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Thermal behavior and pyrolytic kinetics of palm kernel shells and Indian lignite coal at various blending ratios

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Abstract

The study presents the effect of heating rate on thermal degradation kinetics of gasification and cogasification of palm kernel shell (PKS) and low-grade Indian coal (LC) at various blends. The thermogravimetric analysis (TGA) and pyrolytic kinetics of PKS and LC were investigated by heating up to 1000°C at a different heating rate of 10, 20, 30, 40 and 50°C/min. With the increase of heating rate, the TG profile of both PKS and LC were found different. For the gasification kinetics of PKS and LC, the activation energy (E) were 56.92 and 74.69 kJ/mol along with the exponential factor (A) as 9.391×10^3 and $6.740 \times 10^3 \text{ min}^{-1}$ respectively. In case of cogasification studies, the activation energy for the blends of PKS and LC at various ratios were found lowered to the range of 56 - 66 kJ/mol. This study could propose the appropriate blending ratio of PKS with LC for co-gasification at ease.

Keywords: Cogasification; Thermogravimetric analysis; Palm kernel shell; Activation energy; Pyrolytic kinetics.

1. Introduction:

The rapid growth of global energy demand by both developed and developing countries forced the universe to meet its total energy demand from the fossil fuels of around 80% and only 10-15% of the biomass materials (**Singh and Sekhar, 2016; Balasubramanian and Karthickumar, 2012**). As far as India is concerned, one-third of its total energy consumption could be met by bioenergy technology from the available 500 metric tons of biomass per year (**Asok et al., 2013; Karthickumar and Balasubramanian, 2015**). The gasification technology using single biomass as a source of feed material throughout its year of operation experiences the hardship of non-availability of particular biomass throughout the year, hurdle in transportation and non-utilization of locally available biomass in that region. Gasification is one of the promising technology in which the energy sources other

than coal can be used as feedstock. This advantage gives the initiative to probe the possibility of using different fuels at blended proportion.

Biomass gasification has received significant attention in India, while, coal gasification has been less studied due to its lower reactivity and high ash content in domestic coals (**Sharma et al., 2015**). The co-gasification of different fuels makes the possibility of synergistic reactions during the reactor operation for maximized product generation as well as intermediates improve the process performance by reducing the carbon losses and increase the energy content of the synthetic gas (**Singh and Sekhar, 2016**). The blending technology of biomass feedstock gives a path for sustainable growth of continuous and steady operation of gasifiers in remote areas (**Sreejith et al., 2014**). The single feed biomass gasifier working underwood as fuel feed can be operated by multi-feed sources like coconut shells and rubber seed shells blended feed form under cogasification technology (**Inayat et al., 2017**). Cogasification of wood chips and coconut shells in a downdraft gasifier showed the carbon conversion efficiency, syngas quality and performance of co-gasification were more responsive to multiple feed particle size and blending ratio (**Inayat et al., 2016**).

The cultivation of oil palm plantation in the agricultural sector is one of the commercial projects in countries like Malaysia, Indonesia, and several other West African countries (**Durst et al., 2004**). Palm oil mill industry in Malaysia produces most abundant residues as shells (**Mubarak et al., 2014**), as it contributes about 47% of the world's supply of palm oil (**Kaman et al., 2017**). However, India is one of the world biggest importers of edible oils in which the palm oil accounts for 80%. Palm is one of the potentially attractive sources because it is a highest perennial edible oil crop which requires a fraction of the area for cultivation compared to other oilseeds. India has planned to promote oil palm development program under the National Mission on Oilseeds and Oil palm (NMOOP). 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. The generation of wastes from palm industries is almost 64 % of PKS from palm fruit bunch during the production of palm crude oil (**Obisean, 2004**). In palm oil refining process, for every ton of palm fruit bunch around 0.7 tons of shells, 0.15 tons of palm fiber and 0.15 tons of empty fruit bunch are generated as solid wastes. The conversion of agricultural solid wastes seems to have possible application and can be developed sustainably for industrial need utilization (**Purevsuren et al., 2003**).

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 resulting specific challenges such as emission issues (**Yusolf, 2006**). After removal of oil-rich and outer cover fiber from palm fruits, the inner part material of PKS covering the palm nut which is hard, fibrous and tough (**Azlina et al., 2010**). However, researchers around the globe explored the possibilities of utilizing PKS in other environmental applications such as for biogas applications (**Garcia-Nunez et al., 2016**), anion resin preparation for fluoride adsorption (**Bashir et al., 2018; Abu-Bakar et al., 2016**), activated carbon (**Yacob et al., 2013; Luka et al., 2018**) for supercapacitor applications (**Misonon et al., 2018**) and heavy metal removal (**Sylvia et al., 2018; Pam et al., 2018**) aggregates in concrete (**Yusuf et al., 2018**), biofertilizer for oyster cultivation (**Nam et al., 2018**), biochar production (**Liew et al., 2018**), phenol synthesis (**Chang et al., 2018**) and various other applications (**Yahayu et al., 2018**). Recently, **Monir et al., (2018)** modelled the gasification of palm oil empty fruit brunches in pilot plant downdraft reactor.

Keeping the view of physical characteristics of PKS and the possibility of energy extraction through thermochemical routes give an initiative for co-gasification of palm kernel and low-grade Indian lignite coal. 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 (Thiagarajan et al., 2016; 2017). The thermal kinetics for cogasification of jatropha seed cake residues with wood chips was earlier reported by the authors (Thiagarajan et al., 2018). In this present work, the thermogravimetric analysis was carried out to study the thermal behavior and comprehend the pyrolytic kinetics of palm kernels and low-grade Indian lignite coal. Further, the syngas production during thermal decomposition of PKS and LC at individual as well as at mixed blends were reported.

2. MATERIAL AND METHODS

2.1 Materials

In this study, the palm kernel shells (PKS) derived from the oil palm industry is used as a biomass feedstock. PKS is a residue of palm oil production technology using palm fruits as feed materials, which were procured from local palm oil production unit of Godrej Agrovet Ltd. of Ariyalur, Tamilnadu, India and the low-grade Indian lignite dry coal was purchased from Raju enterprise Pvt. Ltd. of Cuddalore, Tamilnadu, India. This experimental work was carried out to study the pyrolytic kinetics of PKS and low-grade Indian coal along with their blends at different ratios.

For the TGA analysis, the PKS and LC were powdered to 250-350 μm by using the mini household grinder and subsequently, the gasification studies were carried out with 100% samples (100PKS and 100LC). For co-gasification studies, both the LC and PKS blended samples were prepared with a mass ratio of 10:90 (10LC90PKS), 20:80 (20LC80PKS), 30:70 (30LC70PKS), 40:60 (40LC60PKS) and 50:50 (50 LC50PKS).

2.2. Thermogravimetric analysis (TGA):

The thermogravimetric analysis was carried out with the PKS, LC and their respective blended mixtures to comprehend the thermal degradation behavior and pyrolytic kinetics in view of energy recovery through pyrolysis of those feedstocks. Approximately 5-6 mg of the pure powdered samples of the individual as well as various blended ratios were subjected to TGA studies by performing non-isothermal experiments using Shimadzu TGA50H analyzer. TGA analysis of the individual samples of PKS and LC were done at five different heating rates of 10, 20, 30, 40 and 50°C/min using Nitrogen as an inert gas at the flow rate of 20 ml/min by heating from the ambient temperature to 1000°C. The TGA tests were carried out on mixed blends of PKS and LC at different ratios of 90, 80, 70, 60 and 50% at the heating rate of 40°C/min to study the effect of blending ratio on the thermal degradation kinetics.

2.3 Kinetic studies

The modified Arrhenius equation based technique was adopted in this present work to comprehend the kinetics of thermal degradation behavior of materials were earlier followed by **Naveen and Pemelatha, 2014; Jeguirim and Truove, 2009; Mansaray and Ghaly, 1999**. It will relate the effect of different mixing ratios of fuels on activation energy, the order of reaction and frequency factor. From the TGA data, the kinematic parameters were estimated by adopting the general rate equation as in **Eq. 1**.

$$\frac{dx}{dt} = kx^n \quad (1)$$

Where x is the conversion ratio, which is equal to $(w_o - w) / (w_o - w_f)$ where w_o , w_f and w are the initial and final and time-dependent mass sample respectively. Likewise, n is the order of reaction, t is the time (min) and k is the reaction constant.

The reaction rate constant could be experimentally obtained by the Arrhenius decomposition equation as shown in **Eq. 2**.

$$k = Ae^{-\frac{E}{RT}} \quad (2)$$

Where Ea is activation energy in kJ.mol^{-1} and A is 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.

Applying the Arrhenius equation (2) for k in Eq. (1) leads to a linear form of equation as

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

Eq. 3. is similar to the simplified form of equation as

$y = B + Cx + Dz$ where

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

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

From the TGA data, the time and temperature at which maximum weight loss occurred during the reaction can be obtained. Using this constant x , y , and z were calculated. Constants B , C , D are calculated by multilinear regression of TGA data by using the LINEST function in MS-Excel. By obtaining out the values of constants, the activation energy, pre-exponential factor and reaction order kinetic parameters could be calculated. However, it is noteworthy to mention that the use of pre-exponential factor without understanding the limitations of the corresponding equation might end-up on misleading kinetic and thermodynamic data (Ali, 2018).

2.4 Gasification and cogasification studies

The gasification of palm kernel shells (PKS) and cogasification with low grade Indian lignite coal (LC) at different blending ratios were performed. These experiments were carried out on a lab scale 1 kW fixed bed down draft type biomass gasifier equipped with wet scrubbing and filtering units for downstream process of gasification. LC was pulverized evenly to a particle size of 10-15mm and uniformly mixed with PKS to the required proportions for cogasification studies. The cogasification was performed using the blended feed materials PKS and LC and the effects on different blending ratios were studied. The tests were conducted on batch type process by loading the prepared feed materials from the top of the reactor. Each test run on gasification and cogasification of biomass (PKS) with coal (LC) was carried out by loading the prepared feed material of 4 ± 0.5 kg and using air as gasifying agent. The reduction zone temperature of the gasifier was monitored by K-type thermocouple fitted with data logger. The temperature of output gas from the reactor was reduced by passing through the wet scrubber and filtering units. The filtered synthetic gas was collected in gas sampling bladder through designated gas sampling ports.

The feedstocks for cogasification were prepared by mixing the LC and PKS at different proportional ratios of 10:90, 20:80, 30:70, 40:60 and 50:50. Each run of experiment was conducted for about 2hr by initial loading of stipulated 4 ± 0.5 kg of fuel feed material and during the operational run of every 30 min, 0.5 kg of feed was topped up for maintaining the fuel head at hopper portion of the gasifier. At the beginning, the loaded feed material was ignited and it takes about 10 to 15 min of initial run for reaching the steady state. After reaching the steady state of operation, by monitoring the temperature as well as continuous flame of output gas burning at firing flare condition, the gaseous samples were collected through gas sampling ports. Three samples were collected for every 30 min of continuous run of operation by maintaining the head of feed at hopper and steady state of operational

condition. The collected syngas samples were quantitatively analyzed for its composition of CO, H₂, CH₄ and CO₂ by using gas chromatography [(Shimadzu GC- 2014 with TCD detector and Shin carbon ST column (100/120 mesh, 1.00mm I.D × 2000mm length)] using nitrogen as carrier gas at the flow rate of 10 ml/min. Before analysis of gas samples, the calibration was done using the standard gas with known composition. The calorific value (LHV) of the syngas was calculated by taking into account the CO, H₂ and CH₄ by using Eq. 4 as follows:

$$LHV \text{ of the syngas } \left(\frac{MJ}{m^3} \right) = (12.62 * V_{CO}) + (10.71 * V_{H_2}) + (35.81 * V_{CH_4}) \quad (4)$$

Where, V_{CO}, V_{H₂} and V_{CH₄} are the volume fraction of each gas (Wu et al., 2012).

3. Results and Discussion

The physicochemical characteristics of the feedstocks (PKS and LC) were comprehended by subjecting the samples for both ultimate and proximate analysis. PKS are the leftover shell fractions after the oil extraction process, however, it is fibrous and hard. The fixed carbon and ash content of the PKS are comparable with LC. TGA analysis revealed the effect on thermal degradation of the individual as well as blended samples of PKS and the low-grade Indian lignite coal (LC) at various heating rates and blending ratios. To study the thermal degradation kinetics of individual samples of PKS and LC, TGA analysis was carried out at different heating rates of 10, 20, 30, 40 and 50°C/min on a temperature range of 35-1000°C. Similarly, the co-gasification studies were carried out at different blending ratios of LC with PKS at 10, 20, 30, 40 and 50% of mixed nature were studied at the heating rate of 40 °C/min for the temperature range of 35-1000°C. The profiles of the weight loss and the kinetic parameters of the individual as well as the blended samples were analyzed.

3.1 Effect of heating rates on thermal degradation profiles of PKS:

The thermal degradation (TG and DTG) patterns of the PKS at the heating rates of 10, 20, 30, 40 and 50°C/min under nitrogen atmosphere are shown in **Fig. 1**. In the case of gasification studies with PKS, the weight loss due to thermal degradation is maximum between the temperature range of 190-590°C. The thermal decomposition summary of the PKS at various heating rates is shown in **Table 1**. The comprehension of the TGA profile was done based on the consideration of 10 well-defined points for the characterization of a thermogravimetric experiment of a biomass sample as outlined by **Gronli et al., (2002)**. With the increase of heating rate, the weight loss of material occurred with a number of peaks. At 40°C/min of heating rate, the complete degradation of the sample about 87.65% was found in a single peak with DTG_{max} of -14.61%.min⁻¹. However, at a heating rate of 50°C/min, the weight loss was found with less value of 52.57% with DTG_{max} of -18.99%.min⁻¹ by leaving the mass of 28.99% as residues.

The TGA tests at different heating rates showed that the initial peak at a temperature range of 190-210°C represents the removal of moisture and initial volatile matter. At 10°C/min, the weight loss of the sample at peak P₂ was found as 45.72% between the temperatures of 205 to 405°C with DTG_{max} -7.53%.min⁻¹ at peak temperature (T_p) 335°C. During this reaction peak, the thermal decomposition of biomass components such as hemicelluloses (200-280 °C) cellulose (280-350 °C) and lignin (200-550 °C) might initiated and converted into volatile phase. In the third peak (P₃) between the temperatures of 375-760°C further weight loss of about 24.33% with DTG_{max} -2.73%.min⁻¹ at peak temperature (T_p) 690°C were observed, which signified the degradation of hard components such as lignin and other hard fibrous contents of PKS. At the heating rates of 20 and 30°C/min, the mass reduction was found with increasing derivative maximum value in the second peak (P₂) indicates the pyrolytic reactions of major part of lignin, cellulose and hemicelluloses were effected. The

thermal degradation of the sample material with a further increase of heating rates to 40 and 50°C/min, the entire mass loss was found in second peak itself might be due to high reactivity and efficient thermal degradation of fibre hard nature of PKS. By observing the degradation profile parameters at 40°C/min, the maximum weight reduction of the sample about 87.65% was found with DTG_{max} -14.61%.min⁻¹ at T_p of 310.33°C as 4.08% as residues.

The sample test at an increased rate of 50°C/min the weight loss found to be 52.57% at increased DTG_{max} of -18.99%.min⁻¹ at T_p value about 320.46°C with high sample residue of about 28.49%. At the heating rate of 40°C/min, the percentage of weight loss found high compared to other degradation profiles and it may be due to the fiber and hard nature of the palm kernel shell material.

3.2 Effect of heating rates on thermal degradation profiles of LC:

The TGA and DTG profiles of the low-grade Lignite Indian coal (LC) at different heating rates 10, 20, 30, 40 and 50°C/min are shown in **Fig. 2**. In the case of Lignite coal at all heating rates, the weight loss was found between the temperature range of 200-935°C at different peaks. The degradation parameters of the LC was summarized in **Table 2**. From the degradation profile of Lignite coal at 10 and 20°C/min, the maximum mass loss and derivative were observed in third peak (P_3) with 81.93% (DTG_{max} -2.926%.min⁻¹ at T_p 460°C) and 84.97% (DTG_{max} - 4.479%.min⁻¹ at T_p 480°C). The TG curve and reaction parameters of LC revealed that the mass loss of the lignite coal was with low decaying rate in the entire reaction at peak temperature of 460-480°C. It could be due to the low reactivity nature, and less volatile content in LC, which need comparatively higher temperature for degradation with high rate of DTG. This would exhibit that low carbon and volatile matter content nature of the LC might have required more heat for pyrolytic reactions.

At increased heating rate 30, 40 and 50°C/min, the profile indicated that at third peak (P_3), the derivative value increased with more or less same maximum weight loss percentage. However, at the rate of heating 40°C/min a remarkable difference in degradation nature of profile of single peak with a weight loss of 87.42% ($DTG_{max} -14.51\% \cdot \text{min}^{-1}$ at T_p 480.42°C). The difference in degradation nature of lignite coal at different heating rates are due to low volatile, high carbon content and low reactivity characteristics of the coal material.

3.3 Cogasification thermal reaction parameters of PKS and LC at various blending ratios

The degradation of the blended samples of PKS with LC at 10, 20, 30, 40 and 50% were carried out at a temperature range of 35-1000°C at the heating rate of 40°C/min under an inert atmosphere of nitrogen gas. The effect on thermal degradation of blended samples of PKS and LC at different ratios were shown in TG and DTG curves in **Fig. 3**. From the degradation profile of the each mixed sample, the initial peak at a temperature range of 35-195°C was relating to the removal of moisture and initial volatile matter.

The degradation profile of the respective blended sample shows that the weight loss of material occurred at different stages during the reaction. The summary of the degradation parameters of the PKS and LC at various blending ratios are shown in **Table 3**. For all the samples at different blending ratios, it was observed that the weight loss during reaction occurred between the temperature of 190-950°C at the various stages.

For the samples 10LC90PKS and 30LC70PKS, the material degradation was found to be 56.86% ($DTG_{max} -17.86\% \cdot \text{min}^{-1}$ at T_p 325.26°C) and 46.89% ($DTG_{max} -16.09\% \cdot \text{min}^{-1}$ at T_p 335.01°C) respectively. At 10% LC with 90% PKS blend the available weight content of PKS with high volatile and oxygen content, could not dissipate the generated pyrolytic products for developing thermal interaction during reaction which resulted high amount of

residue material. With the 30% of LC with 70% of PKS decaying of mixed materials got affected due to sluggish thermal interactions between the biomass and fossil material mixture. In this ratio the available mass content of LC with low reactivity and carbon content may dominate and affect the thermal interactive reaction of mixture. The residual percentage was found high about 19.48 and 33.03 for 10% and 30% blended samples of LC with PKS respectively. On contrary, the residues were found lowered to 7.65 and 9.89% in 20LC80PKS and 40LC60PKS mixtures. At an equal ratio of PKS and LC (50LC50PKS), the weight loss was found to the value of 84.98% with a maximum derivative value of $-18.10\%.\text{min}^{-1}$ at peak temperature T_p of 305.35°C with the final residue of 4.74%. The overall analysis of thermal degradation and reaction parameters predicted a view of that 20% LC with 80% of PKS mixed blend (20LC80PKS) have better thermal interaction for the pyrolytic and gasification reactions due to the appropriate volatile and oxygen content from PKS.

The possible synergy effect during the cogasification of PKS and LC can be verified by Eq. 5.

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

Where, X_{LC} and X_{PKS} are the percentage of LC and PKS in the blend respectively, W_{LC} and W_{PKS} is the normalized weight loss of LC and PKS respectively under same operating conditions (Idris et al., 2012). It was found that the synergistic effect on thermal degradation behavior was observed with slight deviation from the experimental values, might be due to the fact that the PKS biomass is complexed structure with hard fiber content material. However, the combined feedstock of LC with PKS for gasification could offer many advantages in both energy and environmental aspects: as less dependence on finite fossil fuels, ease on waste disposal methods of PKS and recovery of energy from waste

PKS. Thus the blending could sustain industrial ecology and lessen the reliance on coal for power production (Wu et al., 2012).

3.4 Thermal kinetics of PKS and LC at various heating rates

The reaction kinetics parameters are determined by considering the maximum weight loss zones. **Table 4** shows the summary of kinetic reaction parameters at various heating rates of 10, 20, 30, 40 and 50°C/min. The thermal kinetic parameters such as activation energy, pre-exponential factor and the reaction order were determined by linear regression analysis using Microsoft LINEST function. For both samples of PKS and LC at all heating rates, the correlation coefficient (R^2) value was greater than 0.90. The calculated kinetic parameters of PKS and LC at different heating rates were shown in **Table 4**. For the biomass material of PKS, the activation energy (E) was found between 50-57 kJ/mole. From the derivative result at all heating rates, the peak temperature (T_p) for the maximum weight loss rate was found between the temperature range of 305-335°C. For the material lignite coal, the maximum mass reduction due to the reaction was observed in the temperature range of 165-750°C and derivative peak temperature (T_p) for highest mass reduction rate determined to be 475-585°C which is greater than the biomass material PKS. The minimum energy required for the reaction was in the range of 24–75 kJ/mol. It was observed at higher heating rates that the energy needed for the material degradation was quite less. The overall resulted thermal kinetic parameters of this analysis at different heating rates showed the possibility of cogasification of low-grade lignite coal (LC) with palm kernel shells (PKS).

3.5 Cogasification kinetics of PKS and LC at different blending ratios:

The thermal decomposition of PKS, LC and their blends were found with major weight loss at the reaction zone of peak 2. With the use of Microsoft Excel LINEST function for linear regression analysis, the activation energy (E), pre-exponential factor (A) and the reaction

order (n) for the blending sample were found out at the reaction zone P_2 . The correlation coefficient (R^2) values for all samples were found more than 0.96. The results of the kinetic parameters are reliable for predicting the weight loss of these samples at different conditions.

The results of thermal degradation kinetics for mixed blends of LC and PKS at various ratios when heated to a temperature range of 35-1000°C at 40°C/min heating rate were shown in **Table 5**. It was observed from the analysis that the increase in percentage of LC with PKS, the activation energy for degradation of the blended sample is getting reduced subsequently up to 40% of LC. Further increase in the coal percentage increases the energy required for activating the material degradation. With the increase in blending proportion of coal, the necessary energy for the reaction were found in the range of 56 – 65 kJ/mol which is almost the similar value obtained by using Model-free kinetics method for the blend of palm kernel shells and coal at an equal ratio (Naveen and Premelatha, 2016). Yet, the exponential factor (A) value also reduced due to the low reactivity nature of the coal.

3.6 Syngas production during gasification of PKS and cogasification with LC at different blending ratios

The experimental run on gasification using PKS as single feed (100%) and cogasification with LC at different blending percentages of 10, 20, 30, 40 and 50 were carried out. In the bioenergy conversion through gasification technology, the produced output syngas contains varying composition of carbon monoxide (CO), hydrogen (H_2), methane (CH_4) and carbondioxide (CO_2). **Figure 4** shows the results of the composition of syngas produced and the obtained calorific value (LHV) during the cogasification run of PKS and LC at the various blending ratios. With the increase in blending percentage of LC, it was

found that the conversion of carbon and production of hydrogen and methane varied slightly.

The analysis of produced syngas by cogasification showed that the blended sample of 10% LC with 90 % of biomass (10LC90PKS) having the higher content of combustible gases such as CO (5.16%), H₂ (4.12%) and CH₄ (2.99%) by volume than results of all other blended mixtures. It might be due to the fact that the high percentage of PKS with higher volatile matter and hydrocarbons while compared to LC are more favorable for pyrolytic reactions. Moreover, in cogasification of coal with biomass, the production of hydrogen was also unpredictable because of the more percentage of biomass content would effect the hydrogen production due its higher volatile content which causes reduction in gasification temperature. The CO concentration was found be more because of higher reactivity and the its oxygen content compared to lignite coal (**Emami-Taba et al., 2013**). The sample of 80% PKS with 20% LC (20LC80PKS) resulted on increase in conversion of carbon into carbon monoxide (CO) but decrease in production of hydrogen (H₂) and methane (CH₄). Further increase of LC with PKS blends of 30LC70PKS and 40LC60PKS, it was found that the production of CO getting lowerd with the little increase of H₂ and CH₄. In case of cogasification run with the increase in percentage of coal the produced CO concentration would be consumed in water shift and boudourd reactions (**Alzate et al., 2009; Vreugdenhil, 2009**). At the equal percentage of bended sample (50LC50PKS), the composition of combustible gases in the output syngas were found very low. The experiments on cogasification of PKS with LC revealed that, with the increase in LC upto 20%, the carbon conversion into gas was high and further increasing of coal to 40% enhanced the production of hydrogen (H₂). At equal percentage of the blended feed, the combustible gases production getting reduced. It would be attributed to more content of oxygen and hydrogen in biomass, the improvement in reactivity of LC led to increase and

subsequent conversion of volatile matter into free radicals resulted improvement in gasification reaction (Sharma et al., 2105; Naidu et al., 2016). For the blended samples of 10, 20 and 30 % of LC with PKS, the calculated lower heating value (LHV) was found as 2.4, 2.2 and 2.0 MJ/m³, whereas for the blended samples of 40 and 50%, the calorific value got reduced to 1.8 and 1.5 MJ/m³ respectively. The resulted output fluctuation in cogasification of PKS and LC at different blending ratios due to prevailing thermal degradation characteristics of the raw materials could produce adverse impact on carbon conversion ratio during gasification which may depends upon the reactivity of blended materials at pyrolysis stage of gasification.

4. Conclusion

The thermal degradation kinetics of palm kernel shells (PKS) and Lignite coal (LC) along with their respective blends were evaluated in this study at various heating rates and blending ratios. For PKS and LC as individual feed, the activation energy (E) was found to be ranged between 48-57 and 24-75 kJ/mol. The thermal degradation profile of PKS and LC blends at different proportion indicated that with an increased composition of LC in the blend mixture resulted in rising weight loss during thermal degradation at lower temperature of 335°C and E was ranged between 56–66 kJ/mol. The experimental analysis by thermogravimetry (TGA) and syngas analysis revealed that 30% of LC could be cogasified with 70% of PKS to promote the biomass/coal blended gasification for energy conversion. The combined feedstock of LC with PKS for gasification could offer many advantages in both energy and environmental aspects: as less dependence on finite fossil fuels, ease on waste disposal as well as energy recovery from PKS and less sulphur emissions to the atmosphere.

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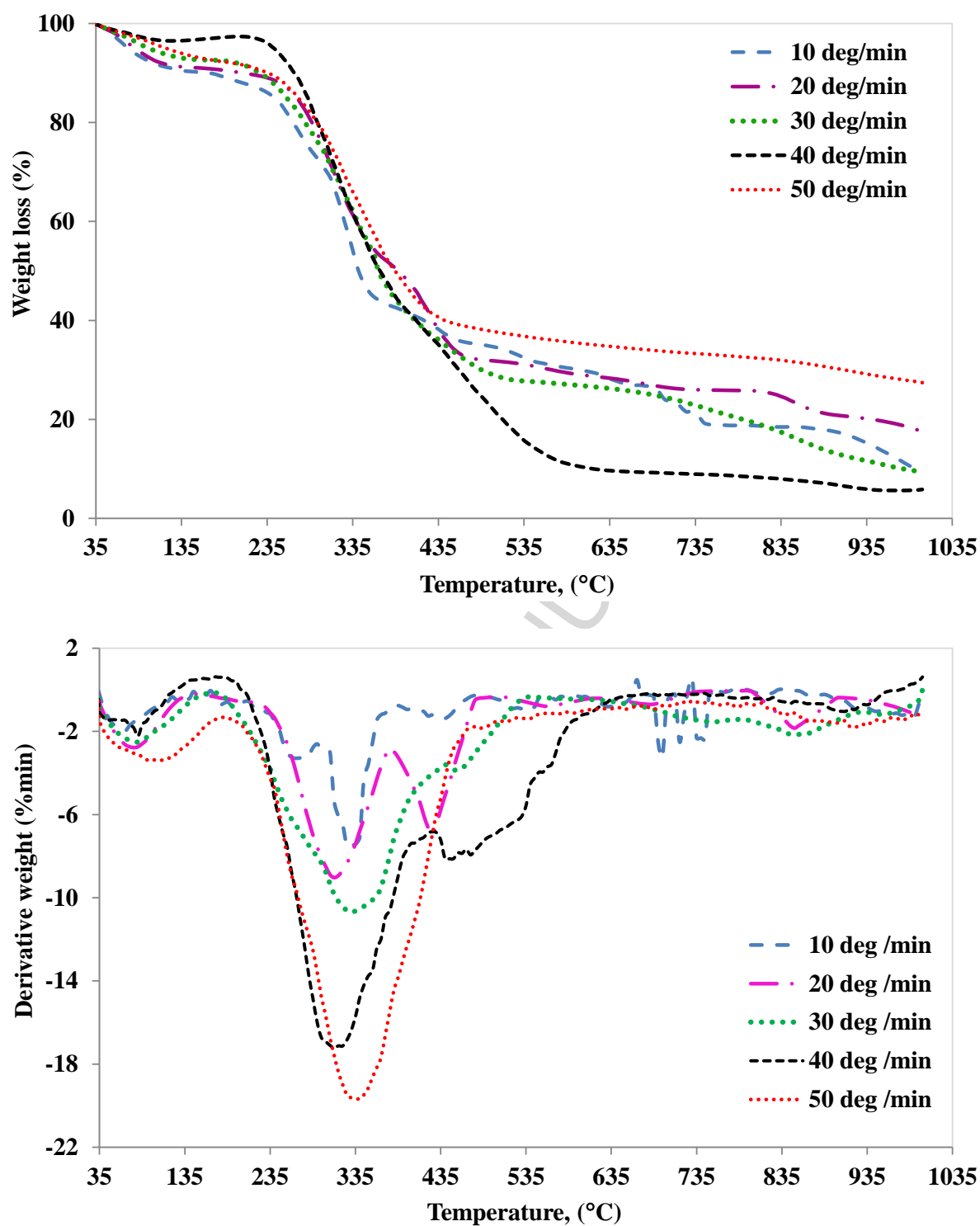


Fig. 1: TG and DTG curves of palm kernel shells (PKS) at various heating rates

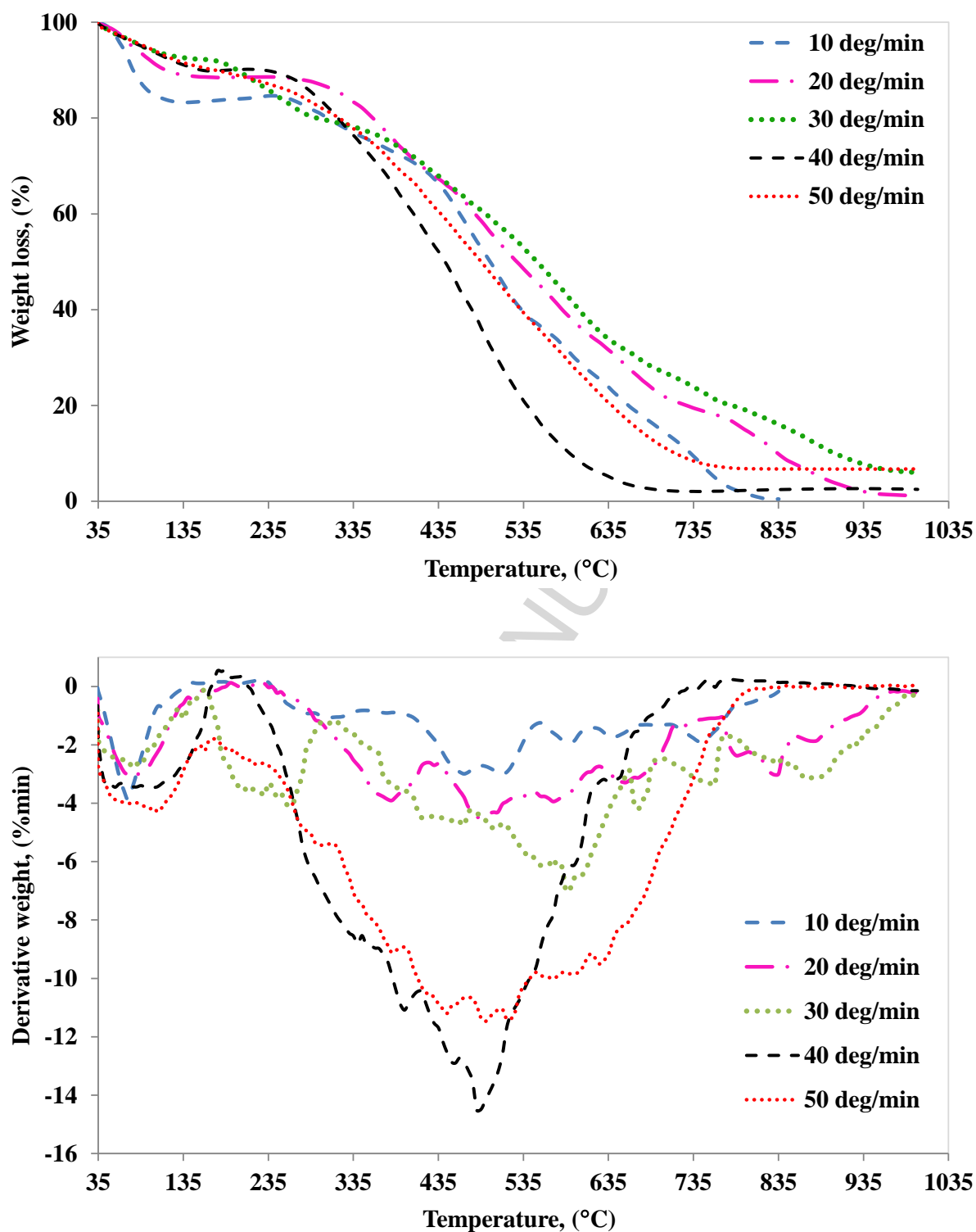


Fig. 2: TG and DTG curves of low grade Indian lignite coal (LC) at various heating rates

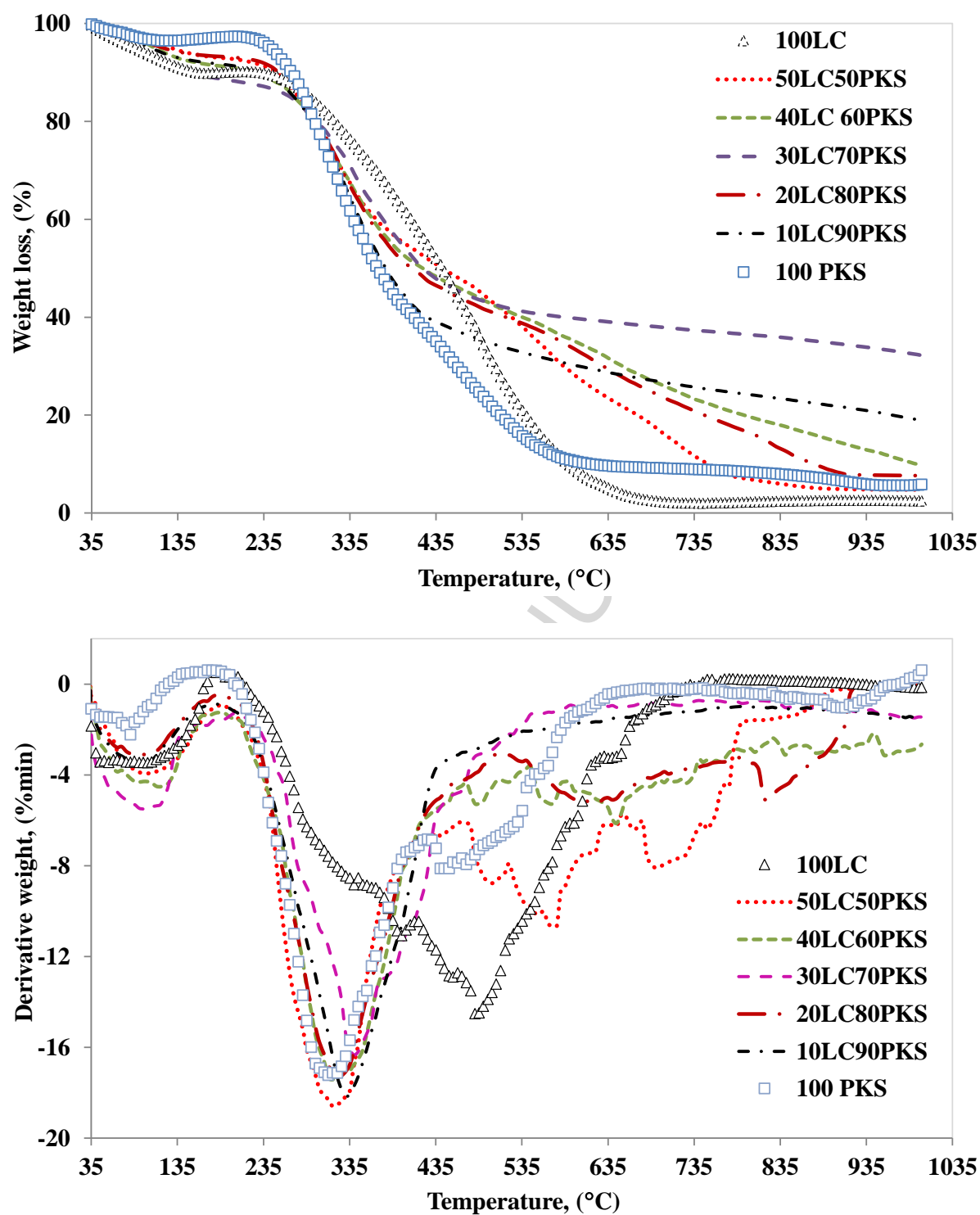


Fig. 3. TG and DTG profiles of palm kernel shells (PKS) and low grade Indian lignite coal (LC) blends

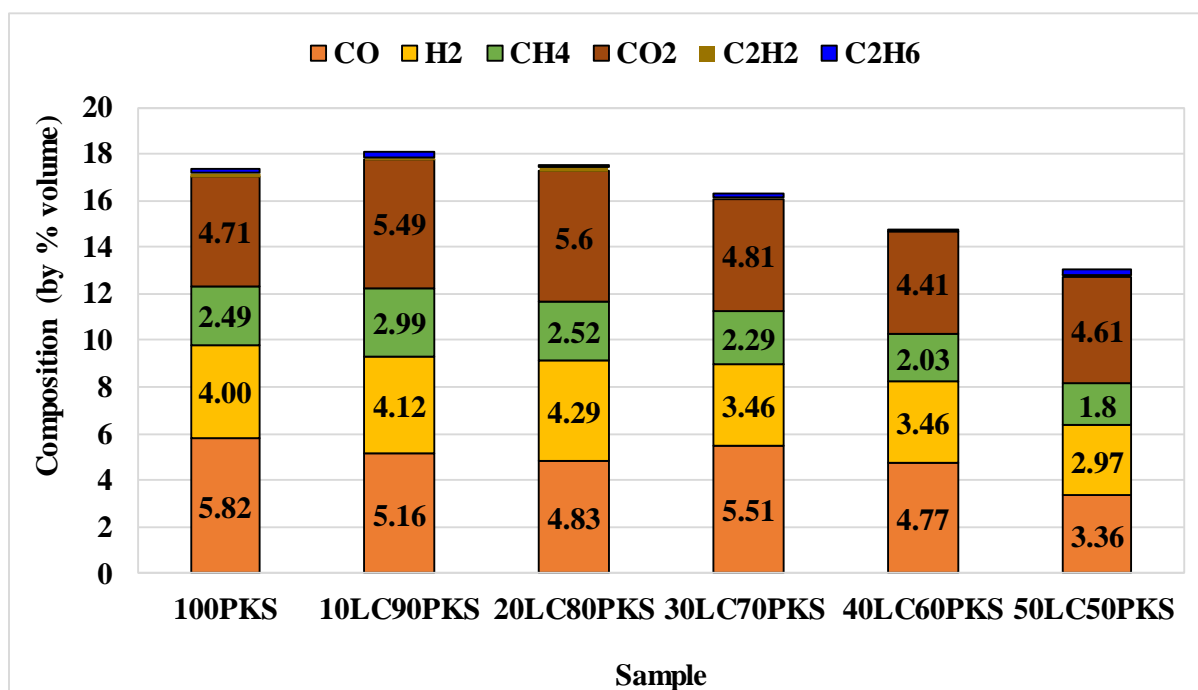


Fig. 4. Syngas composition of palm kernel shells (PKS) along with the blends of low grade Indian lignite Coal (LC) at different ratios

Table 1: Reaction parameters for palm kernel shells (PKS) at different heating rates

Heating rate (°C/min)	P ₂ PKS				P ₃ PKS				T _f (°C)	Residue, (%)
	Temp range, (°C)	Weight loss, (%)	T _p , (°C)	DTG _{max} (% min ⁻¹)	Temp range (°C)	Weight loss, (%)	T _p , (°C)	DTG _{max} (% min ⁻¹)		
10	205.06 – 405.07	45.72	335.27	-7.53	375.20 – 760.20	24.33	690.07	-2.53	970	12.13
20	210.14 – 365.12	36.52	305.21	-8.89	375.06 – 465.41	19.14	420.10	-6.63	960	19.28
30	185.36 – 520.41	64.26	330.40	- 10.71	570.31 – 950.09	16.12	850.06	-2.08	975	10.24
40	200.45 – 635.23	87.65	310.33	- 14.61					960	4.08
50	190.55 – 450.18	52.57	320.46	- 18.99					970	28.49

Table 2: Reaction parameters for low grade lignite Indian coal (LC) at different heating rates

Heating rate (°C/min)	P ₂ LC				P ₃ LC					
	Temp range, (°C)	Weight loss, (%)	T _p , (°C)	DTG _{max} (% min ⁻¹)	Temp range (°C)	Weight loss, (%)	T _p , (°C)	DTG _{max} (% min ⁻¹)	T _f (°C)	Residue, (%)
10	40.08 – 130.18	13.35	70.03	- 3.872	230.06 – 780.10	81.90	460.12	- 2.926	790	2.01
20	35.24 – 150.33	11.11	70.15	- 3.041	215.42 – 905.44	84.97	480.32	- 4.479	920	2.73
30	150.28 – 300.69	12.63	255.12	- 3.982	325.30 – 935.17	71.23	585.44	- 7.010	955	6.82
40	200.66 – 680.03	87.43	480.42	- 14.51					710	2.15
50	40.43 – 171.03	8.79	80.462	-4.02	185.04 – 735.41	81.00	505.57	- 11.18	960	6.73

Table 3: Reaction parameters for palm kernel shells (PKS) at different blending ratios

Sample	Temp range (°C)	Weight loss (%)	T_p (°C)	DTG_{max} (% min⁻¹)	T_f (°C)	Residue (%)
100LC	200.66 – 680.03	87.73	480.42	-14.51	710	2.15
100 PKS	200.45 – 635.23	87.65	310.33	-14.61	960	4.08
10LC90PKS	200.30 – 485.35	55.86	325.26	-17.86	980	19.48
20LC80PKS	200.05 – 900.55	84.71	315.08	-17.16	980	7.65
30LC70PKS	200.24 – 530.48	46.89	335.01	-16.09	970	33.03
40LC60PKS	190.39 – 950.39	79.63	310.55	-17.33	995	9.89
50LC50PKS	195.23 – 775.24	84.98	305.31	-18.10	965	4.74

Table 4: Thermal kinetics of palm kernel shells (PKS) and lignite coal (LC) at different heating rates

Sample	Heating rate (°C/min)	Temperature range (°C) in which max. weight loss occurred	T _p °C	E (kJ/mol)	A (min ⁻¹)	n (dimension less)	R ² (dimension less)
PKS	10	175.15 – 410.01	325.08	56.92	9.399×10 ³	2.69	0.93
	20	205.35 – 460.43	305.21	50.03	2.593×10 ³	1.83	0.95
	30	180.20 – 525.26	320.18	54.09	1.084×10 ³	2.77	0.91
	40	195.54 – 630.02	310.33	47.80	5.475×10 ³	2.65	0.96
	50	195.75 – 400.18	320.46	52.49	1.403×10 ⁴	2.56	0.99
LC	10	245.07 – 750.01	500.05	74.69	6.740×10 ³	1.24	0.99
	20	240.15 – 745.24	475.20	62.85	5.867×10 ³	3.96	0.93
	30	165.11 – 720.21	585.40	44.63	1.170×10 ²	1.63	0.98
	40	210.27 – 675.20	480.42	56.84	1.070×10 ⁴	3.67	0.90
	50	165.57 – 490.14	490.14	23.63	7.199	1.33	0.99

Table 5: Thermal kinetics of palm kernel shells (PKS) and lignite coal (LC) at different blending ratios

Sample	Temp range (°C)	E (kJ/mol)	A (min ⁻¹)	n (dimensionless)	R ² (dimensionless)
100PKS	195.54 – 630.02	47.80	5.48×10 ³	2.65	0.96
100LC	210.27 – 675.20	56.84	1.07×10 ⁴	4.01	0.90
10LC90PKS	200.30 – 485.35	62.40	1.05×10 ⁵	3.90	0.99
20LC80PKS	200.05 – 900.55	65.74	1.57×10 ⁵	3.77	0.96
30LC70PKS	200.24 – 530.48	55.71	1.68×10 ⁴	2.90	0.97
40LC60PKS	190.39 – 950.39	59.01	3.95×10 ⁴	4.31	0.99
50LC50PKS	195.23 – 775.24	61.01	5.80×10 ⁴	3.92	0.97

Highlights:

- Palm kernel shells (PKS) and Indian Coal (LC) are substrates for gasification
- Cogasification studies were done at varying blending ratios and heating rates
- Thermogravimetric analysis, pyrolytic kinetics and syngas were evaluated
- Activation energy (E) of PKS and LC were 56.92 and 74.69 kJ/mol at 40°C/min
- Activation energy for the blended substrates varied from 56 - 66 kJ/mol