Journal of Hazardous Materials 185 (2011) 1205–1213

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Devolatilization of oil sludge in a lab-scale bubbling fluidized bed

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ARTICLE INFO

Article history:
Received 27 May 2010
Received in revised form 4 September 2010
Accepted 9 October 2010
Available online 15 October 2010

Keywords:
Oil sludge
Devolatilization time
Fragmentation
Fluidized bed

ABSTRACT

Devolatilization of oil sludge pellets was investigated in nitrogen and air atmosphere in a lab-scale bubbling fluidized bed (BFB). Devolatilization times were measured by the degree of completion of the evolution of the volatiles for individual oil sludge pellets in the 5–15 mm diameter range. The influences of pellet size, bed temperature and superficial fluidization velocity on devolatilization time were evaluated. The variation of devolatilization time with particle diameter was expressed by the correlation, $\tau_\mathrm{d} = Ad_\mathrm{p}^N$. The devolatilization time to pellet diameter curve shows nearly a linear increase in nitrogen, whereas an exponential increase in air. No noticeable effect of superficial fluidization velocity on devolatilization time in air atmosphere was observed. The behavior of the sludge pellets in the BFB was also focused during combustion experiments, primary fragmentation (a micro-explosive combustion phenomenon) was observed for bigger pellets (>10 mm) at high bed temperatures (>700 °C), which occurred towards the end of combustion and remarkably reduce the devolatilization time of the oil sludge pellet. The size analysis of bed materials and fly ash showed that entire ash particle was entrained or elutriated out of the BFB furnace due to the fragile structure of oil sludge ash particles.

1. Introduction

In the petroleum refineries, a considerable quantity of oil sludge accumulates from refining processes. The major sources of the oil sludge include the oil storage tank sludge, the biological sludge, the dissolved air flotation (DAF) scum. In China, most of the oil sludge is from the treating process of cleaning of oil storage tanks, more than 1,000,000 tonnes of this kind of sludge are generated annually. Oily sludge usually contains a considerable quantity of water, oil, and solids, in which there are many of toxic, mutagenic and carcinogenic components. It is designated as hazardous waste in Resource Conservation and Recovery Act (RCRA) [1], and represents a major source of several contaminants that pollute the soil and the ground water (e.g. petroleum hydrocarbons, metals), and the air (e.g. volatile organic carbons). Typically, oil sludge can be handled via microbial degradation and/or recycling into reusable oils. However, it has been found that such methods cause secondary pollutants. The oily sludge, consisting mainly of heavy organic compounds and a large amount of combustible matters, is recognized as a valuable energy resource that can be recycled as fuel [2]. Fluidized bed (FB) incineration has been proven an alternative to dispose many kinds of wastes such as municipal sludge, biomass waste, and industrial wastes (such as oil sludge), due to its fuel flexibility, high mixing efficiency, high combustion efficiency and low pollutant emissions [3–8]. Using such a process can not only minimize the solid waste but also recover energy.

Oil sludge is a kind of low caloric value fuel, characterized by very high yields of volatiles (~93 wt.% on free ash basis) and very low fixed carbon [8,9]. The studies [10,11] have shown that the high volatile content of some alternative fuels leads to longer devolatilization times and larger quantities of volatiles evolved. Consequently, a distinctive feature of these fuels is the larger heat release associated with homogeneous combustion of volatile matter. The devolatilization time and the rate of fuel particle mixing within a fluidized-bed will control the distribution of volatiles throughout the bed, and then has a great influence on the location of combustion of volatiles along fluidized-bed furnace, which is direct relating to their design and operation [12]. Thus, understanding volatile release and their subsequent combustion with oxygen is of paramount importance.

The devolatilization times of fuel particles pertaining to their utilization in fluidized-bed combustion have been extensively reported in the literature [12–19]. Previous measurements [12–16] showed that the devolatilization times under fluidized bed conditions range between 10 and 100 s for coals of varying rank in the size range of 5–15 mm diameter. These results have been typically correlated using a power-law relation in the form of

$$\tau_d = Ad_p^N \qquad (1)$$

where τ_d, is devolatilization time (s), and d_p, is the pellet initial diameter (mm), the exponent, N, is reported to be range between 0.27 and 2.0, and increase with an increase in the moisture content

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0304-3894/$ – see front matter
doi:10.1016/j.jhazmat.2010.10.032

Table 1
Proximate and ultimate analysis of the oil sludge samples.

Proximate analysis		Ultimate analysis (as received, wt.%)	
Moisture (as received, wt.%)	16.95	C	20.85
Combustible[a] (as received, wt.%)	31.06	H	2.70
Ash (as received, wt.%)	51.99	O	6.00
Fixed carbon (daf, wt.%)	6.83	N	0.11
Volatile matter (daf, wt.%)	93.17	S	1.40
Net calorific value (kJ/kg^{-})	8530	Clinkering property	Weakly clinkered

[a] Volatile + fixed carbon.

Table 2
Main organic chemical composition of the oil sludge (wt.%).

Organic materials in oil sludge	Chemical composition of organic materials				
	Bituminous	Satisfied hydrocarbon	Aromatic hydrocarbon	Non-hydrocarbon	TOC (%)
26.07	3.32	11.80	5.44	5.51	21.97

and temperature, and also depends on the fuel type. Generally, fuel particle devolatilization may be controlled by three main factors, heat transfer to and within the particle, chemical kinetics of pyrolysis and mass transfer of volatile products within the particle. It has been suggested that the value of the exponential constant N can give an indication of the rate-controlling process [17,18]. In the region of reaction control, τ_d should be independent of d_p, so the value of N is zero. However, assuming shrinking-core behavior with kinetic control can give $N = 1$. If internal heat transfer controls, the value of N should be 2; on the other hand, if external heat transfer governs devolatilization, N will lie between 1 and 2, depending on the size of the particle. If there is internal mass transfer control, the resulting value of N is also 2. Devolatilization time was found to be influenced by bed temperature, gas environment, moisture content and fuel type [18]. Measurements of devolatilization time using various techniques in fluidized-beds [14–16], have shown that the exponential constant N is mainly between 1 and 2 for coal particles with sizes ranging between 6 and 20 mm, thus supporting that devolatilization time for large coal particle is heat transfer controlled. While, the analysis of Werther and Ogada [17] of sewage sludge particles with various moisture contents showed that the exponential constant N increased with moisture content and equal to 0.27 and 0.72 in air atmosphere for dry and wet sludge, respectively, thus supporting that devolatilization for dry sewage sludge particles was in the region of reaction control.

Although fluidized bed technology has been applied to oil sludge incineration [8] and preliminary combustion characteristics have been studied [9], the study on the fluidized bed combustion of oily sludge characterized by very high yields of volatiles is still very limited. In addition, the experimental investigations of combustion behavior with respect to gaseous emission in the progress of the combustion of oil sludge in a fluidized bed are very limited. In the present work, the pyrolysis and combustion experiments of a number of oil sludge pellets have been carried out to understand the volatiles release and its subsequence combustion under bubbling fluidized bed conditions. The devolatilization times of the oil sludge pellets, primary fragmentation in the hot lab-scale bubbling fluidized bed were focused. The influences of pellet size, bed temperature and superficial fluidization velocity on volatiles release and combustion of oil sludge pellet were evaluated.

2. Experimental

2.1. Fuels and bed material

The oil sludge sample used in this work was generated from tanker cleaning processes from Shengli Oil Field, Shandong province, northern China. 'As-received' sample appears to be black, viscous and in the form of semisolid cake at ambient temperature. The proximate analysis and ultimate analysis of the as-received oil sludge are given in Table 1. The heating value of the sample measured by employing a bomb calorimeter is also listed in Table 1. The proximate analysis indicates that oily sludge is characterized by very high yields of volatiles and very low fixed carbon. Therefore, special attention should be paid to the release and combustion of volatiles during oily sludge combustion. The contents and group composition of chloroform extract on the oil sludge are shown in Table 2. Table 2 shows that the oil sludge contains 26.07 wt.% of chloroform extractable including bituminous (3.32%), satisfied hydrocarbons (11.80%), aromatic hydrocarbons (5.44%) and non-hydrocarbons (5.51%). The inorganic materials of the oil sludge were analyzed by an Inductively Coupled Plasma Atomic Emission Spectrometry (ICP/AES) after the chloroform extraction, the total concentration of the metals are listed in Table 3.

In order to make the viscous oil sludge into pellets, the as-received oil sludge was dried in advance at 105 °C in a horizontal electric heated reactor under the nitrogen atmosphere with the flow rate of 200 ml/min for 9 h. The final moisture content of the pre-dried sample would be 0 wt.% according to the standard test method of moisture in coal (ASTM D5142–09, Standard Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures). Then the pre-dried sample was made into a number of pellets with diameter of 5–15 mm.

2.2. Experimental facility

The schematic diagram of the experimental system is shown in Fig. 1. The system consisted of an electrical air heater, a fluidized bed furnace and two stage separators (a cyclone and a bag house filter). The fluidized bed furnace was made of a high-temperature

Table 3
Analysis of metal elements in the oil sludge after chloroform extraction (wt.%).

Element	Weight fraction	Element	Weight fraction
Ca	8.758	Cu	0.11
Fe	5.16	Mn	0.0882
AL	3.754	Se	0.0601
Ba	2.583	Ni	0.05
K	1.369	Pb	0.0186
Na	1.237	Co	0.0164
Mg	0.4889	Cr	0.0159
Sr	0.4779	As	0.0083
Ti	0.1313	Mo	0.006
Zn	0.1285	Cd	0.0004
Total	24.4615		