Available online at www.sciencedirect.com
SCIENCE DIRECT
Thermochimica Acta 428 (2005) 63–70
thermochimica acta
www.elsevier.com/locate/tca

Pyrolysis and thermal oxidation kinetics of sugar mill press mud

P.B. Gangavati[b], M.J. Safi[a], A. Singh[a], B. Prasad[a], I.M. Mishra[a,*]

[a] *Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee 247667, India*
[b] *Department of Mechanical Engineering, Basaveshwar Engineering College, Bagalkot 587102, India*

Received 24 October 2003; received in revised form 24 August 2004; accepted 27 September 2004
Available online 11 November 2004

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

* Corresponding author. Tel.: +91 1332 285720; fax: +91 1332 273560.
E-mail address: imishfch@iitr.ernet.in (I.M. Mishra).

0040-6031/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2004.09.026

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.