Research on the law of hydrogen production by supercritical water gasification of oily sludge

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Abstract. As China's oil consumption continues to increase, the amount of oily sludge generated increases yearly. Aiming at the limitations of the traditional oil-containing sludge treatment technology, supercritical water is used to dissolve and convert organic components into hydrogen for hydrogen energy recovery to realize the reduction, harmlessness, and resourcefulness of the oily sludge treatment. The influences of reaction temperature, pressure, time, material ratio, and other parameters on hydrogen production from supercritical water gasification of oily sludge were experimentally examined. Results indicated that hydrogen yield increases with increased response temperature, pressure, and time, and hydrogen yield decreases with increased response mass ratio.

1. Introduction

Currently, a considerable amount of oily sludge is generated in China in the process of crude petroleum extraction, gathering and transportation, and oil refining, and the production of oily sludge is increasing yearly. The composition of oily sludge is very complex, and the on-site sludge often contains crude oil, emulsion breakers, viscosity reducers, inorganic salts, and a small number of heavy metal compounds. It also contains benzene, phenolics, anthracene, and other toxic substances with a lousy odor[1]. When oily sludge is not handled correctly, it will pollute the surrounding environment and deteriorate the ecological environment[2].

The generation of oily sludge is unavoidable, and oily sludge contains a high number of hydrocarbons, metals, inorganic salts, etc., which contains a large amount of hydrocarbons is also a vital resource if the direct reduction treatment not only causes a resource waste but also lead to CO₂ pollution. Traditional oily sludge treatment technologies include fluidization, conditioning, centrifugation, solvent extraction, electrochemical treatment, ultrasonic treatment, membrane separation technology, etc. However, each sludge treatment technology has certain defects, such as the shortcomings of fluidization-conditioning-centrifugal technology treatment, which has a low sludge treatment capacity, and the process being more complex. In solvent extraction technology, many chemicals are added, and the excess chemicals must be reused later, which increases the operating cost of oily sludge. In treating oily sludge, Membrane separation technology can only block the solid phase components of large particles. It cannot upgrade the quality of oil products, so the subsequent waste membrane must still be treated. The disadvantage of electrochemical treatment technology is that too much sludge treatment will lead to an unstable electric field and poor electric dehydration quality when recovering sludge. The disadvantage of ultrasonic treatment technology is that the requirements for ultrasonic sound intensity processing time and other parameters are relatively strict. Otherwise, it is easy to cause re-emulsification [3].

Supercritical water gasification hydrogen production technology places organic matter in supercritical water, and supercritical water not only provides a good reaction environment for organic solvents but participates in hydrogen production reaction as a reactant[4]. The advantage of this technology is that the reactants are water and organic matter, and new drugs do not need to be added to the reactants with high water content, avoiding the shortcomings of the traditional treatment technology that drugs are not easy to separate and the cost of dehydration is high[5].

It is considered to use supercritical water to treat oily sludge, dissolve organic matter in oily sludge, and convert it into hydrogen. Firstly, the cost of dewatering traditional oily sludge can be avoided; secondly, oily sludge can produce a large amount of combustible gas such as hydrogen to achieve energy recovery.; finally, organic components in solid phase residue after supercritical water treatment can be rapidly reduced. The oily sludge's reduction, harmlessness, and resorization are completely realized [6]. However, because oily sludge contains a significant amount of crude petroleum and other organics, and different organic waste gasification laws have different impacts on hydrogen production, this paper examines the feasibility of hydrogen production from oily sludge gasification, optimizes the reaction parameters of hydrogen generation from oily sludge gasification, and

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explores the experimental mechanism of hydrogen production from gasification. It offers theoretical and experimental evidence for applying supercritical water gasification of oily sludge for hydrogen generation.

2. Experimental stage

The crude oil is obtained from the field. As shown in Figure 1. To ensure the repeatability and uniformity of the extracted crude oil, the crude oil is pre-treated before the experiment. The specific method is: the crude oil of the Xinjiang oilfield is placed in a grinding bottle with a grinding bottle stopper, and the grinding bottle is placed in the oven. Slowly heat to 80°C, constant temperature for 2 hours, remove and put into vacuum drying box to cool to chamber temperature. Then, please take out the grinding bottle and put it in a place with little difference in ambient temperature for 48 hours to complete the crude oil pretreatment[6].

After adding the quantitative oily sludge and distilled water into the reactor, tighten the kettle cover bolts, connect the argon cylinder, adjust the pressure of the argon cylinder to 1MPa, and slowly open the exhaust valve to purge the inside of the reactor for 5 min. Then, close the vent valve and pressurize the kettle at the original pressure of the experimental design scheme. After adding to the experimental pressure, close the air inlet valve and gas cylinder, carry out heating according to the experimental design program, keep the heating rate each time at 400°C/h, and calculate the heating time according to the required reaction temperature. The heating time inside the reaction kettle is usually 20-30 min longer than the heating time set by the heating furnace. When the temperature at the top of the reaction kettle reaches the set temperature, start timing, stop heating after reaching the target time, remove the reaction kettle and rapidly cool it down to room temperature, then collect the gases from the exhaust port by applying the drainage collection method, and then introduce it into the gas chromatograph for analysis, and ultimately get the percentage of the various gas-phase components in the product.

2.1. Influence of temperature on the hydrogen constant

The variation of experimental results of hydrogen production from the supercritical water gasification of oily sludge at 400°C-- 544°C was investigated under initial reactor pressure of 1.8 MPa, time of 60 min, and constant concentration of 10%. From Figure 2, It was observed that the hydrogen production increased from 0.128 mmol/g to 3.179 mmol/g with the increase in reaction temperature. Methane yield increased from 0.21 mmol/g to 6.62 mmol/g, carbon dioxide yield increased from 0.704 mmol/g to 2.691 mmol/g, and carbon monoxide yield decreased to 0.002 mmol/g at 490 °C. The results showed that hydrogen, methane, and carbon dioxide yields increased significantly with increasing temperature, and carbon monoxide yield increased and then decreased[7-8].
2.2. Influence of pressure on the hydrogen constant

From the results in Figure 3, it can be shown that the hydrogen production increases from 3.89 mmol/g to 4.46 mmol/g with increasing reaction pressure. Methane production decreases from 6.61 mmol/g to 6.34 mmol/g and then rises to 6.78 mmol/g with pressure production. CO₂ production is strongly affected by the pressure production rate, increasing from 7.59 mmol/g to 2.84 mmol/g and then to 2.95 mmol/g. The pressure had the least effect on the CO yield in the range of 0.186 mmol/g ~ 0.009 mmol/g. As the reaction pressure increased, the hydrogen yield gradually increased, the methane and carbon dioxide yields decreased and then increased, and the carbon monoxide yield decreased.

![Figure 3. Effect of reaction pressure on gas production](image)

2.3. Influence of reaction time on the hydrogen constant

As shown in Figure 4, the reaction time varied from 15 to 150 min, and the hydrogen production per unit of sludge increased from 2.38 mmol/g to 5.92 mmol/g as the reaction time increased. Methane production also increased dramatically from 4.90 mmol/g to 8.32 mmol/g. CO production increased from 0.072 mmol/g at 20 min to CO production increased from 0.072 mmol/g at 20 min to 0.0025 mmol/g at 150 min. 150 min co2 yield increased from 1.90 mmol/g to 4.05 mmol/g. With the increase in reaction time, the hydrogen and methane yields significantly increased, the carbon dioxide yield increased, and the carbon monoxide yield decreased.

![Figure 4. Effect of reaction time on gas production.](image)

2.4. Influence of Material Ratio on the Hydrogen Constant

As seen in Figure 5, along with the increase in the material ratio from 10% to 100%, the hydrogen production per unit of sludge decreased from 5.86 mmol/g to 1.65 mmol/g. The methane production increased from 8.29 to 9.71 mmol/g. The carbon monoxide production increased from 0.0012 to 0.44 mmol/g and then decreased to 0.25 mmol/g. The carbon dioxide production increased from 13.67 to 2.46 mmol/g. The carbon dioxide production decreased from 0.0012 to 0.44 mmol/g. Carbon dioxide production decreased from 13.67 mmol/g to 2.46 mmol/g finally.
3. Conclusion

In this thesis, the influence of each reaction factor on the supercritical water gasification hydrogen production experiment of oily sludge was investigated by using a one-way experimental design, and the specific conclusions are as follows:

1. The reaction temperature plays a role in promoting the hydrogen yield experiment of oily sludge. Accompanied by the increase of reaction temperature from 400°C to 544°C, hydrogen yield increased from 0.128 mmol/g to 3.179 mmol/g.

2. The reaction pressure played a facilitating role in the hydrogen yield experiments with oily sludge. Accompanied by the increase of reaction pressure from 1.0 MPa to 2.2 MPa, hydrogen yield increased from 3.89 mmol/g to 4.46 mmol/g.

3. The reaction time plays a facilitating role in the oily sludge hydrogen production experiment. Accompanied by the increase in reaction time from 15 min to 150 min, hydrogen yield increased from 2.38 mmol/g to 5.92 mmol/g.

4. The reaction material ratio inhibited the hydrogen yield experiment of oily sludge. Along with the increase of reaction material ratio from 10% to 100%, the hydrogen yield of 5.86 mmol/g.

5. This paper mainly explores the feasibility of hydrogen production from supercritical water gasification of oily sludge and finds that oily sludge can still produce a large amount of hydrogen in supercritical water. On this basis, the hydrogen production law under different reaction parameters is explored, which provides a theoretical basis for realizing hydrogen production from supercritical water gasification of oily sludge. The following research direction should be to solve the energy consumption problem of heating water and oily sludge to a supercritical state, which can be combined with supercritical hydrothermal combustion technology to produce energy after oily sludge combustion to realize the whole process of treating and utilizing oily sludge.

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References