

# Thermal Kinetics and Syngas Production on Co-Gasification of Deoiled Jatropha Seed Cake Residues With Wood Chips

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**Abstract-** The total energy demand has been escalating day to day globally as well as the quest for sustainable and affordable energy enforcing the paradigm shifts of predominant fossil fuels. The prospective bioavailability of biomass residues in India could induct the gasification and co-gasification technologies through the interaction of various sources either by adopting biochemical or thermochemical methods. Both gasification and co-gasification studies experimented with deoiled jatropha seed cake (JC) residues and wood chips (WC) from juliflora shrub along with their blends at the mass ratio of 75:25, 50:50 and 25:75 in the lab scale downdraft type biomass gasifier. Thermogravimetric analysis at the heating rate of 30°C per min in the nitrogen atmosphere was carried out to investigate the thermal decomposition behavior along with pyrolytic kinetics. The produced syngas was analyzed for its chemical composition (CO, H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>, and O<sub>2</sub>) by a portable gas analyzer. The co-gasification of 75JC:25WC exhibited the higher calorific value than the gasification of JC and WC individually at the respective pyrolytic regimes. It acts as evidence for substantial synergetic effects and thermal interaction for blending JC with WC during co-gasification for syngas production. The JC residues with low activation energy could be cogasified with WC to overcome the demand for fuel sources with higher activation energies.

**Keywords-** Co-gasification, De-oiled jatropha seed cake, Pyrolytic kinetics, Syngas, Thermogravimetric analysis, Wood chips.

## 1. Introduction

Energy is the central key to sustainable development of any nation and promotion of clean and renewable energy sources are indispensable for meeting the energy demand of developing countries such as India [1-3]. Globally, fossil fuels contributed more than two-thirds of total energy demand and the rest by other resources. In India, biomass based energy technologies with the available 500 metric tons of biomass per year are contributing to one-third of total energy consumption [4-6]. Moreover, gasification and co-gasification methodologies through the interaction of various sources either by adopting biochemical or thermochemical methods yield low carbon footprint on the environment and also increases the H<sub>2</sub>/CO ratio in the produced gas which is essential for liquid fuel synthesis. Gasification using single biomass as a source of feed material throughout its year of operation experiences the hardship of non-availability of particular biomass round the year, hurdle in transportation and non-utilization of locally available biomass in that region. Hence co-gasification technology is a promising approach for deriving additional energy sources other than the

predominant feedstock, where it gives the initiative to probe the possibility of using different fuels at blended proportion. The synergistic impact of various biomasses during co-gasification processes generates products and intermediates which improve the performance by reducing the carbon losses and increase the energy content of the synthetic gas [7]. The blending technology of biomass feedstock gives a path for sustainable growth of continuous and steady operation of gasifiers in remote areas [8]. The gasifier designed for wood as a fuel source can be operated by using coconut shells and rubber seed shells as single feed or blended feed source [4].

Currently, non-edible oilseeds are the virtuous source for the biodiesel generation, and its sustainable development of massive production may result in the production of non-edible deoiled seed cakes as residues [9]. Non-edible oil generation from jatropha seeds rendered about 50-75% weight residues as jatropha seed cakes [10]. Besides, every ton of jatropha biodiesel yields nearly 3 tons of seed cake residues generated depending upon the seed quality [11]. Due to its toxicity and heavy oil content nature of enormous quantity of Jatropha seed

cake biomass, neither it can be used as cattle feed, nor it can be disposed of as waste which is a grave concern in view of environmental management [12]. Many other researchers has evaluated the jatropha and castor [13], rice husk [14], Poinciana pods [15], and oil palm shell [16] as a feedstock for gasification studies. The rich content of volatile matter and low ash prefers the thermochemical method of gasification process for energy extraction.

The authors have earlier studied the thermal kinetic behavior of jatropha, pongamia, and castor deoiled seed cakes as a biomass resource for energy recovery through gasification [17, 18]. Although the comprehension of co-gasification studies is complicated, it offers numerous benefits over gasification research. Hence, this study is directed towards the investigation on the blending mixture of deoiled jatropha seed cake (JC) residues and wood chips (WC) using co-gasification process and also examine the effect of blending ratio on thermal degradation kinetics and synthetic gas concentration.

## 2. Materials and Methods

### 2.1 Materials

This work was carried out to study the thermochemical behavior and co-gasification performance of two different type of biomass agro-residues and their blends at various ratios. Wood chips (WC) derived from juliflora shrub and non-edible, deoiled jatropha seed cake residues (JC) were used as feedstock materials. JC is a residue of biodiesel production technology from jatropha seeds. The jatropha seed cake was procured from Kanmani nursery garden, Coimbatore, Tamilnadu, India and the juliflora wood was obtained from local firewood vendor of Thanjavur, Tamilnadu, India.

For gasification and co-gasification studies, the wood chips of size with a diameter of 15-20 mm and to the length of 20-25 mm were made by cutting the juliflora wood using single blade wood cutting machine. The biomass feed material was dried at ambient room temperature up to the required moisture content 5-15%. Both the agroresidues were initially subjected to gasification studies followed by co-gasification studies with various mass ratios of 75:25 (75WC25JC), 50:50 (50WC50JC) and 25:75 (25WC75JC). The 100% samples of wood chips and deoiled jatropha seed cake residues were named as 100WC and 100JC.

### 2.2 Proximate and ultimate analysis

The physical and chemical characteristics of the feed materials were analyzed by proximate and ultimate analysis. As per the ASTM D3173, ASTM D3174 and ASTM3175, the moisture content, ash content and volatile materials of the JC and WC were determined. The ultimate analysis was carried out on Thermoscientific flash 2000 organic elemental analyzer on CHNS mode for the determination of Carbon (C), Hydrogen (H), Nitrogen (N) and Sulfur (S) content of the feed samples.

### 2.3 Thermogravimetric analysis

The raw material of JC, WC and their respective blended mixtures were subjected to thermogravimetric analysis (TGA) to evaluate the parameters for an efficient pyrolysis in view of energy recovery purpose. For the TGA analysis, the JC was powdered by using the mini household grinder and WC were

milled by using a circular blade with the size of 250-350 $\mu$ m. This analysis was carried out by using TGA analyzer Perkin Elmer TGA 4000 series. The sample weight (5 $\pm$ 1mg) of both individual feedstocks and their blends were prepared and further subjected to TGA analysis under the normal isothermal condition for a temperature range of 30 $^{\circ}$ C to 800 $^{\circ}$ C at the heating rate of 30 $^{\circ}$ C/min under nitrogen atmosphere.

### 2.4 Kinetic studies

The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of the JC, WC and their respective mixed blends were analyzed at the heating rate of 30 $^{\circ}$ C/min at N<sub>2</sub> atmosphere. In this present work, the kinetics of thermal degradation behavior was studied by using the modified Arrhenius equation based technique [10]. It relates the effect of different mixing ratios of fuels on activation energy, the order of reaction and frequency factor. The kinetic parameters were estimated from TGA data by adopting the general rate equation as outlined in earlier studies [19] and as shown in Eq. 1.

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

Where,  $x$  is the conversion ratio, which is equal to  $(W_o - W) / (W_o - W_f)$ .  $W_o$ ,  $W_f$  and  $W$  are the initial, final and time-dependent mass of the samples respectively.  $n$  is the order of reaction,  $t$  is the reaction time (min) and  $k$  is the reaction constant.

The reaction rate constant ( $k$ ) could be experimentally obtained by the Arrhenius decomposition equation as shown in Eq. 2.

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

Where  $Ea$  is activation energy in kJ/mol and  $A$  is the pre-exponential factor in S<sup>-1</sup> are the Arrhenius parameters,  $R$  is the universal gas constant (8.314 kJ/mol.K) and  $T$  is the temperature in degree K.

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

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

This Eq. (3) is similar to the simplified form of equation as  $y = B + Cx + Dz$  where

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

$$B = \ln(A), \quad C = \frac{E}{RT}, \quad D = n \quad (5)$$

From the TGA data, the time and temperature at which maximum weight loss occurred at during reaction can be obtained. By using this constant  $x$ ,  $y$  and  $z$  were also calculated. Constants  $B$ ,  $C$ ,  $D$  have been computed by multilinear regression of TGA data by using the LINEST function in MS-Excel. Thus by obtaining out the values of constants, the activation energy, pre-exponential factor and reaction order kinetic parameters could also be calculated.

## 2.5 Gasification and co-gasification studies

Experiments on gasification and co-gasification of JC, WC and their mixed, blended feed were carried out on a lab scale 1 kW fixed bed downdraft gasifier at Periyar research and development centre for solar and bioenergies of Periyar Maniammai University, Tanjore, India. The influences of varying the blending ratios in co-gasification were analyzed. This downdraft type gasification unit was equipped with a scrubber and packed bed filter for filtering the producer gas. The blended feed material for the experimental run was fed into gasifier unit from the top of the gasifier. The gasification and co-gasification experiments were run on batch type process with a batch size of  $4\pm 0.5$  kg using air as a gasifying agent. The gasification of single as well as blended feed at different ratios performed in a set of experiments with three trials. From the gasifier, the product gas was allowed to pass through the scrubber and packed bed filter for reducing the temperature and filtering. The gasification reduction zone temperature was measured by using K-type thermocouples fitted with an automatic data logger. The output gas composition and the heating value is analyzed by a portable gas analyzer (Wahun Cubic of model Gas board 3100P) with a resolution of 0.01% by tapping through the product gas sample port.



**Fig. 1:** Experimental setup for gasification and co-gasification studies

Each run of the experiment was performed by mixing the prepared feed material of JC and WC at different ratios of 100, 75:25, 50:50, 25:75 and 100. Each trial of the experiment was conducted for about 2 hours by loading the gasifier initially with  $4\pm 0.5$  kg of the prepared mixed blend, and in between every 30 minutes of operation, it was topped up with 0.5 kg of feed to maintain the height of the bed during gasification run. The gasification run was started by igniting the fuel feed and almost it took 15 minutes of initial run for reaching the steady state. In that continuous series of operating condition for every 5 minutes the temperature, product gas composition ( $\text{CO}$ ,  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{O}_2$ ) and the lower heating value (LHV) were recorded directly with the portable gas analyzer.

## 2. Results and Discussion

The physical and chemical characteristics of both biomass feedstocks such as JC and WC were evaluated by subjecting to proximate and ultimate analysis. The detailed physicochemical characterization of JC and WC were shown in Table 1.

**Table 1:** Proximate and ultimate analysis of deoiled jatropha seed cake (JC) and wood chips (WC)

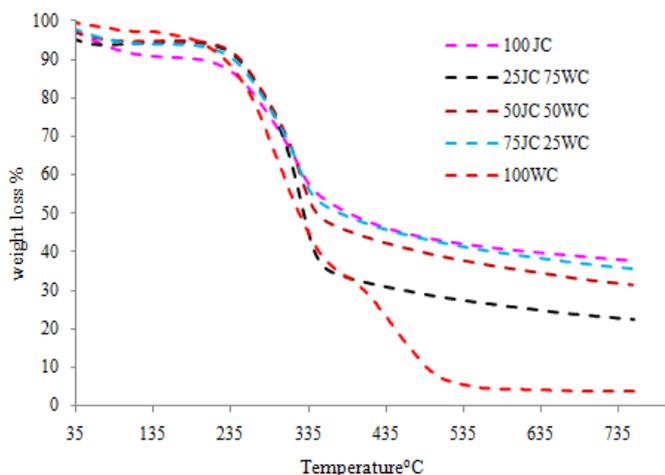
Properties (%)	JC	WC
Lignin	20.78	14.00
Cellulose	6.16	42.50
Hemicellulose	11.16	27.50
Moisture content	7.70	6.32
Volatile content	64.99	82.46
Fixed carbon	22.58	9.20
Ash content	2.31	2.52
Carbon	44.02	47.39
Hydrogen	6.00	6.12
Nitrogen	6.67	0.40
Sulphur	0.00	0.00
Oxygen	43.02	45.92

### 3.1 Thermal degradation of jatropha seed cake, wood and their blends

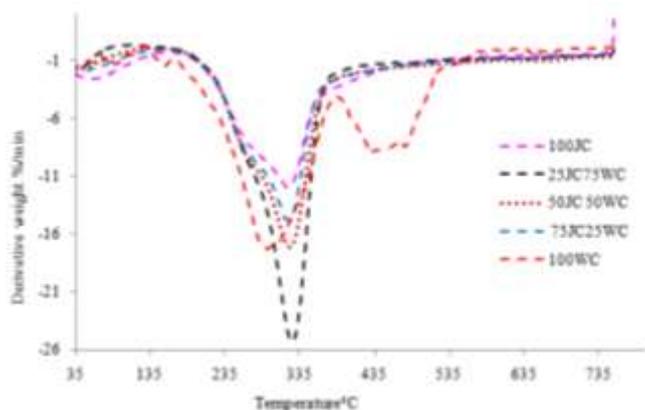
In TGA analysis the individual and blended samples were heated to a temperature from  $30^\circ\text{C}$  to  $800^\circ\text{C}$  at the heating rate of  $30^\circ\text{C}/\text{min}$ . The loss of weight conversion profiles and the kinetic parameters of the JC and WC with their blends were analyzed. From the TG curve, the ignition, peak, final and burnout temperature were also compared.  $T_{\text{ignition}}$  ( $^\circ\text{C}$ ) is the temperature at which the sudden decrease in weight loss is observed in DTG curve. Peak temperature ( $T_p$ ) is the temperature at which the maximum rate of combustion  $DTG_{\text{max}}$  occurs on DTG curve. Burnout temperature ( $T_b$ ) is the temperature at which no further mass loss is observed DTG curve.

The thermochemical conversion rates of JC, WC and their mixed blends have represented by the TG and DTG curves as shown in Fig. 2 and Fig. 3. The overall thermal degradation profile of JC, WC and their blends were summarized in Table 2. Three different stages of degradation occur when wood chips (WC at 100 %) was heated to a temperature up to  $800^\circ\text{C}$  at the heating rate of  $30^\circ\text{C}/\text{min}$ . The first peak ( $P_1$ ) between  $35$  to  $170^\circ\text{C}$  due to moisture evaporation. The second peak ( $P_2$ ) occurred  $181$ – $394^\circ\text{C}$  due to degradation of components hemicellulose, cellulose and lignin of the wood material. In the second peak, the  $DTG_{\text{max}}$  was around  $-16.36\%$ /min.

The third peak occurred between  $397$ – $583^\circ\text{C}$ , where the lignin gets converted with  $DTG_{\text{max}}$  around  $8.88\%$ /min. The degradation of deoiled jatropha seed cake (100% of JC) occurred with two different stages under a heating rate of  $30^\circ\text{C}/\text{min}$  up to the temperature of  $800^\circ\text{C}$ . The first stage peak ( $P_1$ ) represents the removal of moisture between  $35$  to  $194^\circ\text{C}$ . The peak ( $P_2$ ) occurred between  $201$ – $397^\circ\text{C}$  due to the devolatilization and oxidation together with the maximum rate of combustion  $DTG_{\text{max}}$  as  $-11.40\%$ /min.



**Fig. 2:** Thermogravimetric analysis of deoiled jatropha seed cake (JC), wood chips (WC) and their blends



**Fig. 3:** Derivative thermogravimetric analysis of deoiled jatropha seed cake (JC), wood chips (WC) and their blends

The stages of decomposition occurred for the blended samples of JC and WC (25JC75WC, 50JC50WC and 75JC25WC) when heated to a temperature of 800 °C at the heating rate of 30 °C/min under nitrogen atmosphere. For all the blends, the small peak ( $P_1$ ) occurred between 35 to 195 °C where the moisture get evaporated. The second peak ( $P_2$ ) in the temperature range of 204 to 442 °C showing the devolatilization and oxidation of the blended material. The peak ( $P_3$ ) between 425-767 °C mainly due to the oxidation of char formed within the material. The ignition temperature of the blended samples was at 205°C and it has been observed that

there was no remarkable change in the ignition temperature compared to 100WC and 100JC. However, it has been observed that with an increase of blending ratio of JC and WC there are few variations in the peak height.

### 3.2 Determination of thermokinetic parameters

The major weight loss of the WC, JC and their blends were observed in the zone of peak 2. The kinetic parameters such as exponential factor ( $A$ ), activation energy ( $E$ ) and the order of reaction ( $n$ ) for WC, JC and their several blends were calculated for the reaction zone  $P_2$  by using linear regression analysis of LINEST function in Microsoft Excel. The kinetic parameter for the blending ratios at 30°C/min are shown in Table 3. The maximum rate of combustion ( $DTG_{max}$ ) of  $P_2$  curve of the blended samples increased considerably from -14.24 %/min to -24.19 %/min, while compared to 100WC and 100JC. The peak temperature ( $T_p$  in °C) and the  $DTG_{max}$  of peak  $P_2$  curve was found almost same for the mixed blends.

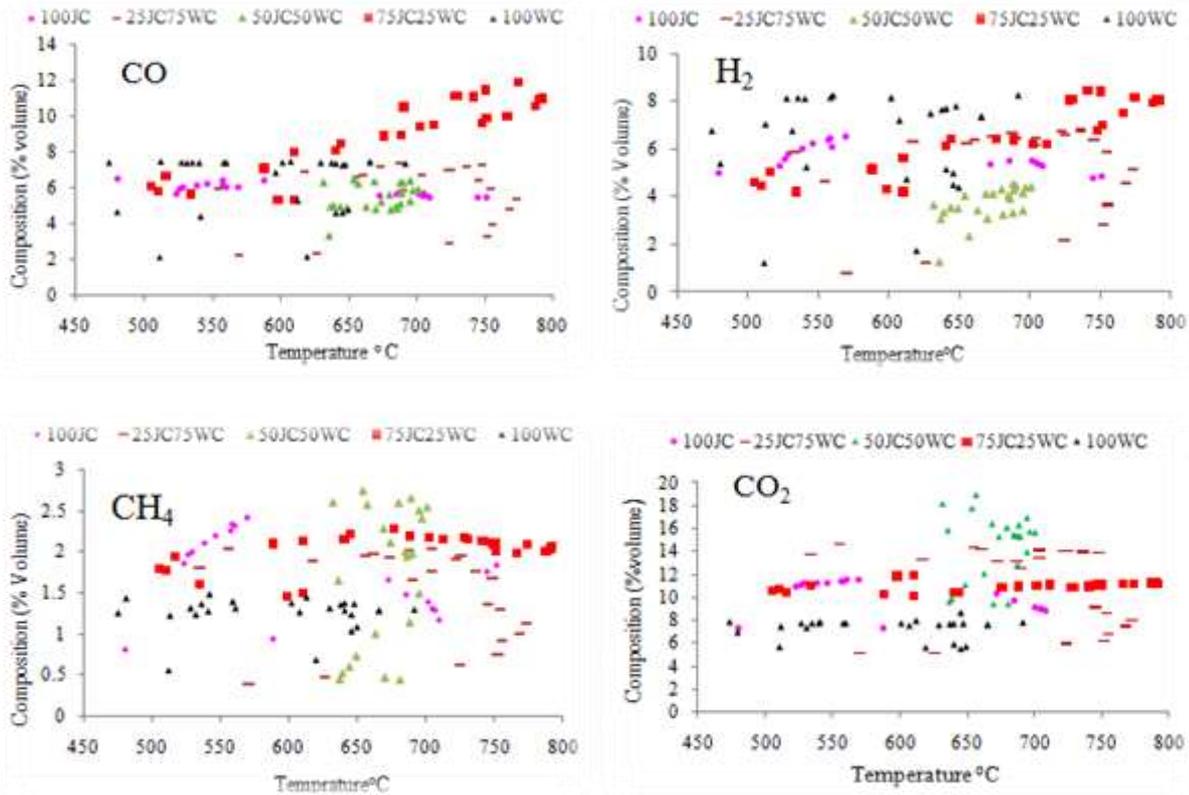
**Table 3:** Thermal kinetics of deoiled jatropha seed cake (JC), wood chips (WC) and their blends

Sample	Temp range (°C)	E (kJ mol <sup>-1</sup> )	A (min <sup>-1</sup> )	n	R <sup>2</sup>
100JC	204-404	51.24	$2.70 \times 10^3$	0.86	0.9038
25JC75WC	212-418	67.65	$6.50 \times 10^4$	0.64	0.9261
50JC50WC	231-415	69.50	$1.00 \times 10^5$	0.73	0.9337
75JC25WC	227-406	58.38	$1.16 \times 10^4$	0.86	0.9082
100WC	210-405	70.25	$1.31 \times 10^5$	1.20	0.9650

The correlation coefficient ( $R^2$ ) value of all the samples found greater than 0.9 for the maximum weight loss region. Thus the kinetic parameters are reliable to predict the weight loss at different conditions. In this study, it has found the activation energy ( $E$ ) for the blend of 75JC25W with the value of 58.38 kJ/mol and there is no significant difference in 50% and 25% of deoiled jatropha seed cake blend with wood chips. Since the JC and the WC are the biomass resources with components of cellulose, hemicellulose and lignin so that jatropha residue seed cakes can be co-gasified with fuel sources which require higher activation energy. The increased percentage of blending JC showed that the pre-exponential factor ( $A$ ) decreases with increase in the order of reaction ( $n$ ).

**Table 2:** Thermal degradation profile of deoiled jatropha seed cake (JC), juliflora wood chips (WC) and their blends

Sample	P <sub>2</sub>			P <sub>3</sub>			T <sub>f</sub> (°C)	Residue
	Temp range (°C)	T <sub>p</sub> (°C)	DTG <sub>max</sub> (%/min)	Temp range (°C)	T <sub>p</sub> (°C)	DTG <sub>max</sub> (%/min)		
100JC	201-397	347	-11.40	401-710			701	39.09
25JC75WC	204-422	354	-24.19	425-735			735	23.29
50JC50WC	204-443	351	-16.51	448-767			768	31.02
75JC25WC	207-441	335	-14.24	449-766			767	35.81
100WC	181-394	314	-16.36	397-583	466	-8.88	584	4.84



**Fig. 4:** Syngas concentration of deoiled jatropha seed cake (JC), wood chips (WC) and their blends

### 3.3 Syngas generation during gasification of JC, WC and their blends

The experimental run on gasification of JC, WC and their blends were carried out at various blending ratios of 100%, 75%, 50% and 25%. Syngas with the changing composition of carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), Hydrogen (H<sub>2</sub>) and methane (CH<sub>4</sub>) was usually generated during the gasification and co-gasification of any agro-residues. The variation in the syngas generation during gasification of JC, WC and their blends were shown in Fig. 4. It could be inferred that the syngas producing trends were varying once the steady state is attained.

Table 4 shows the minimum and maximum value of gas composition generated during the co-gasification run at a reduction zone temperature range of 450°C to 800°C. At 100% of using jatropha seed cake and wood chips as single feed for gasification, there is no remarkable effect on gas product composition and calorific value. In the case of co-gasification of JC and WC at different blending ratios of 75%, 50% and 25%, there was a significant change in syngas generation. However, the blended sample of 75JC25WC resulted in a higher gas composition with CO (11.48%), H<sub>2</sub> (8.46%) and CH<sub>4</sub> (2.28%) with a higher calorific value of 790 kcal/m<sup>3</sup>.

The co-gasification of biomass blend at an equal ratio of JC and WC (50JC50WC) resulted in lower product gas generation compared to the output of other two blends of 25% and 75%. It might be because the two agro-residues such as JC and WC were exhibiting different structural properties, bulk density, as well as, the significant difference in the content of molecular components of hemicellulose, cellulose and lignin. In the case of a 75JC25WC blend, the concentration of CO, H<sub>2</sub>, CH<sub>4</sub> production was higher at the respective temperature which results in a higher calorific value. For the blending ratio 25JC75WC and 50JC50WC, the more generation, as well as less conversion of CO<sub>2</sub>, resulted in lower calorific value.

Fig. 5. shows the average value of individual components of syngas produced at different blending ratios of biomass. The blended feed of 75JC25WC showed the gas components CO and H<sub>2</sub> with a higher value of 8.94% and 6.66% respectively. The average calorific value of the product gas generated during the co-gasification of JC and WC at different ratios were shown in Fig. 6. During the gasification of single feeds of 100% of JC and WC, the lower heating value (LHV) are 2.09 and 2.18 MJ/m<sup>3</sup>. However, for the co-gasification of blends 75JC25WC, 50JC50WC and 25JC75WC resulted in LHV of 2.7, 1.87 and 2.06 MJ/m<sup>3</sup> respectively.

### 3.4 Total combustible gas of syngas:

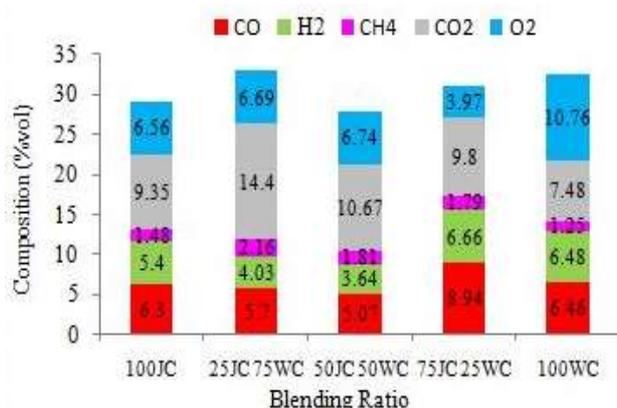
The total combustible gas (TCG) is the mole fraction of the all combustible gases found in the syngas which includes CO, H<sub>2</sub> and CH<sub>4</sub>. TCG can be used to determine the quality of the syngas and is calculated by the Eq. 6. [11].

$$TCG \text{ of syngas} = [Y_{CO} + Y_{H_2} + Y_{CH_4}] * 100 \quad (6)$$

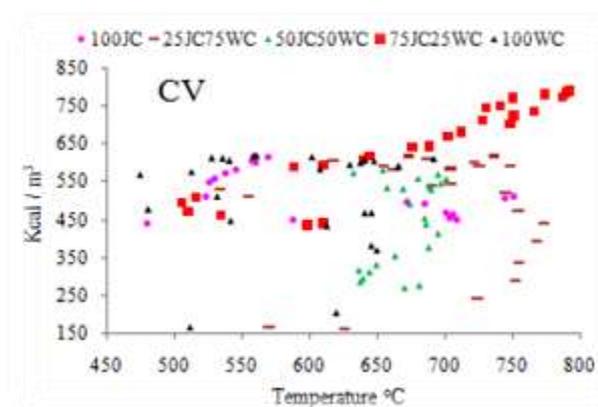
**Table 4:** Syngas concentration of deoiled jatropha seed cake (JC), juliflora wood chips (WC) and their blends

Sample	Percentage by volume								TCG		
	CO		H <sub>2</sub>		CH <sub>4</sub>		CO <sub>2</sub>		CV (Kcal/m <sup>3</sup> )		(Volume %)
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	
<b>100JC</b>	5.43	6.56	4.30	6.51	0.54	2.43	6.32	11.57	441	617	13.18
<b>25JC75WC</b>	2.20	7.42	0.79	6.91	0.39	2.21	5.17	14.63	160	618	11.89
<b>50JC50WC</b>	3.36	6.46	1.29	4.45	0.45	2.75	9.39	16.89	273	584	10.52
<b>75JC25WC</b>	5.32	11.48	4.19	8.46	1.46	2.28	10.31	11.91	436	790	17.39
<b>100WC</b>	2.13	7.53	1.23	8.22	0.55	1.39	5.56	8.71	169	619	14.19

Where,  $Y_{CO}$ ,  $Y_{H_2}$  and  $Y_{CH_4}$  are the mole fraction of CO, H<sub>2</sub> and CH<sub>4</sub> respectively. Table 4 shows the average TCG of the syngas produced from gasification of JC, WC and their blends at different ratios. In co-gasification with the increase of blending JC with WC, the sample of 75JC25WC blend was with a higher value of TCG than the gasification of 100% of JC and WC. Fig. 6 represents the calorific value during the experimental runs at individual and blended biomass residues.



**Fig. 4:** Syngas composition of deoiled jatropha seed cake (JC), wood chips (WC) and their blends



**Fig. 5:** Calorific values of deoiled jatropha seed cake (JC), wood chips (WC) and their blends

### 3. Conclusion

This paper evaluated the thermal kinetics of feedstock mixtures such as deoiled jatropha seed cake residues (JC) and wood chips (WC) from a lab scale downdraft gasifier and studied its effect on produced syngas composition. Thermogravimetric analysis was performed to investigate the thermal decomposition behavior and reaction kinetics further revealed that the pyrolysis occurred in three stages comprising of dehydration, devolatilization and solid decomposition. The effect of JC and WC ratio on the syngas composition and syngas energy efficiency were also evaluated. The blending ratio of JC: WC of 75:25 exhibited the higher calorific values while comparing with their resources at the corresponding temperature regimes. The pyrolytic kinetics of co-gasification studies showed that the deoiled jatropha seed cake residue with low activation energy could be co-gasified with fuel source which requires high activation energy.

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