



Research article

Co-pyrolysis of oily sludge and rice husk for improving pyrolysis oil quality

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ABSTRACT

Co-pyrolysis of oily sludge and rice husk was conducted in a fixed-bed reactor to investigate the effects of interactions on the products and improve the quality of the pyrolysis oil. The synergy can be attributed to the catalytic effects of ash and alkali metals derived from biomass. SARA results showed that synergy enhanced the quality of oil product by promoting the content of saturates and aromatics and reducing heavy fractions. Gas chromatography/mass spectrometry results showed that the interaction increased the concentration of chain hydrocarbons and significantly reduced the content of oxygenated compounds by 46–93%. The gas yield was improved due to the promotion of secondary reactions and more H₂, CO and C₁–C₂ hydrocarbons were generated. Additionally, though the emission of H₂S was restrained, the distribution of sulfur in oil and gas phases was promoted.

1. Introduction

Oily sludge is a waste accumulated during the processes of crude oil exploitation, storage, transportation, and refining [1]. Generally, oily sludge is a complex emulsion of water, heavy oil and solid particles [2]. Oily sludge has already been classified as a hazardous waste in many countries for its high content of toxic petroleum hydrocarbons, and inappropriate disposal may lead to severe environmental pollutions [3]. Traditional methods such as incineration and landfilling may cause secondary pollution and a waste of petroleum resource [4]. In recent years, widespread attention has been attracted to the oil recovery from this waste, and many methods have been developed, such as solvent extraction [5], centrifugation [6], pyrolysis [7], etc. Pyrolysis is the most concerned method due to its high energy recovery potential and low pollutants emission [8]. It is reported that the pyrolysis products of oily sludge will be influenced by the heating rate, the temperature, the oxygen content and the catalysts [9,10]. Gong et al. [11] found that the cracking of heavy fractions was more pronounced at high heating rates during the pyrolysis of oilfield sludge, thus the gas yield was increased while the oil and char yields were decreased. Schmidt et al. [12] investigated the products distribution from pyrolysis of tank cleaning oily sludge between 460 °C and 650 °C, and an oil yield of 70–84% was achieved. However, the oil product obtained through pyrolysis is still poor due to the high fraction of heavy components [9].

In addition to oily sludge, pyrolysis is also widely used for producing oil from various biomass streams, such as rice husk [13], cotton stalk [14], etc. However, due to the high O/C molar ratio in biomass,

the derived bio-oil is composed of a complex mixture of oxygenated compounds and is unstable for chemical utilization [15]. Therefore, it is of great importance to reduce the content of oxygenated compounds and increase the fraction of hydrocarbons.

Co-pyrolysis is considered as a simple and effective way to improve the quantity and quality of pyrolysis products [16]. Several studies have been conducted to investigate the co-pyrolysis characteristics of biomass with other organic wastes, such as municipal sewage sludge, plastics, and agricultural wastes [17]. Zhang et al. [18] found that the addition of plastic in the pyrolysis of sawdust can decrease the activation energy. Wang et al. [19] found that the synergetic effect between sewage sludge and wheat straw resulted in an increase in gas and liquid yield but a decrease in char yield, and the strongest interaction appeared at the biomass proportion of 60 wt%. Zhang et al. [20] also observed an increase in gas yield during co-pyrolysis of sewage sludge and rice husk, and the syngas content and gas lower heating value were significantly improved. Zhang et al. [21] revealed that the optimum temperature for synergetic effects in the co-pyrolysis of straw and lignite was 600 °C at which enough free radicals and hydrogen-donors were generated. Martínez et al. [22] obtained an oil product with higher stability from co-pyrolysis of pine woodchips and waste tyre in terms of lower oxygen content and higher calorific value.

However, limited research has been conducted on the co-pyrolysis of oily sludge and biomass. Generally, biomass and oily sludge are different in chemical and physical properties such as ash content, volatile matter and oxygen content, which can result in a synergetic interaction during co-pyrolysis [23]. Thus in this study, the co-pyrolysis

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Table 1
Primary components of oily sludge and rice husk.

Sample	Proximate analysis (wt%, ad ^a)				LHV ^f (MJ kg ⁻¹)	Ultimate analysis (wt%, ad)				
	M ^b	V ^c	A ^d	FC ^e		C	H	O	N	S
OS	3.1	88.5	–	8.4	43.1	81.2	9.2	4.1	0.4	2.0
RH	12.3	61.0	12.0	14.7	15.2	38.8	4.9	31.3	0.6	0.1

Sample	Alkali metal (mg g ⁻¹)		
	Potassium	Calcium	Magnesium
OS	–	0.28	0.005
RH	6.36	1.59	0.48

Sample	Components (wt%)			SARA analysis of oil (wt%)			
	Oil	Water	Solid	Saturates	Aromatics	Resins	Asphaltenes
OS	92.0	3.1	4.9	25.9	38.4	24.5	11.2

^a ad: air dry basis.

^b M: moisture.

^c V: volatile.

^d A: ash.

^e FC: fixed carbon.

^f LHV: lower heating value.

of oily sludge and biomass (rice husk) were carried out in a fixed-bed reactor to investigate the synergetic effect on the pyrolysis products. The main compositions of the gas and oil products were identified by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS), respectively. Moreover, the release of sulfur was also detected. The findings of this study may provide an alternative way for the utilization of hazardous oily sludge.

2. Materials and methods

2.1. Materials preparation

The oily sludge (OS) sample was obtained from the bottom of crude oil tanks at Nahai Solid Waste Central Disposal Co., Ltd. The rice husk (RH) sample was collected from Zhejiang Province, China. Proximate and ultimate analysis of both samples and the primary components of oily sludge are listed in Table 1. The water content was determined by ASTM-D95-13 and the total oil fraction was evaluated by Soxhlet extraction using toluene as solvent [2]. SARA (saturates, aromatics, resins, asphaltenes) were first separated by precipitation of asphaltenes by *n*-hexane, followed by further separation through a chromatographic column according to the Chinese standard SY/T 5119–2008. The content of major alkali metals (potassium, calcium, magnesium) was detected by inductively coupled plasma-atomic emission spectrometer (ICP-AES). Prior to analysis, about 0.1 g samples were digested with HNO₃, HF and H₂O₂ (volume ratio 4:2:2).

Before test, the rice husk was ground into small particles with size between 100 and 150 μm. For the co-pyrolysis experiments, oily sludge and rice husk particles were mixed with blending ratios of 2:1, 1:1 and 1:2. To ensure the mixing uniformity, the oily sludge was first mildly heated to 50 °C to reduce its viscosity, and then the rice husk was added and stirred for 10 min.

2.2. Co-pyrolysis experiments

The product distribution from co-pyrolysis of oily sludge and rice husk was investigated by the pyrolysis experiments in a horizontal quartz tube fixed-bed reactor, which was equipped with a temperature-programmed device. The inert atmosphere was maintained by nitrogen

with a flow rate of 150 mL min⁻¹. For each run, about 4 g of sample were loaded into the reaction zone and the reactor was heated to 600 °C and maintained for 20 min. The volatile products were swept out through a condenser filled with cold water, where the liquid product was collected. The non-condensable gas was then scrubbed with 4% Zn (Ac)₂ solution to absorb H₂S (in the form of ZnS precipitate) before collected in a gas bag. After pyrolysis, the yields of liquid product and residues were determined by weight and the gas yield was calculated by mass balance. Duplicated experiments were performed and average results were discussed. The theoretical results were obtained by linear combination of experimental results for individual samples, and then the experimental (Exp.) values were compared with calculated (Cal.) values to investigate the effect of interactions on the products during co-pyrolysis.

2.3. Analysis methods

Prior to the analysis, the aqueous fraction in the liquid product was removed by absorption with anhydrous sodium sulfate. Then the oil phase was subject to SARA analysis. Gas chromatography/mass spectrometry (GC/MS, DSQII) was applied to study the compositions of the oil product. The chromatographic separation was conducted with a DB-WAX column (30 m × 0.25 mm × 0.25 mm) and the oven temperature was programmed from 50 °C (hold 5 min) to 240 °C at a rate of 10 °C min⁻¹ and held for 10 min. Helium was the carrier gas at a flow rate of 1.0 mL min⁻¹ and the split ratio was 50. Data were analyzed by Xcalibur software and the chromatographic peaks were identified by NIST library. The relative concentration of the chemical compounds was calculated by a semi-quantitative analysis based on the peak area [24]. The sulfur content of oil was detected by sulfur elemental analyzer (Vario MAX cube).

The compositions of the gas product (H₂, N₂, CO, CO₂ and C₁–C₂ hydrocarbons) were detected by gas chromatograph (GC) with FID and TCD detectors (Agilent 490 Micro GC). The released H₂S (ZnS precipitate) was determined by iodometric titration according to the Chinese Standard GB/T 11060.1-1998 [25]. First, the ZnS was oxidized by excess iodine in an acid solution. Then the excess iodine was titrated by Na₂S₂O₃ solution. The different forms of sulfur in the solid residues were characterized by X-ray photoelectron spectroscopy (XPS) and a

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