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

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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, $\tau_d = Ad_p^N$. 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.

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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

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

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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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		

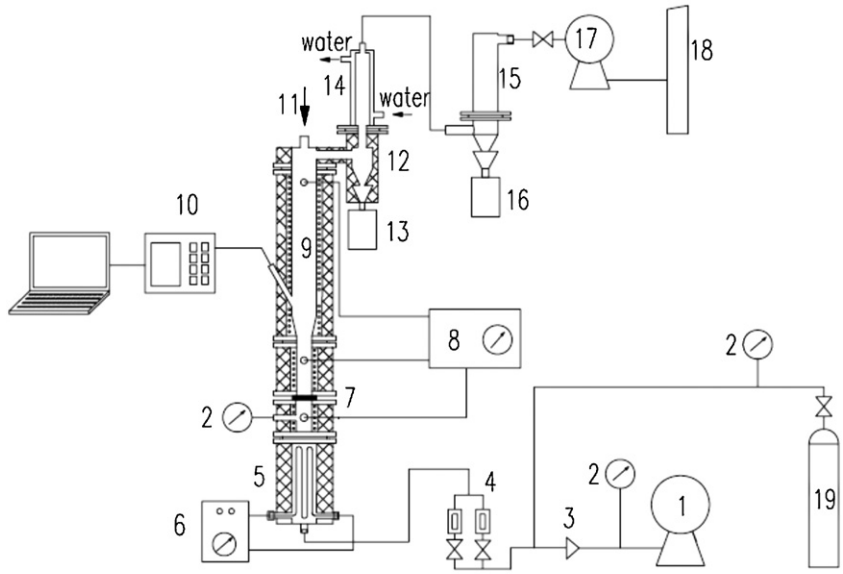

Fig. 1. Schematic diagram of experimental system.

austenitic stainless steel containing a dense phase region (50 mm ID with the height of 200 mm) and a lean phase region (80 mm ID with the height of 600 mm). The fluidized bed furnace could be heated by electric resistances winded around the fluidized bed furnace. The temperatures of the fluidized bed furnace were measured and controlled by the temperature controllers equipped with a number of type K thermocouples. The fine particles entrained by flue gas stream could be caught by two stage separators (a cyclone and a bag house filter), and were gathered in ash vessels.

Quartzite particles with average size of 1.62 mm were employed as bed material in this study; the minimum fluidizing velocity for the bed particles ranges between 1.19 and 1.31 m/s under dense bed temperatures ranging from 600 to 800 °C. The gaseous products evolved from heating process were analyzed by Vario Plus emission monitoring system made in Germany.

2.3. Devolatilization in nitrogen

Assessment of fuel devolatilization was carried out by a technique based on analysis of time series of gas concentrations (CO, H_2, and CHs) during devolatilization at the bed temperature of 700 °C in nitrogen of batches of oil sludge pellets of preset size and mass in the BFB. Nitrogen as fluidization medium was supplied by a high-pressure bottle (No. 19 in Fig. 1) and heated up to 700 °C when it passed through the electrical heater. Its flow rate was measured by a rotameter. The experimental conditions are shown in Table 4.

2.4. Devolatilization in air

Assessment of devolatilization was carried out by a technique based on analysis of time series of gas concentrations (O_2, CO_2, CO, H_2, SO_2, CH_x and NO_x,) during devolatilization at the bed temperature of 650–750 °C in air of batches of fuel particles of preset size and mass in BFB. Air as fluidization medium was supplied by a compressor (No. 1 in Fig. 1). Its flow rate was measured by a rotameter and adjusted by a pressure regulator. The air was heated up to a specific temperature between 650 and 750 °C according to experimental conditions when it passed through the electrical heater.

Table 4
Design and operating variables of the pyrolysis experiments.

Operating variables	Operating parameters
Bed temperature T_b (°C)	700
Bed material	Quartzite particle (with 1.62 mm average diameter)
Bed solids height h (mm)	70
Nitrogen flux (Nm^3/h)	4
Initial size range of particles d_0 (mm)	9–15

Table 5
Design and operating variables of the combustion experiments.

Operating variables	Operating parameters
Bed temperature T_b (°C)	650–750
Bed material	Quartzite particle (with 1.62 mm average diameter)
Bed solids height h (mm)	70
Air flux (Nm^3/h)	7,8,9
Oil sludge ball size d_0 (mm)	5–15

Two main factors, such as the bed temperature (T_b) and the initial size (d_0) of oil sludge pellet, were taken into account to study the combustion of the oil sludge pellets in the lab-scale BFB. The experimental conditions are shown in Table 5.

For combustion experiments, two different techniques were used to measure the devolatilization times of single particles: the oxygen concentration profile in the exhaust gas (O_2) and Flame extinction time. Flame extinction time was the time from injection of the particle into the bed until the end of the visible volatile flame above the bed and measured using a stopwatch [12]. For the oxygen concentration profile method, the devolatilization times with pellet sizes were estimated by the degree of evolution of the consumption of the O_2 during combustion experiments. Attempts of using different percentages (75%, 80%, 85%, 90% and 95%) of the total consumption of the O_2 to defined end point of devolatilization were conducted.

3. Results and discussion

3.1. Devolatilization in nitrogen

3.1.1. Gas compositions of individual pellet pyrolysis

Under nitrogen atmosphere and bed temperature of 700 °C, the gas compositions of oil sludge pellet pyrolysis in the BFB reactor are shown in Fig. 2. The quantities of the evolved combustible gas obtained by integrating the area under the curves are shown in Fig. 3. Figs. 2 and 3 indicate that the major combustible gaseous products are CHs (Hydrocarbons), H_2 and CO. CHs is the largest fraction gaseous product in pyrolysis process, and this is different from the dominant gaseous product, carbon monoxide, from the pyrolysis of sewage sludge [17]. CHs are released significantly in the range of 30–80 s of residence time and attain a peak residence time of 47 s. More than 90% of CHs is released before 78 s of residence time, thereafter the release decay slowly till the end of experiment. H_2 and CO release have a similar behavior of CHs release but with relatively minor release intensity. The volume fractions of the three major combustible gas products from Fig. 3 are 56.4–66.6, 26.8–30 and 6.5–13.7 vol.%, respectively. The quantities of these products change with the pellet size, increasing the pellet size leads to a decrease in the fraction of CO and an increase in the fraction of CHs. This can be explained on the basis that heating rate can influence competitive reaction between carbon and hydrogen with oxygen, increasing heating rate is in favor of the reaction of carbon and oxygen. Obviously, the smaller pellet usually obtains a higher heating rate when it drops into a hot FB, resulting in a higher fraction evolution of CO for the smaller ones [19]. Generally, increasing the pellet size can also decrease the volume fraction of H_2. However, this kind of influence shows a decay tendency with the pellet diameter increase. This might result from the fact that H_2 formation is from the cracking reaction of petroleum hydrocarbons under high temperature condition (over 400 °C) [20,21]. As analysis above, smaller pellet usually obtains a higher heating rate after it drops into a hot FB, leading to a higher average pellet temperature than big one, and therefore increasing the volume fraction of H_2 evolved for cracking reaction shown in Eq. (2).

$$C_mH_{2m+2} \leftrightarrow C_mH_{2m} + H_2 \quad (2)$$

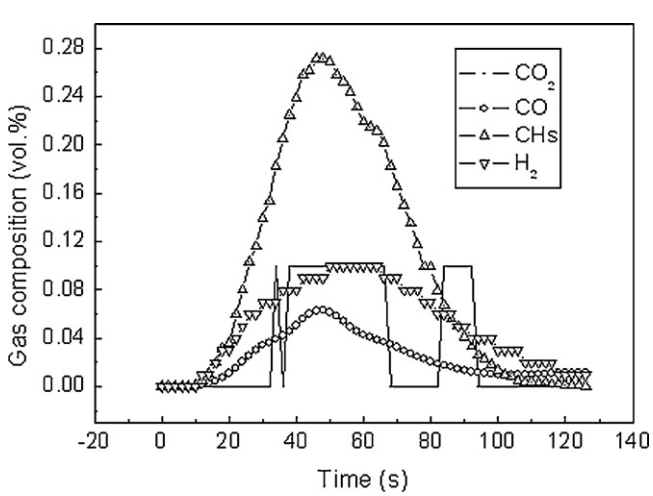

Fig. 2. Gas composition to time curves of the oil sludge pellet pyrolysis with initial diameter of 9.5 mm.

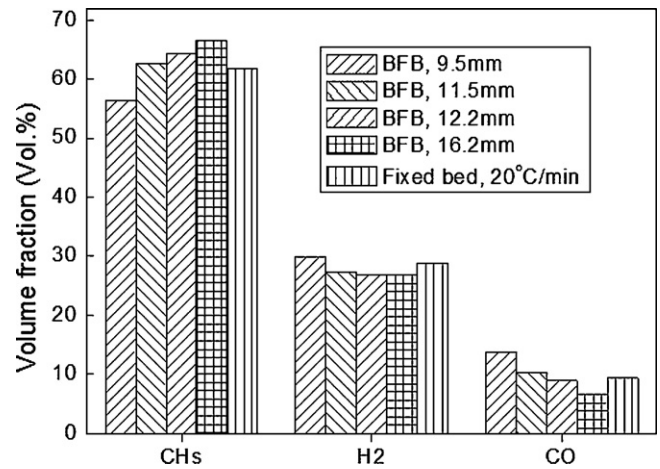

Fig. 3. Combustible gaseous products for the pyrolysis of oil sludge pellets with different diameters in the BFB and a pyrolysis in a fixed bed.

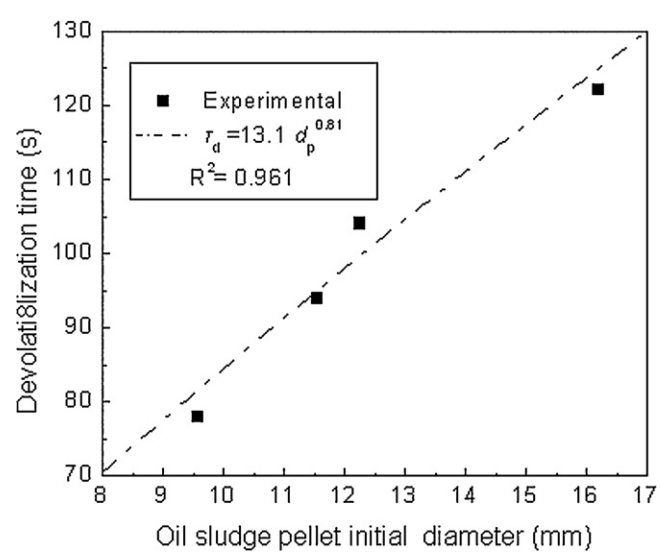

Fig. 4. Devolatilization time curve of pre-dried oil sludge pellet with different initial diameter.

Table 6
Correlations of the devolatilization time with fuel particle diameter in FBs by using various measurement techniques.

Fuel	Measurement techniques	Devolatilization time correlation parameters		Atmosphere
		A	*N*	
Oil sludge	Volatile evolution Present work	13.1	0.81	N_2
Bowmans coal	Temperature response [14]	8.96	0.99	N_2
Australian coal	Volatile evolution [13]	9.77	1.08	N_2
Australian coal	Volatile evolution [13]	4.61	1.48	N_2
Australian coal	Volatile evolution [13]	5.18	1.23	N_2
Indian coals	Mass profile [16]	0.74	2.0	Ar
Oil sludge	O_2 profile Present work	0.39	1.85	Air
Bowmans coal	Temperature response [14]	4.43	1.16	Air
Bowmans coal	Flame extinction time [14]	1.65	1.52	Air
Australian coal	Flame extinction time and CO_2 profile [12]	1.84	1.50	Air
Indian coals	Mass profile [16]	0.55	2.0	Air
Sewage sludge	Volatile evolution [17]	–	0.27	Air

For comparing the influence of heating process on gaseous products, the volume fraction of combustible gaseous products from a fixed bed pyrolysis during a heating process from room temperature to 700 °C at heating rate of 20 °C/min [22] also is listed in Fig. 3. It can be seen that the gaseous volume fractions from the fixed bed are similar to that from the BFB, indicating that heating progress does not remarkably influence the combustible gaseous products release of oil sludge.

3.1.2. Devolatilization time in nitrogen

The devolatilization times of oil sludge pellets in the BFB were determined by the degree of completion of the evolution of the CHs (95% of the evolution of the CHs). The experimental results showed that the devolatilization times range between 75 and 125 s for the pre-dried oil sludge pellets of 9–15 mm diameter.

Fig. 4 tells the relation of devolatilization time with initial pellet diameter. Devolatilization time (τ_d) was correlated with the pellet initial mass (d_p) by the power law correlation shown as follows.

$$\tau_d = 13.1 d_p^{0.81} \quad R^2 = 0.961 \tag{3}$$

Eq. (3) shows that the devolatilization time was nearly proportional to the particle initial diameter for the pre-dried oil sludge particles.

Various measurement techniques have been used to estimate the devolatilization time of fuel particles in fluidized-beds under an inert atmosphere. Table 6 shows the values of constant *A* and *N* of devolatilization time correlations for various fuels and measurement techniques in fluidized-beds. Good agreement of current volatile evolution data is obtained when compare with similar data reported by Stubington and Sumaryono [13] and temperature time data by Ross et al. [14], they measured the devolatilization of coal particles in FB conditions in nitrogen atmosphere. However, a poor agreement is observed when compare the present data to the data by Borah et al. [16], who defined devolatilization time as the point of intersection of the two linear portions of the mass versus time curve, and gave a apparently higher exponent *N* in inert atmosphere than other researchers' from Table 6. For oil sludge pellets, majority of volatiles release in heating process is related to the volatilization of hydrocarbons in oil sludge especially when particle temperature is below 400 °C [22]. The intensive devolatilization because of very high volatile contents in oil sludge (93 wt.% on free ash basis) results in a stream of low temperature volatiles from the interior of the particle to the outer surface which lower the surface temperature. Thus, it is expected that heat transfer to and within the particle are main rate controlling mechanism. From the exponent $N = 0.81$, the volatiles release for pre-dried oil sludge is assumed to proceed with a shrinking core of virgin oil sludge pellet surrounded by char and ash, which, because of its relatively high porosity, offers no resistance to the gases leaving the thin reaction zone, where sludge undergoes volatilization or thermal decomposition.

3.2. Devolatilization in air

3.2.1. Gas compositions of individual pellet combustion

Devolatilization experiments of batches of pre-dried oil sludge pellets of preset size and mass were carried out in the BFB in air atmosphere. The compositions of the flue gases, such as O_2, CO_2, CO, H_2, SO_2, CH_x and NO_x, were measured. The typical compositions to residence time curves are shown in Fig. 5. It can be seen from Fig. 5 that the devolatilization time is within 60 s for an oil sludge pellet with initial mass of 2.433 g (12.8 mm in diameter) at bed temperature of 700 °C. The high-level combustible gases in the gas are CO and H_2 with the maximum concentrations of 1600 and 400 ppm, respectively, at the minimum oxygen concentration of 17.3 vol.%, whereas the level of CHs, which is the largest fraction gaseous product in pyrolysis process, is less than 10 ppm, or essentially zero. Therefore, it is necessary to maintain a high temperature circumstance in freeboard to keep the components of CO and H_2 to a lower level. Fig. 5 shows that the emissions of SO_2 and NO_x corresponding to the minimum oxygen concentration of 17.3 vol.% are lower than 80 and 120 ppm, respectively. The low emission of SO_2 is attributed to the large amount of limestone ($CaCO_3$) contained in the oil sludge [22]. The low emission of NO_x might lay in the following facts: (1) nitrogen content in the oil sludge is far lower than conventional fuels (see Table 1); (2) fluidized bed as a low temperature combustion technology can inhibit the oxidation of the nitrogen of the combustion air to thermal NO_x.

3.2.2. Fragmentation

The behavior of oil sludge pellets in the BFB was observed visually during combustion experiments. Observation showed that the pellets were surrounded by bright yellow flame just after injection in the hot BFB from the feeding entrance located at the top of the fluidized bed furnace. Due to the density difference between the sludge pellets and the bed material (densities of oil sludge and bed material were 2200 and 2630 kg/m^3, respectively), the sludge pellets spent most of the time floating on the bed surface, and immersing occasionally. The flame was bright and continuous except the case of the pellet immersed in the bed. Primary fragmentation (a micro-explosive combustion phenomenon) of oil sludge pellets could be observed for some cases, especially for bigger pellets (>10 mm) at higher bed temperatures (>700 °C) during the BFB combustion. Due to the moisture content of the pre-dried oil sludge pellet is 0 wt.%, the primary fragmentation is mainly induced by the

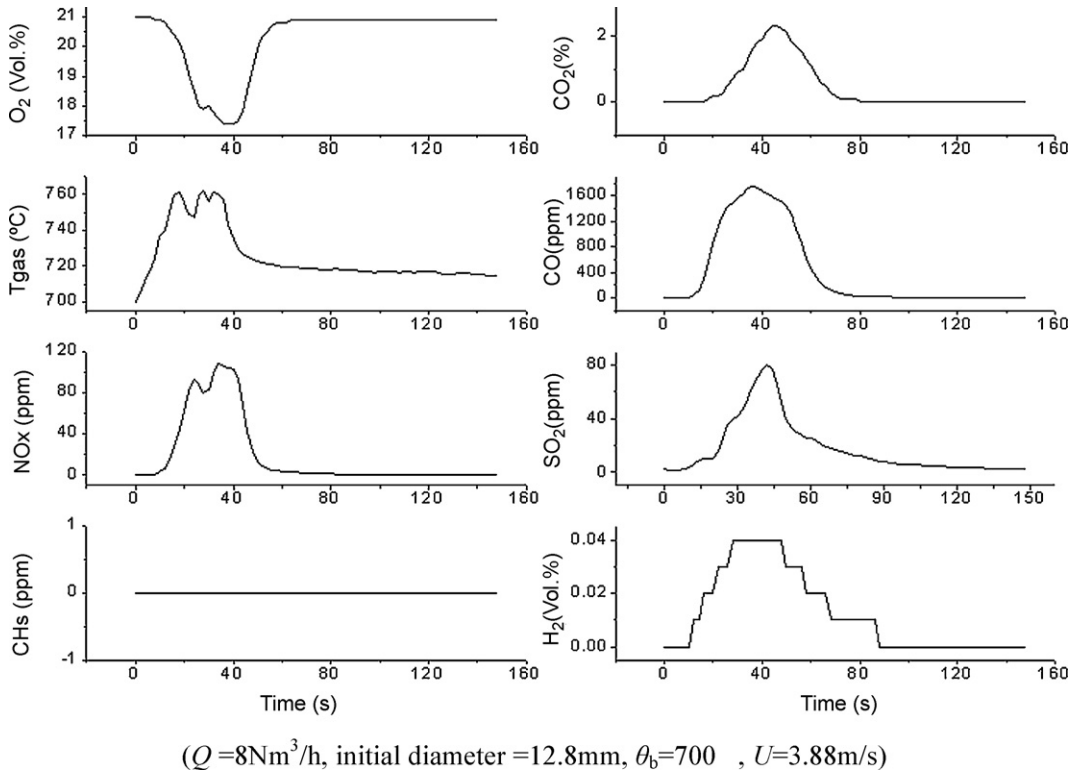

Fig. 5. Typical gas composition to residence time curves of oil sludge pellet combustion in the BFB.

fast volatiles release based on previous study [11]. A digital camera located at the sample entrance recorded the detail process of the primary fragmentation; some typical stages are shown in Fig. 6.

Primary fragmentation is important, not only for its effect on devolatilization time but also for its effect on particle size distribution and therefore burnout time for char combustion. Observation showed that the primary fragmentation occurred towards the end of combustion, broke the pellet into several smaller fragments, and remarkably reduced the devolatilization time of the pellet. After combustion experiments were completed, the size and contents of the bed materials were analyzed, the analysis showed that entire ash particles were entrained out of the fluidized bed furnace under the present experimental conditions. The fines captured by two stage separators were further sieved to determine the size distribution of the fine particles, indicating that the fly ash ranged from 40 to 450 μm, majority of the fine particles (93 wt.%) were in the range of 40–250 μm. Based on the above analysis, some general conclusions might be drawn. (1) Oil sludge having a high propensity of the primary fragmentation induced by devolatilization cause a drastic size reduction of ash particles under FB combustion condition. (2) Oil sludge ash is fragile, the forces, caused by the collision from the fiercely turbulent action of bed materials under FB combustion condition are large enough to fracture the oil sludge ash panicles into fines and then result in intense elutriation. (3) Adding inert bed material into the dense region is necessary to maintain mass balance in BFB combustion condition because no bottom ash was formed during the oil sludge pellet combustion in the BFB furnace.

3.2.3. Devolatilization time in air

The measurement of the devolatilization time was based on flame extinction and gas analysis for the fluidized bed combustion experiments. Flame extinction time was the time from injection of the particle into the bed until the end of the visible volatile flame above the bed and measured using a stopwatch [12]. For gas analysis method, the end point definition of the devolatilization time would be crucial to justice of measurement results due to the char combustion and fragmentation. Previous study by Stubington et al. [12] has based on CO_2 evolution profiles to determine the devolatilization time of coal particles during combustion experiments, a reasonable agreement for CO_2 evolution data with the flame distinction time method was obtained when the end point was defined as the first increase in slope after the maximum of the CO_2 versus time profile. However, for oil sludge, devolatilization time estimated by the time-resolved exhaust gas analysis need to be reconsidered. Firstly, the determination of end point based on the gas compositions profile might be more complex because only single stage could be observed for oil sludge combustion due to the very low fixed carbon contents in the sludge (6.83 wt.%, daf), no distinct char combustion stage could be observed. This is very different from coal particles FB combustion studied by Stubington et al. [12], who indicated a char combustion stage was formed after volatiles combustion. Secondly, the determination of start point by using CO_2 evolution profile would be delayed due to the very intensive CO release at the earlier stage from Fig. 6. Finally, the release of CO_2 from the decomposition of inorganic carbonate such as $CaCO_3$, $MgCO_3$ contained in the oil sludge would influence the CO_2 evolution profiles at high particle temperature condition [22]. Thus the devolatilization times with pellet sizes, in present paper, were estimated by the degree of evolution of the consumption of the O_2 during combustion experiments at the bed temperatures of 650–750 °C.

In order to determine a suitable end point definition of the devolatilization time during combustion experiments, attempts of using different percentages (75%, 80%, 85%, 90% and 95%) of the total consumption of the O_2 to defined end point of devolatilization were conducted at bed temperature of 750 °C. For comparison purpose, flame extinction time technique was also used to measure the devolatilization time for identical experiments. Fig. 7 illustrates the comparison of the devolatilization times determined by the degrees (from 75% to 95%) of evolution of the total consumption of the O_2

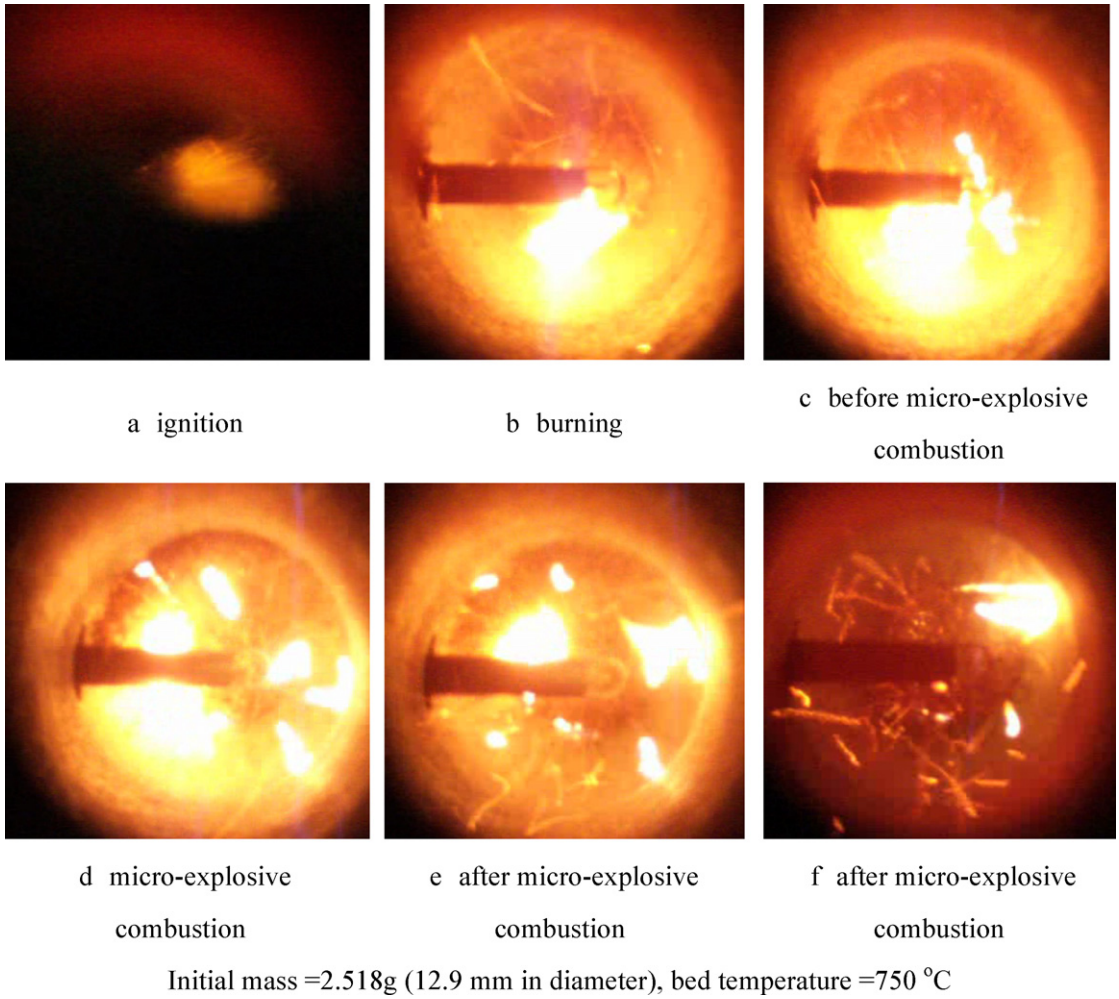

Fig. 6. Fragmentation process of a pre-dried oil sludge pellet in the hot BFB.

to the flame extinction time. The comparison with flame extinction time data shows that better agreement of the O_2 profiles data is obtained when the devolatilization time is defined as the 75% of the total consumption of the O_2 during the oil sludge pellet combustion experiments. The cases for the definition by over 75% of the total consumption of the O_2 result in a significantly longer estimate of devolatilization time especially for big pellets. Therefore, the devolatilization time defined as the time to 75% the final cumulative consumption of the O_2 was used for combustion experiments. Accordingly, the curves of devolatilization time versus time at bed temperatures of 650–750 °C are plotted in Fig. 8. It is can be seen from Fig. 8 that the devolatilization time is nearly an exponential increase with the pellet diameter. Generally, the devolatilization

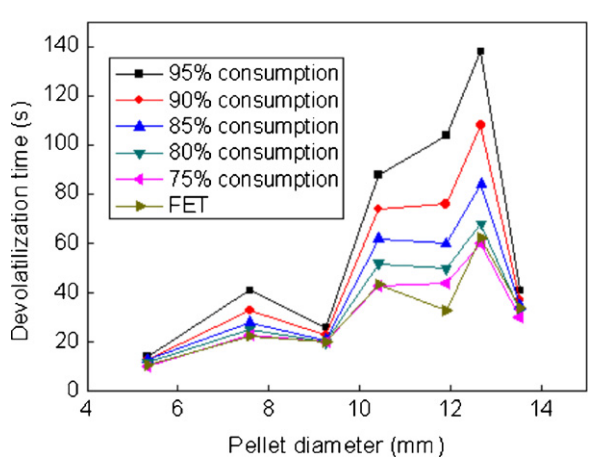

Fig. 7. Comparison of devolatilization time between the two methods.

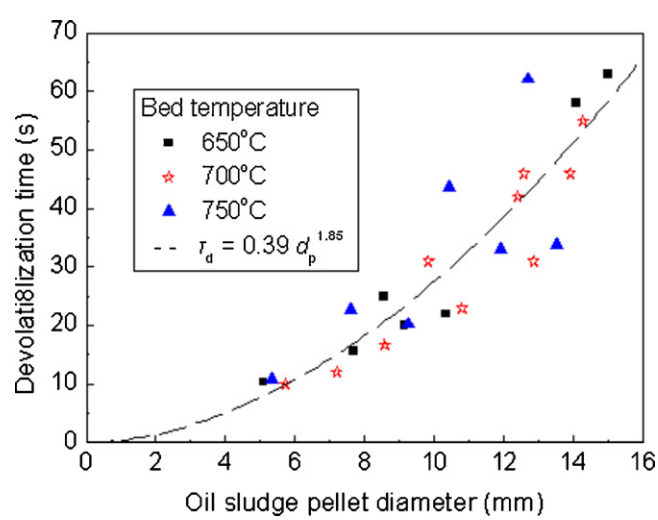

Fig. 8. Devolatilization time to pellet diameter curves at different bed temperatures under 8 Nm^3/h air flow rate.

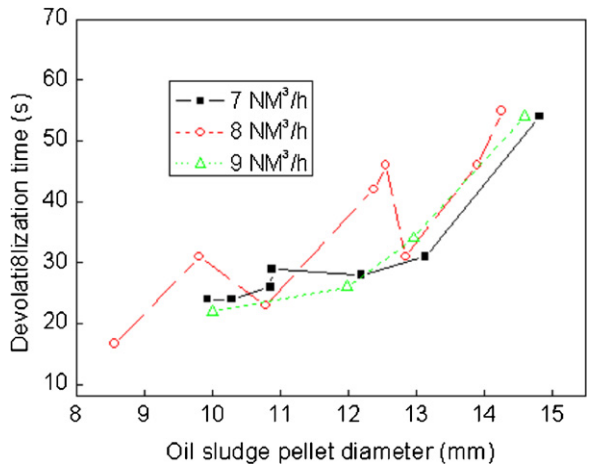

Fig. 9. Devolatilization time to pellet diameter curves at 700 °C bed temperature and different air flow rates.

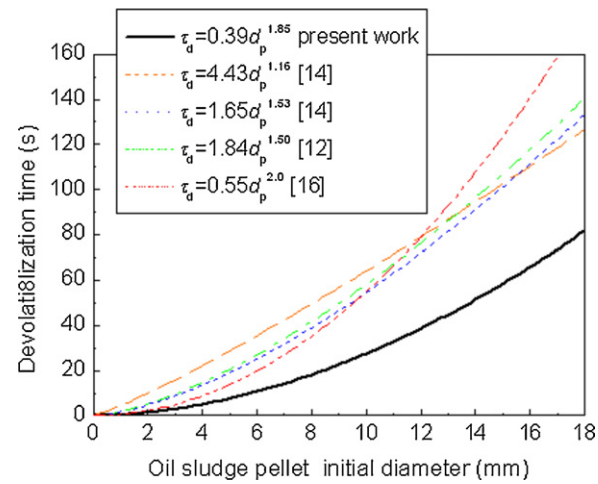

Fig. 10. Comparison of devolatilization time between the oil sludge and coals in fluidized-bed combustion conditions.

time increased with an increase of the pellet size under the BFB combustion condition. However, it is not always the case, the primary fragmentation (a micro-explosive combustion phenomenon) visually observed for bigger pellets (<10 mm) under high bed temperatures (>700 °C), distinctly decreased the devolatilization time as seen in Fig. 8.

The devolatilization times range from 10 to 70 s for pre-dried oil sludge pellets of 5–15 mm diameter in BFB combustion conditions, it were found to be about 50% shorter than in nitrogen for the same sized oil sludge pellet under the same bed temperature. This result is in agreement with Ross et al. [14], who indicated that the devolatilization times for coal particles in a nitrogen atmosphere were found to be 38% and 24% longer than in air, respectively. The decrease in devolatilization time with changing atmosphere from nitrogen to air has been attributed to the formation of the volatile diffusion flame around the fuel particle, which increases the particle heating rate, and therefore decreasing the devolatilization time [14].

The devolatilization times for oil sludge pellets can also be described using the power law relationship. Fitting Eq. (1) to the combustion experimental data, the values of the coefficient A and N were obtained; the corresponding correlation is listed as follows:

$$\tau_d = 0.39 d_p^{1.85} \quad (R^2 = 0.8) \tag{4}$$

From the exponent $N = 1.85$, it is expected that heat transfer to and through the oil sludge particle controls the rate of devolatilization for particle sizes relevant to fluidized bed combustion [13]. This is consistent with the fact that volatiles release in heating process is mainly related to the volatilization of hydrocarbons in oil sludge especially when particle temperature is below 400 °C [22]. The intensive devolatilization because of very high volatile contents in oil sludge (93 wt.% on free ash basis) results in a stream of low temperature volatiles from the interior of the particle to the outer surface which lower the surface temperature. Thus, heat transfer to and within the particle is the main rate controlling mechanism.

Various measurement techniques have been used to determine the devolatilization time of fuel particles in fluidized-bed combustion conditions. Table 6 also lists the values of constant A and N of devolatilization time correlations for various fuels and measurement techniques under FB combustion conditions. It can be seen from Table 6 that the exponent N varies from 1.16 to 2.0 for coal particles. The variability of N might be attributed to the differences in the definition of devolatilisation time (temperature response [14], flame extinction time [14], flame extinction time and CO_2 profile [12], mass profile [16]) and coal type. Obviously, the exponent N of coal particles is generally smaller than that of oil sludge. As far as volatile evolution definitions are concerned, relatively good agreement of current volatile evolution data is obtained when compare with similar data reported by Stubington et al. [12]. Fig. 9 shows the comparison of devolatilization time between the oil sludge pellet and coal particles in fluidized bed combustion conditions. It can be clearly seen that the devolatilization time of oil sludge pellet is much shorter than that of coal particle with the same size, this might lay in the following facts: Firstly, oil sludge pellet is a mixture of oil and solid, its inner structure is looser than that of coals. Therefore, the resistance of gas diffusivity within the oil sludge pellet is much lower than that of coal particle. Secondly, volatiles release of oil sludge is mainly related to the volatilization of hydrocarbons, especially when particle temperature is below 400 °C. The average activation energy in oil sludge pyrolysis is only 80 kJ/mol [22], being much lower that that of coals with an average activation energy of 100–200 kJ/mol depending on coal type. The value of activation energy reflects the difficulty in releasing volatiles, smaller value of activation energy means volatiles release being easier. Therefore, volatiles release from oil sludge pellet is intense than coals under the same heat transfer condition (both in fluidized bed condition).

It is also necessary to compare the present date with the date of sewage sludge because of their similar semisolid state at ambient temperature. Werther and Ogada [17] measured devolatilization times of about 50 s for pre-dried sewage sludge particles of diameter 4–20 mm, the corresponding values of exponential constant N was equal to 0.27. Distinct difference of exponential constant N between the two kinds of pre-dried sledges indicates different devolatilization mechanisms. The volatiles release of oil sludge is mainly related to the volatilization of hydrocarbons. This is very different from that of sewage sludge, whose volatiles release mainly resulted from thermal decomposition of carbonaceous substances, consisting of a series of complex chemical reactions, which leads to the decomposition, and breakage of the organic matter and the separation of different components into individual gases. From the exponential constant $N = 0.27$ for pre-dried sewage sludge, the devolatilization process might be mainly controlled by chemical reaction kinetics of pyrolysis.

3.2.4. *Influence of fluidization velocity on devolatilization*

The devolatilization of the pellets in air at the bed temperature of 700 °C under the air flow rates of 7, 8 and 9 Nm^3/h (corresponding fluidization velocities are 3.5, 4.0 and 4.5 m/s, respectively) were conducted, the effect of fluidization velocity on devolatilization time is shown in Fig. 10. It can be seen that the fluidization velocity does not play a noticeable role on devolatilization time of the oil

sludge pellet in air atmosphere. This is consistent with the study by Jia et al. [23], who undertook experiments on pyrolysis and combustion of several coals in FB reactor, and found that superficial gas velocity play a little role on release and burnout of volatiles.

4. Conclusions

Devolatilization of the individual pre-dried oil sludge pellet in a lab-scale bubbling fluidized bed was investigated in both nitrogen and air atmosphere. The volatiles release and combustion of oily sludge mainly occurred on the surface of the dense bed, primary fragmentation (a micro-explosive combustion phenomenon) was visually observed for bigger pellets (>10 mm) at high bed temperatures (>700 °C). The primary fragmentation occurred towards the end of combustion, and remarkably reduced the devolatilization time. The size analysis of bed materials and fly ash showed that entire ash particles were entrained or elutriated out of the fluidized bed furnace due to the fragile structure of ash particles.

The end point of devolatilization from O_2 evolution profiles for oil sludge pellet FB combustion must be carefully defined. When devolatilization time is defined as the 75% of the total consumption of the O_2, the measured O_2 evolution data agrees well with the flame extinction data. Both bed temperature and pellet size had a significant influence on devolatilization time, however, fluidization velocity did not play a noticeable role on devolatilization time. Correlations for the devolatilization time in nitrogen and air with particle size were developed. The devolatilization time to pellet diameter curve shows nearly a linear increase in nitrogen, whereas an exponential increase in air. The exponent $N = 1.85$ indicates that heat transfer to and through the oil sludge particle controls the rate of devolatilization for particle sizes relevant to fluidized bed combustion. The comparison indicates that the devolatilization time of oil sludge pellet is much shorter than that of coal particle with the same size because of loose structure and low activation energy in pyrolysis of oil sludge.

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