Analysis on Energy Recovery Efficiency of Oily Sludge Gasification

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Abstract: The harmless treatment of oily sludge is a long-term and arduous task. It is always a hotspot that is worthy of discussion for how to maximize the utilization of oily sludge and control the pollution to the lowest level. In this paper, the CO_2 in waste gas from oily sludge combustion is reused by gasification to produce syngas rich in CO and H_2, so as to reduce CO_2 emission and realize efficient recovery of oily sludge energy. The effects of gasification temperature and dosage of gasification agent on the gasification efficiency of oily sludge were investigated. It is found that with the increase of gasification temperature and dosage of CO_2, the energy recovery efficiency and the yield of CO are greatly improved. It is found that the CO production can be greatly increased when the temperature reaches 900 °C, while the CO_2/oily sludge ratio will not significantly affect the experiment result when it exceeds 2.

1 INTRODUCTION

As a kind of representative by-product of petrochemical industry, oily sludge treatment is imminent (Gong, Du, Wang, Bai, Wang, 2019); (Gong, Du, Wang, Sun, Fang, Wang, 2019); (Gong, Fang, Wang, Li, Li, Meng, 2020). According to rough statistics, the production of oily sludge exceeds 5 million tons only in China (Gong, Liu, Wang, Wang, Li, 2020). Moreover, the existence of toxic substances such as heavy metals, PHCs and PAHs undoubtedly increases the difficulty of oily sludge treatment. On the other hand, oily sludge also contains a considerable amount of energy. If reasonable methods can be used for energy recovery, it will greatly promote the development and promotion of oily sludge treatment technology. Therefore, there are new requirements for oily sludge treatment, that is, based on realizing the harmless and reduction of oily sludge, to achieve the efficient recovery and utilization of energy as far as possible. Among many treatment methods, combustion treatment method is the first choice because of the characteristics of fast treatment speed, strong adaptability, thorough treatment, etc.

However, the application of combustion technology for oily sludge treatment is difficult to solve the problem of low energy recovery efficiency, and the impact of a large amount of CO_2 emissions from the combustion of a large quantity of petroleum hydrocarbons is also negative.

Therefore, it is of great significance to discuss how to achieve efficient energy recovery and CO_2 emission reduction of oily sludge.

Gasification has great potential although it has not been widely used for oily sludge treatment at present. Using CO_2 as gasification agent can reduce CO_2 emissions, as well as realize the recovery of oily sludge energy products, which is an ideal treatment scheme. In the report of Guo et al. (Guo, Xiong, Che, Liu, Sun, 2021), due to the existence of CO_2, the formation of CO increases with the increase of temperature, while the formation of NO_x and SO_x is inhibited. Michel et al. (Michel, Rapagna, Di Marcello, Burg, Matt, Courson, 2011) investigated the effects of gasification technology and the results showed that the content of H_2 and CO account for 45.89% and 24.35% 880 °C, respectively.

In particular, the combination of gasification technology and combustion technology is more hopeful to realize the low-priced and thorough treatment of oily sludge.

In this paper, the gasification experiment of oily sludge in a fixed bed reactor was carried out, and the effects of temperature and gasifying agent dosage on the composition and distribution of gasification

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products were investigated, which provided basic theory and data support for the large-scale promotion of the technology.

2 EXPERIMENT AND MATERIAL

Oily sludge is collected from Liaohe Oilfield, Liaoning Province, China. The basic physical and chemical properties of the samples were tested as ASTM method D482-87, and the results are shown in Table 1. In order to facilitate the follow-up experiments, the original oily sludge samples were dehydrated at 105 °C by oven and segmented to the size of less than 5mm.

Table 1: Basic physical and chemical characteristics of PS.

		Data
Proximate analysis $_{ad}$ (ad. wt%)	*A*	48.53
	V	49.76
	FC	1.71
Ultimate analysis $_{ad}$ (ad. wt%)	C	53.78
	H	8.32
	S	0.96
	N	0.39

ad: air-dry base; *By difference; *A*: ash, *V*: volatile matter, *FC*: fixed carbon

Gasification experiment was carried out in a fixed bed reactor as Fig.1. N_2 was injected as carrier gas and protection gas at a rate of 40 ml/min to produce inert environment and CO_2 is used as gasifier. The effect of gasifier on gasification process is tested by adjusting the amount of CO_2 flux. 4g of LSOS samples were taken in each experiment and placed in corundum crucible. Temperature and CO_2/oily sludge ratio (*R*) was set as 500/600/700/800°C with *R*=1 and *R* was adjusted as 0.6/1/2/2.5 at 800°C, respectively. The gasification experiment was determined as 25 minutes, during which the CO_2 and N_2 were injected stable. The actual amount of CO_2 is shown as Eq. 1:

$$Q_{CO_2} = \frac{m_{OS} \times n_i}{M_{CO_2} \times 25\,\text{min}} \times 22.4\text{mL/mol} \times 1000\text{mL/L} \quad (1)$$

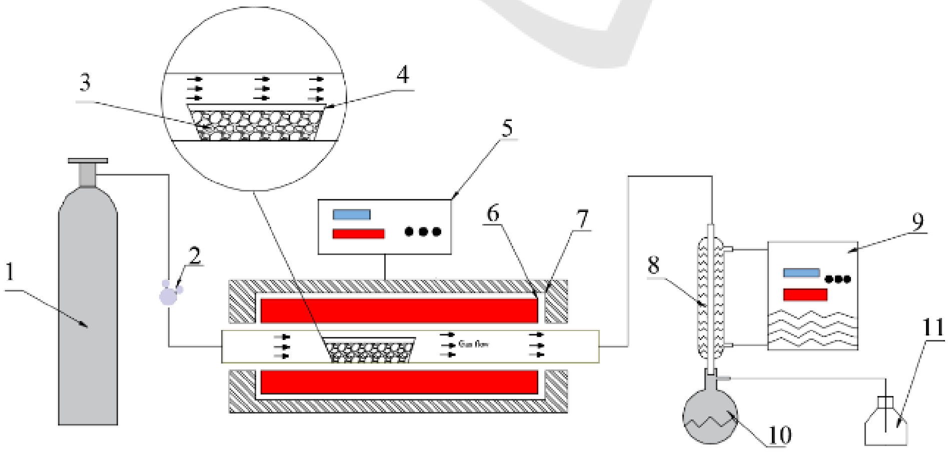
The yields of gasification char could be calculated as Eq.2 and Eq.3.

$$\eta_c = \frac{m_c}{m_{os}} \times 100\% \quad (2)$$

$$\eta_g = (1-\eta_c) \times 100\% \quad (3)$$

m_c—Weight of gasification char;
m_{os}—Weight of oily sludge sample;
η_c—Yield of char;
η_g—Yield of syngas.

The syngas was collected with aluminum foil gas bag. The composition of gasification syngas is detected by GC-456-Gas Chromatograph detector.



1. High pressure gas cylinder 2. pressure reducing valve 3. sample 4. crucible 5. heating furnace temperature controller 6. heating wire 7. furnace body 8. condenser tube 9. condenser tube temperature controller 10. flask 11. gas recovery device

Figure 1: Experiment flow chart.

3 RESULT AND DISCUSSION

The application of incineration technology for oily sludge treatment not only can recycle the energy contained in oily sludge, but also can realize the thorough treatment of oily sludge. However, a large quantity of hydrocarbons contained in oily sludge will produce CO_2 during combustion. In order to reduce CO_2 emission and recover as much as possible, combustion waste gas can be added into the gasification process as gasification agent in a certain proportion to produce high calorific value syngas rich in H_2 and CO, which can be used as industrial raw material to create certain economic value. Therefore, as an important part of the treatment process, the CO_2 gasification characteristics of oily sludge need to be further investigated.

3.1 Effect of Temperature on Production Yield

High temperature environment provides energy for the gasification of oily sludge. Organic components in oily sludge are cracked to produce small molecules of gaseous organic matter. The non-decomposable components and inorganic substances exist in the form of char. Different from the combustion process, the gasification process of oily sludge is always in the endothermic state, which means that in the conversion process, the external energy needs to be continuously input for the gasification process. As one of the key parameters, temperature is an important basis to measure the energy input in the treatment process. Especially for large-scale process, it is very important to determine the optimal temperature. The influence of temperature on the treatment effect is mainly reflected in two aspects: the energy recovery rate and the composition of gas products. The effect of temperature on the yield is the most intuitive. Generally, high temperature environment is conducive to the decomposition of organic components, and the increase if temperature can promote the recovery of organic components. For the gasification process of oily sludge, organic components recovered in the form of syngas have higher recycling value. In Fig.2a, the ratio of oily sludge to gasifier was controlled to 1, and the temperature change and energy recovery ratio were studied separately. In the environment above 600 °C, more than 90% of organic components can be recovered even without oxygen and other oxidants. However, when the temperature is raised from 600 °C to 900 °C, the yield of gas products has not been greatly improved. The yield of syngas only increased from 45.5% to 47.9%.

From the perspective of energy recovery, the energy recovery rate of oily sludge increased by about 5%. This feature shows that for oily sludge, a substantial increase in environmental temperature has a positive effect on energy recovery, but the increase is no longer obvious when the temperature exceeds 600 °C, even the energy input is far greater than the energy output, which is not in line with the economic balance.

However, the yield of the product is often not a single determinant, and the influence of temperature on the product composition is also crucial. For the gasification product, only syngas and char residue and oil phase production are lack. Therefore, the calorific value and purity of syngas determines the value of products. Especially CO and H_2 are the most ideal components.

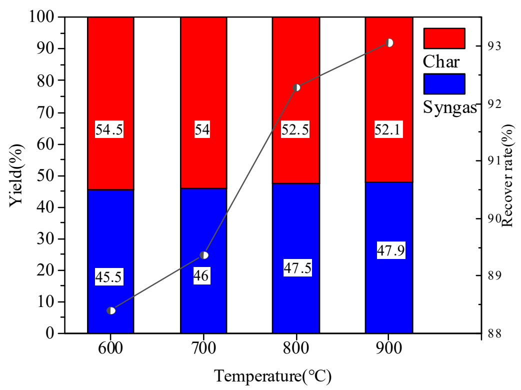


Figure 2: Recovery rate yield of syngas and char of LSOS at 600/700/800/900°C.

3.2 Effect Of Gasifier Dosage on Gasification Effect

Since the gasifier will participate in the specific reaction, the amount of gasifier often has a significant impact on the yield of the product. The CO_2/oily sludge ratio (*R*) was adjusted and the product distribution of oily sludge was investigated. According to Eq. (1), the injection volume of CO_2 is set as 24/40/80/100ml/min, and the corresponding product distribution is shown in Fig. 3. It can be found that the injection amount of gasification agent has a significant impact on the gasification effect of oily sludge. Although the effect is far less than that caused by oxidant, the gasification of oily sludge is limited when the amount of gasifying agent is relatively low, resulting in incomplete gasification reaction and the low yield of syngas. Nevertheless, the planned recovery rate of oily sludge has reached a very high level, that is, the recovery rate has exceeded 91%. With the increase of *R*, the gasifier is no longer the obstacle of syngas formation, and the syngas production increased slightly. With the increase of *R* value from 0.6 to 2.5, the yield of syngas increases from 46.92% to 47.75, showing an obvious upward trend. However, the increase of gasifying agent will not increase the recovery of product without limit. It can be clearly seen from Figure 3 that when R increases from 0.6 to 2, increasing the ratio of gasifying agent again will not increase the yield of syngas, and will basically remain at a high level. At this stage, the energy recovery efficiency is above 92%.

Although it is to combine CO_2 gasification and combustion treatment of oily sludge at present, excessive CO_2 injection is meaningless. Excessive CO_2 injection may also cause heat loss and energy waste. Therefore, it can be preliminarily determined that when the *R*=2, it can meet the processing requirements and obtain a better processing effect.

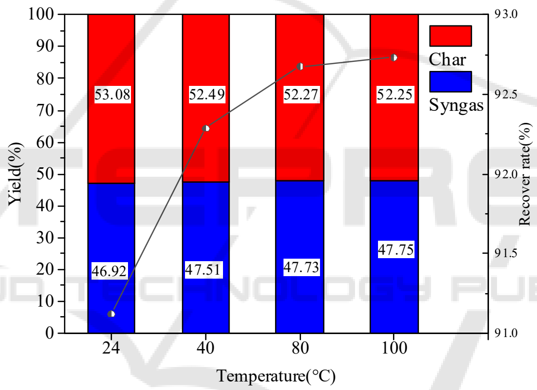


Figure 3: Distribution of gasification productions of LSOS with different R.

3.3 Effect of Temperature on Syngas Composition

The gasification products of oily sludge mainly contain char of gas and solid phase. Syngas, as a target product, composition greatly determines the economic value. As can be seen from Fig. 4, the composition of syngas is extremely complex. In addition to the target products CO and H_2, there are many kinds of impurity gases including methane, ethane, ethylene, propane, propylene, isobutane, n-butane, trans-2-butene, butene-1, isobutene, cis-2-butene, isopentane, n-pentane, C5+, etc. In syngas, CO and H_2 account for 21.89% and 21.01% respectively, which are the main components of syngas. The proportion of methane, ethylene and other small molecular hydrocarbon products is also quite high, accounting for 22.35% and 19.41% respectively, which is equivalent to the production of CO and H_2. Although there are many kinds of other impurity gases, the proportion is quite low, most of them are about 1%, which can be ignored. This phenomenon shows that in the process of gasification, the purity of gas products is quite high, which has a very positive impact on the subsequent recycling. By comparing the gasification effect with the previous pyrolysis study, it can be found that there is a certain gap with pyrolysis (Wang, Gong, Wang, Li, Liu, Tang, 2021); (Wang, Gong, Wang, Li, Liu, Tang, 2020). There are not only differences in the form of products, but also obvious differences in the composition of products. For pyrolysis in inert environment, the syngas is mainly composed of C1-C6 components and H_2 and CO only occupy a small proportion. By adding CO_2 as oxygen donor, the composition of CO and H_2 in the product greatly improved. In Fig.4, the ratio of CO and H_2 increased greatly and the proportion of miscellaneous gases decreased significantly. In particular, the gas ratio of C5 and C6 decreased significantly.

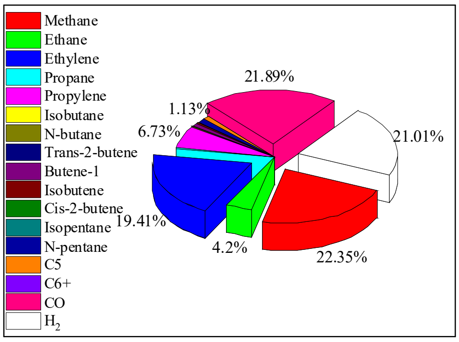


Figure 4: Main syngas components at 600 °C.

In the gasification process of oily sludge, temperature and *R*, as important indexes, not only affect the product distribution, but also the product composition. The results show that the proportion of C3 + in syngas composition is low and does not meet the expected goal of the experiment. Therefore, this experiment focuses on CO, H_2, C1-C3 components. It can be seen from Figure 5 that when the gasification temperature is only 600 °C, the yield of each component is at a very low level. When the temperature rises to 700 °C, the yield of each component does not change significantly. Only the yield of CO increased significantly. When the gasification temperature was further increased to 800 °C, the CO production increased significantly, but it was still at a relatively low level. The composition of syngas changed obviously when the temperature increased to 900 °C.

The composition of syngas is affected by temperature and can be divided into two stages. When the temperature is lower than 900 °C, the increase of temperature has little effect on the increase of components, and CO_2 cannot fully participate in the gas-phase reaction. Organic components tend to recombine freely in high temperature environment to form gaseous products with small molecules. Due to the participation of CO_2, the difficulty of the reaction is greatly reduced, and the chain breaking and recombination of organic components can occur at low temperature. It is worth noting that when the temperature increases from 600 °C to 800 °C, the proportion of C3+ in syngas decreased, even disappeared.

At present, the common views on the production of H_2 and CO include $CH_4+2H_2O \rightarrow 4H_2+CO_2$ and $C+2H_2O \rightarrow 2H_2+CO_2$ (Zhu, Zhao, Fu, Yang, Li, Yuan, 2019) and Boudouard reaction ($C+CO_2 \leftrightarrow 2CO$; ΔH=172 kJ·mol^{-1}) which is proceeded spontaneously in the forward direction to produce CO above 973K. Therefore, when the temperature rises to 900 °C, the production of CO increases by leaps and bounds. While due to the lack of water and energy input in low temperature environment, the yield of H_2 is difficult to reach a high level. This conclusion is consistent with the experimental results.

When the temperature was maintained at 800 °C, the effect of syngas composition was investigated by adjusting the amount of CO_2. Overall, the increase of the amount of gasifying agent has a certain effect on the increase of the yield of each component. Especially for CO, when the gasifier is increased from 1 to 2, the yield is more than twice as high. However, when R further increases, the increase of CO production is not obvious. When R>2, the increase of the amount of gasifying agent will not have a great impact on the yield of the product.

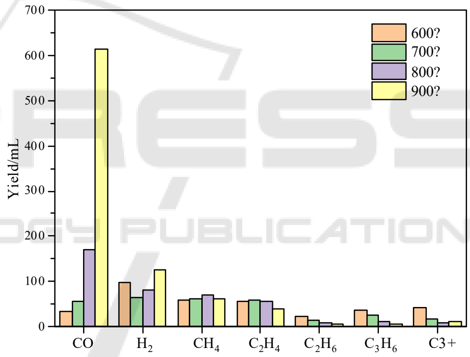


Figure 5: LSOS syngas composition at different temperature.

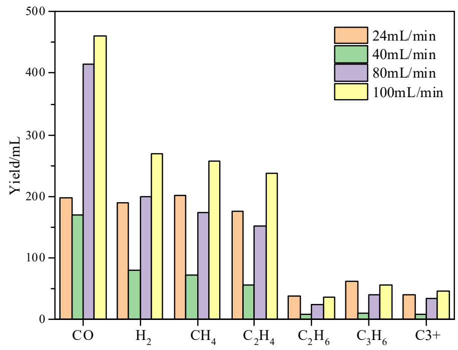


Figure 6. Syngas production composition.

4 CONCLUSION

The gasification treatment of oily sludge has short treatment cycle and high efficiency, which is an excellent treatment technology with good prospects. The results show that the effect caused by the increase of temperature is more significant than that caused by the increase of gasifying agent dosage. When the temperature is increased from 600 °C to 900 °C, the CO production is increased by 4 times, while when the temperature is increased from 600 °C to 900 °C, the CO production is increased by 12 times while the effect of temperature on H_2 production is not obvious. The increase of gasifier will also increase the yield of H_2, and the yield of H_2 is nearly doubled when R is increased from 1 to 2. The syngas obtained in the environment of high temperature and sufficient gasifier is rich in H2 and Co, and the impurity gas content is low. It is a gas product with high calorific value and high added value. It has a good industrial application prospect, which lays a foundation for the promotion of oily sludge gasification technology.

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