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# Catalytic pyrolysis of petroleum sludge for production of hydrogen-enriched syngas

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ABSTRACT

Petroleum sludge has attracted wide attention owing to its large quantity, hazardous character, and difficulty in processing. Furthermore, petroleum sludge contains a high proportion of hydrocarbons which are valuable for recovery. In this paper, the possibility of producing hydrogen-enriched syngas from different petroleum sludge by a two-stage catalytic pyrolysis under different temperature has been examined. X-ray photoelectron spectroscopy and $C^{13}$ nuclear magnetic resonance were employed to characterize the pyrolysis residues. The pyrolysis of three different petroleum sludge samples was discussed along with possible reaction mechanisms. It was found that heavy oil components vaporized in the first stage of pyrolysis. Thereafter, the gaseous compounds were cracked in the second catalytic stage forming $H_2$, $CH_4$, CO, and other small molecules. Higher catalytic temperatures can enhance the yield of $H_2$ while lower temperatures would favor the generation of $CH_4$ and CO. The pyrolysis of samples collected from a sludge storage tank gave the highest $H_2$ yield (0.13 $Nm^3$ per kg sludge) among the three sludge samples examined. Additionally, after solid particles were removed by extraction (dissolution and centrifugation), catalytic pyrolysis produced 30% more $H_2$ at 1000 °C. Finding of this paper indicates staged-catalytic pyrolysis is a promising method to convert hazardous petroleum sludge into high valuable syngas.


## Introduction

China has become one of the largest crude oil consumers in recent years as a result of rapid economic development and industrialization [1]. Many processes in the petroleum industry including storage, transportation, and refining generate massive oily wastes. In 2012, more than 3 million tons of petroleum sludge was produced [2] in China. Petroleum sludge is a complex mixture of water, oil, and solid particles. Water and oil are in the form of an emulsion, which is stabilized by heavy asphaltene and fine solid particles [3]. Generally, about 30% of the petroleum sludge is oil, 40% is water, and the remainder is solid particles. The oil components can be categorized into four typical fractions i.e., aliphatics, aromatics, asphaltenes, and nitrogen-sulfur-oxygen-containing compounds [4,5]. Many of these components are toxic and may cause serious environmental and human health problems [6,7]. Similar to many other countries,

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petroleum sludge is classified as a hazardous waste (*No. HW08, National Catalogue of Hazardous Wastes, 2007, Ministry of Environmental Protection of the People's Republic of China*) in China.

The treatment of petroleum sludge has attracted intense attention and various treatment methods have been developed including physical methods, chemical methods, and biological methods. Among them, landfill and incineration are the most common approaches. However, petroleum sludge is harmful to soils and sanitary landfill is expensive and time consuming, and it is difficult to eliminate oil leakage [3]. Currently, most petroleum sludge is burned directly in rotary kilns, but the flue gas cleaning facilities required to meet emission regulations are very expensive [8]. In addition to disposal treatment processes, centrifugation is also widely used to recover valuable oil fractions from petroleum sludge. The quality and quantity of recovered oil strongly depend on the viscosity of the sludge, and the centrifugation residue must be given further careful treatment. Biological approaches are also considered promising methods for the treatment of petroleum sludge. However, the solids, iron fragments, and heavy metals in petroleum sludge make it unsuitable for biological treatment [9]. For solvent extraction, large amounts of toxic organic chemical reagents are required and treatments with such chemicals are expensive and may cause secondary pollution.

In the past few years, transforming industrial waste into effective energy sources has become attractive. Because of the high content of heavy oil components, converting petroleum sludge into various light weight liquid compounds and small gaseous molecules has become a vibrant research topic [10]. Previous studies have found that, compared with direct incineration, the emission of pollutants such as $NO_x$ and $SO_x$ from pyrolysis is much lower and the heavy metals present in petroleum sludge can be retained in the bottom ash [11]. The advantages of pyrolysis have made it a promising method for energy recovery from petroleum sludge.

Hydrogen has been considered as an ideal energy carrier owing to its zero emissions and high energy density [12–15]. $H_2$ can be generated from various feed stocks bearing H-containing compounds. Furthermore, the production of $H_2$ from renewable biomass or organic wastes through pyrolysis/gasification has been intensively explored because of the cheap cost and high possibility for commercialization [16]. Maoyun He et al. studied the production of $H_2$ from waste polyethylene (PE). It was found that high temperatures would enhance the $H_2$ yield and production was maximized at 900 °C [17]. Ligang Wei et al. used biomass as a substrate and the results showed that the content of $H_2$ increased with higher reaction temperatures owing to endothermic water–gas reactions [19]. Nimit Nipattummakul et al. tried to produce $H_2$ from sewage sludge and it was noted that $H_2$ yield was maximized at 1000 °C [21]. Similarly, using sewage sludge as the starting material, Tae-Young et al. discovered that dolomite favored the generation of $H_2$ and reduced tar at the same time [22]. Gonzalez reported that 800 °C was a promising catalytic temperature for producing $H_2$ from olive cake [23]. Although many works have been concerned with enhancing the $H_2$ yield from various wastes, the production of $H_2$ from petroleum sludge has not been studied.

In this article, the production of hydrogen-enriched syngas from different petroleum sludges using a two-stage catalytic pyrolysis has been studied. The reaction mechanism and the effects of sludge components and temperature are investigated to identify favorable experimental conditions. The results of this research will contribute to a clean and improved use of hazardous petroleum sludge, and reducing its environmental pollution and treatment costs.

## Experimental

### *Samples*

Three representative petroleum sludge samples were investigated. Nahai petroleum sludge, supplied by Nahai Solid Waste Central Disposal Co., Ltd, was collected from the bottom of tanks containing oily waste water [24]. Xingzhong petroleum sludge was collected directly from the bottom of crude oil storage tanks at Sinochem Xingzhong Oil Staging Co., Ltd. (Zhoushan). Zhonghai petroleum sludge sample, the residue from a tank washed by heavy oil, diesel, and hot water, was provided by the China National Offshore Oil Petrochemical Co., Ltd. (Zhousan).

Before pyrolysis tests, the compositions of the sludge samples were determined and the SARA (saturates, aromatics, resins, asphaltenes) content of the oily components were obtained according to the ASTM method D2007-02.

### *Experimental setups*

The pyrolysis system used in this paper was illustrated in Fig. 1. The pyrolysis process was carried out in a two-stage, quartz tube fixed-bed reactor, which was electrically heated. According to the temperatures used in previous research [25], pyrolysis for the first stage was controlled at 600 °C and temperatures for the second stage were set at 800 °C, 900 °C, and 1000 °C, respectively, to assess the effect of different catalytic temperatures on pyrolysis performance.

During the experiments, an inert environment in the quartz tube was maintained with nitrogen at a flow rate of 1.0 L/min. The sample held in a ceramic crucible was put into the first stage at 600 °C. The products generated in the first stage were catalytically cracked and reformed in the second stage. After cooling and cleaning, the syngas was analyzed with a gas chromatograph (Agilent 490 Micro GC).

Similar to previous research, the catalyst used in this work was dolomite, which was inexpensive, readily available, and gave good catalytic activity for heavy oil component cracking. The dolomite, which contained about 30% (w/w) CaO, 20% (w/w) MgO, and other minor mineral impurities such as the trace minerals $SiO_2$, $Fe_2O_3$, and $Al_2O_3$, was milled into small (6–9 mm) particles before use [25].

### *Analysis methods*

A DMAX-RA X-ray diffractometer system with Cu K$\alpha$ radiation ($\lambda$ = 0.15406 nm) (Rigaku, Tokyo, Japan) was used to identify the main components of the solid particles contained in the sludge.

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