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Characteristics of oily sludge combustion in circulating fluidized beds

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ABSTRACT

Incineration of oily sludge in circulating fluidized beds may be an effective way for its management in some cases. The objective of the present paper is to investigate combustion characteristics of oily sludge, which would be helpful and useful for the design and simulation of a circulating fluidized bed.

Firstly, the pyrolysis and combustion of oily sludge were studied through some thermal analyses, which included the thermogravimetric (TG) analysis and the differential thermal analytical (DTA) analysis. It was found that the combustion of oily sludge might be the combustion of its pyrolysis products. Secondly, an experiment for measuring of main components of the volatile from oily sludge pyrolysis was carried out. Some mathematic correlations about the compositions of volatile from oily sludge devolatilization were achieved from the experimental results. Finally, the combustion characteristics of oily sludge was studied in a lab-scale circulating fluidized bed, which could obtain some information about the location of release and combustion of the volatiles.

1. Introduction

Vast amounts of oily sludge is generated during the crude oil exploitation and processing activities [1,2]. Oily sludge usually contains a considerable quantity of water, oil and solids, in which there are many of toxic, mutagenic and carcinogenic components [2–6]. Therefore, the release and treatment of oily sludge are strictly controlled, due to their adverse impact on human health and environment. For the treatment of oily sludge, incineration is generally acknowledged as the most efficient measure because of its usefulness for energy recovery [7].

On the other hand, for the incineration of typical low-quality sludge such as municipal solid waste [8] and oil shale [9], petroleum coke, sewage, coal watery rejects, peat, biomass residues, paper mill sludge [10] and so on, the circulating fluidized bed technology has been recommended, due to its fuel flexibility, high mixing efficiency, high combustion efficiency and low pollutant emissions [10–13]. Thus, it is feasible that the circulating fluidized bed technology is adopted to treat oily sludge.

Some papers [3,5,14–16] have been published about the pyrolysis and biodegradation of oil sludge. However, to date, few studies have been found considering the combustion characteristics of oily sludge. In order to simulate and calculate the flue components of oily sludge combustion and incinerate this oily sludge effectively in the circulating fluidized bed, we need know combustion characteristics of oily sludge. The so-called combustion characteristics of oily sludge in this work, which is also the objective of the present work, mainly refer to four aspects as follows:

(1) where the combustible products for the combustion of oily sludge come from;
(2) what main combustible products are from oily sludge;
(3) what mass distribution of the main combustible products;
(4) what location of release and combustion of the volatiles in the circulating fluidized bed.

2. Experimental

2.1. Samples

The oily sludge investigated in this study was obtained from Sheng Li oil field in China, whose proximate analysis, ultimate analysis and low heating value are given in Table 1. The elementary analysis indicates that oily sludge is characterized by very high yields of volatiles and very low fixed carbon. Therefore, special attention is required for the treatment of volatiles release and combustion during oily sludge combustion modeling.

The contents and group composition of chloroform extract on the oily sludge are shown in Table 2. Table 2 shows that the oily sludge contains 26.07 wt.% of chloroform extractable including bituminous (3.32%), satisfied hydrocarbons (11.80%), aromatichydrocarbons (5.44%) and non-hydrocarbons (5.51%). The use of residue after treatment depends on the heavy metal contents. The inorganic materials of the oily sludge were analyzed

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Table 1
Characteristics of oily sludge sample in this study.

Proximate analysis	
Moisture (as received, wt.%)	16.95
Ash (as received, wt.%)	51.99
Volatile (daf, wt.%)	93.17
Fixed carbon (daf, wt.%)	6.83
Ultimate analysis (as received)	
C (wt.%)	20.85
H (wt.%)	2.7
O (wt.%)	6.0
N (wt.%)	1.4
S (wt.%)	0.11
Low heating value (kJ/kg)	8530

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.

2.2. TG and DTA experiments

The sample, weighing approximately 10 mg, was placed in a platinum pan and heated in an inert atmosphere of nitrogen gas at a constant flow rate of 80 ml/min at a constant preset heating rate of 20 and 80 K/min from room temperature to 1073 K for pyrolysis. In the case of combustion test, an atmosphere of air at a constant flow rate of 80 ml/min was used as the carrier gas at a heating rate of 20 and 80 K/min. In these thermogravimetric experiments, a computerized TA instrument, model TGA 2050 thermogravimetric analyzer (TA Instruments Inc., USA), simultaneously recorded the thermographs.

In order to further investigate and differentiate the pyrolysis and combustion of oily sludge, the differential thermal analytical (DTA) experiment has been carried out by TA Instruments 1600 DTA (TA Instruments Inc., USA). At first, the oily sludge sample was dried previously for about nine hours at 378 K in a convection laboratory furnace with an inert atmosphere of nitrogen gas at a constant flow rate of 200 ml/min. TG analysis was carried out in a computerized TA instrument, model TGA 2050 thermogravimetric analyzer (TA Instruments Inc., USA), coupled with differential thermal analyzer (DTA). The sample, weighing approximately 10 mg, was placed in a platinum pan and heated in an inert atmosphere of nitrogen gas at a constant flow rate of 80 ml/min at a constant preset heating rate of 20 K/min from room temperature to 1073 K for pyrolysis. In the case of combustion test, an atmosphere of air at a constant flow rate of 80 ml/min was used as the carrier gas at the heating rate of 20 K/min.

2.3. Measurements of main components of the volatile from oily sludge

In order to obtain information about main components of the volatile devolatilisation from oily sludge, measurements of main components of the volatile devolatilisation were taken under given temperatures.

Firstly, the heating furnace in Fig. 1 was heated to the fixed temperature (923, 1023, 1123 and 1223 K). Secondly, the sample in a tube with a flow of nitrogen gas was inserted into the heating furnace immediately. And then the main components of the volatile devolatilisation were measured by a flue gas analyzer (MRU Vario Plus, Germany).

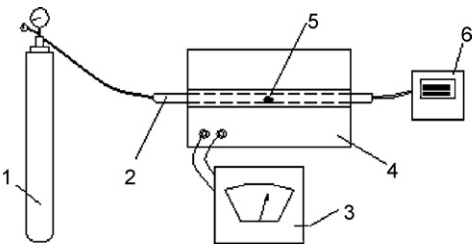

Fig. 1. Schematic diagram of experimental system for measurements of main components of the volatile from oily sludge.

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

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

2.4. Experiments in a lab-scale fluidized bed

2.4.1. Experimental apparatus

The incineration of oily sludge was conducted in a lab-scale fluidized bed shown in Fig. 2. The experimental apparatus of the lab-scale fluidized bed consists of fluidized bed main part, an air pre-heater, air supply system, compressor and so on. The inner diameter of the fluidized bed main part is 51 mm at the bottom and a height of 220 mm. At a height of 300 mm above the distributor plate, the freeboard of the FBC is enlarged to 82 mm diameter. This expanded section is 410 mm long. The air preheated is injected through a porous plate type distributor with 200 holes of 25.4 mm in length. The required combustion temperature is maintained through electrical heating of the walls of the combustor. The outer wall of the combustor is surrounded with ceramic wool to reduce heat loss. The bed material is quartz sand of Sauter diameter 0.55 mm, minimum fluidization velocity 0.18 ms^{-1} and density 2650 $kg\,m^{-3}$. The concentrations of flue gas species (O_2, C_xH_y, H_2, CO and CO_2) were measured with a flue gas analyzer (MRU Vario Plus, Germany).

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

Organic materials in oily 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

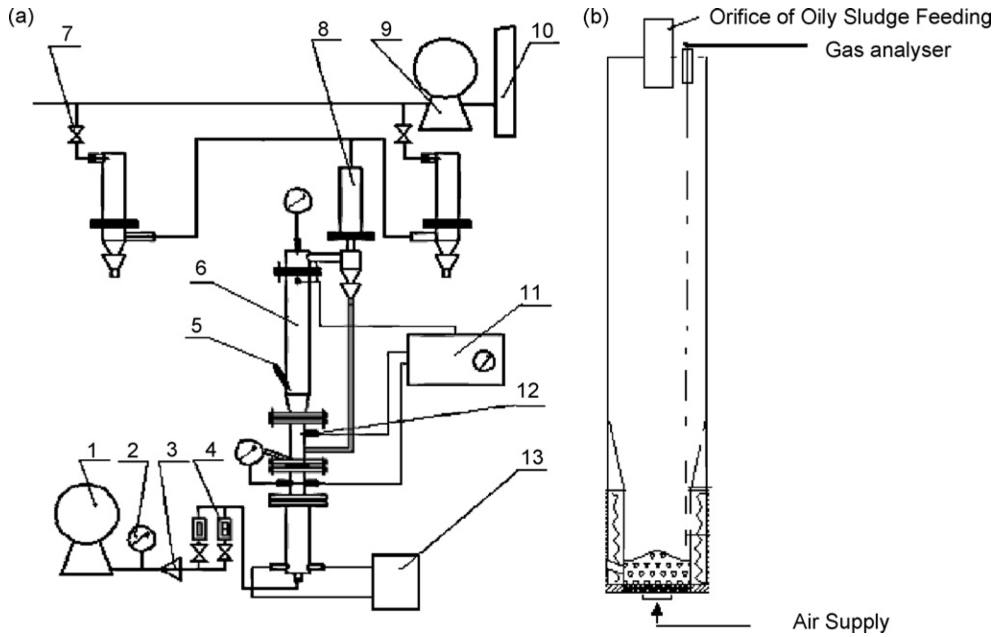

Fig. 2. Schematic diagram of experimental system. (a) The diagram of the lab-scale fluidized bed. (b) The sampling location in the fluidized bed main part.

2.4.2. Continuous combustion of oily sludge

While the bed temperature was heated up to a preset operational temperature by pre-heated air passing through the bed, the oily sludge was fed through the fuel injection port located on the top of the combustor, and the measurement instruments were operated. Under stationary combustion conditions, the oily sludge feed was cut off and the concentrations of O_2, C_xH_y, H_2, CO and CO_2 were continuously recorded until the burnout of the fed oily sludge.

3. Results and discussion

3.1. Pyrolysis and combustion of oily sludge

The mass loss (TG) carried out at a heating rate of 10 and 80 K/min in an inert atmosphere (pyrolysis) and in an oxidative atmosphere (combustion) were obtained. Fig. 3 shows these variations for pyrolysis and combustion of oily sludge at various heating rates.

In Fig. 3, the TG profiles at two different heating rates show that initially there is a large loss of moisture from about 290 to 380 K, which contributes about 20% of the total mass loss. Above 380 K, the degradation rates are comparatively slow. However, at temperatures above about 550 K very rapid degradation of the oily sludge is observed until about 770 K. In the temperature range 380–770 K, the most abundant of volatile matter of oily sludge might be released. By raising the temperature, from 770 to 940 K, the TG data is independent of the temperature. The mass loss at higher temperature (>940 K) is also observed probably as a consequence of the decomposition of the inorganic matter such as calcium carbonate.

On the other hand, some differences could be shown in Fig. 3 when comparing the combustion profiles with the corresponding pyrolysis profiles. The oily sludge at the heating rate of 10 K/min has a combustion profile that is close to the corresponding pyrolysis profile in the 380–550 K temperature range and then shows a strong decay at 550–700 K. However, the oily sludge at the heating rate of 80 K/min has a combustion profile under the corresponding pyrolytic one in the 380–550 K temperature range. This phenomenon indicates that the higher heating rate seems to accelerate the volatile decomposition rate in comparison with the

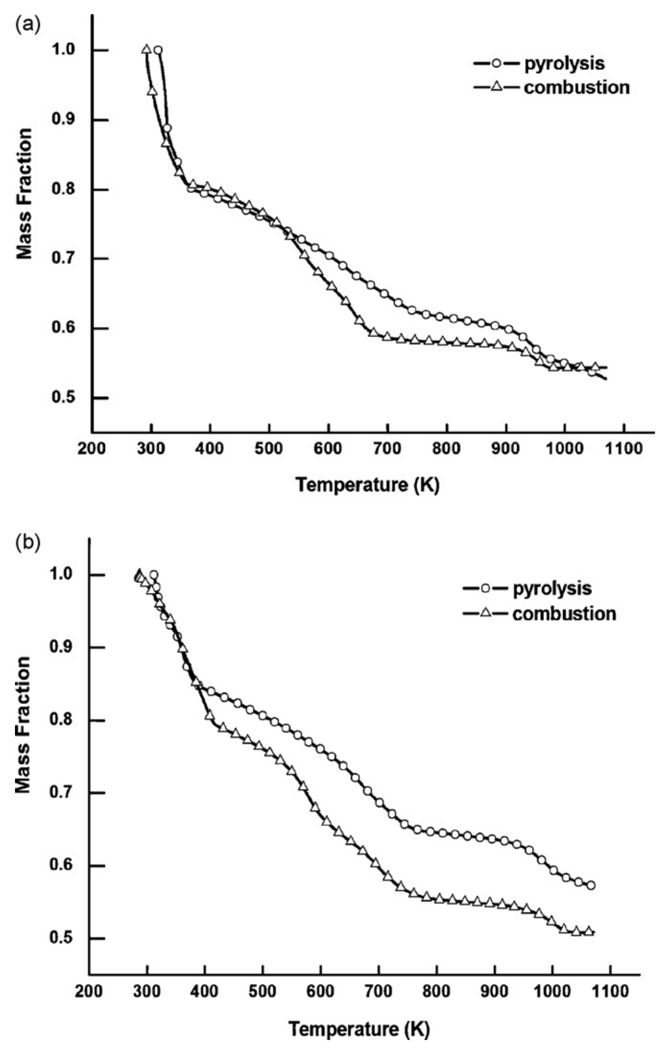

Fig. 3. Pyrolysis and combustion TG thermal analysis profile for oily sludge. (a) At a heating rate of 10 K/min. (b) At a heating rate of 80 K/min.

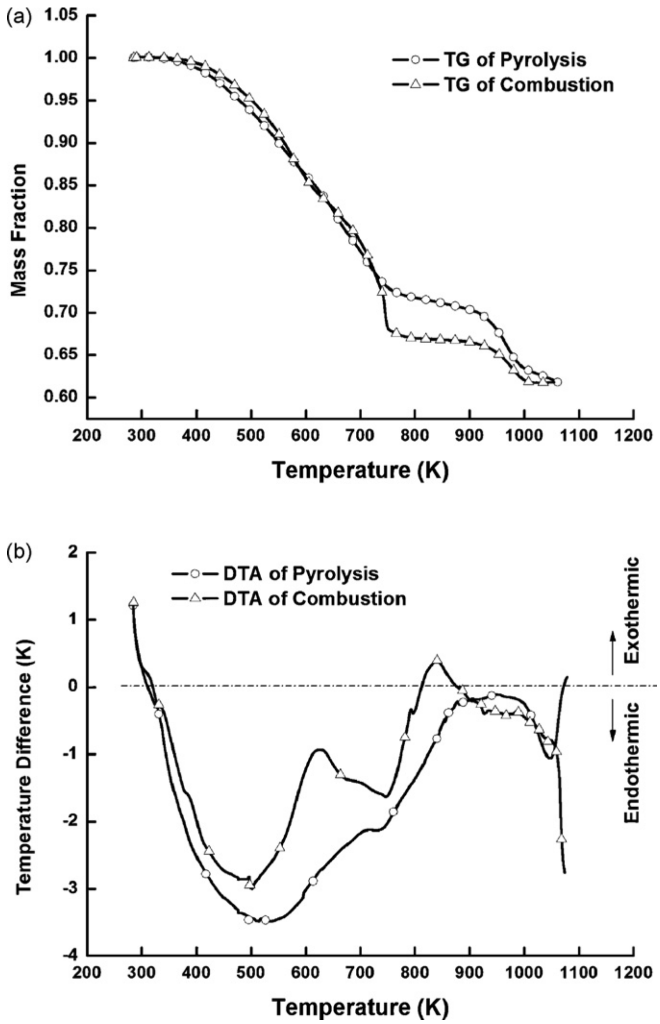

Fig. 4. The thermal analysis profiles of the pyrolysis and combustion of dried oily sludge samples at the heating rate of 20 K/min. (a) The thermogravimetric (TG). (b) The differential thermal analytical (DTA).

pyrolysis. However, despite the different heating rates, the combustion profile is always under the corresponding pyrolysis profile from 380 to 920 K. This behavior can be due to the combustion of the volatile released from the oily sludge sample, which could result in high release of energy as a consequence of some oxidation reactions accompanied in the combustion of oily sludge and then hasten the mass loss.

The thermogravimetric (TG) and the differential thermal analytical profiles of the pyrolysis and combustion of dried oily sludge samples at the heating rate of 20 K/min are shown in Fig. 4. From this figure, TG profile of combustion is close to the corresponding pyrolysis profile under about 550 K, and a mass loss is observed with a big endothermic peak in the DTA profiles for both pyrolysis and combustion. This might be due to the decomposition and devolatilization of a great deal of light hydrocarbons products with the lower boiling points in the oily sludge. At approximately 750 K, the second endothermic peak are observed in both pyrolysis and combustion DTA profiles. This absorption of heat might be caused by the decomposition of the more complex organic structures. In the DTA profile of combustion at around 840 K (Fig. 4b), an exothermic peak can be observed with yielding the high release of energy. This behavior can be attributed to the combustion of the volatile released from the oily sludge sample. At the same time, a rapid mass loss is observed from the TG profile of combustion (Fig. 4a). The third endothermic peak in both pyrolysis and combustion DTA profiles is observed, which might be as a consequence of the decomposition of the inorganic matter.

From above thermal analyses, we could find that the combustion of oily sludge might take place after its pyrolysis. In other words, the combustion of oily sludge might be the combustion of the products of its pyrolysis.

3.2. Empirical correlations of volatiles from the oily sludge

For the convenience of engineering computation, the volatiles generated from the oily sludge during its devolatilisation are considered as a mixture of C_xH_y, H_2, CO and CO_2 in this work. According to above thermal analyses, the combustion of oily sludge might be the combustion of the products of its pyrolysis. Hence, it is necessary to know the quantity of each gas ingredient in the volatiles at every given operational conditions, which could be helpful for simulation and design of the combustion of oily sludge in the fluidized bed. Since it is generally considered that the bed temperature has enormous influence on the quantity of the total volatiles release, some experiments were carried out to determine the quantity of volatiles release from the oily sludge at different bed temperatures [17]. In those experiments, the sample in a tube with a flow of nitrogen gas was taken into the heating furnace at a preset operational temperature in Fig. 1 described above. Time-resolved concentrations of C_xH_y, H_2, CO and CO_2 from volatiles release were continuously recorded until decayed to zero by a flue gas analyzer. The quantity of each gas ingredient was obtained by integrating the area under its decay curve at different bed temperatures. The results of the volume distribution of each gas ingredient (C_xH_y, H_2, CO and CO_2) and the volatile mass fraction in oily sludge at different temperature (923, 1023, 1123 and 1223 K) were illustrated in Fig. 5.

Through dealing with experimental results, the following correlations were achieved:

$$\begin{aligned} [C_xH_y] &= 131.778 - 0.297T + 1.75 \times 10^{-4}T^2 \\ [H_2] &= -454.555 + 0.923T - 4.25 \times 10^{-4}T^2 \\ [CO_2] &= 998.382 - 1.729T + 7.5 \times 10^{-4}T^2 \\ [CO] &= -607.544 + 1.16T - 5.25 \times 10^{-4}T^2 \end{aligned} \quad (1)$$

where $[C_xH_y]$, $[H_2]$, $[CO_2]$ and [CO] are the volume percentages of C_xH_y, H_2, CO and CO_2 in the volatiles, respectively; T is the bed temperature in K. The volatile yield from the oily sludge at different temperatures is estimated by the following empirical correlation:

$$[V] = (0.71988 - 7.604 \times 10^{-4}T + 4.0 \times 10^{-7}T^2)\text{VM} \quad (2)$$

where VM is the volatile mass fraction in oily sludge.

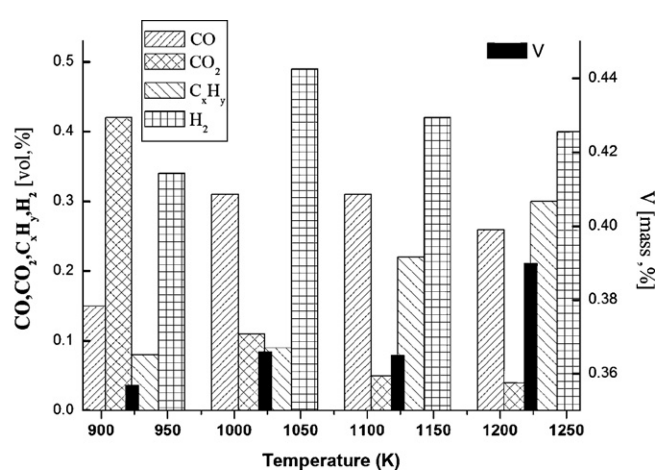

Fig. 5. The volume distribution of components of the volatile devolatilisation and the volatile mass fraction of oily sludge at different temperature (923, 1023, 1123 and 1223 K).

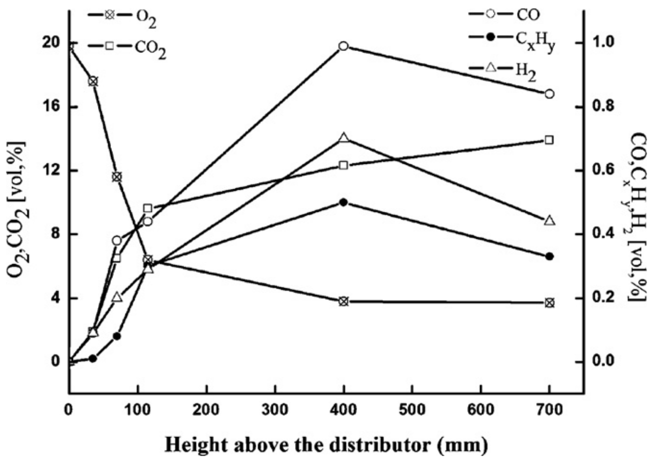

Fig. 6. Axial profiles of O_2, C_xH_y, H_2, CO_2 and CO (the volume flow of fluidized gas is 9 N m^3/h).

3.3. Combustion of oily sludge in a lab-scale fluidized bed

For the sake of rational design of one circulating fluidized bed for the incineration of oily sludge, the information about the location of release and combustion of the volatiles in the circulating fluidized bed is particularly important. Therefore, in order to analyze the location of the release and combustion of the volatiles of oily sludge, measurements of axial profiles of O_2, C_xH_y, H_2, CO and CO_2 were taken under steady-state operating conditions in the lab-scale fluidized bed (Fig. 2) mentioned above.

Fig. 6 shows the axial profiles of O_2, C_xH_y, H_2, CO and CO_2. The oxygen concentration decreases rapidly from about 20 vol.% on the surface of the distributor plate to about 6 vol.% near the surface of the dense region (Generally, the fluidized bed could be divided into the dense region in the bottom of bed and the dilute region in the upper of bed according to the solids concentration in the bed. The dense region refers to the zone with the relatively high solids concentration and the dilute region refers to the zone with the lower solids concentration [18]. In this work, the dense region is from the surface of the distributor plate to about 110 mm above the distributor plate), whereas the CO_2 concentration rises from 0 to about 9 vol.%. The profiles of O_2 and CO_2 in the dense region indicate that a strong oxidation takes place in the dense region. Because of high volatile matter and very low fixed carbon in the oily sludge, it can be assumed that this rapid consumption of the O_2 is due to the combustion of the volatiles in the dense region. However, in the dilute region, the oxygen concentration decreases slowly compared with that in the dense region. Similarly, the CO_2 concentration increases slowly in the dilute region. This indicates that there are comparatively weak oxidation reactions in the dilute region.

On the other hand, the concentration profiles of CO, C_xH_y and H_2, as the main combustible components of volatile in the oily sludge, have some particular features. Near the surface of the distributor plate, the volume contents of CO, C_xH_y and H_2 are close to zero seen in Fig. 6. This behavior may be owing to the rise of volatiles from oily sludge due to feeding air through the gas distributor. And then, the CO, C_xH_y and H_2 concentrations increase rapidly from 0 to the peaks at 400 mm above the distributor plate in the dilute region. Above the 400 mm from the distributor plate, the concentrations of CO, C_xH_y and H_2 decrease in the upper section of dilute region.

Therefore, we could conclude that the location of the release and combustion of the volatiles of oily sludge should take place not only in the dense region but also in the dilute region.

4. Conclusions

In present work, some experiments were performed in order to obtain some information about combustion characteristics of oily sludge in fluidized beds. Firstly, through TG and DTA experiments of oily sludge including its pyrolysis and combustion, it was found that the combustion of oily sludge may be the combustion of the products of its pyrolysis. Secondly, some mathematic correlations to assess the quantity of gas compositions in the volatiles from oily sludge were achieved. Finally, the combustion experiments of oily sludge were carried out in a lab-scale circulating fluidized bed. It was found that the release and combustion of volatiles from oily sludge took place not only in the dense region but also in the dilute region.

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