



Thermochemical behaviors and co-gasification kinetics of palm kernel shells with bituminous coal

J. Thiagarajan¹ · P. K. Srividhya¹ · P. Balasubramanian²

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Abstract

This work presents the effect of heating rate on thermal degradation behavior and kinetics of the imported bituminous coal (IC) and co-gasification of its blended form with palm kernel shells (PKS) of oil palm industry waste at different blending ratios. Thermogravimetry and pyrolytic kinetics of IC were determined by heating up to 1000 °C at various heating rates of 10, 20, 30, 40, and 50 °C/min. With the increase in heating rate, the degradation behavior of the IC improved with activation energy (E_a) and was found to be between 25 and 92 kJ/mol. While co-gasification with the blended form of IC with PKS at different ratios improved the degradation pattern, as well as the reaction and kinetic parameters with E_a ranged between 36 and 54 kJ/mol. The outcome of the study proposes the suitable blended form of this bituminous coal with PKS for efficient co-gasification on promoting energy mix and environmental aspects.

Keywords Co-gasification · Thermogravimetric analysis · Palm kernel shell · Activation energy · Pyrolytic kinetics

1 Introduction

Significant agriculture development in Southeast Asia provides abundant biomass from large-scale agricultural activities such as palm plantation. Around 90% of the world's palm oil production is ensuing in Southeast Asia with home to three ASEAN countries such as Indonesia, Malaysia, and Thailand. Palm oil is utilized for a wide range of purposes such as cooking, soaps, cosmetics, paints, and for biodiesel production [1–3]. Palm oil accounts 80% among import of edible oils

by India demands the promotion of oil palm development program under the National Mission on Oilseeds and Oil palm (NMOOP). It is due to the fact that palm is the main perennial edible oil crop that requires a section of the cultivation lands compared to other oilseeds [4].

The oil palm biomass may be defined as organic materials (edible/non-edible) in a solid or liquid form which is produced by oil palm industry during harvesting, crushing, refining, and milling of palm kernel oil [5]. In palm oil processing industries, quite a few residues such as empty fruit bunch (EFB), palm oil fiber (PFF), palm oil effluents (POMF), and palm kernel shells (PKS) have been generated. During the production of palm crude oil, around 64% of PKS is being generated as waste from palm fruit bunch in palm industries. In palm oil refining process, for every ton of palm fruit bunch, around 0.07 tons of shells, 0.15 tons of palm fiber, and 0.2 tons of empty fruit bunch are generated as solid wastes [6].

The waste PKS can be used as fuel for thermochemical methods as biomass energy conversion technologies. However, utilization of waste PKS as a single fuel results in specific challenges such as emission issues [7]. After removal of oil-rich and outer cover fiber from palm fruits, the inner part material of PKS covering the palm nut is hard, fibrous, and tough [8]. However, researchers around the globe explored the possibilities of utilizing PKS in other ways of energy applications such as resin, supercapacitor, and environmental

Highlights

- Palm kernel shells (PKS) and imported bituminous coal (IC) were feed-stocks.
- Co-gasification studies were carried out at various blending ratios.
- Thermogravimetric analysis, pyrolytic kinetics, and syngas production were evaluated.
- Activation energy of bituminous coal were 25–92 kJ/mol.
- Activation energy for the blended substrates varied from 36 to 54 kJ/mol

✉ J. Thiagarajan
rethiagarajan@gmail.com; thiagarajan@pmu.edu

¹ Department of Mechanical Engineering, Periyar Maniammai Institute of Science and Technology, Thanjavur 613404, India

² Department of Biotechnology and Medical Engineering, National Institute of Technology, Rourkela 769008, India

applications such as biogas, biofertilizer, and biochar along with few exquisite applications. For instance, Obi [9] demonstrated the utilization of ground palm kernel shell to make composite briquette with sawdust using cassava starch as the binding agent.

The swift growth of global energy demand enforced the universe to meet its total energy demand from fossil fuels around 80% and only 10–15% from the biomass [10]. India meets almost one-third of its energy consumption through bioenergy conversion technologies by existing 500 metric tons of different biomass sources per year, which is equivalent to about 250 million tons of coal having the potential of producing 17GW power [11, 12]. The biomass gasification in India reached adaptable status whereas gasification of coal is still under study because of the low reactivity and high ash content in Indian coal. Therefore, recent research is focused on the problems on co-gasification of coal having moderate ash content with biomass in fixed bed downdraft gasifiers [13]. Different agro-industrial wastes were utilized with coal in blended form as fuel feedstocks for co-gasification technology attributed process development with high carbon conversion efficiency and generation of improved-quality high-energy mix syngas and leads to the sustainable development of gasification technology for electrical power generation in remote areas [14].

Taking into consideration the physical characteristics of PKS and the possibility of energy extraction through thermochemical routes gives an initiative for co-gasification of palm kernel and imported bituminous coal, which could pave the way for scaling down the consumption of coal as a single feed. The authors have earlier reported the thermal behavior and pyrolytic kinetics of deoiled seed cake residues of jatropha, castor, and pongamia by thermogravimetric analysis for gasification studies [15, 16]. The thermal kinetics for co-gasification of jatropha seed cake residues with wood chips as well as palm kernels with low-grade Indian lignite coal was earlier reported by the authors [17, 18]. In this present work, the thermogravimetric analysis was carried out to study the thermal behavior of imported bituminous coal (IC) and realize the co-gasification kinetics of palm kernel shells (PKS) along with IC. Further, the syngas production during thermal decomposition of PKS and IC at individual as well as at mixed blends was also reported in detail.

2 Materials and methods

2.1 Materials

The biomass feed material such as palm kernel shells (PKS), a residue of oil palm industry, was obtained from palm oil production company of Godrej Agrovat Ltd. of Ariyalur, Tamil Nadu, India, and the imported bituminous coal (IC) was procured from a cement factory at Dalmiapuram, Tamil Nadu,

India. This work was carried out to study the thermal degradation behavior and co-gasification kinetics of PKS and IC at different blending ratios. For the thermal behavior and kinetic analysis, the feedstocks such as PKS and IC were grounded to 250–350 μm by using a mini household grinder and the co-gasification studies were performed at various blending percentages of 90, 80, 70, 60, and 50 of PKS with coal.

2.2 Thermogravimetric analysis

The degradation behavior and thermal kinetics of the IC individually at different heating rates as well as blend with PKS biomass at pyrolysis mode were studied by thermogravimetric analysis (TGA) technique. The experiments of pyrolysis on non-isothermal mode were performed by using Shimadzu 50H TGA analyzer with an accuracy of $\pm 0.5^\circ\text{K}$ temperature and readability of 0.001 mg on microbalance sensitivity. The fuel material, bituminous coal (IC), was subjected to thermogravimetric analysis at different heating rates of 10, 20, 30, 40, and 50 $^\circ\text{C}/\text{min}$ for the temperature range from ambient to 1000 $^\circ\text{C}$ under the inert atmosphere of nitrogen flowing at 20 ml/min. The co-pyrolysis of PKS and IC at different blending ratios of 90:10 (90PKS10IC), 80:20 (80PKS20IC), 70:30 (70PKS30IC), 60:40 (60PKS40IC), and 50:50 (50PKS50IC) by TGA was carried out at the heating rate of 40 $^\circ\text{C}/\text{min}$ for understanding the effect of blending ratio on thermal degradation behavior and kinetics.

2.3 Kinetic studies

By using the modified Arrhenius equation adopted in earlier studies [17–19], the effect of heating rates on TG and DTG profiles and the kinetic parameters such as activation energy (E_a), reaction order (n), and the frequency factor (A) were determined. The reaction rate constant (k) can be determined by using the following general Arrhenius equation as given in Eq. 1:

$$k = Ae^{-\frac{E_a}{RT}} \quad (1)$$

Where E_a as activation energy in kJ mol^{-1} and A as the pre-exponential factor in S^{-1} are the Arrhenius parameters, R is the universal gas constant $8.314 \text{ kJ mol}^{-1} \text{ K}^{-1}$, and T is the temperature in K.

Total kinetics can be determined by using the Eq. 2 as outlined in Jeguirim and Trouve [20]:

$$\left[\frac{-1}{w_o - w_f} \frac{dw}{dt} \right] = k \left(\frac{w - w_f}{w_o - w_f} \right)^n \quad (2)$$

where w is the sample weight in (mg) at time t , w_f is the final residue weight in (mg), w_o is the initial sample weight in (mg),

dw/dt is the ratio of the change in weight to change in time. By combining Eqs. 1 and 2, the derived linear form of the equation is obtained as given in Eq. 3:

$$\ln \left[\frac{-1}{w_o - w_f} \frac{dw}{dt} \right] = \ln(A) - \left(\frac{E}{RT} \right) + n \ln \left[\frac{w - w_f}{w_o - w_f} \right] \quad (3)$$

The above Eq. 3 can be written in the form of $y = B + Cx + Dz$, where

$$y = \ln \left[\frac{-1}{w_o - w_f} \frac{dw}{dt} \right], \quad x = \frac{1}{T}, \quad z = \left[\frac{w - w_f}{w_o - w_f} \right]$$

$$B = \ln(A), \quad C = -\left(\frac{E}{R} \right), \quad D = n$$

With the data of TG and DTG profile, the occurrence of maximum weight loss concerning time and temperature during the reaction can be determined. The three constants such as x , y , and z can be evaluated from the sample degradation analysis data and by using SigmaPlot 10.0.0 software, the kinetic parameters such as the activation energy (E_a), pre-exponential factor (A), and reaction order (n) were calculated.

2.4 Co-gasification studies

The co-gasification of the blended form of palm kernel shells and bituminous coal at the desired ratios were carried out on a 1 kW fixed bed, downdraft type, biomass gasifier system having reactor size of 300 mm diameter and 475 mm length. This lab-scale gasifier is equipped with wet scrubbing and filtering units for the post process of gasification run. The blending fuel of bituminous coal was prepared to the particle size of about 10–15 mm and uniformly mixed with preferred proportions of PKS. A batch-type co-gasification experimental runs were carried out by initial loading 4 ± 0.5 kg of the mixed form of feed materials (PKS and IC). During the entire gasification process, the air was being used as a gasifying agent and by fitting a K-type thermocouple with a data logger, the temperature of the reduction zone was being monitored. By passing reactor output gas through the wet scrubber and filtering units, the temperature was controlled and the filtered synthesis gas was collected through sampling ports in a gas sampling bladder.

The blended form of feedstocks was prepared in various proportional ratios of 90:10 (90PKS10IC), 80:20 (80PKS20IC), 70:30 (70PKS30IC), 60:40 (60PKS40IC), and 50:50 (50PKS50IC) for co-gasification studies. By loading the designated quantity of 4 ± 0.5 kg of the blended feedstocks, each experiment was carried out for 2 h and every 30 min of operational run, 0.5 kg of feed material was topped up to maintain fuel head till the complete run of the operation. After igniting the loaded feedstock, the initial run of about 10 to 15 min was processed for reaching the steady state of

operation. By observing the temperature as well as continuous flame of syngas burning condition at firing flare, the gas samples were collected in sampling bladders. Under steady-state process condition, three gas samples were collected for every 30 min of the process run. The composition of the product output gas was quantitatively analyzed by using gas chromatography [(Shimadzu GC-2014 with TCD detector and Shin carbon ST column (100/120 mesh, 1.00 mm I.D \times 2000 mm length) using nitrogen as carrier gas at the flow rate of 10 ml/min] for the content of carbon monoxide (CO), hydrogen (H_2), methane (CH_4), and carbon dioxide (CO_2). Calibration of the gas chromatography analyzer was done using standard gas before each gas sample analysis. By considering the produced volumetric quantity of combustible gases CO, H_2 , and CH_4 , the lower heating value (LHV) of the syngas was determined by using Eq. 4:

LHV of the syngas (4)

$$\left(\frac{MJ}{m^3} \right) = (12.62 * V_{CO}) + (10.71 * V_{H_2}) + (35.81 * V_{CH_4})$$

where, V_{CO} , V_{H_2} , and V_{CH_4} are the volume fraction of each gas [21].

3 Results and discussion

The physical and chemical characteristics of PKS and bituminous coal (IC) were determined by proximate and ultimate analysis. The moisture content, volatile matter, fixed carbon, and ash content of PKS and IC were analyzed as per the ASTM D3173, ASTM D3174, and ASTM D3175. The elemental content of carbon, hydrogen, nitrogen, and sulfur was analyzed by CHNSO analyzer. Table 1 shows the characteristics of PKS and IC in view of proximate and ultimate analysis. The thermal degradation pattern, thermal reaction, and kinetics were studied by TGA analysis of feed materials.

3.1 Effect of heating rates on thermal degradation pattern of bituminous coal (IC)

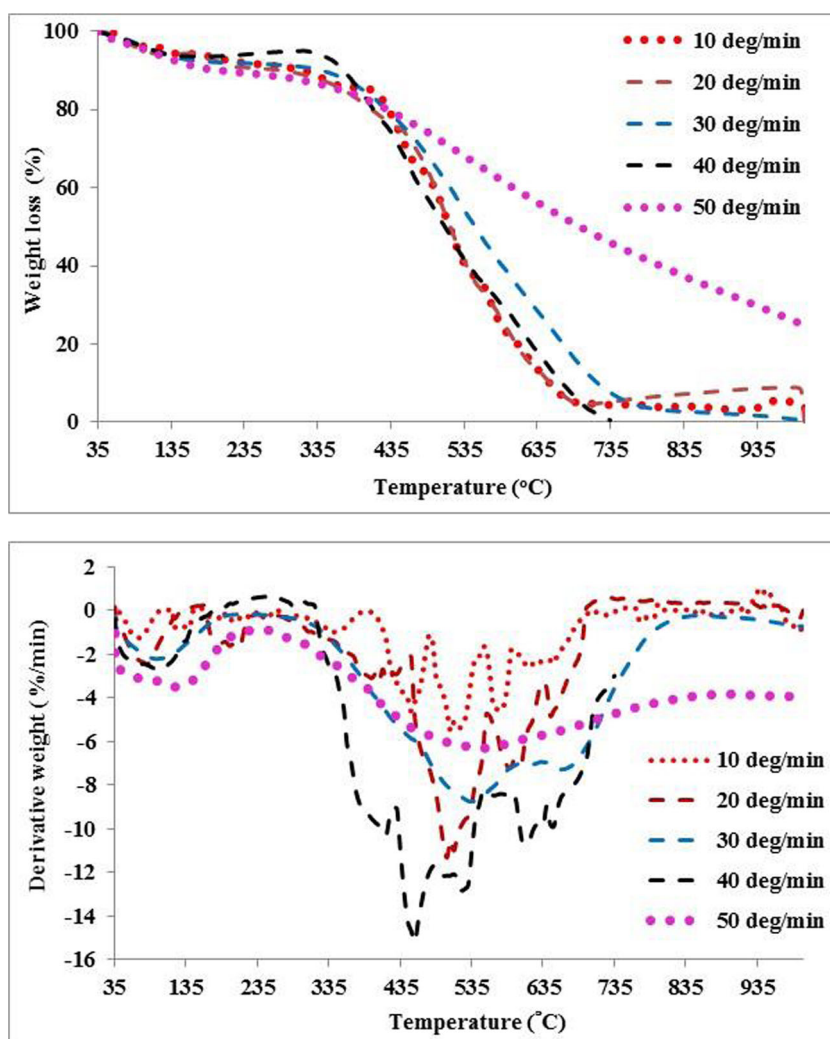
The thermal degradation pattern (TG and DTG) of the fuel material coal (IC) at various heating rates 10, 20, 30, 40, and 50 °C/min is shown in Fig. 1. It was observed that the slope of weight loss profile with respect to temperature is constant at the heating rates of 10, 20, and 40 °C/min. From the TG profile of the given coal material, the weight loss was found between the temperature range of 165 °C and 970 °C at all heating rates with different peaks of weight loss rate relative to temperature and the number of derivative weight loss peaks reduced with the increase of heating rate. The degradation of coal sample at the heating rates of 10 and 20 °C/min resulted in more number of peaks with low decaying rate.

Table 1 Proximate and ultimate analysis of palm kernel shells (PKS) and imported bituminous coal (IC)

Properties (%)	Palm kernel shells (PKS)	Imported bituminous coal (IC)
<i>Proximate analysis (mass % on dry basis)</i>		
Volatile content	73.21	42.20
Fixed carbon	20.74	48.88
Ash content	0.79	4.50
Moisture	5.26	4.42
<i>Ultimate analysis (mass % on ash free basis)</i>		
Carbon	46.32	64.94
Hydrogen	5.48	5.50
Nitrogen	0.45	1.40
Sulfur	Nil	0.12
Oxygen	47.45	28.04

At the heating rate of 10 °C/min, the coal sample was fully degraded having small three peaks at the maximum

rate (DTG_{max}) of -4.59 to $-5.5\% \text{ min}^{-1}$ with an equal percentage of weight loss. The same sample when heated at a rate of 20 °C/min exhibited with the same three peaks of slightly improved degradation pattern with DTG_{max} of -7.17 to $-11.29\% \text{ min}^{-1}$. It could be due to the fact that the coal is having amorphous structural composition and inorganic minerals and moisture. At 30 °C/min, the degradation profile of the sample resulted in a slow and steady manner with maximum derivative weight loss of $-8.61\% \text{ min}^{-1}$ at peak temperature (T_p) of 845 °C. The heating rate, pyrolysis temperature, and the residence time of reaction play a vital role in the distribution of yield products during the reaction [22]. When the heating rate further increased to 40 °C/min, the reaction was completed with three peaks with an increased height from -12.80 to $-17.15\% \text{ min}^{-1}$ at reduced temperature. It could be revealed that the coal is made up of principal organic components such as vitrinite, liptinite, and inertinite groups of inorganic minerals [23]. The increase of temperature and residence time of reaction at 30 and 40 °C/min was found suited for degradation of

Fig. 1 TG and DTG profiles of bituminous coal (IC) at different heating rates

coal and converting into products. The total mass of the sample was degraded, leaving the lowest residue at the end of reaction. It would be due to the occurrence of complete thermal reaction at related residence time at a high rate of increasing temperature. Further, the thermal reaction of coal sample at 50 °C/min resulted in about 25.17% of sample weight as end residue and it might be due to a lesser residential period of reaction which affects the production of products during pyrolysis stage and its distribution. Comparing to PKS biomass, the fuel coal has lower volatile matter and high fixed carbon content with low reactive nature. The high heating rate of reaction will affect low reactive material, thermally degrading with a lower rate of weight loss in relation to the temperature. It was found that the IC was fully degraded at the heating rate of 40 °C/min resulting in high rate of weight loss within the temperature range of 415 to 520 °C. Table 2 summarizes the thermal reaction parameters of the IC at all heating rates.

3.2 Thermal reaction parameters in co-gasification of PKS and IC

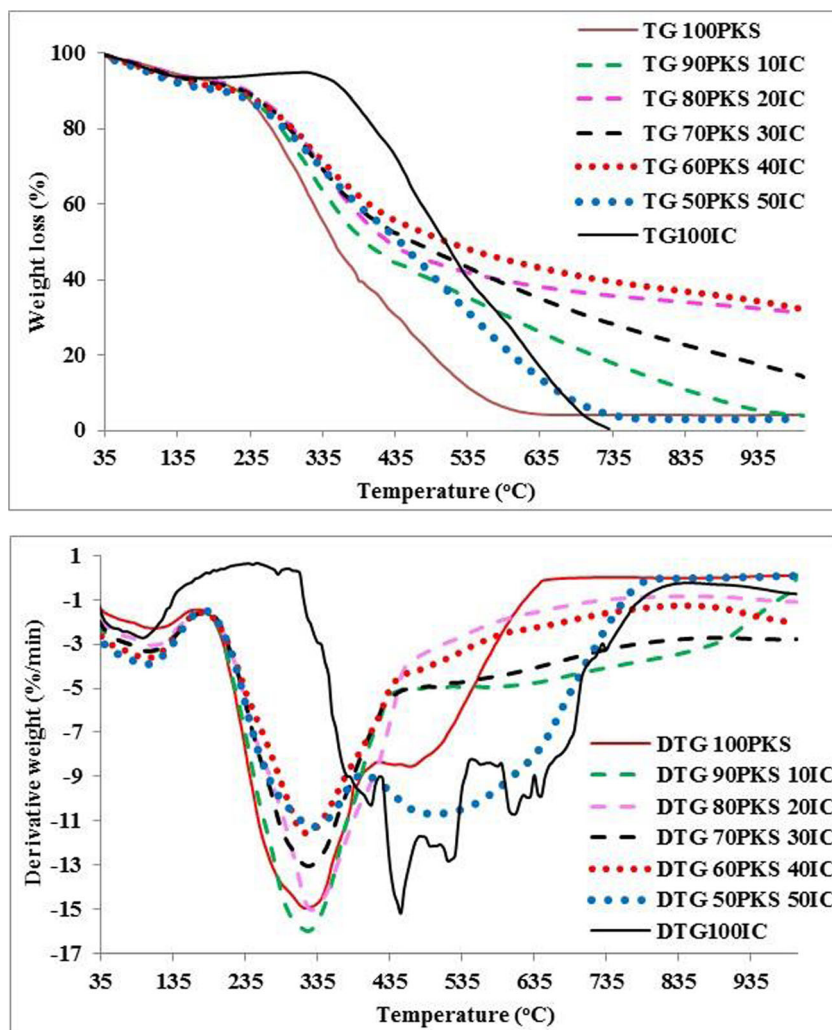
Figure 2. shows the TG and DTG degradation profiles of the blended feedstocks of PKS and IC at various ratios of 90:10 (90PKS10IC), 80:20 (80PKS20IC), 70:30 (70PKS30IC), 60:40 (60PKS40IC), and 50:50 (50PKS50IC) heated to temperature range of ambient to 1000 °C at the rate of 40 °C/min. For the blended samples with an increase in the percentage of coal with PKS, the percentage of weight loss was lowered as well as the maximum derivative weight loss rate with almost equal peak temperature. The summary of the thermal reaction parameters of the blended samples of PKS and IC is shown in Table 3. It was observed that the weight loss of the samples during the reaction occurred between the temperature range of 165–970 °C at different phases for

all the mixed samples except the blended sample at an equal percentage. For the sample 90PKS10IC, there was no significant change on reaction parameters comparing to the individual sample of 100PKS. The mixing of 10% of coal with PKS does not have any significant effect on the reaction kinetics. With the increase of coal to 20% with PKS, the values of peak weight loss rate (DTG_{max}) in relation to temperature (T_p) was not affected, yet the percentage of weight loss was reduced. The weight content of PKS existed with high oxygen and volatile content that could not develop effective thermal interaction by the generated pyrolytic products resulted in a higher amount of residue material. The increase of coal content up to 40% had a significant impact on derivative weight loss percentage and the degrading amount of sample material getting affected without a remarkable change in peak temperature. It may be due to the fact that the presence of coal with low reactive and high fixed carbon content biomass of PKS, resulting in low synergetic effect during the pyrolytic reaction. For the sample at an equal percentage (50PKS50IC), the total weight loss of the sample effected with a comparatively lower rate of derivative percentage (DTG_{max}) and increase of peak temperature. It would be due to the dominant coal reaction at high temperature in low residence period. The mixing of biomass (PKS) with IC changes the height of the peak during the oxidative pyrolysis regime. The PKS-IC blend took more time for their combustion with an increase of PKS percentage. It has been observed that the ignition temperature of the PKS-IC blends corresponds to the biomass present in the mixed sample. It would be due to the high volatile content and rapid release of volatile matter at low temperature [24]. Similar results have been reported on coal with PKS by Idris et al. [25], on lignite biomass (cotton, pine pruning, olive residues and sewage sludge) by Vamvuka and Sfakiotakis [26] and coal and biomass by Gil et al. [27]. By considering the differences in degradation pattern

Table 2 Reaction parameters for bituminous coal (IC) at different heating rates

Heating rate (°C/min)	P ₂				P ₃				P ₄					
	Temp range (°C)	Weight Loss (%)	T _p (°C)	DTG _{max} (% min ⁻¹)	Temp range (°C)	Weight loss (%)	T _p (°C)	DTG _{max} (% min ⁻¹)	Temp (°C)	WeightLoss (%)	T _p (°C)	DTG _{max} (% min ⁻¹)	T _f (°C)	Residue, (%)
10	150–470	28.53	450	−4.61	475–550	27.56	505	−5.50	560 - 680	29.75	575	−4.59	920	3.33
20	165–440	18.01	400	−3.09	445–550	38.11	505	−11.29	555 - 695	31.23	595	−7.17	970	8.70
30	165–780	88.14	545	−8.61	—	—	—	—	—	—	—	—	945	1.51
40	150–435	19.26	415	−10.26	440–490	17.15	455	−15.17	495–695	49.44	520	−12.80	725	1.30
50	165–945	62.59	545	−6.30	—	—	—	—	—	—	—	—	995	25.17

Fig. 2 TG and DTG profiles of palm kernel shells (PKS) and bituminous coal (IC) blends



of sample feedstock in both single and mixed form, the possible synergistic effect could be verified by Eq. 5:

$$W_{blend} = (X_{IC} * W_{IC}) + (X_{PKS} * W_{PKS}) \quad (5)$$

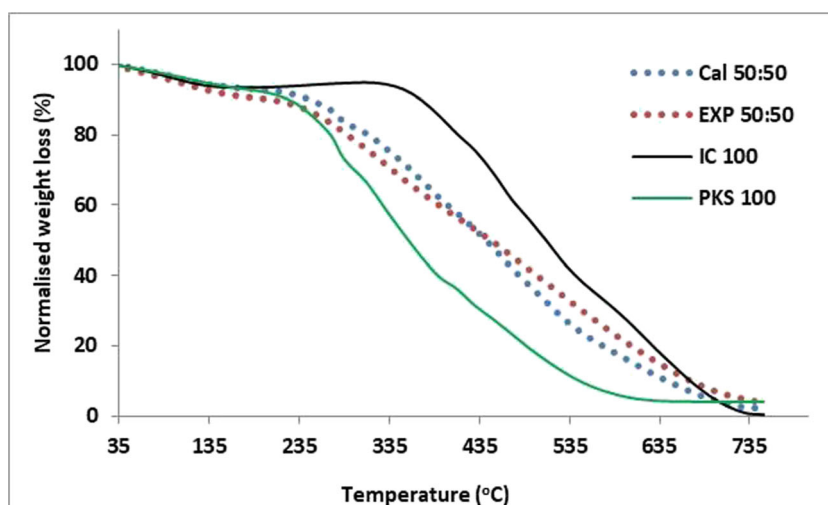
where X_{IC} and X_{PKS} are the percentages of IC and PKS in the blend, respectively. W_{IC} and W_{PKS} is the normalized weight

loss of IC and PKS, respectively under the same operating conditions [25]. The comparison of calculated and experimental weight loss curves for the blended sample of PKS and IC is shown in Fig. 3. It was found that the degradation behavior of the blended sample PKS and coal having a substantial synergistic effect and the minimum deviation from the experimental values would have been due to the complex structure and lignocelluloses content of the PKS biomass.

Table 3 Reaction parameters for palm kernel shells (PKS) and bituminous coal (IC) at different blending ratios

Sample	Temp range (°C)	Weight loss (%)	T _p (°C)	DTG _{max} (% min ⁻¹)	T _f (°C)	Residue (%)
100IC	150.64–695.55	85.85	455	–15.17	725	1.30
100 PKS	200.45–635.23	87.65	310	–14.61	960	4.08
90PKS10IC	165.53–960.45	87.80	320	–15.98	990	4.03
80PKS20IC	165.24–965.43	61.33	325	–15.02	995	30.98
70PKS30IC	160.59–970.42	76.75	320	–13.01	995	14.62
60PKS40IC	160.48–965.56	58.54	325	–11.52	995	32.23
50PKS50IC	160.30–760.33	87.80	335	–11.29	965	3.14

Fig. 3 Comparison of calculated and experimental thermogravimetric curve of palm kernel shells (PKS) and bituminous coal (IC) for the blending proportion of 50:50



3.3 Thermal kinetics of coal (IC) at various heating rates

By utilizing the TGA data, the thermal kinetic parameters such as activation energy (E_a), exponential factor (A), and the reaction order (n) were obtained by linear regression analysis using Sigmaplot 10.0 software. The kinetic parameters were evaluated by considering the maximum weight loss zone in thermal degradation profile. The calculated kinetic parameters for bituminous coal at all heating rates are shown in Table 4. As the fuel coal sample with low volatile and low reactive nature, the rate of heating plays a role in the minimum energy required for the thermal reaction. The activation energy (E_a) for this coal was to be 25–92 kJ/mol and from the DTG profile data, the peak temperature at which the maximum weight loss rate was found between the temperature range of 415–595 °C irrespective of the heating rates. From the results of the kinematic parameters, E_a found lowered for the heating rate of more than 20 °C/min. At a heating rate of 10 °C/min for IC, the energy required was found to be maximum (91.83 kJ/mol) with a high frequency rate of molecular collision. With increase of heating rate to 20 °C/min, the energy required for the reaction reduced

to half (46.56 kJ/mol) due to a low individual frequency rate of collision of molecules. At heating rates of 30 and 40 °C/min, the temperature range and the frequency factor were differed, resulting in lower E_a due to high temperature in low residence time. For the 50 °C/min heating rate, the reaction at the lowest residence time resulted with lowest E_a and the exponential factor. The obtained thermal reaction kinetic parameters such as activation energy (E_a) and exponential factor (A) of this imported bituminous coal were similar to the findings of low-rank Indian coal by Naidu et al. [28].

3.4 Co-gasification kinetics of PKS and IC at different blending ratios

The pyrolytic reaction kinetics for the mixed samples PKS and IC were found out by linear regression analysis using SigmaPlot software 10.0. For the co-gasification kinetics of all the blended samples, the correlation coefficient ($R[2]$) values were more than 0.97. The resulted kinetic parameters for the thermal reaction of mixed PKS and IC at different blending ratios were consistent for predicting the degradation behavior of these samples at different conditions. The resulted kinetic parameters of thermal

Table 4 Thermal kinetics of bituminous coal (IC) at different heating rates

Sample	Heating rate (°C/min)	Temperature range (°C)	T_p (°C)	E (kJ/mol)	A (min^{-1})	n (dimensionless)	R^2 (dimensionless)	F value	P value
IC	10	290.00–680.14	505	91.83	7.836×10^5	0.985	0.9700	438.01	< 0.0001
	20	285.00–695.55	505	46.56	1.304×10^2	0.638	0.9835	1371.98	
	30	215.19–780.00	545	47.81	1.635×10^2	0.599	0.9754	2462.71	
	40	325.53–695.55	415	53.04	1.161×10^3	0.425	0.8599	159.64	
	50	235.07–945.00	545	25.16	4.197	0.408	0.9785	2777.39	

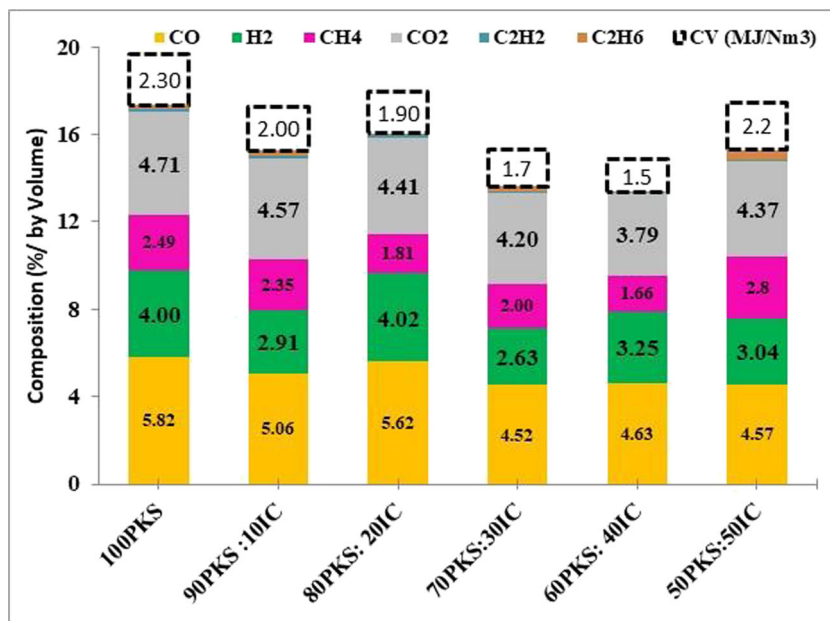
Table 5 Thermal kinetics of palm kernel shells (PKS) and bituminous coal (IC) at different blending ratios

Sample	Temp range (°C)	E (kJ/mol)	A (min ⁻¹)	n (dimensionless)	R ² (dimensionless)	F value	P value
100IC	325–695	53.04	1.161×10^3	0.425	0.8599	159.64	< 0.0001
100PKS	200–280	47.80	5.475×10^5	0.735	0.9582	343.81	
90PKS10IC	200–280	45.81	2.596×10^3	0.694	0.9811	1092.89	
80PKS20IC	175–300	40.08	7.607×10^2	0.411	0.9706	495.27	
70PKS30IC	175–295	42.85	1.210×10^3	0.815	0.9820	1203.16	
60PKS40IC	180–310	36.16	1.593×10^3	0.352	0.9845	1592.93	
50PKS50IC	200–285	49.45	3.899×10^3	0.544	0.9844	883.63	

reaction for the temperature range of 35–1000 °C at the heating rate of 40 °C/min for various blends of PKS-IC is shown in Table 5. E_a for all the samples at different proportions was found to be 36–49 kJ/mol, which is similar to the findings of co-firing of methanated distillery effluent solid waste and Indian coal [29]. With the increase of coal with PKS from 10 to 40% proportions, the resulted E_a was found decreased and the low reactive nature of IC affected the collision frequency. PKS biomass comprises of lignocelluloses with high volatile matter and reactive nature, whereas the coal is the fossil fuel containing high energy and fixed carbon and nature of low reactivity. Mixing of coal with PKS has an insignificant effect on the required activation energy for thermal reaction, whereas the biomass improves the degradation behavior and thermal reaction rate of the fossil fuel. E_a was found increasing in case of 50PKS50IC. The outcome of this co-gasification kinetics revealed that PKS is a suitable material for energy mix with the imported coal.

3.5 Characterization of syngas produced during co-gasification of PKS-IC blends

The synthesis gas produced by the gasification technology contains CO, H₂, CH₄, and CO₂ at varying compositions. The co-gasification experimental run using the blended feedstocks of PKS and IC at different ratios of 90:10 (90PKS10IC), 80:20 (80PKS20IC), 70:30 (70PKS30IC), 60:40 (60PKS40IC), and 50:50 (50PKS50IC) were carried out. The output syngas composition and the obtained heating value (LHV) by considering the combustible gases during the co-gasification of PKS and IC at the desired blending ratios are shown in Fig. 4. The syngas characteristics were found to be different while increase in the percentage of coal with PKS. At 10% of coal mixing, the syngas generated were of CO (5.06%), CH₄ (2.35%) and H₂ (2.91%). With increase of coal to 20%, the output resulted in more CO (5.62%) and H₂ (4.02%) with less percentage of CH₄ (1.81%). The biomass is favorable for pyrolytic reaction due to higher volatile and

Fig. 4 Syngas composition of palm kernel shells (PKS) along with the blends of bituminous coal (IC) at different ratios

hydrocarbons while compared to coal (IC). For the run on blended mixtures (70PKS30IC) and (60PKS40IC), the syngas analysis revealed that the composition of H_2 and CH_4 have differed with an equal percentage of CO. For 50PKS50IC, higher volatile content in blends causes the reduction of gasification temperature, which might further lead the production of H_2 as inconsistent. The increment quantity of CO compared to other components could be due to higher oxygen content and reactivity of the biomass [30]. The resulted syngas was found with a higher content of H_2 and CH_4 by lowering of CO was observed in the case of 50PKS50IC. The increase in the percentage of coal having high carbon thermally reacted with produced CO and hydrogen could promote the water shift and Boudouard reactions [31, 32]. The natural content of oxygen and hydrogen would be promoted the reactivity of the coal (IC) and adaptation of volatile matter into free radicals resulting on the development of gasification reactions [13, 28]. In co-gasification of PKS with coal at the ratios of 90:10, 80:20, 70:30, and 60:40, the obtained calorific value (LHV) was found to be 2.0, 1.9, 1.7, and 1.5 MJ/Nm³ while at an equal percentage of PKS and IC, the LHV increased to 2.2 MJ/Nm³. Similar observations were reported in co-gasification of wood and miscanthus pellets with lignite coal by De Jong et al. [33] as well with PKS sub-bituminous coal by Valdés et al. [34]. The variation in resulted calorific values in co-gasification of PKS and coal (IC) at different ratios could occur due to existing behavior of the feed materials during thermal degradation reaction which would affect the reactivity of blended materials at pyrolysis stage and carbon conversion ratio during gasification.

4 Conclusion

The thermal behavior and kinetics of the imported bituminous coal (IC) sample at various heating rates and its blended form with biomass palm kernel shells (PKS) at the heating rate of 40 °C/min were evaluated. The activation energy for coal at different heating rates was found between 25 and 92 kJ/mol. With the increase in heating rate, the degradation pattern was improved by increasing the peak height and leaving more end residue material. The degrading behavior of the IC with PKS at different blending ratios improved the weight loss percentage of the sample at a lower peak temperature of 310–325 °C with the activation energy ranged between 36 and 54 kJ/mol. The TGA and syngas analysis revealed that the co-gasification of IC and PKS at the ratios of 10:90, 80:20, and 50:50 will promote the biomass/coal blended gasification for energy conversion. The blended feedstock of IC and PKS at desired ratios can promote the energy and environmental benefits for the sustainable development of gasification process at rural areas.

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