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## Thermogravimetric study on the Co-combustion characteristics of oily sludge with plant biomass



Shuanghui Deng<sup>a</sup>, Xuebin Wang<sup>a</sup>, Houzhang Tan<sup>a,\*</sup>, Hrvoje Mikulčić<sup>b</sup>, Fuxin Yang<sup>a</sup>, Zhifeng Li<sup>a</sup>, Neven Duić<sup>b</sup>

<sup>a</sup> MOE Key Laboratory of Thermo-Fluid Science and Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, China <sup>b</sup> Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb, 10000 Zagreb, Croatia

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#### ABSTRACT

Thermal utilization of oily sludge has attracted increased attention. This work studies the combustion characteristics of oily sludge, and its interaction with biomass as well as the reaction heat during the drying and combustion processes of oily sludge. All the experiments were performed by thermogravimetry. Results showed that the co-combustion process of oily sludge with biomass could be divided into three stages with the increase of the temperature. Different interactions between components of oily sludge and biomass existed at different temperatures. At low temperatures (280–390 °C) the interaction between these two fuels slowed down the combustion process of the mixtures, however, it accelerated the combustion process at high temperatures (390–620 °C). The caloric requirement curves of oily sludge with various water contents were obtained by DSC (differential scanning calorimetry) curves. The reaction heat of oily sludge or biomass combustion was also presented. The results obtained can improve the understanding of oily sludge during the combustion process and consequently can be used to develop more efficient sludge combustion equipment.

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#### 1. Introduction

It is of great interest to gain energy from solid waste in order to reduce its landfilling and decrease the consumption of fossil fuels. Oily sludge is a by-product of oil refineries and considered as a solid waste. In the petroleum industry, oily sludge is generated during crude oil exploitation and processing activities [1]. Oily sludge is primarily composed of large quantities of water, various petroleum hydrocarbons, heavy metals and solid particles [2]. Due to the increasing of oilfields worldwide, the production of oily sludge is growing. In China, approximately 3 million tons of oily sludge is produced annually in petrochemical industry [3]. Since it can be used as an energy resource, its thermal utilization has attracted increasing attention. Oily sludge without proper pretreatment not only endangers the environment, but also wastes available resources. Many conventional methods were used to treat the oily sludge, such as farmland application and sludge disposal in landfills and oceans. However, because they can either cause

\* Corresponding author. *E-mail address:* tanhz@mail.xjtu.edu.cn (H. Tan). serious pollution accidents or need high treatment costs, they are not environmentally friendly or cost-effective. Development green processing measures for oily sludge is essential for sustainability and environmental protection. Various thermal processes, e.g. pyrolysis, gasification, combustion, melting or vitrification, have been proposed for treating oily sludge, since they can destroy the sludge organic fractions and convert the sludge inorganic fractions into stable ash or slag; the thermal processes are considered as the promising methods for the use of oily sludge [4]. Using these thermal processes, oily sludge can either be advantageously reused, or harmlessly disposed at a landfill. To meet the increasingly stringent standards, it is necessary to study the stored energy in sludge and minimize environmental impacts [5].

Combustion is a set of complex exothermic chemical reaction, where the fuel oxidization will not only release the heat but also produce new chemical species including different gas, liquid and solid products [6]. The yield and composition of the products are affected by a range of combustion parameters (i.e. the fuel type, particle size, reaction system, reaction temperature, reaction time and heating rate). The combustion of oily sludge can reduce the space needed for its disposal, decomposing harmful poisonous substance and recovering energy. Due to the high moisture content,

Samples	Ultimate analysis/wt.%					Proximate analysis/wt.%				$LHV/MJkg^{-1}$	
	C <sub>ad</sub>	H <sub>ad</sub>	O <sub>ad</sub>	N <sub>ad</sub>	S <sub>ad</sub>	M <sub>ad</sub> <sup>a</sup>	V <sub>ad</sub> <sup>b</sup>	FC <sub>ad</sub> <sup>c</sup>	A <sub>ad</sub> <sup>d</sup>	$Q_{net,ad}^{e}$	
Oily sludge	40.81	4.60	20.32	5.97	1.05	6.28	60.05	12.69	20.98	17.01	
Wood	44.75	4.98	39.85	0.12	0.01	9.87	76.77	12.94	0.42	17.40	

#### Ultimate and proximate analysis of two different samples.

<sup>a</sup> Moisture as air dried basis.

<sup>b</sup> Volatile matter as air dried basis.

<sup>c</sup> Fixed carbon as air dried basis.

<sup>d</sup> Ash as air dried basis.

<sup>e</sup> Low heating value.

dewatering and drying are the prerequisites for an efficient combustion processing of oily sludge [7]. Based on its components, combustion of oily sludge is regarded as a potential way for solid waste utilization. Some researchers [8-10] reported that the combustion of sewage sludge with other fuels could be significantly improved and better than using sewage sludge as a single fuel. The co-combustion of sewage sludge mixed with different fuels, such as biomass and coal, not only promotes the combustion characteristic of sludge but also improves the environmental impact and creates additional economic value. Biomass has a higher combustion rate than coal, resulting in faster expansion of ignition flame. Compared to coal combustion, biomass combustion has a number of other advantages such as its low ash content, and low S and N content that results in low NOx and SO<sub>2</sub> emissions as well as its neutrality on CO<sub>2</sub> emissions during its life cycle [11]. Based on the advantages, biomass is regarded as a potential feedstock for thermal conversion.

The literature is rich in resources regarding the disposal of oily sludge; however the research about the combustion characteristics of oily sludge has been rarely reported. The co-combustion of oily sludge with biomass and their interaction have not been also extensively studied. Therefore, further research is necessary to study the combustion characteristics and interactions between oily sludge and biomass. Moreover, He et al. investigated the heat of pyrolysis and combustion of biomass over the integral of differential scanning calorimetry (DSC) curves [12]. To our knowledge, this research method is not used in the drying and combustion processes of oily sludge. The methods of calculating reaction heat for the drying and combustion processes of oily sludge by DSC curves have been not reported. Reaction heat of oily sludge combustion will be discussed in this work.

This work studies the combustion behavior of oily sludge and the co-combustion characteristics of oily sludge with biomass. Moreover, the calorific value was determined by DSC curves during sludge drying and combustion processes. The experimental results provide reference data for the use of new heat sources, such as boiler flue gas and metallurgy flue gas, as drying medium in order to commercialize drying and combustion of oily sludge.

#### 2. Materials and methods

#### 2.1. Sample preparation

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Oily sludge used in this work was obtained from Sinopec Luoyang Company in Luoyang city Henan Province, China. Sinopec Luoyang Company applies the two-stage aerobic biological treat-

Table 2	
Ash composition of the two tested materials.	

ment to treat wastewater. Oily sludge is produced by biological treatment of wastewater. After the biological treatment the flocculation is employed to obtain oily sludge. Total discharge of wastewater includes industrial and living wastewater. Large amounts of aerobic bacteria are used to treat wastewater. In addition, living wastewater contains a large amount of proteins and fats. After the second-stage sedimentation pool, the compositions of oily sludge mainly contain the products of microbial residues decomposition. These products contain proteins, fats and a small quantity of untreated oils. Wood was taken as the representative material of plant biomass. The wood material was obtained from a wood factory around Xi'an in Shaanxi Province, Western China. The release of the volatile components of oily sludge started at a relatively high temperature and it generally occurred in the temperature range of 200–650 °C [13]. Initial oily sludge was dried in the oven at 105 °C until its mass did not change [14]. The oily sludge obtained by this process refers to dried oily sludge in this work. After milling and sieving into particles of 50–200 µm in diameter, the dried oily sludge and wood were dried in the oven at 105 °C for 24 h. The ultimate and proximate analyses of two different samples are shown in Table 1, while Table 2 presents ash composition of the two tested materials in weight. Oily sludge samples with different water contents (20%, 40%, 60% and 90% for initial oily sludge) were obtained under different drying time at 105 °C from a constant temperature oven. Dried oily sludge and wood were mixed together, with wood weight percentages of 20%, 40% and 60%.

#### 2.2. Combustion experiments

Thermogravimetric analysis was performed in a STA-409PC thermal analyzer (NETZSCH, German), and its temperature ranges from 30 °C to 900 °C, with the heating rates of 20 °C/min and weight precision of 0.001 mg. Prior to thermogravimetric analysis, the thermogravimetry baseline was adopted to reduce measurement errors after sample insertion. It was corrected by subtraction of predetermined baselines determined under identical conditions except for the absence of a sample. In the thermal analyzer system, each sample was heated in a micro-furnace enclosed by a cooling jacket, and water was used as the cooling agent. The sample temperature was measured with a type S (Pt-Rh/Pt) thermocouple set under the crucible ( $Al_2O_3$ ). Sample ( $10 \pm 0.01$  mg) was loaded into an Al<sub>2</sub>O<sub>3</sub> crucible for each run. In the experiments, combustion of the samples was carried out over a temperature range of 30–900 °C, with a heating rate of 20 °C/min, and the total carrier gas (20/80 in O<sub>2</sub>/N<sub>2</sub>) flow were constant as 100 mL/min. Tempera-

Ash samples	Ash composition/wt.%									
	SiO <sub>2</sub>	CaO	K <sub>2</sub> O	KCl	$Al_2O_3$	MgO	$P_2O_5$	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	SO <sub>3</sub>
Oily sludge Wood	4.29 23.91	3.82 18.2	0.56 3.99	0.89 0.39	2.47 9.32	0.63 7.70	3.76 1.11	2.83 19.3	1.27 1.92	6.53 6.19

Table 1

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