis of the slow-pyrolysis process and its potential application toward energy generation from genetically different carbon-source materials.

2. MATERIALS AND METHODS

2.1. Sample Preparation and Characterization. Before the pyrolysis experiments are carried out using the TGA–DSC analysis tool, it is essential to determine and understand the physical properties and characteristics of the materials. The materials of the present study can be categorized into five groups—(i) high and medium ash coals from the Talcher region coal mines, India (C-1 to C-3), (ii) commercial gasification feed coal with post- and pre-ash treatment, respectively (C-4 and C-5), (iii) petcoke sample from the Paradip Indian oil refinery, India. (RPC-1), (iv) lignite samples from the mines of the Rajasthan region, India (LG-1 and LG-

Table 2. XRF Analysis of Ash Samples of Different Carbonaceous Materials

sample code	LOI (wt. %)	XRF data (wt. %)												
		Fe ₂ O ₃	TiO ₂	CaO	K ₂ O	Cl	SO ₃	P ₂ O ₅	SiO ₂	Al ₂ O ₃	MgO	Na ₂ O	BaO	MnO
C-1	63.91	1.81	0.49	0.49	0.60	N.D.	0.13	0.30	22.21	9.55	0.42	0.04	0.05	N.D.
C-2	54.27	0.60	0.69	0.74	0.72	N.D.	0.08	0.56	29.25	12.69	0.36	0.04	N.D.	N.D.
C-3	62.50	3.73	0.62	0.93	0.57	N.D.	0.38	0.70	20.54	9.34	0.67	0.03	N.D.	N.D.
C-4	68.58	0.86	0.53	0.27	0.31	N.D.	0.07	0.16	18.53	10.23	0.36	0.04	0.01	0.01
C-5	59.44	1.05	0.72	0.32	0.25	N.D.	0.07	0.21	23.77	13.78	0.30	0.04	N.D.	0.01
LG-1	73.92	2.55	0.58	0.53	0.10	N.D.	0.89	0.01	11.29	7.56	0.82	1.69	N.D.	0.03
LG-2	74.47	2.79	0.67	0.44	0.13	N.D.	0.73	0.02	10.84	6.70	0.64	2.52	N.D.	0.02
BM-1	87.48	0.08	0.01	1.17	0.99	0.02	0.51	0.30	8.66	0.08	0.51	0.02	0.02	0.16
BM-2	89.89	0.07	N.D.	2.32	1.67	0.11	0.81	0.53	3.13	0.11	1.27	0.01	N.D.	0.09

2), (v) biomass feedstock from Odisha region, India (paddy straw as BM-1 and banana leaf as BM-2).

Proximate, ultimate, and gross calorific values (GCVs) of all the above samples are listed in Table 1, which were determined by using standard analytical methods such as—(i) complete proximate analysis was performed as per IS 1350 (Part-I) 2013 using a LECO TGA 701 instrument, (ii) ultimate analysis (C, H, N, S, and O) was performed as per IS-1350 (Part-IV) 2013 using LECO CHNS 628 and LECO brand Truspec micro elemental analyzer, and (iii) all the samples' GCVs were determined using the standard method of IS 1350 (Part-II) 2013 using the LECO AC350 and AC500 instruments.

Here, the proximate analysis was performed on an air-dry basis for the pulverized sample per the IS standard. Similarly, GCV and ultimate analysis were performed on an air-dry basis per IS methods; however, the ultimate analysis was further converted to a DMMF (dry, mineral matter-free) basis to determine the C, H, N, S, and O values. All the as-received samples were pulverized and sieved to <212 μ (72 mesh) before conducting all the experiments and analysis. A very small quantity (a few milligrams) of fine samples contributes toward achieving the minimal heat and mass transfer resistances during the slow pyrolysis experiments, also highlighted by different researchers.^{24,25}

2.2. Experimental Procedure. During all the TGA–DSC experiments, the specimen weight for this analysis was kept at around 5 to 30 mg, and the heating rate was kept constant at 10 °C/min until around 1000 °C from room temperature. Before the TGA–DSC experiment, the samples were dried in an oven at 40 °C to ensure uniformity before sample loading. Since the DSC analysis was also coupled with the TGA, simultaneous TGA–DSC studies were conducted using the instrument of model NETZSCH STA 449F3 in an inert atmosphere using Argon as a carrier gas at an 80 mL/min flow rate. For the DSC analysis, a blank reference condition was kept in an Al₂O₃ pan, which is inert until 1700 °C. Using DSC, we recorded the heat flow delta profile to and from the samples w.r.t. the blank reference as a temperature- and time-controlled function.

2.3. TG–DTG Model-Fitting Analysis. In this work, we evaluate the properties of various potential gasification feedstocks using TGA–DSC and assess their performance for combinatorial application for optimized gasification process development. As reported in the literature,²⁶ TG/DTG analysis helps determine the various temperatures and steps involved during the decomposition of carbonaceous material. Without going deep into the complexity of the chemical reactions accompanying the pyrolysis-based thermal degradation process, the kinetic parameters of the material could be

evaluated using the TGA method.¹ There are various analysis methods to determine the kinetic parameters of a pyrolysis process, which can be categorized into two methods—(i) model-independent/free method and (ii) model-based fitting methods. Examples of model-free methods, which are also termed isoconversional methods, can be further categorized as (a) differential method—Friedman method and (b) integral methods—Flynn–Wall–Ozawa (FWO) method, Kissinger method, Kissinger–Akahira–Sunose (KAS), Miura–Maki method, etc.²⁷ However, these model-free methods do not provide knowledge about the reaction mechanism. On the contrary, the model-fitting methods are very informative concerning the reaction mechanism estimation. In the present work, to determine the kinetic parameters by applying the TGA experimental data, we assume and evaluate the first-order reaction mechanism of the pyrolysis process using the CR method.²⁸ This model-fitting method is considered one of the most extensively applied and popular methods, as explained in the introductory section and the Supporting Information. The detailed analytical derivation of the CR method is also provided in the Supporting Information associated with this article.

3. RESULTS AND DISCUSSION

3.1. Characterization Results. Table 1 represents the proximate, ultimate, and GCVs of all of the carbonaceous substances and the biomass samples utilized for the TGA–DSC experiments.

For all the samples in Table 1, the ash content varies from as low as 0.5% in petcoke to as high as 40.35% in the commercial coal sample. Similarly, fixed carbon is the highest for the petcoke sample at 89.21% and the lowest for the biomass samples, with a below 6% content. Accordingly, the petcoke sample has the maximum GCV at around 8436 kcal/kg, while that for the lignite samples is a minimum with less than 3300 kcal/kg. All the characterization results for the different substances showed repeatability and reproducibility within the range of ± 0.3 –0.5%.

X-ray fluorescence (XRF) analysis of the coal, biomass, and lignite samples is highlighted in Table 2, along with their loss on ignition (LOI) values in weight percentage. Since the petcoke sample has very low ash content (<0.5 wt %), XRF analysis is not performed for it. The very high degree of LOI, with more than 85% in biomass samples, indicates a significant amount of volatiles and moisture content. SiO₂ and Al₂O₃ are the two primary elemental oxides in all of the solid substances under investigation. The presence of alkali (Na and K) and alkaline (Ca and Mg) oxides in the ash content of these

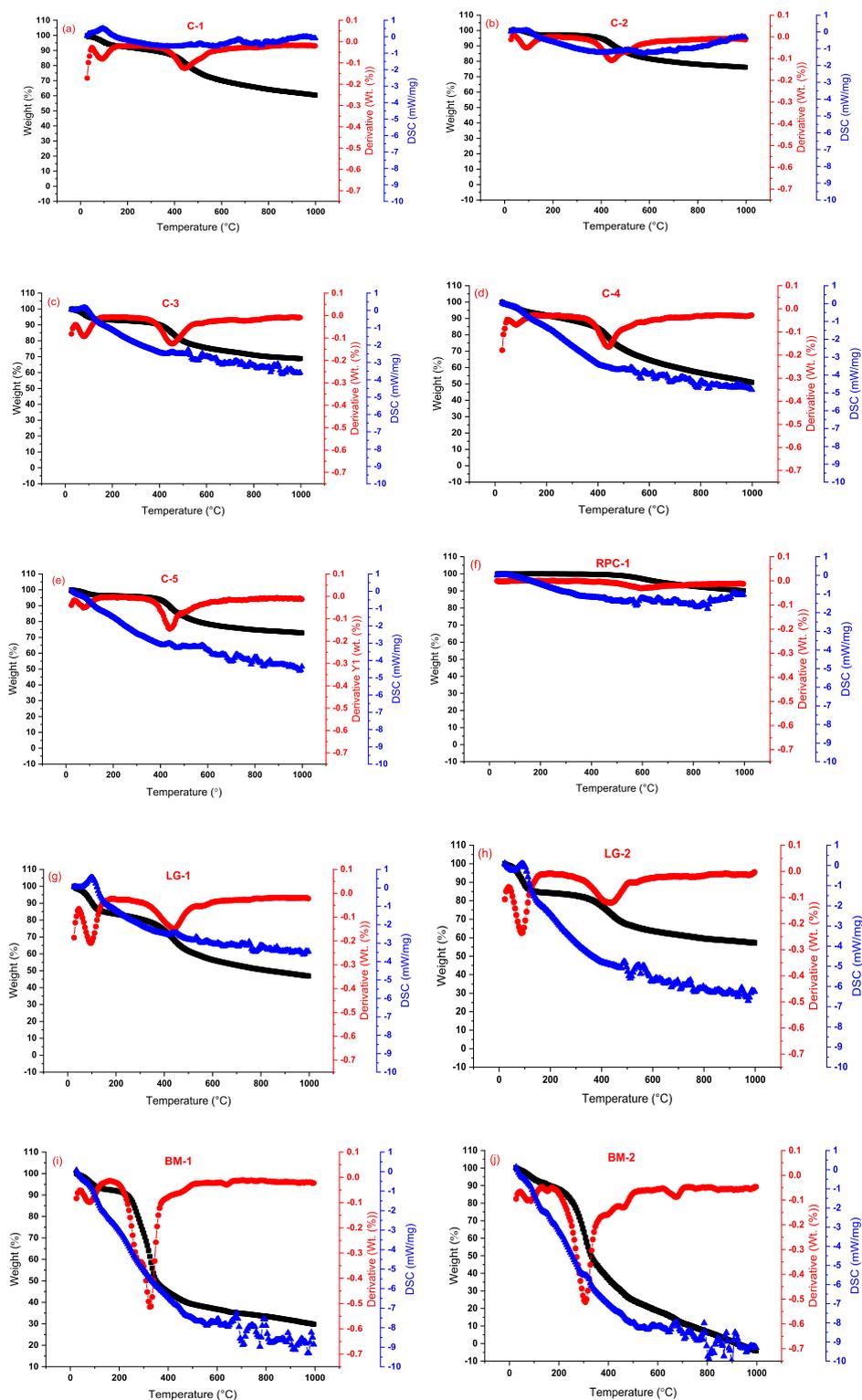


Figure 1. TG–DTG–DSC profile of coal samples (a) C-1 to (e) C-5, petcoke sample (f) RPC-1, lignite samples (g) LG-1, (h) LG-2 and biomass samples, (i) BM-1, and (j) BM-2.

materials shows their potential for catalytic activity during the thermochemical conversion process of slow pyrolysis.

3.2. TGA–DSC Results. Figure 1 shows the TGA–DSC profile with the DTG behavior of different solid energy feedstocks to identify their potential for pyrolysis and gasification applications. In this figure, the TG graph represents the substance's weight change as a temperature function,

whereas the DTG profile is based on the derivative of the TG graph. Therefore, TG and DTG profiles depict precise information about the material's temperature-based processes. The performance of these pyrolysis experiments could be validated during the bench-scale or pilot-scale gasification application processes.

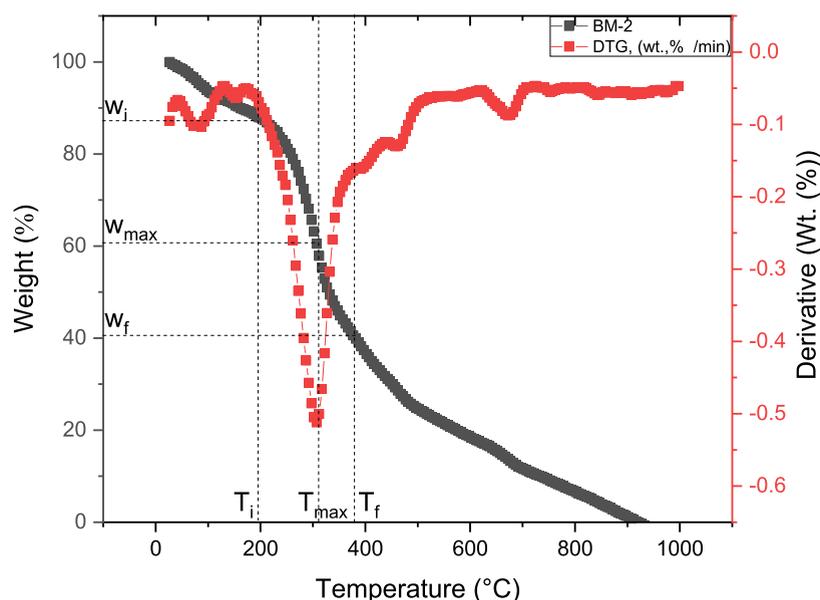


Figure 2. TG–DTG analysis plot for determining the activation energy (E_a) for biomass BM-2.

Figure 1 shows the high moisture and volatile contents in biomass and lignite samples compared to the coal and petcoke samples, as evident by the derived degradation profiles of all of the samples. Considering the high fixed carbon and energy contents (higher heating value—HHV) of petcoke and coal samples, a synergistic effect of all these compounds can be utilized during the energy generation using the gasification process. Much research has been conducted to identify the synergy during gasification for petcoke, coal, and biomass samples.^{29–31} Therefore, all the samples have the potential for pyrolysis and gasification if applied in a coprocessing mode subject to a detailed investigation.

Out of the detailed TG–DTG–DSC profiles explained in Figure 1, we illustrate the analysis of one of the above-represented thermograms (TGs) and derivative thermograms (DTGs), i.e., biomass sample BM-2 of banana leaf in Figure 2 and evaluate the data for the pyrolysis process. Here, we denote the initial, maximum, and final peak pyrolysis temperatures as T_i , T_{max} , and T_f , which correspond to the weight percentage values of W_i , W_{max} , and W_f . Similarly, the analysis is done for all the carbonaceous samples to obtain the devolatilization weight change profile with temperature. It is clear from the data presented in Table 3 that T_{max} is highest for the petcoke sample and lowest for the biomass samples, similar to the other research findings highlighted in the introductory section and the detailed literature work of the Supporting Information. The high carbon content, low volatiles, and low inherent oxygen content make the petcoke sample difficult for pyrolysis, combustion, and gasification^{26,29–31} compared to biomass samples.

The temperature for initiating the devolatilization process varies from 197.74 °C to around 501.78 °C for all the analyzed samples, which primarily depends on the physical and chemical characteristics of the substance. In the present study, the maximum/peak temperature corresponding to the maximum degradation/devolatilization rate, i.e., peak height, varies from 306.02 to 598.29 °C. The final temperature of the devolatilization process ranges from 376.83 to 690.43 °C, as per the physical and chemical nature of the substance. All of the experiments are repeated, and the results for different

Table 3. TG–DTG Analysis Results for Different Stages of Weight Change with Temperature

sample code	T_i —initial DTG temp. (°C)	W_i —initial DTG wt. %	T_{max} —max. DTG temp. (°C)	W_{max} —max. DTG wt. %	T_f —final DTG temp. (°C)	W_f —final DTG wt. %
C-1	365.07	88.04	445.18	82.41	551.26	72.49
C-2	348.67	96.26	442.72	91.29	492.21	86.81
C-3	374.37	91.13	456.94	85.28	544.16	77.47
C-4	362.61	86.47	445.18	78.79	497.13	71.96
C-5	365.07	94.99	440.53	89.34	494.67	83.58
RPC-1	501.78	99.11	598.29	97.21	690.43	94.80
LG-1	221.53	83.03	438.07	69.07	518.18	60.88
LG-2	334.45	79.13	430.96	74.02	499.32	67.37
BM-1	209.50	91.53	327.34	61.76	381.48	47.02
BM-2	197.74	87.76	306.02	61.48	376.83	40.59

kinetic and thermal parameters are in the acceptable range of $\pm 2\%$.

3.3. Kinetic Analysis and Parameter Estimation. In Figure 3a–d, we present the kinetic parameter analysis, especially the activation energies, the pre-exponential factors of pyrolysis experiments, and the linear model fitting. We calculate the kinetic parameters associated with the major thermal degradation curve related to the DTG profile of all of the materials between T_i and T_f . The conversion rate (α) or the fractional conversion is calculated for the weight (w_t) at time t , which varies as per the physical and chemical properties of the material. For the calculated values of α , we determine the model-fitting function of first-order and plot the graph with the inverse of the temperature for estimating the activation energy and the pre-exponential factor associated with the degradation profile of the sample. In the present work, the reaction mechanisms are analyzed using the CR method—with the first-order model-fitting method—and the kinetic plot is drawn using the Arrhenius equation between $y = \ln \left[-\ln \left(\frac{1-\alpha}{T^2} \right) \right]$ and $x = \frac{1}{T}$. The first-order kinetic modeling approach adopted in the present research has also been

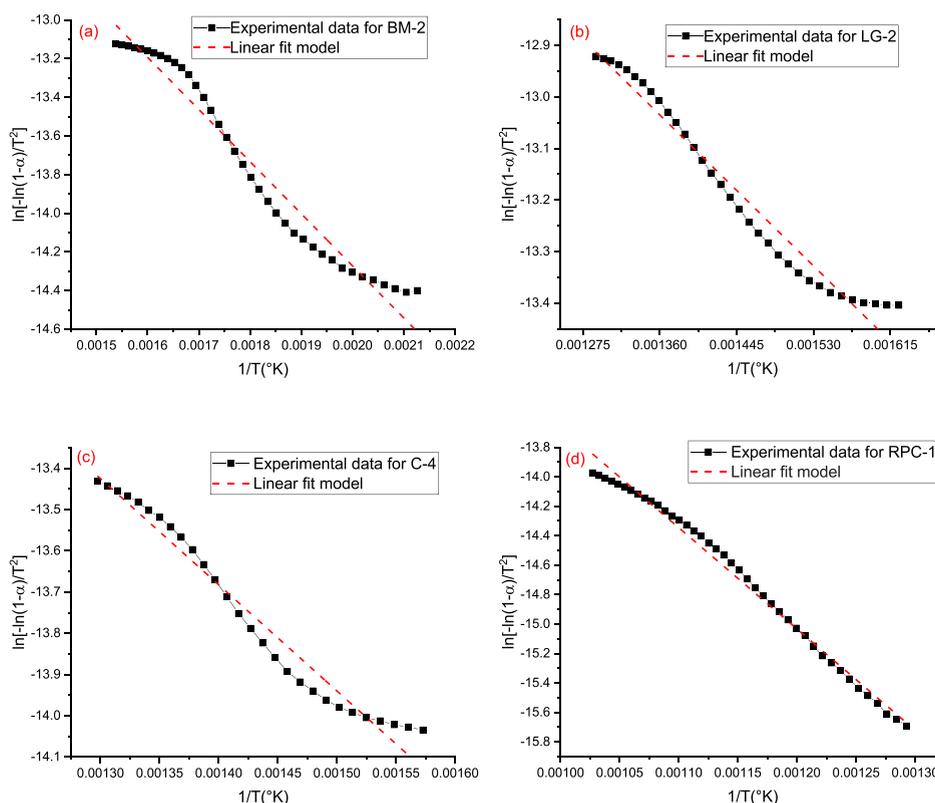


Figure 3. Data analysis and model fitting to (a) biomass BM-2, (b) lignite LG-2, (c) coal C-4, and (d) petcoke RPC- 1.

concluded as one of the most popular and applicable approaches to materials such as agro-industrial solid wastes,²⁵ waste plastics,²⁴ camel manure,²⁸ etc.

Table 4 shows activation energies and pre-exponential factors for the first-order kinetic model fitting curves obtained

Table 4. TG–DTG Analysis Results for Different Materials’ Activation Energy and Pre-exponential Factor at a 10 °C/min Heating Rate

sample code	act. energy E_a (kJ/mol)	pre-exponential factor, A (min^{-1})	adj. R^2 values
C-1	18.65	0.62	0.975
C-2	37.54	22.13	0.956
C-3	27.40	3.83	0.975
C-4	21.40	1.08	0.966
C-5	41.02	48.52	0.967
RPC-1	57.17	77.95	0.990
LG-1	12.84	0.24	0.960
LG-2	14.33	0.39	0.964
BM-1	33.12	66.15	0.977
BM-2	22.42	3.76	0.960

using the CR method and the corresponding R^2 coefficient (coefficient of determination) values. The Supporting Information associated with the present article provides all the best-fit curves of the CR method with the experimental and predicted results for all the substances under investigation. Other statistical parameters are also presented, such as the residual sum of squares (RSS) associated with all the model fittings. As highlighted by different researchers,^{32,33} the R^2 value, along with the other statistical parameters RSS, mean squared error (MSE), root mean squared error (RMSE), etc.,

provide information regarding the model fit quality. The higher values of adjusted R^2 above 0.95 and the low values of RSS for all of the substances prove the applicability and acceptability of the CR model to almost all carbonaceous substances with energy-generation potential. It is evident from the analysis that the petcoke sample has the highest values of the kinetic parameters, i.e., E_a and A . In contrast, lignite samples have the lowest values of activation energies, while coal and biomass samples have intermediate kinetic parameter results. These results are consistent with other findings highlighted in the previous sections.

3.4. Effect of Heating Rate on Kinetic and Thermodynamic Parameters. Thermal degradation of the selected carbonaceous materials from diverse genesis was performed by the TGA analyzer at three different heating rates of 10, 15, and 20 °C/min. Figure 4 shows the corresponding specific temperatures, namely, T_{β} , T_{\max} , and T_{γ} , definitions of which were explained earlier. Consistent with the literature results cited earlier, the increase in the heating rate of the substance leads to an increase in the degradation temperature of that specific decomposition stage. Table 5 shows different materials’ alkali and alkaline metal oxide compositions to explain further the behavior observed during the pyrolysis. The analysis highlights that biomass and lignite have the highest composition of Na, K, Ca, and Mg oxides, which are catalytically active during different thermal conversion processes such as combustion, pyrolysis, and gasification. Also, the higher values of the volatile and moisture contents of the biomass and lignite samples presented in Table 1 contribute toward the lower values of the specific temperatures, as shown in Figure 4.

The conclusions, obtained for the specific temperature profiles, from the catalytic substances in different carbon

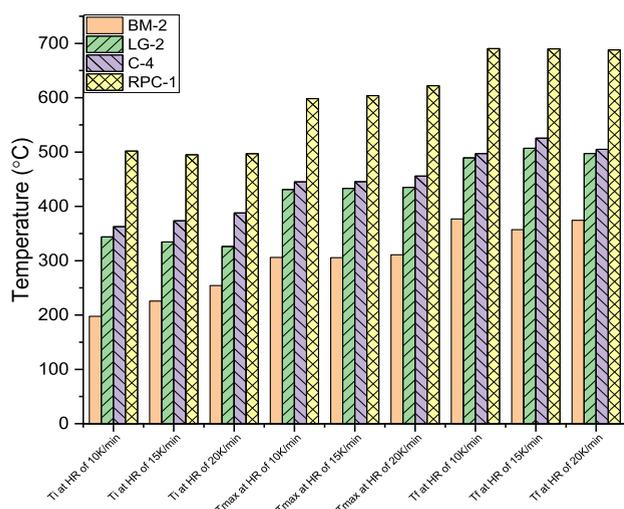


Figure 4. TG–DTG analysis results with different heating rates, where in *x*-axis HR is the heating rate in °C/min during the TGA analysis.

Table 5. Major Alkali and Alkaline Metal Oxide Composition of Solid Ash Samples

sample code↓	ash, A (%)	XRF data of ash samples (wt. %)				
		CaO	K ₂ O	MgO	Na ₂ O	total
BM-2	12.52	2.32	1.67	1.27	0.01	0.66
LG-2	27.47	0.44	0.13	0.64	2.52	1.02
C-4	31.36	0.27	0.31	0.36	0.04	0.31
RPC-1	0.5	ND	ND	ND	ND	<0.50

source materials are consistent with the kinetic parameters obtained in Table 6 at different heating rates.

The results presented in Table 6 show that, with the increase in the heating rate during the pyrolysis process, there is a gradual increase in the activation energy of all the carbonaceous materials. Higher values of the correlation coefficients R^2 for all the experiments prove the higher degree of validity and applicability of the applied model of the CR. Also, it is evident from the results that the petcoke substances have the highest activation energy values at all of the heating rates compared to biomass, lignite, and coal. This effect is due to the complex carbon structure of petcoke material, which is composed of different cyclic and polycyclic compounds with the lowest reactivity toward different reactions. On the other hand, lignite has the highest amount of volatiles and catalytically reactive metal oxides, leading to the lowest energy requirements to initiate the reactions involved in the thermochemical degradation process of pyrolysis. The calculated values of the kinetic parameters are in excellent agreement with those of materials of comparable characteristics, structures, and morphology.

Table 6. Effect of Heating Rate on Kinetic Parameters for Different Carbonaceous Materials

sample code↓	heating rate of 10 °C/min			heating rate of 15 °C/min			heating rate of 20 °C/min		
	act. energy E_a (kJ/mol)	pre-exponential factor, A (min^{-1})	adj. R^2 values	act. energy E_a (kJ/mol)	pre-exponential factor, A (min^{-1})	adj. R^2 values	act. energy E_a (kJ/mol)	pre-exponential factor, A (min^{-1})	adj. R^2 values
BM-2	22.42	3.76	0.9604	32.7	91.06	0.9683	36.49	258.33	0.9135
LG-2	14.33	0.39	0.9645	12.88	0.34	0.9696	16.03	1.15	0.9563
C-4	21.4	1.08	0.9664	34.89	25.61	0.9746	41.38	99.48	0.9792
RPC-1	57.17	77.95	0.9902	62.63	186.57	0.9885	67.58	3041.42	0.9449

3.5. Fourier Transform Infrared Spectroscopy Study.

Since the kinetics of the TGA–DSC performance analysis is strongly affected by the presence of different functional group characteristics of the materials, a more detailed and sensitive study is performed using the FTIR instrument, Bruker, Alpha II (Germany), which is a modular and compact spectrometer. The FTIR study provides information about the investigated materials' different chemical and functional groups.

FTIR data was analyzed based on the detailed investigation of the previous studies.^{34–38} Figure 5 represents the FTIR

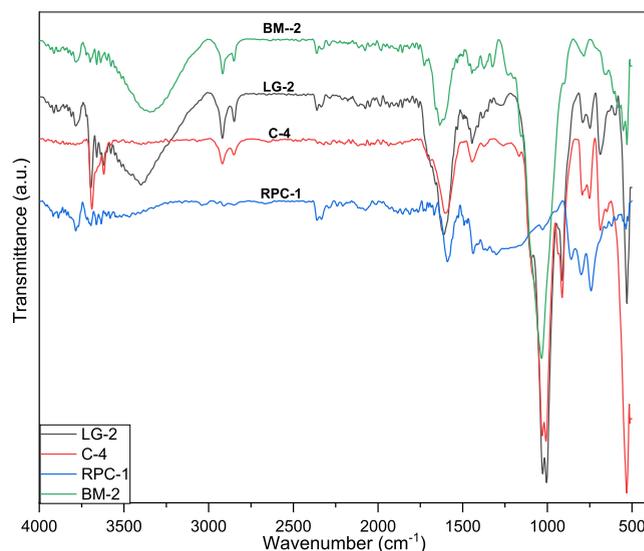


Figure 5. FTIR spectra of genetically different carbon-source materials, lignite (LG-2), coal (C-4), petcoke (RPC-1), and biomass (BM-2).

analysis of the raw petcoke (RPC-1), coal (C-4), biomass (BM-2), and lignite (LG-2) samples with distinguished prominent transmittance bands between 3200 and 3600 cm^{-1} , especially for lignite and biomass samples, indicating the presence of the hydroxyl O–H group, which can be attributed to the presence of water, alcohols, phenols, and other aromatic components. The hemicellulose structure of biomass is also indicated due to the presence of a very dominant peak between 1000 and 1200 cm^{-1} . Inorganic ash materials of the coal samples are identified based on the very significant peak between 500 and 750 cm^{-1} , which was absent for the petcoke sample, having a negligible amount of ash compared with the other samples. Minor peaks between 2750 and 3000 cm^{-1} correspond to the C–H stretching of the aliphatic groups associated with the methyl and methylene groups of different aromatic structures.³⁷ The peak between 1500 and 1700 cm^{-1} confirmed the aromatic C=C stretching for all the substrates under study, which could suggest the

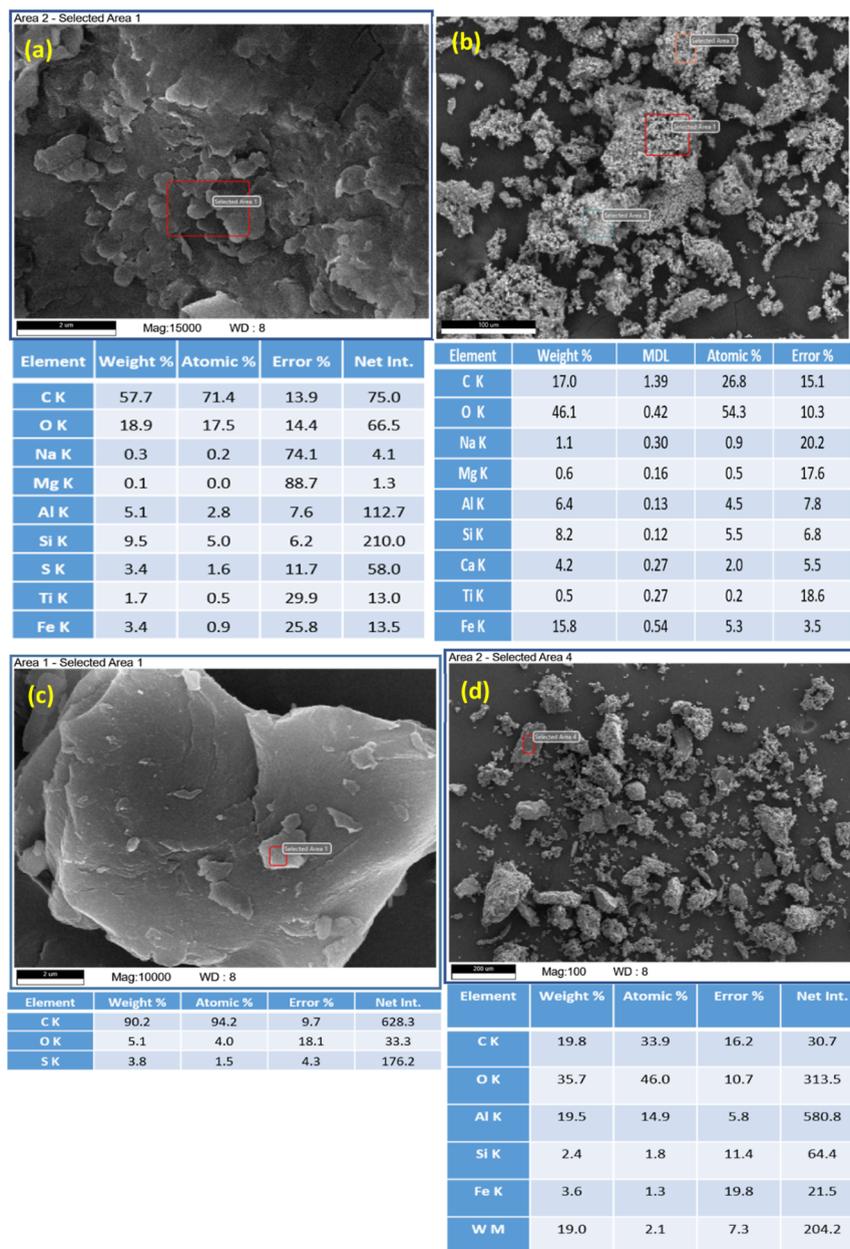


Figure 6. SEM–EDX analysis of (a) lignite feed sample, (b) lignite ash sample, (c) petcoke feed sample, and (d) petcoke ash sample

benzene or similar group structure vibration. The same peaks also point toward the oxygenated (C=O and C–O) groups' presence, like ketones, carboxylic acids, and phenolic structures for all the four diversified group compounds under the TGA–DSC investigation of the present article. The detection of dominated peaks between 700 and 900 cm^{-1} for the petcoke sample indicates the presence of C–H vibrational out-of-plane bonds in the aromatic structures. The study confirmed the presence of alkyl chain-associated polynuclear aromatic compounds in the petcoke sample, such as naphthalene, phenanthrene, pyrene, etc., which are responsible for the highest kinetic parameters for the petcoke sample, indicating the difficulty toward the thermal degradation behavior. Based on the present study, a conclusion can be made about the presence of complex and diverse chemical functional structures, especially for biomass and lignite samples.

3.6. Scanning Electron Microscopic Study. To further investigate the catalytic effect of the alkali and alkaline elements along with the surface and pore morphology of the substances under study on the pyrolysis kinetic behavior, we performed SEM–EDX and FE-SEM analyses of lignite and petcoke samples that showed the two extreme kinetic trends. The authors' recent work details the SEM–EDX and FE-SEM instruments applied in this study.³⁹ Figure 6a–d shows the performance of lignite feed and ash after pyrolysis, petcoke feed, and ash samples with respect to the SEM–EDX and FE-SEM analyses for the grounded samples. The selected area of the lignite ash sample shows the presence of different alkali and alkaline metals, namely Ca, Na, and Mg. In contrast, the petcoke sample has less than 1% ash content with a smoother surface morphology and a greater extent of graphitization than other samples.

This distinct behavior of the petcoke sample makes it challenging for pyrolysis and promotes harsher conditions for gasification studies. Also, the petcoke ash sample shows the scarcity of the alkali and alkaline earth elements compared to the lignite sample, further enhancing the difficulty of the thermochemical processes.

4. CONCLUSIONS

This work analyzed the pyrolysis characteristics of genetically different group materials, coal, petcoke, biomass, and lignite samples, using the TGA/DSC thermal decomposition method. The kinetic parameters of activation energy and pre-exponential factor were determined in nonisothermal conditions using the CR kinetic model of the first order at different heating rates. The summaries of the present research work are presented as follows:

- Only a single significant differential mass loss was present in the thermogravimetric coal and biomass pyrolysis graphs. At the same time, the lignite samples showed dual mass loss functions due to their high moisture and volatile contents.
- Proximate and ultimate analysis of all five coal samples indicated the presence of ash yield in the 30–40% range, with volatile yield varying between 25 and 31%. For the coal samples, the kinetic analysis showed activation energies (E_a) in the range of 18.65 to 41.38 kJ/mol. Since all the coal samples originate from the Talcher coalfield in eastern India, the kinetic parameters do not show significant variation, as the first-order fitting curves show a high adjusted R^2 .
- The petcoke sample has a very low ash yield, below 0.5%. The activation energy associated with the pyrolysis process is the highest among the solid samples studied in this work.
- Lignite samples have an ash yield in the 22–28% range with a high alkali and alkaline metal oxide composition and around 28–31% volatile content. For these samples, E_a values are between 12.84 and 16.03 kJ/mol, the lowest among all the different feedstock materials of diverse nature.
- Biomass samples analyzed using the proximate and ultimate analyses showed ash and volatile yields in the 12–17 and 70–73% ranges, respectively, while the activation energies range from 22.42 to 36.49 kJ/mol.
- SEM–EDX and FE–SEM analyses of the lignite and petcoke samples under investigation explain the distinct extreme behavior of the genetically different substances under the pyrolysis kinetic study.
- FTIR analysis of the genetically different four substrates showed the presence of specific chemical functional groups, which significantly affected the performance during the TGA–DSC study. It resulted in a difference in the kinetic parameters of the TG–DTG analysis study.

The insights and information provided in this work can support designing and scaling up thermochemical process-based units, such as pyrolyzers, gasifiers, combustion reactors, etc. Determination of the reaction kinetics and the corresponding kinetic parameters can contribute to the sizing of these units and generate knowledge about the functionality of these genetically different carbon-source materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c06035>.

Literature review of TG–DSC analysis for different materials, TG–DTG analysis plots, Coats–Redfern kinetic model, and kinetic parameter analysis plots (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank the Director, CSIR-IMMT, Bhubaneswar, for his kind permission to publish this work.

■ ABBREVIATIONS

TGA	thermogravimetric analysis
XRF	X-ray fluorescence
E_a	activation energy
CCUS	carbon capture utilization, and storage
DSC	differential scanning calorimetry
DTA	differential thermal analysis
DAEM	distributed activation energy model
TG–MS	thermogravimetric and mass-spectrometric
CR	Coats–Redfern
SEM–EDX	scanning electron microscopy with energy-dispersive X-ray spectroscopy
FE–SEM	field emission scanning electron microscopy
DMMF	dry mineral matter-free
GCV	gross calorific value
DTG	differential thermogravimetric analysis
FWO	Flynn–Wall–Ozawa
KAS	Kissinger–Akahira–Sunose
FTIR	Fourier-transform infrared spectroscopy
HHV	higher heating value
LOI	loss on ignition

REFERENCES

- (1) Ferrara, F.; Orsini, A.; Plaisant, A.; Pettinau, A. Pyrolysis of coal, biomass and their blends: Performance assessment by thermogravimetric analysis. *Bioresour. Technol.* **2014**, *171*, 433–441.
- (2) Escalante, J.; Chen, W. H.; Tabatabaei, M.; Hoang, A. T.; Kwon, E. E.; Andrew Lin, K. Y.; Saravanakumar, A. Pyrolysis of lignocellulosic, algal, plastic, and other biomass wastes for biofuel production and circular bioeconomy: A review of thermogravimetric analysis (TGA) approach. *Renewable Sustainable Energy Rev.* **2022**, *169*, 112914.
- (3) Mandapati, R. N.; Ghodke, P. K. Kinetic modeling of Indian lignites pyrolysis in the context of underground coal gasification (UCG). *Fuel* **2021**, *283*, 118939.
- (4) Li, J.; Shang, Y.; Wei, W.; Liu, Z.; Qiao, Y.; Qin, S.; Tian, Y. Comparative Study on Pyrolysis Kinetics Behavior and High-Temperature Fast Pyrolysis Product Analysis of Coastal Zone and Land Biomasses. *ACS Omega* **2022**, *7* (12), 10144–10155.
- (5) Polat, S.; Sayan, P. Assessment of the thermal pyrolysis characteristics and kinetic parameters of spent coffee waste: a TGA-MS study. *Energy Sources, Part A* **2023**, *45* (1), 74–87.
- (6) Mahmood, H.; Ramzan, N.; Shakeel, A.; Moniruzzaman, M.; Iqbal, T.; Kazmi, M. A.; Sulaiman, M. Kinetic modeling and optimization of parameters for biomass pyrolysis: A comparison of different lignocellulosic biomass. *Energy Sources, Part A* **2019**, *41* (14), 1690–1700.
- (7) Cheng, Q. P.; Jiang, M.; Chen, Z. H.; Wang, X.; Xiao, B. Pyrolysis and kinetic behavior of banana stem using thermogravimetric analysis. *Energy Sources, Part A* **2016**, *38* (22), 3383–3390.
- (8) Balogun, A. O.; Lasode, O. A.; Li, H.; McDonald, A. G. Fourier Transform Infrared (FTIR) Study and Thermal Decomposition Kinetics of Sorghum bicolor Glume and Albizia pedicellaris Residues. *Waste Biomass Valorization* **2015**, *6* (1), 109–116.
- (9) El-Sayed, S. A.; Mostafa, M. E. Kinetic Parameters Determination of Biomass Pyrolysis Fuels Using TGA and DTA Techniques. *Waste Biomass Valorization* **2015**, *6* (3), 401–415.
- (10) Al-Farraj, A.; Marsh, R.; Steer, J. A Comparison of the Pyrolysis of Olive Kernel Biomass in Fluidised and Fixed Bed Conditions. *Waste Biomass Valorization* **2017**, *8* (4), 1273–1284.
- (11) Balogun, A. O.; Lasode, O. A.; McDonald, A. G. Thermo-physical, Chemical and Structural Modifications in Torrefied Biomass Residues. *Waste Biomass Valorization* **2018**, *9* (1), 131–138.
- (12) Nzioka, A. M.; Kim, M. G.; Hwang, H. U.; Kim, Y. J. Kinetic Study of the Thermal Decomposition Process of Municipal Solid Waste Using TGA. *Waste Biomass Valorization* **2019**, *10* (6), 1679–1691.
- (13) Zhang, J. Z.; Wang, Z. Q.; Zhao, R. D.; Chen, T. J.; Wu, J. H. Release of nitrogen during thermochemical conversion of Shenhua bituminous coal under Ar, CO₂, and air atmospheres. *Can. J. Chem. Eng.* **2023**, *101* (2), 797–804.
- (14) Oner, F. O.; Yurum, A.; Yurum, Y. Non-isothermal kinetics of pyrolysis of Turkish petroleum pitches. *Energy Sources, Part A* **2016**, *38* (15), 2197–2204.
- (15) Jiang, L.; Yang, X. R.; Gao, X.; Xu, Q.; Das, O.; Sun, J. H.; Kuzman, M. K. Pyrolytic Kinetics of Polystyrene Particle in Nitrogen Atmosphere: Particle Size Effects and Application of Distributed Activation Energy Method. *Polymers* **2020**, *12* (2), 421.
- (16) Hu, L.; He, L.; Guo, X. H.; Wang, G. H. Non-isothermal pyrolysis kinetics characteristics of ZhaoTong lignite using thermogravimetric analysis. *Energy Sources, Part A* **2022**, *44* (2), 2963–2972.
- (17) Kabir, G.; Hameed, B. H. Recent progress on catalytic pyrolysis of lignocellulosic biomass to high-grade bio-oil and bio-chemicals. *Renewable Sustainable Energy Rev.* **2017**, *70*, 945–967.
- (18) Shen, Y. F.; Zhang, N. Y.; Zhang, S. Catalytic pyrolysis of biomass with potassium compounds for Co-production of high-quality biofuels and porous carbons. *Energy* **2020**, *190*, 116431.
- (19) Lu, Q.; Yuan, S.; Liu, C.; Zhang, T.; Xie, X.; Deng, X.; He, R. A Fe-Ca/SiO₂ catalyst for efficient production of light aromatics from catalytic pyrolysis of biomass. *Fuel* **2020**, *279*, 118500.
- (20) Nzihou, A.; Stanmore, B.; Lyczko, N.; Minh, D. P. The catalytic effect of inherent and adsorbed metals on the fast/flash pyrolysis of biomass: A review. *Energy* **2019**, *170*, 326–337.
- (21) Zhou, L. M.; Zhang, G. J.; Reimmoller, M.; Meyer, B. Effect of inherent mineral matter on the co-pyrolysis of highly reactive brown coal and wheat straw. *Fuel* **2019**, *239*, 1194–1203.
- (22) Zhang, Y. J.; Lv, P.; Wang, J.; Wei, J.; Cao, P.; Bie, N.; Bai, Y.; Yu, G. Product characteristics of rice straw pyrolysis at different temperature: Role of inherent alkali and alkaline earth metals with different occurrence forms. *J. Energy Inst.* **2022**, *101*, 201–208.
- (23) Zarnegar, S. A review on catalytic-pyrolysis of coal and biomass for value-added fuel and chemicals. *Energy Sources, Part A* **2018**, *40* (12), 1427–1433.
- (24) Brems, A.; Baeyens, J.; Beerlandt, J.; Dewil, R. Thermogravimetric pyrolysis of waste polyethylene-terephthalate and polystyrene: A critical assessment of kinetics modelling. *Resour., Conserv. Recycl.* **2011**, *55* (8), 772–781.
- (25) Fernandez, A.; Soria, J.; Rodriguez, R.; Baeyens, J.; Mazza, G. Macro-TGA steam-assisted gasification of lignocellulosic wastes. *J. Environ. Manage.* **2019**, *233*, 626–635.
- (26) Pan, D. L.; Jiang, W. T.; Guo, R. T.; Huang, Y.; Pan, W. G. Thermogravimetric and Kinetic Analysis of Co-Combustion of Waste Tires and Coal Blends. *ACS Omega* **2021**, *6* (8), 5479–5484.
- (27) Saeed, S.; Saleem, M.; Durrani, A.; Haider, J.; Riaz, M.; Saeed, S.; Qyyum, M. A.; Nizami, A. S.; Rehan, M.; Lee, M. Determination of Kinetic and Thermodynamic Parameters of Pyrolysis of Coal and Sugarcane Bagasse Blends Pretreated by Ionic Liquid: A Step towards Optimization of Energy Systems. *Energies* **2021**, *14* (9), 2544.
- (28) Parthasarathy, P.; Fernandez, A.; Al-Ansari, T.; Mackey, H. R.; Rodriguez, R.; McKay, G. Thermal degradation characteristics and gasification kinetics of camel manure using thermogravimetric analysis. *J. Environ. Manage.* **2021**, *287*, 112345.
- (29) Li, J. L.; Wang, Y. F.; Zhu, L. C.; Zhang, Z. F.; Xiao, H. X. Experimental study on co-pyrolysis of petroleum coke and coals: Synergy effects and co-gasification reactivity. *Fuel* **2020**, *279*, 118368.
- (30) Puig-Gamero, M.; Lara-Díaz, J.; Valverde, J. L.; Sanchez, P.; Sanchez-Silva, L. Synergistic effect in the steam co-gasification of olive pomace, coal and petcoke: Thermogravimetric-mass spectrometric analysis. *Energy Convers. Manage.* **2018**, *159*, 140–150.
- (31) Hamzah, N. S.; Idris, S. S.; Rahman, N. A.; Abu Bakar, N. F.; Matali, S. Thermal Analysis of Co-Utilization of Empty Fruit Bunch and Silantek Coal Under Inert Atmosphere Using Thermogravimetric Analyzer (TGA). *Front. Energy Res.* **2021**, *8*, 608756.
- (32) Torres-Sciancalepore, R.; Fernandez, A.; Asensio, D.; Riveros, M.; Fabani, M. P.; Fouga, G.; Rodriguez, R.; Mazza, G. Kinetic and thermodynamic comparative study of quince bio-waste slow pyrolysis before and after sustainable recovery of pectin compounds. *Energy Convers. Manage.* **2022**, *252*, 115076.
- (33) Torres-Sciancalepore, R.; Asensio, D.; Nassini, D.; Fernandez, A.; Rodriguez, R.; Fouga, G.; Mazza, G. Assessment of the behavior of Rosa rubiginosa seed waste during slow pyrolysis process towards complete recovery: Kinetic modeling and product analysis. *Energy Convers. Manage.* **2022**, *272*, 116340.
- (34) Manasrah, A. D.; Nassar, N. N.; Ortega, L. C. Conversion of petroleum coke into valuable products using oxy-cracking technique. *Fuel* **2018**, *215*, 865–878.
- (35) Manu, J.; Kailas, T. G.; Madav, V. Exploring the synergetic effects of rice husk, cashew shell, and cashew husk biomass blends on fluidized bed gasification for enhanced hydrogen production. *J. Cleaner Prod.* **2023**, *419*, 137991.
- (36) Meng, A. H.; Zhou, H.; Qin, L.; Zhang, Y. G.; Li, Q. H. Quantitative and kinetic TG-FTIR investigation on three kinds of biomass pyrolysis. *J. Anal. Appl. Pyrolysis* **2013**, *104*, 28–37.
- (37) Mishra, S.; Panda, S.; Pradhan, N.; Satapathy, D.; Biswal, S. K.; Mishra, B. K. Insights into DBT biodegradation by a native Rhodococcus strain and its sulphur removal efficacy for two Indian coals and calcined pet coke. *Int. Biodeterior. Biodegrad.* **2017**, *120*, 124–134.

(38) Wei, J. T.; Liu, X.; Guo, Q. H.; Chen, X. L.; Yu, G. S. A comparative study on pyrolysis reactivity and gas release characteristics of biomass and coal using TG-MS analysis. *Energy Sources, Part A* **2018**, *40* (17), 2063–2069.

(39) Saini, R.; Deb Barma, S.; Srinivas Rao, D.; Basu, S.; Mahajani, S. M. Applied mineralogical investigation on coal gasification ash. *Waste Manage.* **2023**, *167*, 1–12.