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Pyrolysis and thermal oxidation kinetics of sugar mill press mud

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Abstract

Press mud, a solid waste obtained from the sugar mills, has the potential of energy generation through pyrolysis and gasification. The paper reports its proximate and ultimate analyses, deformation and fusion ash temperatures, lower and higher heating values, physico-chemical and thermal degradation in nitrogen and air atmospheres. The thermal degradation was conducted in a thermogravimetric analyzer from room temperature to 900 °C at heating rates of 20 and 40 K min^{-1}. The thermogravimetric, derivative thermogravimetric and differential thermal analyses were carried out to determine the rate of volatiles evolution, the effect of heating rates on the thermal degradation characteristics and to determine the global mass loss kinetics of thermal degradation. The thermal degradation was found to occur in several distinct phases: each phase giving volatile evolution in an independent parallel lump. Each decomposition phase was modeled by a single irreversible reaction with respect to the solid mass. Global mass loss kinetics was also determined for the entire decomposition process, as if occurring in one single step. The integral and differential techniques were used for the determination of kinetic parameters. Using the method of Agrawal and Sivasubramanian [R.K. Agrawal, M.S. Sivasubramanian, AIChE J. 33 (1987) 7] for the total degradation zone, the orders of reaction were found in the range of 1.00–2.50 in both the atmospheres (i.e. nitrogen and air) and the activation energy in the range of 27.84–33.44 and 57.41–88.92 kJ mol^{-1} in nitrogen and air, respectively.

The pre-exponential factor was found in the range of 32.1–95.1 and 5.10×10^4 to 5.46×10^9 min^{-1} in nitrogen and air atmospheres, respectively.

Keywords: Thermal degradation; Press mud; Thermogravimetric analysis; Kinetic parameters

1. Introduction

Press mud is an industrial waste available from the sugar mills. Most of the sugar mills in India are situated in the rural setting where the problem of fuel and power supply is encountered almost round the year. In monsoon months, fuel availability for domestic cooking and other purposes are acute. Indian sugar mills, using double sulphitation process for clarification, produce about 12 million tonnes [1] of press mud (filter cake) as a waste. Press mud has about 68–70% of moisture, 24–28% of combustibles and 6–8% of ash [1]. It is very rich in micronutrients for agricultural crops and horticulture: nitrogen 1.9%, phosphorous 1.8%, potassium 0.9%, calcium 4.3%, magnesium 0.7%, sulfur 3.2%, sodium 0.1%, manganese 0.034%, zinc 0.008% and copper 0.053% [1]. Press mud is either disposed off in heaps in open fields or sold as immature manure to farmers. Dry press mud has higher percentage of combustibles which could be exploited for energy generation. One of the most promising routes of extracting energy from such biomass waste materials is through thermochemical processing, viz., pyrolysis and gasification. Pyrolysis produces solid charcoal, liquid and gaseous products. It is the initial stage and a major controlling step in the process of gasification and combustion. Press mud can be dried and densified and can be used for pyrolysis and gasification.

Thermogravimetric studies under isothermal and non-isothermal conditions are normally used to understand the

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pyrolysis and gasification phenomena. A number of researchers have performed thermogravimetric analysis to understand the process of thermal degradation, (pyrolysis and gasification) and its kinetics [1–6] for various biomass materials. However, it appears that no study has been undertaken so far on press mud, an important agro-industrial waste, which is available in plenty in sugar mills. The thermal degradation kinetics will help the sugar mills in exploiting this waste for cogeneration purposes.

The thermogravimetric, derivative thermogravimetric and differential thermal analyses have been carried out to understand the process of thermal degradation in purging nitrogen and air atmospheres and its kinetics. DTG and DTA characteristics have also been studied to understand the rate of volatization and the distribution of volatiles in different temperature ranges. The kinetics of thermal degradation in nitrogen and air has been determined by using different models based on integral and differential methods.

2. Materials and methods

Press mud was procured from a local RBNS Sugar Mill, Laksar, Hardwar, India. The press mud was in powdery form. The press mud was brought to the Department of Chemical Engineering, I.I.T., Roorkee and was sun-dried. Dried material was stored in a polyethylene bag for future use. For the physico-chemical and thermal characterization of press mud, a sample of approximately 1 kg of press mud was further oven-dried at 105 °C for 2 h and ground in a laboratory ball mill. The ground matter was further classified by using two IS sieves in the size range of 200 and 600 μm. This sieved powdery sample was stored in airtight plastic containers for future use. The proximate analysis of sieved press mud sample was carried out as per procedure laid down by ASTM standard method for proximate analysis [D-3172-73 through D-3174-82 and D-3175-82 (1)]. The ultimate analysis of the sample was determined by using Perkin-Elmer CHN Elemental Analyser (Model 2700, available at the Centre of Advanced Study, Chemical Engineering Department, Institute of Technology, Banaras Hindu University, Varanasi, India). The higher heating value of press mud sample was determined in a standard bomb calorimeter according to ASTM-2015-17 [1]. Ash deformation and fusion temperatures were found using the standard tests for the fusibility of coal and coke ash (ASTM D-1857-68) as guidelines. A Stanton Redcroft Model STA-781 thermogravimetric analyzer was used to continuously monitor weight changes of press mud sample due to drying, volatilization, and gasification as the sample followed a linear heating programme. This instrument was available in the Institute Instrumentation Centre, I.I.T., Roorkee. The instrument also provided the continuous recording of the DTG and DTA curves, in terms of percentage weight loss per minute and temperature difference in mV (for DTA) which could be converted as per calibration chart to obtain temperature difference between the alumina sample and the press mud sample at any temperature under temperature programmed heating rates (from 10 to 40 K min^{-1}).

Table 1
Characteristics of press mud

Characteristic	Value
Proximate analysis (Moisture-Free basis) (%)	
Volatile matter	54.0–58.0
Fixed carbon	25.7–26.2
Ash	12.9–18.2
Ultimate analysis (%)	
C	41.30–44.50
H	5.00–5.60
N	1.10–2.50
S	2.80–3.40
O (by difference)	24.90–25.80
Higher heating value (MJ kg^{-1})	13.60–20.50
Lower heating value (MJ kg^{-1})	11.98–17.05
Ash deformation temperature (°C)	1285–1310
Ash fusion temperature (°C)	1340–1360

The principal experimental variables which could affect the thermal degradation characteristics in nitrogen and air flow rates in a TGA are the pressure, the purge gas flow rate, the heating rate, the weight of the sample and the sample size fraction. In the present study, the operating pressure was kept slightly positive; the purge gas (nitrogen and air) flow rate was maintained at 50 ml min^{-1} and four heating rates viz. 10, 20, 30 and 40 K min^{-1} were employed. The uniformity of the sample was maintained by using a 10 mg sample from the stored lot and spreading it uniformly over the crucible base in all the experiments.

3. Results and discussion

The results of proximate analysis, ultimate analysis, fusion and deformation temperatures, and the lower and higher heating values of a number of press mud samples are shown in Table 1. It may be emphasized that physico-chemical characteristics of press mud vary from mill to mill and even the wastes produced on different days in a mill differ in their characteristics due to the differing cane quality and processing techniques. Press mud has energy content more than half of the energy content of the average coal found in India [2]. It has high ash content, comparable to coal and high volatile matter and fixed carbon as compared to average coal. Thus, it may be readily amenable to gasification at lower temperatures. However, it has sulfur which may get converted to SO_2 in oxidative environment or may complex and form pyrolysis liquid. It can be seen that the temperatures of ash deformation and fusion of press mud in oxidizing atmosphere are higher (>1300 °C) than the normal operating temperature range of a fluidized bed gasifier (650–850 °C) and therefore, press mud can easily be gasified in a fluidized bed. Under reducing atmospheres, the ash fusion temperature will be lower than that reported in Table 1.

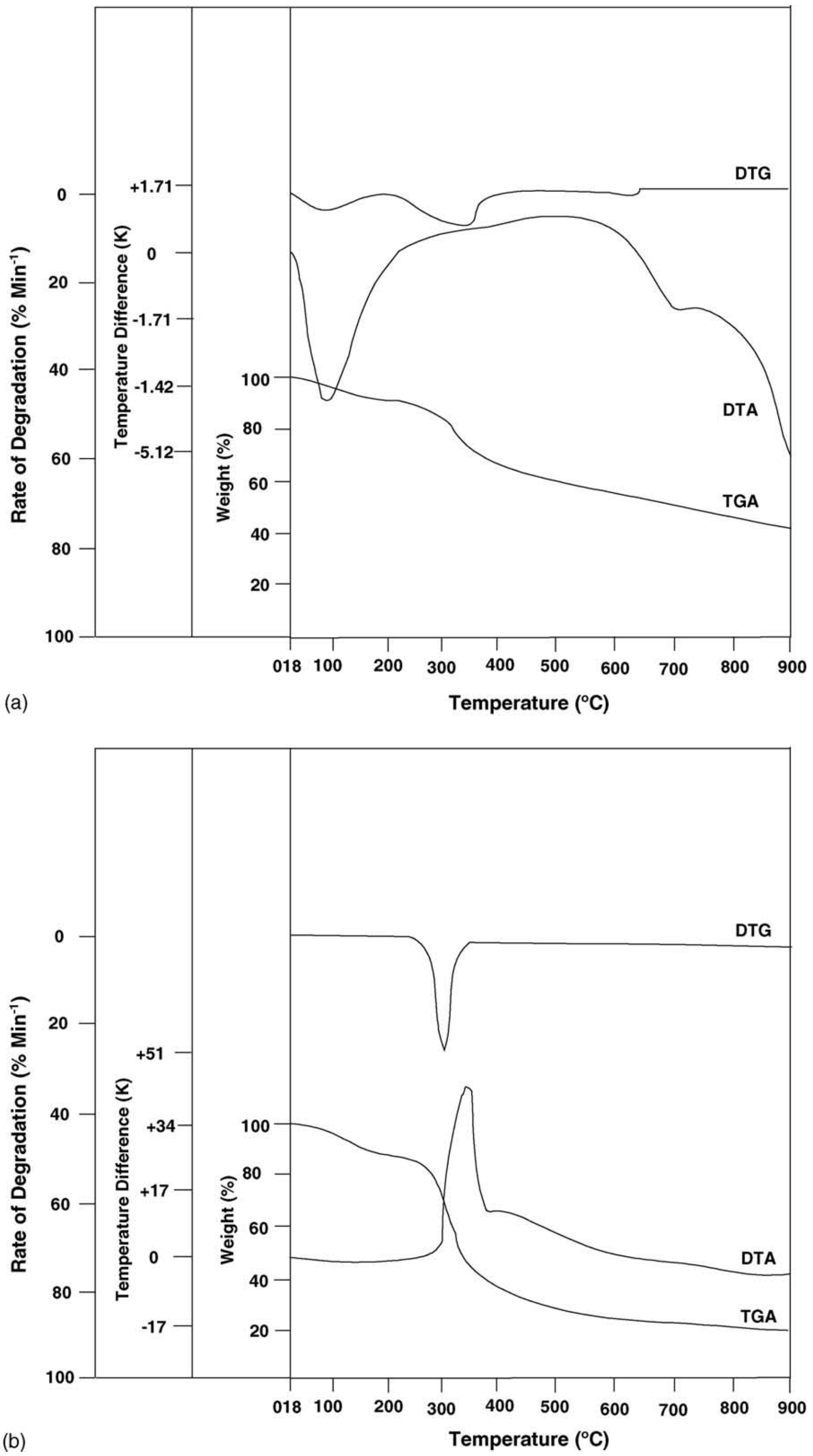

Fig. 1. Thermogravimetric and differential thermal analysis of press mud in (a) nitrogen, and (b) air, heating rate = 20 K min^{-1}.

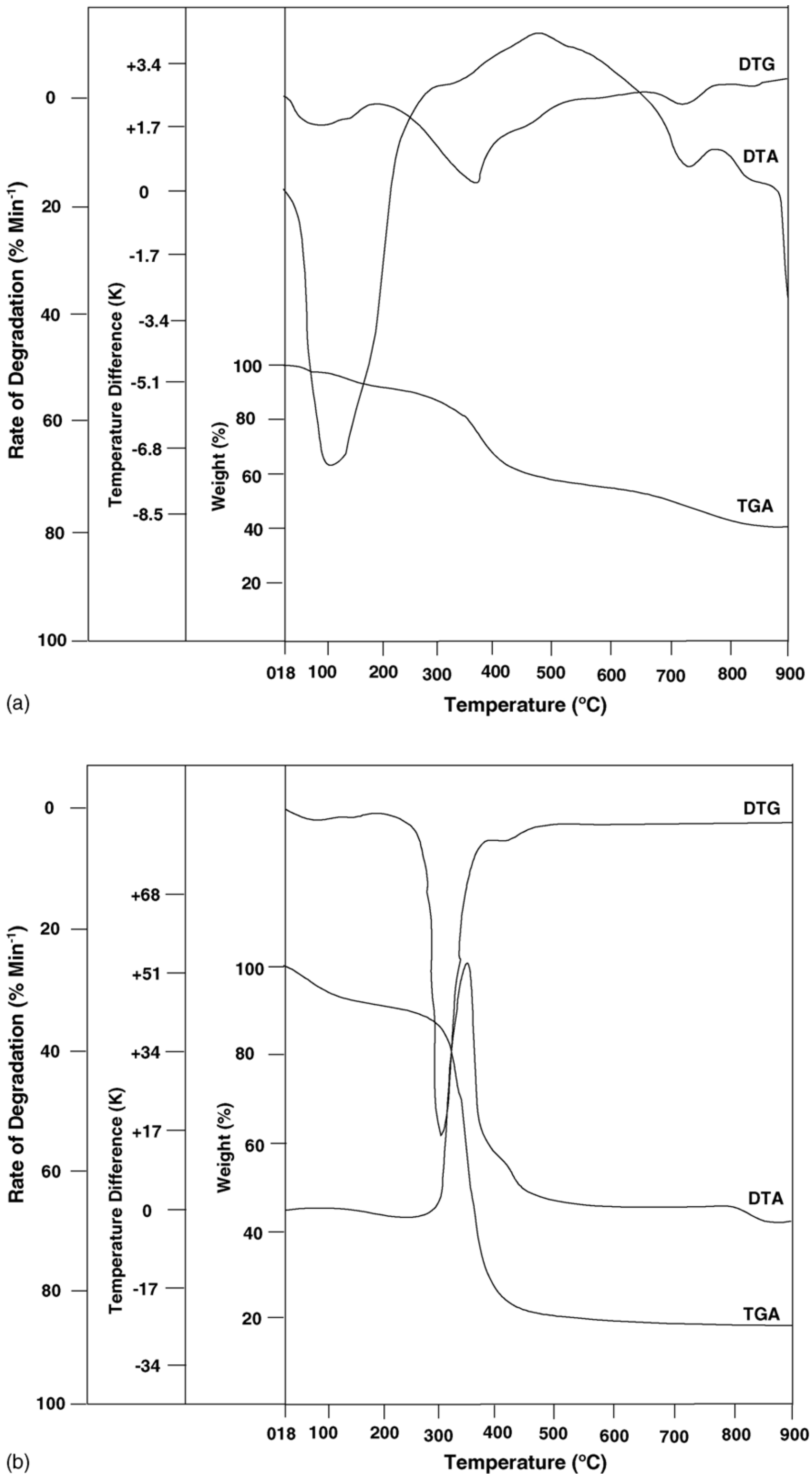

Fig. 2. Thermogravimetric and differential thermal analysis of press mud in (a) nitrogen, and (b) air, heating rate = 40 K min^{-1}.

Table 2
Thermal degradation of press mud in different reaction zones (nitrogen purging rate: 50 ml min^{-1})

Reaction zone	Heating rate (K min^{-1})	Water evolved (%)	Degradation temperature (°C)			Total degradation (wt.%)	Degradation rate (wt.% min^{-1})		Residue at 850 °C (wt.%)
			Initial	Final	Maximum		Average	Maximum	
I	20	8.1	145	310	265	5.6	–	6.2	–
	40	8.1	169	279	279	3.0	–	7.7	–
II	20	–	310	409	341	16.7	7.0	9.7	–
	40	–	279	419	360	16.1	9.3	14.0	–
III	20	–	409	850	–	20.5	–	2.0	49.1
	40	–	419	850	–	19.9	2.8	3.8	52.8

The thermal degradation characteristics of press mud under flowing nitrogen and air are given in Figs. 1 and 2, for the two heating rates viz., 20 and 40 K min^{-1}, respectively. Press mud looses moisture ($\sim$8%) followed by volatile evolution and thermal degradation under nitrogen atmosphere (Figs. 1(a) and 2(a)). The zone of degradation started at 145 °C and ended at 310 °C, with the maximum degradation rate of 6.2% min^{-1} at $T_{\max} = 265$ °C at 20 K min^{-1} heating rate. Total degradation in this phase was found to be 5.6%. With 40 K min^{-1} heating rate, the degradation started at 169 °C and ended at 279 °C. Total degradation at this heating rate was only 3%, with the maximum degradation rate of 7.7% min^{-1}. This initial phase was followed by the second and faster degradation phase which continued upto 409–419 °C. The total degradation, maximum degradation rate and the temperature at which this occurred, for 20 and 40 K min^{-1} heating rates, were respectively, 16.7%, 9.7% min^{-1} and 341 °C; 16.1%, 14.0% min^{-1} and 360 °C. This phase was followed by at least two other phases. One very short phase of degradation occures at 642 °C and 772 °C (peak temperature) for 20 and 40 K min^{-1} heating rates, respectively. Before this short phase the rate of degradation was found to be almost constant. For calculation purposes, the total degradation from the end of the second reaction zone to 850 °C has been taken to be occurring as if in one single zone. The total degradations so calculated were, respectively 20.5% and 19.9% for the two heating rates (Table 2). Under nitrogen atmosphere, press mud degradation is incomplete even at 900 °C, and the residues obtained at 850 °C were, respectively, 49.1% and 52.8% for 20 and 40 K min^{-1} heating rates. DTG and DTA curves also characterize the degradation.

Changing the atmosphere from flowing nitrogen to flowing air at 50 ml min^{-1} catapults the degradation characteristics in contrast to pyrolysis. DTG and DTA curves exemplify the acceleration in degradation rate and the heat evolution due to exothermic reactions at different temperatures (Figs. 1(b) and 2(b)). The first phase of degradation is slow giving a total degradation of 16.3% and 9.3% at 20 and 40 K min^{-1} heating rates, respectively. This phase is seen to start at 169 °C ending at 320 °C for 20 K min^{-1} heating rate. A small kink is seen during this phase in both DTG and DTA curves. The second phase showed very fast degradation ending at 362 °C and 385 °C for 20 and 40 K min^{-1} heating rates, respectively. The maximum degradation rate was found to be 78.3% min^{-1} at 304 °C at 40 K min^{-1} (Table 3). During this reaction zone, total degradation was found to be 24.4% at 20 K min^{-1} and 46.9% at 40 K min^{-1}. Last phase of degradation was found to be very slow. Taking the degradation up to 700 °C as if in a single reaction zone, total degradations were found to be 16.7% and 18.5% and the residue obtained were 34.1% and 16.5% at 700 °C for 20 and 40 K min^{-1} heating rates, respectively.

It is, thus, very clear that the oxidation helps achieve much larger overall degradation in flowing air atmosphere with the remaining residue being only 34.1% and 16.5% of the original sample in comparison to 49.1% and 52.8% with nitrogen at 20 and 40 K min^{-1} heating rates, respectively.

The DTA curves obtained under oxidizing atmosphere at 20 K min^{-1} heating rate showed that the exothermic oxidation of press mud started at 370 °C and ended at 530 °C. Dual peak exotherms were observed, with the first exotherm peak starting at 341 °C and terminating at $\sim$370 °C. The temperature difference was $\sim$50 K. The second peak was observed

Table 3
Thermal degradation of press mud in different reaction zones (air purging rate: 50 ml min^{-1})

Reaction zone	Heating rate (K min^{-1})	Degradation temperature (°C)			Total degradation (wt.%)	Degradation rate (wt.% min^{-1})		Residue at 700 °C (wt.%)
		Initial	Final	Maximum		Average	Maximum	
I	20	169	320	290	16.9	15.5	26.4	–
	40	133	304	–	9.3	–	–	–
II	20	300	362	290	24.4	5.7	90.0	–
	40	304	385	304	46.9	–	78.3	–
III	20	362	700	400	16.7	1.0	1.9	34.1
	40	385	700	–	18.5	–	–	16.5

Table 4
Determination of kinetic parameters by using different methods

Method of analysis	The equations of determination of the kinetic parameters
Coats and Redfern [7]	$\ln\left[\frac{-\ln(1-x)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT}$, for $n = 1.0$, $\ln\left[\frac{-\ln\{1-(1-x)^{1-n}\}}{(1-n)T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT}$, for $n \neq 1.0$
Agrawal and Sivasubramanian [8]	$\ln\left[\frac{-\ln(1-x)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(\frac{1-2(RT/E)}{1-5(RT/E)^2}\right)\right] - \frac{E}{RT}$, for $n = 1.0$, $\ln\left[\frac{-\ln\{1-(1-x)^{1-n}\}}{(1-n)T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(\frac{1-2(RT/E)}{1-5(RT/E)^2}\right)\right] - \frac{E}{RT}$, for $n \neq 1.0$
Freeman and Carroll [9]	$\frac{\Delta\log(\beta\,\mathrm{d}x/\mathrm{d}T)}{\Delta\log(1-x)} = n - \frac{E}{2.303R}\frac{\Delta(1/T)}{\Delta\log(1-x)}$
Horowitz and Metzger [10]	$\ln[\ln(1-\omega)] = \frac{E}{RT_\mathrm{P}^2}$, when $n = 1$, $\ln\left[\frac{1-(1-\omega)^{1-n}}{1-n}\right] = \frac{E\theta}{RT_\mathrm{P}^2}$, when $n \neq 1$, where $\theta = T - T_\mathrm{P}$, T_P is the peak temperature as taken from the DTG curve
Reich and Stivala [11]	$\ln\left[\frac{1-(1-\omega_i)^{1-n}}{1-(1-\omega_{i+1})^{1+n}}\left(\frac{T_{i+1}}{T_i}\right)^2\right] = \frac{E}{R}\left(\frac{1}{T_i} - \frac{1}{T_{i+1}}\right)$
Piloyan and Novikova [12]	$\ln\left(\frac{\omega}{T^2}\right) = \ln\frac{AR}{\beta E} - \frac{E}{RT}$

ω: decomposed fraction of solid at time t; $W_r = W_\infty - W_t$, (mg); W_t: weight of biomass at any time, (mg); W_∞: weight of biomass at the completion of degradation, (mg); $x = (W_0 - W_t)/(W_0 - W_\infty)$; fractional conversion, A: pre-exponential factor in the Arrhenius equation, ($\mathrm{mg}^{1-n}\,\mathrm{min}^{-1}$); E: activation energy, ($\mathrm{kJ\,kg}^{-1}$); R: universal gas constant, ($\mathrm{kJ\,mol}^{-1}$); n: order of degradation reaction.

at ∼400 °C giving a temperature difference of ∼10 K. Beyond 530 °C, the degradation was found to be endothermic in nature. For 40 K min^{-1} heating rate, the DTA curve showed similar characteristics as for 20 K min^{-1}. The exothermic oxidation was found to start at 258 °C and ended at 568 °C. Dual peak exotherms were observed with overlapping. The first exothermic peak was observed at 390 °C giving a temperature difference of ∼50 K. The second exothermic peak was observed at ∼477 °C showing a temperature difference of 13 K.

Pyrolytic behavior of press mud is not akin to what has been witnessed for the biomass samples. Press mud showed a larger number of reaction zones in contrast to what is seen in woody biomass samples. However, for our analysis, the pyrolysis and oxidation characteristics have been divided in three reaction zones for 20 and 40 K min^{-1} heating rates, Figs. 1(a) and 2(a)).

The kinetic parameters were determined for each reaction zone separately by using the methods described elsewhere [1,6]. Although, several mechanistic models have been proposed to study the kinetics of thermal degradation using dynamic thermogravimetry, a single-step, irreversible, global reaction model of the type

$$aA(\mathrm{s}) \rightarrow bB(\mathrm{s}) + cC(\mathrm{g}) \quad (1)$$

describes the degradation behavior successfully.

For the reaction, the decomposition of the solid can be described by a general rate expression as

$$\frac{\mathrm{d}X}{\mathrm{d}t} = kf(X) \quad (2)$$

where X is the fractional conversion of A at time, t and $f(X)$ is the conversion function and k the specific reaction rate constant following Arrhenius equation for temperature dependence as,

$$k = A\exp\left(-\frac{E}{RT}\right) \quad (3)$$

where A is the frequency factor, E the activation energy, R the universal gas constant and T the absolute temperature. With a linear constant heating rate, $\beta = \mathrm{d}T/\mathrm{d}t$, Eq. (2) is represented as,

$$\frac{\mathrm{d}X}{\mathrm{d}T} = \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)f(X) \quad (4)$$

Using this equation several investigators have proposed different expressions for the determination of kinetic parameters: A, E and the reaction order, n. In the integral method, the exponential term of Eq. (4) has been approximated initially by Coats and Redfern [7] and improved upon by Agrawal and Sivasubramanian [8] recently. In most of the studies integral method has been used to determine kinetic parameters. For the present analysis we have used the relations proposed by different investigators, as given in Table 4. Gangavati [1] and Safi et al. [6] have given a detailed analysis of the existing models for the kinetic analysis of thermal degradation. The kinetic parameters of pyrolysis of press mud as determined by various methods for 20 K min^{-1} heating rate is given in Table 5. For the first reaction zone, viz., 145–310 °C the differential method of Freeman and Carroll [9] gave the lowest value of n, whereas Horowitz and Metzger [10] and the integral approximations of Agrawal and Sivasubramanian [8] and Coats and Redfern [7] gave the highest values of n for

Table 5
Kinetic parameters of press mud pyrolysis as determined by different methods for heating rate of 20 K min^{-1}

Temperature zone (°C)	Kinetic parameters	Method of analysis					
		Coats and Redfern [7]	Agrawal and Subramanian [8]	Freeman and Carroll [9]	Horowitz and Metzgers [10]	Reich and Stivala [11]	Piloyan and Novikava [12]
145–310	n	2.50	2.50	0.23	2.50	0.90	–
	E (kJ mol^{-1})	47.14	47.14	46.41	7.91	44.43	75.12
	A	8.59×10^3	8.29×10^3	1.99×10^5	2.67	2.04×10^4	2.26×10^5
	R^2	0.9646	0.9646	–	0.9245	0.9359	–
310–409	n	1.50	1.50	0.28	1.50	0.25	–
	E (kJ mol^{-1})	105.88	105.88	34.94	24.22	107.02	82.33
	A	3.05×10^8	3.01×10^8	9.74×10^4	9.51×10^2	2.69×10^5	2.48×10^5
	R^2	0.9695	0.9695	–	0.8976	0.9028	–
409–850	n	2.50	2.50	3.38	–	0.50	–
	E (kJ mol^{-1})	58.90	58.90	82.05	–	55.37	118.68
	A	2.08×10^3	1.95×10^3	9.48×10^3	–	1.03×10^5	3.57×10^5
	R^2	0.9103	0.9103	–	–	0.8846	–
145–850	n	–	1.25	–	–	–	–
	E (kJ mol^{-1})	–	27.84	–	–	–	–
	A	–	3.21×10^1	–	–	–	–
	R^2	–	0.9916	–	–	–	–

A has the dimension of (min^{-1}) for $n = 1$ and ($\text{mg}^{1-n}\ \text{min}^{-1}$) for any other value of n.

20 K min^{-1} heating rate. Reich and Stivala [11] method gave a value of $n = 0.90$ and 0.25 for the first two reaction zones for 20 K min^{-1} heating rate. But the values of E obtained by integral approximation methods and the methods of Reich and Stivala [11] and Freeman and Carroll [9] were similar, i.e. ~45 kJ mol^{-1} for the first reaction zone. The Piloyan and Novikava [12] method yielded the highest value of activation energy, $E = 75.12$ kJ mol^{-1}, whereas the Horowitz and Metzger [10] method gave the lowest value of $E = 7.91$ kJ mol^{-1} for the first reaction zone. For the second reaction zone, the values of E obtained from the integral approximation methods and that of Reich and Stivala [11] gave similar values: $E \approx 106$ kJ mol^{-1}, whereas the values obtained by Horowitz and Metzger [10] and Freeman and Carroll [9] methods were low. The Piloyan and Novikava [12] method gave a value of $E = 82.33$ kJ mol^{-1} which is in between the values reported by other methods.

For the overall degradation zone, the integral method with the approximation of Agrawal and Sivasubramanian [8] gave the best fit of experimental data at $n = 1.25$ for 20 K min^{-1} heating rate. At this n, the values of E and A were, respectively 27.84 kJ mol^{-1} and 32.1. Similar results

Table 6
Kinetic parameters of thermal degradation of press mud in nitrogen and air by Agrawal and Sivasubramanian [8] method for 20 and 40 K min^{-1} heating rates

Temperature zone (°C)	Kinetic parameters	Heating rate (K min^{-1})			
		Nitrogen atmosphere		Air atmosphere	
		20	40	20	40
First reaction zone	n	2.50	2.50	1.25	0.00
	E (kJ mol^{-1})	47.14	72.25	105.79	21.71
	A	8.29×10^3	5.84×10^6	4.19×10^9	2.85×10^1
	R^2	0.9646	0.9341	0.9864	0.9756
Second reaction zone	n	1.50	2.50	0.75	1.00
	E (kJ mol^{-1})	105.88	121.66	232.14	164.65
	A	3.01×10^8	1.69×10^{10}	4.23×10^{19}	6.80×10^{13}
	R^2	0.9695	0.9851	0.9917	0.9977
Third reaction zone	n	2.50	2.50	1.75	2.50
	E (kJ mol^{-1})	58.90	62.82	62.28	105.54
	A	1.95×10^3	5.43×10^3	1.41×10^4	8.66×10^7
	R^2	0.9103	0.9143	0.9859	0.9512
Entire reaction zone	n	1.25	2.50	2.50	1.75
	E (kJ mol^{-1})	27.84	33.44	88.92	57.41
	A	3.21×10^1	9.51×10^1	2.27×10^7	3.27×10^4
	R^2	0.9916	0.9542	0.9935	0.9640

A has the dimension of (min^{-1}) for $n = 1$ and ($\text{mg}^{1-n}\ \text{min}^{-1}$) for any other value of n.

were obtained for 40 K min^{-1} heating rate. However, the values of n, E and A were consistently different for the best fit of experimental values of the conversion function. The optimum values were obtained at $n = 2.50$ for 40 K min^{-1}. Comparison of E values with $n = 1.25$ showed that at higher heating rate of 40 K min^{-1}, lower value of E was obtained: at $n = 1.25$, $E = 27.84$ kJ mol^{-1} and $A = 32.1$ for 20 K min^{-1} heating rate, whereas for 40 K min^{-1} heating rate, at $n = 1.25$, $E = 24.91$ kJ mol^{-1} and $A = 10.6$. The best fit values for 40 K min^{-1} were at $n = 2.50$ giving $E = 33.44$ kJ mol^{-1} and $A = 95.1$. The units of A may be taken as (mg^{1-n} min^{-1}) for all values of n.

The thermal degradation characteristics in air (oxidizing) atmosphere are well described by a single sharp peak followed by a weak slow peak in both DTG and DTA (Figs. 1(b) and 2(b)) curves. Kinetic parameters have been determined for a slow degradation first zone followed by the second fast volatilization zone and a slower volatilization and combustion zone. The values of the activation energy and pre-exponential factor are found to vary with n. The best fit values of n, and their corresponding values for E and A are presented in Table 6 in both the atmospheres (i.e. nitrogen and air) at the two heating rates, i.e. 20 and 40 K min^{-1}. As also shown in Table 5, the value of the activation energy, E obtained by the Coats and Redfern [7] and Agrawal and Sivasuvbramanian [8] approximations at a particular value of n under oxidizing environment is the same. However, A values differ slightly with that obtained by the Agrawal and Sivasubramanian [8] approximation being consistently lower than that obtained by the Coats and Redfern [7] approximation.

The kinetic parameters for the entire range of degradation temperature under oxidizing environment at the two heating rates indicated that the order of reaction $n = 2.50$ for the best-fit of the experimental data for 20 K min^{-1} heating rate and $n = 1.75$ for 40 K min^{-1} heating rate. The best fit values for E and A for 20 K min^{-1} ($n = 2.50$) and 40 K min^{-1} ($n = 1.75$) were, respectively $E = 88.92$ kJ mol^{-1} and $A = 2.27 \times 10^7$; and $E = 57.41$ kJ mol^{-1} and $A = 3.27 \times 10^4$, respectively. With the increase in heating rate, the degradation temperature range widens and the kinetics becomes sluggish. This may be explained by finding the values of E and A at some value on n where the experimental data gives good fit with the model. At one such value of $n = 1.75$, the E values for 20 and 40 K min^{-1} heating rates were, respectively, 69.15 and 57.41 kJ mol^{-1}. The corresponding A values were 2.41×10^5 and 3.27×10^4 with R^2 being 0.9608 and 0.9640, respectively. It is clear that although, the kinetic parameters for each reaction zone may be obtained separately, the parameters obtained for the entire reaction zone are also satisfactory due to very good fit with high R^2 for engineering design of gasifiers.

4. Conclusion

The physico-chemical properties for press mud showed that this waste from the cane sugar mills is a useful fuel for gasification. TGA, DTG and DTA curves showed a number of distinct reaction zones during the thermal degradation process for the press mud. Natural break in the slope of TGA is characterized by the change in the rate of weight loss due to drying, volatilization and degradation. Press mud showed distinct degradation behavior in comparison to other biomass materials. However, for brevity, only three degradation zones were considered. Pyrolysis behavior showed poor volatilization with the maximum volatilization being 9.7% and 14.0% min^{-1} at 20 and 40 K min^{-1} heating rates, respectively. At 850 °C, the total residue obtained was around 50%. However, in the oxidizing environment, the rate of degradation of press mud was as high as 90.0% min^{-1} at 20 K min^{-1} heating rate. The total residue at 40 K min^{-1} heating rate was found to be 16.5% only. This showed that the press mud could be a very important source of clean energy through gasification. For the total degradation zone, the methods of Coats and Redfern [7] and Agrawal and Sivasubramanian [8] were used and the order of reaction was found in the range of 1.00–2.50 in both the atmospheres (i.e. nitrogen and air). The activation energy was found in the range of 27.84–33.44 and 57.41–88.92 kJ mol^{-1} in nitrogen and air, respectively and the pre-exponential factor was found in the range of 32.1–95.1 and 5.10×10^4 to 5.46×10^9 in nitrogen and air, respectively.

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