



Effect of coconut shell in gasification kinetics of palm kernel shells at various blending ratios

Thiagarajan Janakiraman¹ · Abhijeet Pathy² · Srividhya Poosari Kumaravel¹ · Balasubramanian Paramasivan²

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Abstract

This work aims to present the thermal behaviour and pyrolytic kinetics of coconut shell (CS) at various heating rates of 10–50 °C/min to explore the potential of co-gasification with palm kernel shells (PKS) at varying proportions of 10–50%. The degradation profiles have been observed, and the activation energy (E_a) for CS (91.47–50.79 kJ/mol) was found to vary with the increase in heating rate. E_a for the blends of PKS-CS was ranged from 53.35 to 72.21 kJ/mol. The syngas produced through co-gasification had a calorific value of 2.6–3.2 MJ/Nm³ for various PKS-CS blending ratios. This study with predicted possible synergistic effect could propose the appropriate blending ratio of PKS with CS for co-gasification and promote the agro industry process waste PKS as a suitable single feed and multi-feed fuel source for gasification. Moreover, it also helps offset the concerns of fuel feedstock availability due to demand, seasonal variation and transportation cost for the continuous operation of biomass gasifier plants in remote areas.

Keywords Thermogravimetry · Palm kernel shell · Gasification · Syngas · Coconut shell · Activation energy

1 Introduction

The global energy demand has grown exponentially over the past few decades due to population escalation, tremendous urbanization and rapid industrialization. The world energy sectors have startled due to fossil fuel depletion, since 80% of the global energy demand is being met by coal, oil, and natural gas (Gaulin & Billon, 2020). The threats to the environment due to fossil fuels' use encourage the development of new renewable energy sources for sustainable development technologies (Balasubramanian & Karthickumar, 2012; Newell & Simms, 2020). Gasification being more efficient and environmentally friendly is a

✉ Balasubramanian Paramasivan
biobala@nitrrkl.ac.in

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

² Agricultural and Environmental Biotechnology Group, Dept. of Biotechnology and Medical Engineering, National Institute of Technology Rourkela, Rourkela 769008, India

predominant technology that enables the use of all the carbonaceous materials as feedstock to produce syngas that could be used for electricity generation. Other than coal and biomass, many attempts have been made to use organic materials such as plastics, municipal wastes, refinery waste, and many others (Cao et al., 2020; Sharma et al., 2015). Several strategies such as an appropriate collection of biomasses, deashing, utilization of catalyst, and pre-treatment of biomasses to improve the overall process and technology of conventional single feed biomass gasification have been already reported (Dhyani et al., 2018; Perkins et al., 2018). Significant studies on co-gasification technology of blended feedstocks of coal and biomass have been reported in the recent decade (Thiagarajan et al., 2018a; Wei et al., 2021). The solid fuel gasification process involves the reaction stages of pyrolysis, followed by char gasification. The residence period of gasification required for biomass has been reported to be shorter than coal due to high volatile matter; hence, its conversion rate was much faster (Xu et al., 2014). Using two different feedstock blends at the desired proportion could promote synergetic interactions in the thermal reactivity of the samples, thereby enhancing the overall gasification process (Cai et al., 2021).

The exploitation of different feedstocks in blended form results in process development with relatively fewer carbon losses, enhanced syngas production with increased energy content, thus promoting sustainable development of gasifier power plant systems in remote areas. Waste biomass (resources) with benefits of carbon sequestration and low sulphur emissions could be employed as prominent renewable fuel (Naidu et al., 2016). Only 20% of the global primary energy demands of the industrial sector are met by the use of biomass, owing to their underutilization, currently, research and process developments aiming at increasing the contribution of biomass are being increasingly carried out (Popp et al., 2020). Using biomass as feedstocks during co-pyrolysis, co-firing and co-gasification technologies promote its exploitations as renewable energy sources and provide an alternative for the disposal. Wei et al. (2011) reported syngas generation using a blend of hardwood chips with 20% of liquid crude glycerol (a byproduct of biodiesel technology) for operating internal combustion engines. It was observed in many co-gasification studies that synergy at a certain feed rate of blending ratios resulted in improvement in syngas production with fewer pollutant gases compared to those obtained in the single feed gasification process.

Given India's abundance of seasonal availability of agro wastes in large quantities, researchers are promoting the utilization of waste biomass into bioenergy through gasification. The gasifier systems operating on a single feed faces the crisis of continuous source availability due to demand along with seasonal variation, transport cost and non-utilization of different locally available biomass (Inayat et al., 2018). Using a blended form of different biomass as mixed feed fuel in gasifier systems can promote regular operation and be cost-effective in remote provinces (Tamili et al., 2018). Based on the availability, the agricultural waste biomass sources such as coconut shell and rubber seed shell can be utilized in blended form as multi feed-in gasifier systems (Singh & Sekhar, 2016).

About 0.07 tons of palm kernel shells (PKS), 0.2 tons of empty fruit bunches (EMB) and 0.15 tons of palm fibres are generated in the form of wastes for every ton of palm fruit. Generated agro wastes from PKS include the shell fractions obtained after crushing the hard and fibrous palm seeds, which could be used as a potential feedstock during thermochemical conversion into energy (Azlina et al., 2010). Many researchers around the globe have explored the potential of PKS in various applications. A recent study by Chan et al. (2018a) attempted a hydrothermal route to produce bio-oil under subcritical and supercritical conditions and evaluated the reaction kinetics (Chan et al., 2018b). In India, 80% of the edible oil requirement met by importing crude palm oil from outside countries. For curtailing the foreign exchange on crude edible oil imports

and fulfilling the requirements by self-production, India has made a plan for oil palm development and process industries under the scheme of National Mission on Oilseeds and Oil Palm (NMOOP) (Govt. of India, 2019).

India ranks first in coconut productivity in the world and third in the area under plantation as per the base year 2009 (Jose, 2011; Preethi et al., 2019). Coconut shell is one of the best feed for pyrolysis due to high volatiles and lignin content with higher calorific value, low ash, moisture, and CO₂ emission than other biomass materials (Yerima et al., 2018). It is possible to process the large varieties of waste generated into energy and other value-added products through co-gasification mode. In preliminary experiments with gasification of coconut shells, the produced syngas quality was found almost identical with wood/coal gasification under the same operating condition. The coconut shell can be used as a secondary feed with other biomass. Several thermal kinetics and co-gasification experimental works have been done on blends of using coal as a primary source and biomass as a secondary one (Krerkkaiwan et al., 2013; Li et al., 2010; Thiagarajan et al., 2018a). A few studies were found on the gasification of blended forms of regularly available biomass with the seasonal one (Singh & Sekhar, 2016; Thiagarajan et al., 2018b). A recent study by Inayat et al. (2018) focused on the co-gasification of coconut shells and oil palm frond blends in the presence of catalysts such as cement, dolomite, and limestone. Co-gasification of PKS and imported bituminous coal were earlier studied by Thiagarajan et al. (2020). Insights into the co-pyrolysis of PKS with other materials were explored recently by Vasu et al. (2020) and Chen et al. (2021).

Considering the mission of developing edible oil palm technology in India and the proposed generation of oil palm waste like PKS, an attempt has been made to study the co-gasification and thermogravimetric kinetics of PKS with coconut shells (CS) through the gasification process. In this work, the thermal behaviour and pyrolytic kinetics of CS are analysed individually by thermogravimetric analysis (TGA). Further, the co-gasification of multi-feed biomass was carried out using PKS as the primary feedstock with CS at different blended ratios, and the resulted syngas composition was analysed.

2 Materials and methods

2.1 Sample preparation

The biomass oil palm waste (PKS) was collected from the crude palm oil production unit of Godrej Agrovet Ltd. at Ariyalur, Tamilnadu, India. The feed material coconut shell (CS) was obtained from the local coconut oil mill. The collected samples were sundried for 2–3 days, then pulverized and sieved with 250–350 µm sieves to obtain a uniform particle size before subjected to thermogravimetric analysis (TGA). For gasification and co-gasification experimental studies, the CS was pulverized to a size of 15–20 mm, and then the chip forms of CS and the PKS were dried at ambient room temperature up to the moisture content of 10–15%. The TGA and co-gasification experiments were carried out by PKS as a primary feed with the CS as the secondary source. Mixture of biomass (PKS-CS) was blended at different ratios (90:10; 80:20; 70:30; 60:40 and 50:50) for co-gasification studies. Feed material (CS biomass) was pulverized to size about 10–15 mm for uniform mixing with PKS.

2.2 Thermogravimetric analysis (TGA)

TGA was performed under the nitrogen atmosphere for studying the degradation profile of CS and their blends with PKS at various heating rates. The non-isothermal pyrolysis experiments were conducted using Shimadzu 50H TGA analyser with a precision of ± 0.5 K temperature and with a readability of 0.001 mg on microbalance sensitivity. TGA was done with a test sample size of 8 ± 1 mg for individual and blended forms of different proportions. The thermal behaviour and kinetics analysis were carried out with heating rates of 10, 20, 30, 40 and 50 °C/min with a stepwise increment from 35 to 1000 °C under nitrogen atmosphere at the flow rate of 20 ml/min. TGA was carried out at the heating rate of 30 °C/min for comprehending the effect of blending ratio on thermal degradation profile. The kinetic parameters associated with the gasification process were evaluated to identify the feedstock characteristics for the maximum possible energy recovery purpose.

2.3 Evaluation of kinetic parameters

The thermal degradation profiles (TG and DTG) of CS and its blends with PKS at different heating rates were analysed. Modified Arrhenius equation was adopted for the estimation of the relative effect of heating rate and to determine the activation energy (E_a), order of reaction (n) and the pre-exponential factor (A) (Thiagarajan et al., 2018a).

The temperature dependence on the reaction rate constant (R) can be obtained by using the Arrhenius degradation equation as given in Eq. (1).

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

E_a is activation energy in kJ.mol^{-1} , A is the frequency factor in s^{-1} , and R is the universal gas constant $8.314 \text{ kJ.mol}^{-1} \text{ K}^{-1}$ and T is the temperature in K.

Global kinetics can be analysed using Eq. (2)

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

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. Combining Eqs. (1) and (2) gives a linearized representation as shown in Eq. (3)

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

Equation (3) can be further simplified in the form as given in Eq. (4)

$$y = B + Cx + Dz \text{ where } y = \ln \left[\frac{-1}{w_o - w_f} \frac{dw}{dt} \right], x = \frac{1}{T}, z = \ln \left[\frac{w - w_f}{w_o - w_f} \right] \quad (4)$$

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

The temperature at which the maximum weight loss occurred with respect to time during the reaction at different heating rates can be obtained from the TGA data. From the sample degradation profile analysis data, three constant values x , y and z were obtained. The remaining kinetic parameters E_a , A and n were estimated by performing multilinear regression analysis using SigmaPlot 10.0.0 software.

2.4 Gasification studies

Single gasification experimental runs were performed using CS. The co-gasification runs were performed with mixed blends (PKS-CS) having the ratios of 90:10 (90PKS:10CS), 80:20 (80PKS:20CS), 70:30 (70PKS:30CS), 60:40 (60PKS:40CS) and 50:50 (50PKS:50CS). Both gasification and co-gasification runs were performed in a fixed bed downdraft type lab scale (1 kW) biomass gasifier. The gasification and co-gasification runs were performed at batch scale for about two hours with the initial loading of 4 ± 0.5 kg of feed. For every 30 min of the operational run, 0.5 kg of feed was topped up through the hopper to maintain the feed head. 10–15 min was required to attain the steady-state after ignition. The reduction zone temperature was monitored by fitting a K -type thermocouple with a data logger at the bottom of the reactor. The downstream output product gas from the reactor was passed through a wet scrubber unit followed by a filtering unit to control the temperature and moisture in the gas to the minimum level. At the designated sampling ports, the filtered syngas was collected in gas sample bladders. Three gaseous samples were collected for every 30 min of the process run at steady state of operational condition. The composition of the syngas for the presence of carbon monoxide (CO), hydrogen (H_2), methane (CH_4) and carbon dioxide (CO_2) was quantitatively analysed by using gas chromatography (Shimadzu GC-2014) fitted with a TCD detector in shin carbon ST column (100/200 mesh, 1.00 mm ID \times 200 mm length). Nitrogen at the flow rate of 10 ml/min was used as the carrier gas. GC calibration was done using the standard gas with known gas composition preceding the sample gas analysis. From the compositional value of CO , H_2 and CH_4 , the lower heating value (LHV) was calculated using the following equation (Eq. 5) as given by Wu et al. (2012).

$$\text{Lower Heating Value} \left(\frac{\text{MJ}}{\text{m}^3} \right) = (12.628 * V_{\text{CO}}) + (10.71 * V_{\text{H}_2}) + 35.81 * V_{\text{CH}_4} \quad (5)$$

where V_{CO} , V_{H_2} and V_{CH_4} are the fractional volumes of CO , H_2 and CH_4 , respectively.

3 Results and discussion

3.1 Characterization of coconut shells (CS)

The results of the proximate analysis of the coconut shells exhibited a comparatively similar composition to palm kernel shells. The volatile matter, fixed carbon and ash content obtained were 72.80, 19.14 and 0.7%, respectively. Higher volatile content of CS could have more influence on the devolatilization process during pyrolysis, and the presence of higher fixed carbon showed the good production of char for end gasification reaction. The concentration of chemical elements of carbon, hydrogen, nitrogen, sulphur and oxygen present in feedstocks obtained through ultimate analysis is given in Table 1. The carbon and

Table 1 Proximate and ultimate analysis of palm kernel shell (PKS) and coconut shell (CS)

Properties (%)	Palm kernel shell (PKS) [#]	Coconut shell (CS)
<i>Proximate analysis (mass % on dry basis)</i>		
Moisture content	5.26	2.21
volatile content	73.21	72.80
Fixed carbon	20.74	19.14
Ash content	0.79	0.76
<i>Ultimate analysis (mass % on ash free basis)</i>		
Carbon	46.32	46.55
Hydrogen	5.48	5.81
Nitrogen	0.45	0.12
Sulphur	0.00	0.00
Oxygen	47.45	47.52

[#]Thiagarajan et al. (2020)

hydrogen elements present in CS were found to be 46.55 and 5.81%, respectively. The key elements of carbon and fixed carbon suggested that the agro-waste feedstock can be used as fuel for combustion and a higher percentage of oxygen showed that it could be co-gasified with the coal mix. Biomass has higher oxygen content; however, the nitrogen (N) and sulphur (S) content is lesser; hence, the co-gasification of biomass with coal will help reduce the operating problem associated with N and S content of the coal.

3.2 Effect of heating rate on thermal decomposition of the coconut shell (CS)

The thermogravimetric (TG) and derivative thermogravimetric (DTG) patterns of the single feed biomass such as CS at various heating rates are shown in Fig. 1a and b. The derivative profile of CS corresponded to the regions where the TG curve slope was constant at the heating rates of 10, 30 and 40 °C/min. The thermal degradation of biomass consists of 3 stages: removal of moisture, main devolatilization, and continuous devolatilization (Munir et al., 2009). In the DTG profile of CS, the first peak at the temperature around 175 °C might be attributed to the removal of moisture and little volatile substance. It was observed that the CS was getting thermally cracked for the main volatilization between the temperature ranges of 180 and 630 °C. But at the heating rate of 20 and 50 °C/min, the main volatilization zone was obtained within the temperature range of 470–510 °C. For CS, the reaction parameters and the peak temperature (T_p) and corresponding weight loss percentages are recorded in Table 2. The TGA analysis of the fuel coconut shell biomass at the different desired heating rates showed that the conversion of material during the pyrolysis reaction was 50–55% at peak temperature between 310 and 315 °C the maximum rate of degradation.

When the sample CS was tested at 10 °C/min, the material degraded in two stages. After the moisture, volatile matter got removed during the second stage of reaction at the temperature range of 185–370 °C. The weight of the sample was reduced to 50.24% with maximum rate of decomposition (DTG_{max}) of $-6.30\% \cdot \text{min}^{-1}$ at the peak temperature of 310 °C. At this heating rate, with the increased temperature, the weight loss of fuel sample was due to pyrolysis reaction, including the devolatilization of volatile matter and conversion of hemicelluloses and cellulose biomass components into volatile gases and char. The

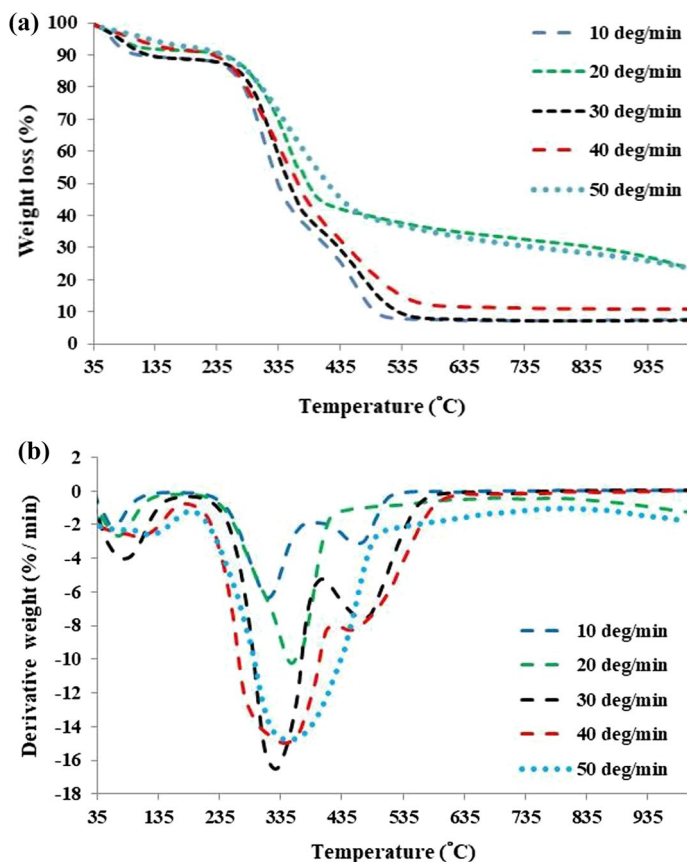


Fig. 1 **a** Thermogravimetric and **b** Derivative thermogravimetric profiles of coconut shell (CS) at various heating rates

credible secondary reaction between the produced volatile gases and solid char continued into the second stage of reaction, and with the rising temperature, the lignin carbonaceous matter and char were subjected to gasification reaction (Overend et al., 2012). The conversion of the sample was about 29.28%, and it was observed between the temperatures of 380–505 °C with DTG_{max} of $-3.05\% \cdot \text{min}^{-1}$ at 450 °C. The thermal reaction of the sample at 10 °C/min proceeded with a low heating process with higher residence time resulting in the maximum conversion of 79.52% of the CS material, leaving 7.62% end residue.

At the heating rate of 20 °C/min, the total mass reduction of the CS material was 62.28%, with leftover 23.44% as of end residue. In this reaction, about 50% of the mass reduction was observed in the second peak between the temperatures 185 and 435 °C with an increased maximum rate of degradation (DTG_{max}) $-10.17\% \cdot \text{min}^{-1}$ occurring at the peak temperature of 350 °C. In Figure of Fig. 1b, the peak temperatures at which the maximum rate of decomposition were getting shifted towards the right with variation in heating rates (Ghaly & Mansaray, 1999). It was observed that the significant conversion of the sample was credited to the pyrolytic reaction of volatile matter and bio components. The heating of the sample at 20 °C/min and residence period of reaction would

Table 2 Reaction parameters of coconut shell (CS) at different heating rates

Heating rate (°C/min)	P_2				P_3					
	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	185.06–370.12	50.24	310.13	–6.30	380.12–505.16	29.28	450.08	–3.05	975	7.62
20	185.19–435.26	49.73	350.25	–10.17	440.08–880.10	12.55	–	–	990	23.44
30	200.08–385.41	50.62	315.23	–16.30	395.49–570.36	28.09	460.25	–7.56	985	7.51
40	180.65–415.20	55.27	330.35	–14.87	420.30–630.57	23.86	445.28	–8.26	995	10.98
50	185.93–510.35	54.71	345.27	–14.75	520.23–945.26	11.92	–	–	998	23.72

Reaction parameters for palm kernel shells (PKS) at different heating rates shall be found from Thiagarajan et al. (2018a, 2018b); Tp Peak temperature; Tf Final temperature

not be effective for the continuation of gasification of the carbonaceous and produced char until the end of reaction, resulting in more residue.

The experiment with the increase of heating rate to 30 °C/min resulted in 79% total weight loss, with 50.62% of the sample was getting converted in the first stage. The TG and DTG profiles indicated that pyrolysis of physiochemical components was accomplished in this stage of between 200 and 385 °C with the highest decomposition rate of $-16.30\%.\text{min}^{-1}$ at the peak temperature 315 °C. The heating with the increase in temperature and the possible reaction between the volatile gases and produced solid char could have supported the gasification of carbonaceous and char till the end of the reaction. At the heating rate of 40 °C/min, the thermal behaviour and decomposition of the CS material had resulted in a total mass reduction of 79% of the sample material. The entire degradation of the sample occurred in three stages. At the heating rate 40 °C/min after the initial stage of removal of moisture and little volatile matter, the pyrolysis of the sample was initiated between temperatures of 180 and 415 °C. In this second peak reaction, 55.27% of the CS material was degraded with a maximum conversion rate of $-14.87\%.\text{min}^{-1}$ at the temperature (T_p) of 330.35 °C. The devolatilization of bio components at the pyrolysis condition released the volatile gases and converted the carbonaceous content into char. The third stage of reaction at the temperature between 420 and 630 °C, the weight loss of 23.86% at maximum decaying rate $-8.26\%.\text{min}^{-1}$ at peak temperature of 445.28 °C was observed. The kinetic parameters obtained for the thermal decomposition of CS are given in Table 3.

At 50 °C/min, the pyrolytic reaction of the sample was found with a maximum conversion rate of $-14.75\%.\text{min}^{-1}$ at the temperature of 345 °C within temperature range of 185–510 °C. Over the complete thermal reaction at this heating rate, the conversion of sample fuel was 54.71% and the residue of 23.72% at the end reaction. It could be because of the faster heating process of the sample and the residential period of the reaction is not effective in converting the pyrolytic products of solid char and the remainder carbon. The biomass CS material is one of the versatile fuel sources rich in volatile matter, containing the hard nature of structured bio components with high carbon and fixed carbon. With the TGA analysis at the increase of heating rates and with the given residential period, the heat energy generated by the CS material found to be more, resulting in more weight loss of sample. (Li et al., 2013).

Table 3 Thermal kinetics parameters of coconut shells (CS) at different heating rates

Sample	Heating rate (°C/min)	<i>E</i> (kJ/mol)	<i>A</i> (min^{-1})	<i>n</i>	<i>R</i> ²	<i>F</i> value	<i>P</i> value
CS	10	91.47	1.8852×10^7	0.149	0.9978	6713.20	<0.0001
	20	79.99	1.8625×10^6	0.138	0.9976	6166.66	
	30	85.90	1.1538×10^7	0.237	0.9957	4385.28	
	40	75.68	2.3428×10^6	0.306	0.9973	5165.13	
	50	50.79	7.290×10^3	0.263	0.9977	6413.39	

Reaction kinetics for palm kernel shells (PKS) at different heating rates shall be found from Thiagarajan et al. (2018a, 2018b)

E Activation energy; *A* Pre-exponential factor; *n* order of the reaction; *R*², *F* and *P* values are statistical parameters

3.3 Thermal kinetics of CS at various heating rates

The kinetic parameters of the thermal degradation of CS at various heating rates are summarized in Table 3. Compared to other biomasses, the agro waste coconut shell material comprises highly volatile matter, bio components of hemicelluloses, cellulose, and lignin with hard nature of thick surface material. Higher volatile matter help in enhancing the gasification rate of the biomasses. Being lignocellulosic biomass, the thermal degradation occurs at various stage of the process (hemicellulose, cellulose, and lignin breakdowns at different temperature ranges); hence their composition could impact the gasification yield (Abhijeet et al., 2020). At various heating rates from 10 to 50 °C/min for the CS, the minimum energy required for the reaction was found to be between 50 and 91 kJ/mol. The thermal decomposition of CS at the rate of 10 °C/min required minimum energy for the reaction that has resulted in the highest value of 91.47 kJ/mol with a molecular collision rate of $1.8852 \times 10^7 \text{ min}^{-1}$. The molecular collision rate is the average number of the collision occurs in a unit time frame for a given defined system. The development of heat flux with the increase of temperature at this lower rate of 10 °C/min might have been insufficient to develop the thermal reaction for the decomposition of the hard material of CS and the weight loss of the sample due to the effect of the residence time of reaction. The higher value of frequency factor (A) indicated that the higher residential period at this rate supported the reaction between the pyrolytic product volatile gases along with pyrolytic char and carbonaceous material content of the sample (Jiang et al., 2010). It has been observed that the activation energy (E_a) and the molecular collision rate (A) declined with the increase in heating rate. Because of higher temperature could be due to the supporting of released pyrolytic gases and the physical content of bio components, pyrolytic acid and lignin for the char and carbonaceous residue gasification till the end of the reaction. From the experiments at an increased heating rate with 20, 30 and 40 °C/min, it was observed that the E_a and A are getting reduced. It could be due to the supporting of CS material for pyrolytic and gasification reaction at their particular temperatures during the entire reaction.

At 50 °C/min of heating rate, E_a required for the thermal reaction was found to be lowered to 50.79 kJ/mol with a frequency factor of 7.290×10^3 . The obtained kinetic parameters in the analyses of CS material at various heating rates showed that the thermal reaction of feed CS at the heating rates of 30–50 °C/min would better convert material through pyrolytic and gasification reaction.

3.4 Thermal degradation and kinetics of PKS and CS blends

The thermal behaviour and reaction parameters during degradation of the blended PKS and CS material samples were evaluated using TGA data. The TG and DTG decomposition profiles of blended samples at different percentages of PKS with CS such as 90:10 (90PKS:10CS), 80:20 (80PKS:20CS), 70:30 (70PKS:30CS), 60:40 (60PKS:40CS) and 50:50 (50PKS:50CS) at the heating rate of 30 °C/min are shown in Fig. 2a and b. The TG profile observed that the sample degradation and the weight loss occurred at various stages between the temperature range of 160 and 960 °C. At all the blending proportions, the peak temperature (T_p) at which the maximum decomposing rate was found almost the same within the range of 310–320 °C. An increase in blending percentage of CS with PKS had no remarkable effect on the maximum value of weight loss rate (DTG_{max}) and the weight

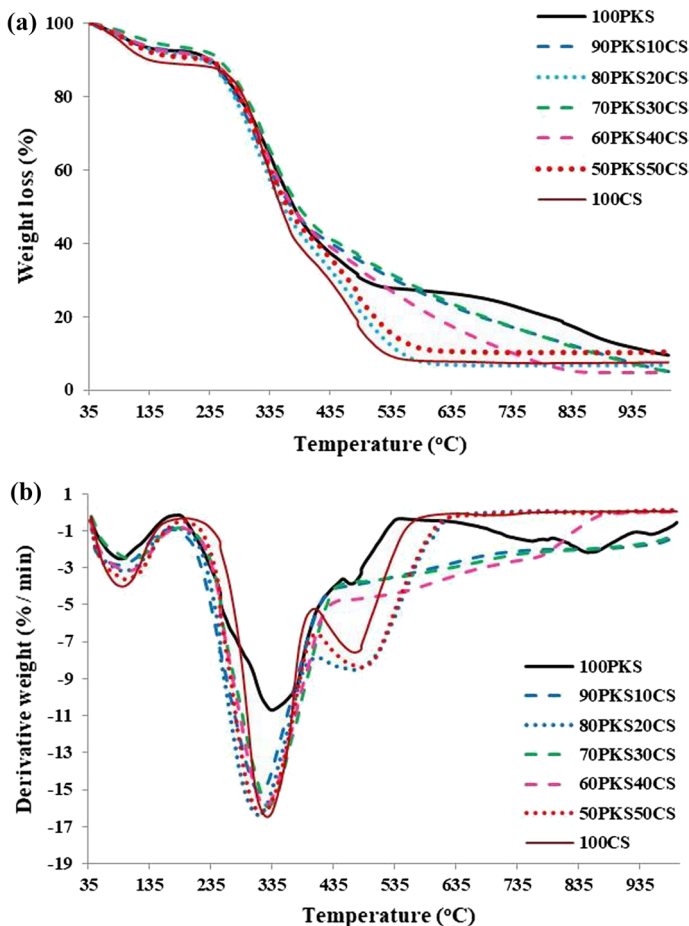


Fig. 2 **a** Thermogravimetric and **b** Derivative thermogravimetric profiles of palm kernel shell (PKS) and coconut shell (CS) blends

loss percentage, while the DTG profiles of the samples at 20 and 50% of CS with PKS resulted in two peaks.

The reaction parameters and the T_p , along with corresponding weight loss percentages for different blends of PKS with CS during the thermal degradation process, are shown in Table 4. The mixing of 10% CS material (90PKS10CS) resulted in degradation of the maximum of 86.38% between the temperatures of 160 and 955 °C with the maximum rate of weight loss of $-15.13 \text{ \%}/\text{min}^{-1}$ at 315 °C. The addition of CS, which is high in volatile and thermal reactions, supported the pyrolysis of palm kernel shells and secondary reaction between the pyrolytic products and char. The sample of 20% mixing of CS (80PKS20CS) with PKS had resulted in the total conversion of the blended sample with three peaks. After removing moisture at the initial stage, the pyrolytic reaction at the second peak between the temperatures of 160 and 395 °C accounted for the mass reduction of 52.22% with a maximum rate of reduction $-16.36 \text{ \%}/\text{min}^{-1}$ at peak temperature 310 °C. During this stage, both PKS and CS materials with higher volatile substances and lignocelluloses components

Table 4 Thermal reaction parameters of palm kernel shell (PKS) and coconut shell (CS) blends at different ratios

Sample	P_2					P_3					
	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 (%)
100CS	200.08–385.41	50.62	315.23	–16.30		395.49–570.36	28.09	460.25	–7.56	985.17	7.51
100PKS	185.36–520.41	64.26	330.40	–10.71		570.31–950.09	16.01	850.06	–2.08	975.28	10.24
90PKS 10CS	160.38–955.04	86.38	315.48	–15.13						995.26	4.91
80PKS 20CS	160.39–395.04	52.22	310.07	–16.36		400.24–620.44	31.88	465.11	–8.54	920.15	6.65
70PKS 30CS	160.01–960.24	86.19	320.47	–15.91						995.13	7.98
60PKS 40CS	160.01–845.43	87.09	315.41	–15.94						965.08	4.69
50PKS 50CS	170.38–395.08	48.99	315.31	–16.26		400.44–615.52	30.52	485.50	–8.36	910.41	10.08

Tp Peak temperature; Tf Final temperature

were subjected to pyrolytic reaction and released volatile gases and char. The thermal reaction of the mixed sample continued to the third stage with the reduced DTG_{max} rate of $-8.537\% \text{ min}^{-1}$ at 465°C accounted for weight loss of 31.88%. It showed that the pyrolytic products char and volatile gases and the carbonaceous matter carbon and fixed carbon of feed materials were subjected to gasification reaction with the increase of temperatures up to 620°C .

For the samples 70PKS30CS and 60PKS40CS, the TG and DTG profiles under thermal reaction revealed that the total decomposition of the blended materials followed the same pattern and resulted in almost the same reaction parameters. Both the feed materials (CS and PKS) are lignocellulosic; the content of pyroligneous acid, gas, charcoal, tannin and potassium in CS increases the degradation rate of PKS of rich fibrous and hardy nature. The TGA analysis of the sample at an equal ratio of PKS and CS (50PKS50CS) resulted in the total conversion of the sample occurred in three peaks. The pyrolysis of mixed sample PKS and CS at the second stage of reaction includes the devolatilization of lignocelluloses material and volatile substances between 170 and 395°C . The reaction was continued with a maximum thermal decaying rate of $-16.26\% \cdot \text{min}^{-1}$ at the temperature 315°C with the mass reduction of the sample material to 48.99%. Due to the difference in density, surface structural hardness and the quantity of the physiochemical components the material CS could support the production of more volatile gases while the PKS was for more conversion of char. There is a possibility of a secondary reaction between the volatile gases and the produced char. This was observed at the third stage, during which the weight reduction was 30.52% at the reduced DTG max rate of $-8.358\% \cdot \text{min}^{-1}$ with an increase in temperatures from 400 to 600°C .

The thermal degradation of the mixed samples of PKS and CS at different ratios 90:10, 80:20, 70:30, 60:40 and 50:50 was recorded when heated through the temperature range from 35 to 1000°C at the heating rate of $30^\circ\text{C}/\text{min}$. For the biomass blends PKS-CS, the increase of % CS up to 40, had seen no significant change in kinetic parameters. The kinetic parameters obtained are given in Table 5. When 40% CS was blended with PKS, the minimum energy (E_a) required for the thermal reaction was found to be in the range of 53–58 kJ/mol. At 50% CS combination with 50% PKS (50PKS:50CS), the activation energy (E_a) and the frequency factor (A) had increased to 72.21 kJ/mol and $7.721 \times 10^5 \text{ min}^{-1}$, respectively. It is because of CS with reactive behaviour of components of pyroligneous matter-dominated PKS in thermal reaction.

Table 5 Thermal kinetic parameters of palm kernel shell (PKS) and coconut shell (CS) blends at different ratios

Sample	Temp range, ($^\circ\text{C}$)	E (kJ/mol)	A (min^{-1})	n	R^2	F value	P value
100CS	200.08–570.36	85.90	1.1538×10^7	0.237	0.9957	4385.28	< 0.0001
100PKS	185.36–520.41	54.09	1.0840×10^4	1.094	0.9100	340.65	
90PKS 10CS	170.34–955.04	53.35	1.1426×10^4	0.684	0.9857	1655.31	
80PKS 20CS	170.24–620.45	58.47	4.4264×10^4	0.641	0.9858	1531.15	
70PKS 30CS	170.18–960.24	53.29	1.0179×10^4	0.710	0.9851	1649.95	
60PKS 40CS	170.13–845.43	55.82	1.9284×10^4	0.633	0.9869	1801.98	
50PKS 50CS	175.44–615.52	72.21	7.7210×10^5	0.890	0.9819	1253.01	

E Activation energy; A Pre-exponential factor; n order of the reaction; R^2 , F and P values are statistical parameters

3.5 Syngas generation during gasification and co-gasification

The thermochemical method of bioenergy production through the gasification process produces syngas with mixed CO, H₂, CH₄, and CO₂. The resulted syngas composition and the calculated calorific values (LHV) of the experimental run at various blending proportions of PKS with CS are shown in Fig. 3. Gasification of PKS as single feed produced syngas having 5.82% CO, 4.0% H₂ and 2.49% CH₄ by volume. Composition analysis of the combustible gases produced during single feed gasification of CS revealed that the % CO and % CH₄ were found to be almost equal to the case of PKS (Thiagarajan et al., 2018a). Because of the higher reactivity of CS material, the resulting H₂ gas composition was relatively lower during gasification of CS than that of PKS. The syngas analysis on co-gasification of PKS with 10% of CS (90PKS:10CS) showed improvement in syngas production. The quantitative analysis of the syngas showed the presence of CO (6.29%), H₂ (4.16%) and CH₄ (2.88%) with a calorific value of 2.6 MJ/Nm³. Blending 10% CS with 90% PKS resulted in an increase of reaction rate at low temperature during the pyrolysis zone of reaction.

For the cases of co-gasification run of 20% (80PKS:20CS) and 30% (70PKS:30CS) of the blended feed resulted in the low production of hydrogen with syngas having a heating value of 2.1 MJ/Nm³. Although both PKS and CS are lignocellulosic materials, the difference in their structural properties, bulk density and biochemical content of cellulose, hemicelluloses and lignin exhibited the variation in syngas composition. In co-gasification of the multi-feed stocks at 40% (60PKS:40CS) and 50% (50PKS:50CS) of CS with PKS, the possible predominant reaction of CS resulted in the production of syngas with an increase in the composition of combustible gases having calorific value of 3.2 and 3.0 MJ/Nm³, respectively. The resulted heating values were similar to that of the values obtained during co-gasification of blends of biomass wood chips (Juliflora) and de-oiled non-edible seed cakes (Jatropha) (Thiagarajan et al., 2018b). This experimental observation established that the PKS as primary feed blended with more than 30% of CS can be used as multi feed source for the co-gasification purposes.

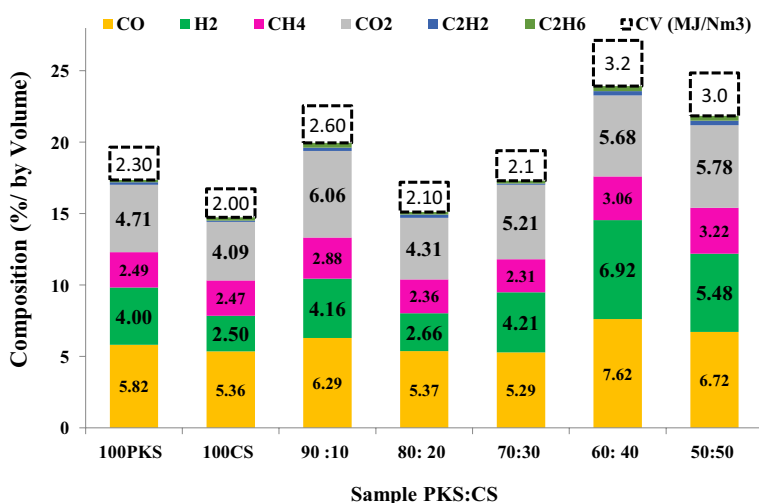


Fig. 3 Syngas composition of palm kernel shell and coconut shell (PKS-CS) blends at different ratios

3.6 Blending effect

The blending effect amidst the co-gasification process of PKS-CS blends was analysed after observing the distinct difference in the TG and DTG plots of PKS and CS. Moreover, a model was implemented and verified for predicting the thermal behaviour of the blended samples. Equation (6) depicts the predictive model of blending effect based on the weighted average of normalized weight loss of the blend (W_{Blend}) as reported by researchers (Idris et al., 2012; Thiagarajan et al., 2018a).

$$W_{\text{Blend}} = X_{\text{PKS}} * W_{\text{PKS}} + X_{\text{CS}} * W_{\text{CS}} \quad (6)$$

where X_{PKS} and X_{CS} are the percentages of PKS and CS blends. W_{PKS} and W_{CS} are the normalized weight loss of PKS and CS blends under the same operating conditions. The comparison of calculated and experimental weight loss curves for blended feed samples of PKS-CS is shown in Fig. 4. Despite having similar chemical compositions, the addition of CS to PKS enhances the gasification kinetics and syngas production. For instance, when the PKS and CS are added in the 70:30 ratios, the activation energy required for gasification is reduced by 33% as that of only CS biomass. Therefore, the blending of CS with PKS would make the gasification process more energetically viable. Similarly, when the PKS and CS are blended in 60:40 ratio, it results in 36% more syngas production. Moreover, the calorific value of the produced syngas increased by 40% as compared to that of only PKS. The difference might be due to the variation in their physical, morphological, and surface properties. However, more experimental verification needs to be done to validate this fact.

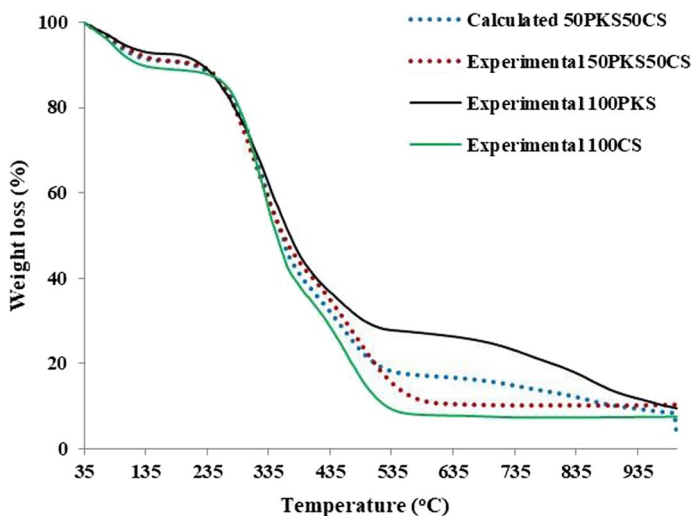


Fig. 4 Comparison of calculated and experimental thermogravimetric profiles for palm kernel shell and coconut shell (PKS-CS) blends at heating rate of 30 °C/min

4 Conclusion

The thermal kinetics of agro-waste biomasses such as coconut shells (CS) for co-gasifying with palm kernel shells (PKS) at various blending ratios were studied. The pyrolytic behaviours showed distinct behaviour in single feed and multi feed at different blended forms, and the activation energy (E_a) was evaluated. The study shows that with PKS and CS added in a 70:30 ratio; the activation energy could be reduced by as much as 40% of the CS gasification. During co-gasification of CS with 30–50% of PKS, the resulted syngas had a higher calorific value. The study promotes the co-gasification by combining locally available biomass for continuous operations of gasifier systems in remote areas. The oil palm industry process waste PKS could be promoted as a suitable single feed and blended multi feed fuel source for gasification and to overcome the issues of fluctuation on its availability due to demand, seasonal variation, and transport cost for the operation of biomass gasifier plants.

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Authors' contributions JT performed the experiments and collected data for analysis and interpretation regarding the kinetics. JT and AP drafted the manuscript. PB and PKS supervised the research work and revised the manuscript. All authors read and approved the final manuscript.

Declarations

Conflict of interest The authors declare that they have no competing interests.

Consent for publication All authors agreed with the content and that all gave explicit consent to submit.

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