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The Effects of Catalysts on the Conversion of Organic Matter and Bio-fuel Production in the Microwave Pyrolysis of Sludge at Different Temperatures

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ABSTRACT: Adding catalyst could improve the yields and qualities of bio-gas and bio-oil, and realize the oriented production. [1]Results showed that the catalytic gas-production capacities of CaO were higher than those of Fe_2O_3, and the bio-gas yield at 800℃ reached a maximum of 35.1 %. Because the polar cracking active sites of CaO reduced the activation energy of the pyrolysis reaction and resulted in high catalytic cracking efficiencies. In addition, the quality of bio-oil produced by CaO was superior to that by Fe_2O_3, although the bio-oil yield of CaO was relatively weak. The light bio-fuel

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oriented catalytic pyrolysis could be realized when adding different catalysts. At 800℃, CaO was 45% higher than Fe_2O_3 in aspect of H_2 production while Fe_2O_3 was 103% higher than CaO in aspect of CH_4 production. Therefore, CaO was more suitable for H_2 production and Fe_2O_3 was more suitable for CH_4 production.

Keywords: Catalytic microwave pyrolysis; CaO catalyst; Fe_2O_3 catalyst; Bio-fuel; Sludge

1. INTRODUCTION

In recent years, with rapid economic development and urbanization, the treatment rates of industrial wastewater and domestic sewage have been gradually increasing, leading to a rapid surge in sludge production. Sludge has a high water content (>80%) (Zhao et al., 2010), a large volume and a complex composition. Besides containing a large amount of organic compounds, sludge contains heavy metals, pathogenic microorganisms, toxic and harmful substances, as well as other inorganic minerals (Namazi et al., 2015; Fonts et al., 2012). If sludge cannot be treated timely and effectively, it becomes a major pollution transfer, re-polluting the soil, water and even the food chain, and causes a considerable threat on the human body and the environment. Therefore, reducing the volume of sludge and its safe treatment and resource recovery are the hot spots of research. The utilization of municipal sludge has become the research focus and development trend of international sludge treatment and disposal.

Sludge pyrolysis is one of the effective ways to realize sludge utilization (Mohamed et al., 2016), it means that the macromolecular organic matter in the sludge is decomposed to produce gaseous, liquid and solid products in an inert environment. The gaseous products mainly include non-condensable small molecule gases, such as H_2 and CH_4, The liquid

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products contain bio-oil and pyrolytic water, and the solid products are the solid residues after pyrolysis. The resulting hydrogen and methane can be used as fuel gas, the bio-oil can be used as a raw material for liquid fuels or chemical reagents, and the solid residues can be used as adsorbents (Borges et al., 2014; Wang et al., 2016). Compared with traditional pyrolysis, microwave pyrolysis is more dominant because of its fast heating rate, high energy efficiency, and ease of operation and control (Huang et al., 2015). It can not only effectively realize the harmlessness, reducing and recycling of sludge, but also improve the quality and safety of the final products. As a result, microwave pyrolysis has become a hot topic of widespread concern.

Nevertheless, how to improve the production and quality of bio-gas and bio-oil generated from the sludge pyrolysis is still one of the most urgent problems to be solved (Deng et al., 2014). For example, the liquid phase products have a high water and oxygen content, a heat value half of that of the petroleum products, poor stability, and are difficult to be used as fuel. Furthermore, liquid phase products are acidic and sticky, and can adversely affect the normal operation of equipment. Meanwhile, sludge also contains a large number of N- and S-containing organic matters, resulting in a stimulant and in an unpleasant odor from the pyrolysates (Tian et al., 2014). Adding catalysts to the microwave pyrolysis of sludge seem to be a good solution to the above bottlenecks. Because adding catalysts can improve the efficiency of pyrolysis and the quality of pyrolysis steam, it is specifically to improve the quality of bio-oil and syngas (Beneroso et al., 2013). There are numerous types of catalysts for catalytic pyrolysis, the two most common are CaO and Fe_2O_3 , which have been thoroughly used as the catalysts for different biomass in traditional pyrolysis and microwave pyrolysis because of their availability, low costs, and particular

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absorption characteristics. Due to its high deoxygenation efficiency and increased gas production, CaO exhibits a relatively high catalytic cracking efficiency (Zhang et al., 2014; Zhou et al., 2014; Fu et al., 2016). However, studies also showed that after a long period of high-temperature pyrolysis, carbon accumulates with CaO, reducing its catalytic activity (Liu et al., 2016). Fe_2O_3 also has a good catalytic effect on the pyrolysis of biomass (Cho et al., 2012; Yu et al., 2014; Shang et al., 2015), Fe_2O_3 appears an effective deployment of the yield of biomass pyrolysis volatiles, including increasing the gas yield and reforming pyrolysis tar components, thereby increasing the relative content of light oil components to improve bio-oil quality. Nevertheless， most of the studies of catalytic pyrolysis are focused on the pyrolysis of coal and biomass (Lin et al., 2010; Veses et al., 2014; Fu et al., 2016), whose ingredient are much simpler than sludge. Quite few studies have been found concentrating on the pyrolysis of sludge catalyzed under microwave irradiation.

In order to improve the production and quality of bio-oil and bio-gas generated from microwave pyrolysis of sludge, CaO and Fe_2O_3 were selected as the catalysts in this study to explore their effect on the pyrolysis of sludge at different final pyrolysis temperatures, and further to investigate the effect on the conversion characteristics of organic matter, the production distribution, and the organic components of bio-oil and bio-gas. Combining with the analysis of the production mechanism of bio-oil and bio-gas, the optimization methods of bio-fuel production from microwave pyrolysis of sludge were proposed.

2. MATERIALS AND METHODS

2.1 Experimental Materials

The sludge sample used in this study was collected from the remaining sludge in the

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secondary sedimentation tank of a sewage treatment plant in Shenzhen, China. The sludge had a moisture content of 84.3%, an ash content of 46.72%, a volatile matter content of 50.42%, and a fixed carbon content of 2.86%. The raw sludge was analyzed by a Vario EL cube elemental analyzer, and the C, H, N and S contents are 28.86 wt.%, 7.35 wt.%, 3.88 wt.% and 0.89 wt.%, respectively. In order to eliminate the interference of water on the analysis of the mechanism of H_2 production from microwave pyrolysis of the biomass in sludge, the wet sludge was placed in an oven for drying at the temperature of 105°C for 12h. After drying, the dry sludge (DS) sample was ground using a mortar into a particle size of 1 mm.

2.2 Experimental Apparatuses and Methods

The experimental device for microwave pyrolysis is shown in Figure 1, including a single-mode and linear adjustable microwave oven with a microwave frequency of 2450±50 MHz, a temperature control system and the product-collecting device. The product-collecting device consisted of a condensing device and a gas collector. A quartz reactor with a volume of 170 ml was used as the microwave cavity, where a mixture of 30g of pretreated sludge samples and 10 wt.% of catalyst was pyrolyzed each time. To ensure the inert reaction environment during the pyrolysis, high purity nitrogen gas was continuously introduced into the quartz reactor for 10 minutes at a flow rate of 200 mL/min before the pyrolysis. After the microwave switch was turned on, the nitrogen flow rate was adjusted to 40 mL/min, and the retention time of the pyrolysis products in the quartz tube reactor was maintained as 255s. The power knob was adjusted according to the displayed temperature to maintain the final temperature of the pyrolysis at a constant. The

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high-temperature pyrolysis gas entered into the condensing device, and part of the gas was liquefied to oil, which was extracted with dichloromethane. The bio-oil was obtained after the removal of dichloromethane with a rotary evaporator. Non-condensable gases were collected using a 2-L air bag.

2.3 Analysis of bio-oil and bio-gas

The pyrolysis bio-oil was analyzed by a gas chromatography-mass spectrometry (GC-MS) system (Agilent, model GCMS-QP2010) and equipped with a DB-5MS column. The operating conditions were as follows: manual injection; injection volume: 1 mL; initial temperature: 40°C; inlet temperature: 250°C; interface temperature: 270°C; carrier gas: helium; and flow rate: 1.0 mL/min. The gaseous products from pyrolysis were determined by a gas chromatography system (FULI, type GC9790) with an external standard method. The chromatography system was equipped with a TXD-01 column with a sampling volume of 1 ml. The detector was a thermal conductivity detector (TCD), high purity N_2 and He were used as the carrier gases, and the temperatures of the detector, the thermal conductivity cell, and the column oven were 120°C, 120°C, and 70°C, respectively.

The experimental data were statistically analyzed by SPSS13.0 data analysis software, the analysis results showed that the significance level p between two data sets was $p \leqslant 0.05$, which indicated that the present datum in this work were useful.

2.4 Calculations of component and yield of bio-oil and bio-gas

2.4.1 The relative content of bio-oil component

The types of organics in the bio-oil were determined by referencing the data in the standard mass spectrometry database, and the relative content was analyzed by calculating

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the peak area in the total ion chromatogram.

Normalization method: Since the amount of component in the sample was proportional to the peak area, the corresponding peak was obtained according to the signal generated by the components in the sample. The conversion formula was as follows:

$$W= [A_i f_i / (A_1 f_1+A_2 f_2+\cdots+A_n f_n)]\times 100\% \quad (1)$$

Since the samples were bio-oil products and the correction factors were similar, the relative content of the component could be approximately calculated using the normalized peak area directly as follows:

$$W= [A_i / (A_1+A_2+\cdots+A_n)]\times 100\% \quad (2)$$

where A represented the peak area, f represented the correction factor, and W represented the relative content of the component.

2.4.2 The yield of the bio-gas components

The yield of each component of the bio-gas was calculated based on the mass of the gas produced per kilogram of dry sludge. First, the volume of each component was calculated by multiplying the amount of bio-gas with the volume content of each component, and then the volume V of the gas under the standard condition (0°C, 101.325 kPa) was calculated according to the ideal gas law PV = nRT. Finally, the gas volume V was converted to the amount of gas per kilogram of dry sludge (unit: L/kg).

2.4.3 The bio-gas production rate

The relative content of each gaseous product (Ci) was obtained according to the results of the gas chromatography analysis using an external standard method, and then the volume of each gas and its production rate were calculated. The formula was as follows:

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Gas volume $V_{total} = (V_1 \times C_1 + V_2 \times C_2 + V_3 \times C_3 + \ldots\ldots + V_n \times C_n)$[a] (3)

Average gas production rate = V_{total}/T[b] (4)

where V_n was the volume of gas collected at each time period, and T was the total duration of pyrolysis.

3. RESULTS AND DISCUSSION

3.1 Conversion of Organic Matter and Production Distribution

With CaO and Fe_2O_3 as catalysts at 500–900°C, the distribution of various products after microwave pyrolysis was shown in table 1, and the conversion process of organic matter was shown in Figure 2. It was seen that the bio-char yields decreased at temperature from 500 to 900°C, When CaO and Fe_2O_3 were used as catalysts, the bio-char yields at 900°C were 51% and 55.3% respectively, which were lower than that when catalysts were not added (60.4%). Thus, CaO and Fe_2O_3 promoted the cracking of organic matter in the sludge. The existence of the catalysts caused the non-condensable gas generated by the pyrolysis to move between the catalyst particles, thus increasing the residence time, promoting the carbonation of the solid matter, the secondary thermal cracking of the organic matter and the pyrolysis reaction of the volatiles, and ultimately resulted in a more complete pyrolysis of the sludge (Liu et al., 2016). When CaO was used as catalyst, the bio-char yields became almost stable above 800°C, which was the lowest in all conditions. Thus, the conversion of organic matter in sludge to organic oil or non-condensable gaseous products was achieved at 800°C with CaO.

The bio-gas yields increased as the temperatures increased, especially adding catalyst CaO and Fe_2O_3 can improve the proportion of gaseous products significantly. At 800°C the

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bio-gas yield with CaO (stabilized to 35.1%) was much higher than that of the raw sludge itself and adding Fe_2O_3, which increased by 132% and 45% respectively. Besides, Adding CaO as catalyst the yields of bio-char and bio-oil increased slightly, yet the bio-gas yield slightly decreased in the temperature range of 800-900°C. It was inferred that CaO rapidly catalyzed the cracking of sludge at the temperature below 800°C due to the polar cracking active sites distributed on the surface and inside of CaO, which reduced the activation energy of the pyrolysis reaction and resulted in high catalytic cracking efficiencies. When the temperature exceeds 800°C, CaO was more easily adsorbed on the surface of the produced bio-char, resulting in decreased catalytic activity. Consequently, the solid residue yield showed a slight increase. Simultaneously, the short-chain gas molecules produced by thermal cracking reorganized on the surface of catalyst, and aromatization, alkylation, isomerization and other reactions occurred, resulting in a phenomenon that the bio-oil yield increase and bio-gas yield decrease slightly. Thus, CaO exhibited a relatively super catalytic effect in the conversion of organic matter during the microwave pyrolysis of sludge at 800°C.

The bio-oil yield exhibited a downward trend after the initial increase as the temperatures rose when no catalyst and Fe_2O_3 was added, moreover the bio-oil yields both reached the maximum at 700°C were 18.4% and 20.4% respectively. An elevated temperature favored the devolatilization reaction, which was the main cause of the increased yield of bio-oil at relatively low temperatures (Loannidou et al., 2009). The bio-oil yields decreased at excessively high temperatures probably due to catalyst deactivation and secondary pyrolysis of the volatiles (Xie et al., 2014). In addition, the carbonization of volatile matter to produce bio-char was also another reason for a decrease

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in the yield of bio-oil. Combined with the change law that the gas yield slightly increased (500-700°C) and significantly increased (800-900°C), It was seen that the conversion of organic matter in sludge to oil products dominated at temperature from 500°C to 700°C, however the conversion of organic matter to gaseous products played a leading role at temperature from 800°C to 900°C. The oxygen-containing groups and the π bonds in the unsaturated hydrocarbons were attracted by the empty d orbit of Fe_2O_3. This phenomenon resulted in the enhanced conversion efficiency of organic matter in the microwave pyrolysis of sludge when Fe_2O_3 was used as the catalyst.

3.2 Analysis of Bio-Oil Composition and Production Mechanism

The component composition of the bio-oil produced by the microwave pyrolysis of sludge was complex and could be grouped into aliphatic hydrocarbons, aromatic hydrocarbons, oxygen-containing aliphatic compounds, oxygen-containing aromatic compounds, nitrogen-containing aliphatic compounds, nitrogen-containing aromatic compounds and other undetected compounds. The effect of catalyst on the distribution of the organic component contents of the oil products at different final pyrolysis temperatures was shown in Figure 3.

Microwave pyrolysis gradually boosted the level of the aliphatic hydrocarbons as the temperature rose. Owing to the stronger interactions between the high frequency electromagnetic field of the microwave and the negatively charged π-electron system of the organic molecules with higher temperatures. The maximum content of the aliphatic hydrocarbons with CaO at 900°C was 15.77%, which was 72% and 28% higher than no adding catalyst (9.18%) and adding Fe_2O_3 catalyst (12.33%), respectively. CaO exhibited a better catalytic effect on the pyrolysis of organic compounds during the microwave

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pyrolysis primarily due to the surface of CaO contained positively charged ions, and most organic molecules in bio-oil have negative π electron systems. Therefore, in the pyrolysis process, the positive ions on the surface of CaO interacted with the organic molecules containing the π electron system, which changed the stability of the molecular structure of the organics, reduced the activation energy of the cleavage of these organic compounds, and made the C-C bond easier to break.

The aromatics yields reached the maximum at 800°C in all conditions, and the maximum yields was 16.73% when adding CaO, which was 91% higher than not adding catalyst. Moreover, the average content of the oxygen-containing aromatics was 58% higher than no adding catalyst. Thus, CaO promoted the formation of the aromatic compounds significantly. It was because that CaO promoted the cleavage of large-molecule oligomers and produced low-molecular-weight stable aromatic compounds. In addition, the aromatic hydrocarbons contained a negative cyclic π electron system that was attracted by the interaction between Ca^{2+} and O^{2-} (Ellig et al., 1985), reduced the stability of this system to the aromatic side chain cleavage and increased the yield of the aromatic hydrocarbons. The average content of the oxygen-containing aromatic compounds was 7.24% when adding Fe_2O_3, which was lower than other two conditions, indicating that Fe_2O_3 inhibited the formation of the aromatic compounds. Phenol is an important member of the oxygen-containing aromatic compounds, and its lowest content was obtained with Fe_2O_3. Under microwave induction, Fe_2O_3 catalyzed OH• and HO_2• free radicals produced during the microwave pyrolysis, occurred a series of reactions with phenol, thereby reducing the relative content of phenol.

A high oxygen content increases the viscosity and the flash point of the bio-oil,

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leading to a deterioration in its stability (Tian et al., 2011; Oasmaa et al., 2012). It also reduces the energy density of the oil products, and renders them unsuitable as energy sources. The oxygen content attained the lowest at 800°C under different conditions, the average content of the oxygen-containing aliphatic compound was 54.95% when not adding catalyst, which was higher than adding CaO (34.90%) and Fe_2O_3 (44.67%), It was seen that CaO reduced the oxygen content significantly, thus achieved the deoxygenation of bio-oil. The similar conclusions were observed in some previous studies that reported that CaO had a significant deoxygenation on bio-oil (Lin et al., 2010; Li et al., 2012). Also, Ca^{2+} promoted the dehydration in the catalytic pyrolysis process, which was an important factor in reducing the oxygen content. During the microwave pyrolysis process, the positive ions on the surface of CaO interacted with the carboxylic acids organic molecules containing the negatively charged π electron system, which changed the stability of the molecular structure of the organics, reduced the activation energy of the cleavage of these organic compounds, and reduced the bond energy between the oxygen-containing functional groups and the main chain, thus promoting the breakage of the oxygen-containing functional groups such as carboxyl group. The pyrolysis of Carboxylic acid compounds (RCOOH) by CaO catalytic microwave can be divided into two reaction pathways. One, under the microwave irradiation, RH and CO_2 was produced directly from cracking. Second, with CaO catalyst, $(RCOO)_2Ca$ the organic calcium salt of carboxylic acid was produced after the dehydrogenation and dehydration, thus carboxyl oxygen groups were fixed in the form of the organic calcium salts, and $(RCOO)_2Ca$ during the high temperature microwave pyrolysis continued to crack and produced $CaCO_3$ and the ketone functional compounds (RCOR), while $CaCO_3$ can decompose to produce CaO and CO_2, and the CaO production

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can be recycled to be used as catalyst again. Besides, the interaction between Ca^{2+} and O^{2-} both attracted and activated the oxygen-containing groups, thus interfering the electron-cloud trajectory of carbon-oxygen double bond, and achieving deoxygenation.

When the contents of the aromatic hydrocarbons and the aliphatic hydrocarbons were higher in the bio-oil, the oxygen content was lower, thus the quality of bio-oil was better, and the bio-oil was a superior raw material for use as fuel energy or valuable chemical products. The contents of the aliphatic hydrocarbons and the aromatic hydrocarbons when adding CaO at 800°C were 12.02% and 16.73%, respectively, and the average content of the oxygen-containing aliphatic compounds was as low as 34.9%. In summary, 800°C is considered to be the optimum temperature and adding CaO catalyst for improving the bio-oil quality significantly.

3.3 Analysis of Bio-gas Production and Process Optimization

H_2 and CH_4 are the main gas components (>80%) produced from the microwave pyrolysis of sludge. The effects of CaO and Fe_2O_3 as catalysts on the production of H_2 and CH_4 at different temperature are shown in Figure 4. The results indicated that as the temperature increases, the CaO and Fe_2O_3 catalysts improve the gas production of H_2 and CH_4 significantly, compared to the absence of catalyst. Adding catalyst reduced the activation energy of the pyrolysis reaction effectively, thereby reducing temperature required for the reaction. During the pyrolysis of sludge, a higher temperature led to a faster heating rate and a shorter gas residence time in the reactor， although the gas residence time was more influenced by the sweep gas flow rate. Additionally, an increase in temperature promoted the secondary cleavage of volatiles, which was conducive to the production of H_2,

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CH_4 and other small-molecule gases. The resulting pyrolysis gas had a higher calorific value and a better combustion performance, and the mass generated of H_2 and CH_4 also increased the recycling value of the sludge pyrolysis gas as fuel (Domínguez et al., 2006).

The total production of H_2 and CH_4 rose with increasing temperatures and reached the maximum at 900°C under different catalytic conditions, at this moment, the maximum total production of H_2 and CH_4 with CaO (46.39 L/kg) and Fe_2O_3 (45.46 L/kg) was 87% and 83% higher than not adding catalyst, respectively. At 800°C, the fuel gas production with CaO and Fe_2O_3 improved 105% and 84% respectively, compared to the addition of no catalyst. This shows the addition of CaO and Fe_2O_3 catalysts improved the efficiency of the fuel gas production significantly, and 800°C was the optimum temperature for producing H_2 and CH_4 high quality gas.

H_2 production also increased with increasing temperatures, tended to stabilize (15.4 L/kg) above 700°C without catalysts. H_2 production reached the maximum (29.56 L/kg) at 900°C with Fe_2O_3, was 92% higher than that with no catalyst. Adding CaO as the catalyst, the H_2 production (38.56 L/kg) stabilized at 800°C and increased by 162% than no adding catalyst, the effect of CaO on enhancing the H_2 production was more splendid than that of Fe_2O_3. Adding CaO, the H_2 production at 900°C was slightly lower than that at 800°C, which was directly related to the increase in the reaction rate and the gas outflowing rate at 900°C higher temperature. The highest hydrogen production rate occurred (Figure 5) with CaO catalyst at 900°C, the residence time of the pyrolysis gas in the microwave environment shortened, the probability of water gasification reaction reduced, and resulted in the reduction of H_2 production. Based on the above findings, CaO exhibited a superior catalytic effect on hydrogen production at 800°C, and an apparent advantage in promoting

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H_2 production, which was consistent with Ying Yu's conclusion that CaO favored the H_2 production via catalytic pyrolysis (Yu et al., 2014).

CH_4 is generally formed by the breakage of aliphatic side chains in the organics at low temperatures. As the pyrolysis temperature rose, the oil products occurred a secondary cracking reaction at high temperatures and continued to produce CH_4 and other small-molecule substances, which caused an increase in CH_4 production with increasing temperatures. CaO reacted with CH_4 to generate CH_3OH while serving as the catalyst (Lin et al., 2009), so the CH_4 production with CaO was lower than that with no catalyst above 500°C. The catalytic effect of Fe_2O_3 on the CH_4 production was significant. CH_4 production with Fe_2O_3 (14.6 L/kg) was 92% higher than that without catalyst at 800°C. At 900°C, the CH_4 production under different catalytic conditions all reached their peak values. The maximum CH_4 production with Fe_2O_3 (15.9 L/kg) increased by 60% than that without catalyst (9.9 L/kg). Therefore, Fe_2O_3 exhibited a strong catalytic effect on CH_4 production when temperature above 800°C, especially the most significant upgrade efficiency occurred at 800°C.

The effects of different catalysts on the H_2 and CH_4 production processes at different final pyrolysis temperatures were further analyzed, and the results were shown in Figure 5. The H_2 and CH_4 production rates trended downward over time after their initial increase, and the rates of production for both gases increased sharply at about 2 minutes. The H_2 and CH_4 production rates rose with increasing temperatures, reached maximum at 900°C. The H_2 production rates at the different pyrolysis final temperatures were higher than the corresponding CH_4 production rates, and the duration of the H_2 production rate was longer than that of CH_4 production rate, which resulted in the H_2 production to be greater than the

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CH_4 production.

The law of changes in the H_2 production rate with Fe_2O_3 showed similar trends with those no catalyst added, and reached the maximum production rate within 3 minutes. In the last stage, the rate of gas production decreased sharply, and H_2 stopped producing at 20 minutes. The maximum production rates with CaO were reached after 10 minutes of pyrolysis at 500°C, 600°C and 800°C, those were reached within 5 minutes at 700°C and 900°C, and H_2 production stopped at about 35 minutes. The maximum H_2 production rates with CaO (134 mL/min) and Fe_2O_3 (128 mL/min) at 900°C improved by 23% and 17.4% than those without catalysts (109 mL/min), respectively. At 800°C, CaO (increasing by 50%) was more conducive to catalytic hydrogen production than Fe_2O_3(increasing by 35%), and the increase in the H_2 production rate at 800°C was greater than that at 900°C. At different temperatures, the duration of high H_2 generation rate (> 20 mL/min) with CaO was the longest, followed by Fe_2O_3 and no catalyst. At 800°C, the duration of hydrogen generation rate adding CaO (25 minutes) increased by 17 minutes compared with Fe_2O_3. CaO、Fe_2O_3 catalyst increased the H_2 production rate and prolonged the duration of high H_2 production rate, thereby enhancing H_2 production, and CaO was more suitable for H_2 production. Because CaO was easier to reduce the reaction activation energy of the cracking of long-chain hydrocarbons, which allowed polymerization, cyclization and aromatization to easily proceed.

Compared with the H_2 production, the CH_4 production rate all reached the maximum within 3 minutes, stopped producing at 15 minutes, and the duration for CH_4 production was relatively short. Fe_2O_3 provided the highest CH_4 production rate, followed by no

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catalyst and CaO, CH_4 production rate with Fe_2O_3 was affected little between 500-700°C, but significantly increased at 800-900°C until reached the maximum value of 89 mL/min, which was 71% higher than that without adding catalysts. At 800°C, the maximum CH_4 production rate increased by 81% than that without catalyst, so the improve performance was better than that at 900°C. The duration of high CH_4 production rate (>10 mL/min) with Fe_2O_3 was significantly longer than CaO and without a catalyst, the duration of high CH_4 production rate with Fe_2O_3 (8 minutes) increased by 5 minutes compared with CaO at 800°C. Therefore, the increase in the CH_4 production rate and the prolongation of the duration of a high CH_4 production rate were the important factors for the increased CH_4 production by adding Fe_2O_3 catalyst. Fe_2O_3 promoted the decomposition and hydrogenation of the methyl side chain, so that the reaction easily advanced. However, while acting as a catalyst, CaO also reacted with CH_4 to produce CH_3OH (Yu et al., 2014). Therefore, Fe_2O_3 had a better enhancing effect on the rate of CH_4 production than CaO.

4. CONCLUSIONS

Adding catalyst to the microwave pyrolysis system could improve the yields and qualities of the bio-gas and bio-oil and realize the oriented production, which provided a possibility for the microwave pyrolysis technology in application of sludge recycling. CaO was a better catalyst for the production of bio-gas while Fe_2O_3 was better for bio-oil. The best quality of bio-oil could be realized at 800°C when catalyzed by CaO, while the maximum bio-gas production could both be catalyzed by CaO and Fe_2O_3 at 900°C. CaO was suitable for oriented catalytic production of H_2 while Fe_2O_3 was preferred for CH_4 production.

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Figure Captions:

Table.1. Production distribution in the microwave pyrolysis of sludge under different temperature (no catalyst，10 wt.% CaO，10 wt.% Fe_2O_3)

Fig.1. The experimental reaction device of microwave pyrolysis sludge.

1-Temperature indicator; 2-Ammeter;3-Thepoweradjustingknob;4-Operating interface; 5-Microwavetransmitter; 6-Quartzreactor; 7-waveguide; 8-magnetron; 9-PC with fuzzy logic algorithm; 10-Gas flow meter; 11-condenser pipe; 12-Tar products collection unit; 13-Heavy metals in the gas collection device; and 14-Air pocket.

Fig.2. The distribution of various products and the transformation mode of organic matter during the microwave pyrolysis.

Fig.3. The distribution curve of organic matter in bio oil under different catalysts: (a) no catalyst; (b) CaO; and (c) Fe_2O_3.

Fig.4. Effects of catalysts on the gas production at different final pyrolysis temperatures: (a) H_2; (b) CH_4; and (c) $H_2 + CH_4$.

Fig.5. Effects of catalysts on H_2 and CH_4 production rate at different final pyrolysis temperatures: (H_2: (a) no catalyst, (b) CaO, (c) Fe_2O_3; CH_4: (d) no catalyst, (e) CaO, (f) Fe_2O_3.)

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Table1

Additive	Temperature (℃)	Bio-char (%)	Bio-oil (%)	Pyrolysis water (%)	Bio-gas (%)
no catalyst	500	70.0±3.4	14.5±0.7	4.2±0.2	11.3±0.6
	600	70.2±3.0	15.4±0.8	4.4±0.2	10.0±0.5
	700	68.0±3.1	18.4±0.7	3.2±0.1	10.4±0.5
	800	65.0±2.8	16.5±0.7	3.4±0.1	15.1±0.7
	900	60.0±2.0	14.4±0.5	2.1±0.1	23.5±1.1
CaO	500	65.2±2.7	15.5±0.7	2.2±0.1	17.1±0.8
	600	60.2±1.6	14.4±0.6	2.4±0.2	23.0±1.2
	700	55.0±2.0	12.4±0.6	1.2±0.1	31.4±1.6
	800	50.0±1.9	13.5±0.7	1.1±0.1	35.1±2.0
	900	51.0±0.8	15.8±0.6	1.1±0.1	33.1±1.6
Fe_2O_3	500	70.2±2.9	11.5±0.5	3.2±0.2	15.1±0.7
	600	66.2±2.0	16.4±0.8	2.4±0.1	15.0±0.7
	700	60.0±2.8	20.4±1.1	2.2±0.1	17.4±0.9
	800	58.0±2.0	16.5±0.7	1.4±0.1	24.1±1.1
	900	55.0±1.4	14.4±0.6	1.1±0.1	29.5±0.8

($P \leqslant 0.05$)

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Highlights:

1. CaO was a better catalyst for the production of bio-gas while Fe_2O_3 for bio-oil.
2. The best quality of bio-oil could be catalyzed by CaO at 800°C.
3. The maximum bio-gas production could both be catalyzed by CaO and Fe_2O_3 at 900°C.
4. CaO was more suitable for oriented catalytic production of H_2 while Fe_2O_3 for CH_4.

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Figure1

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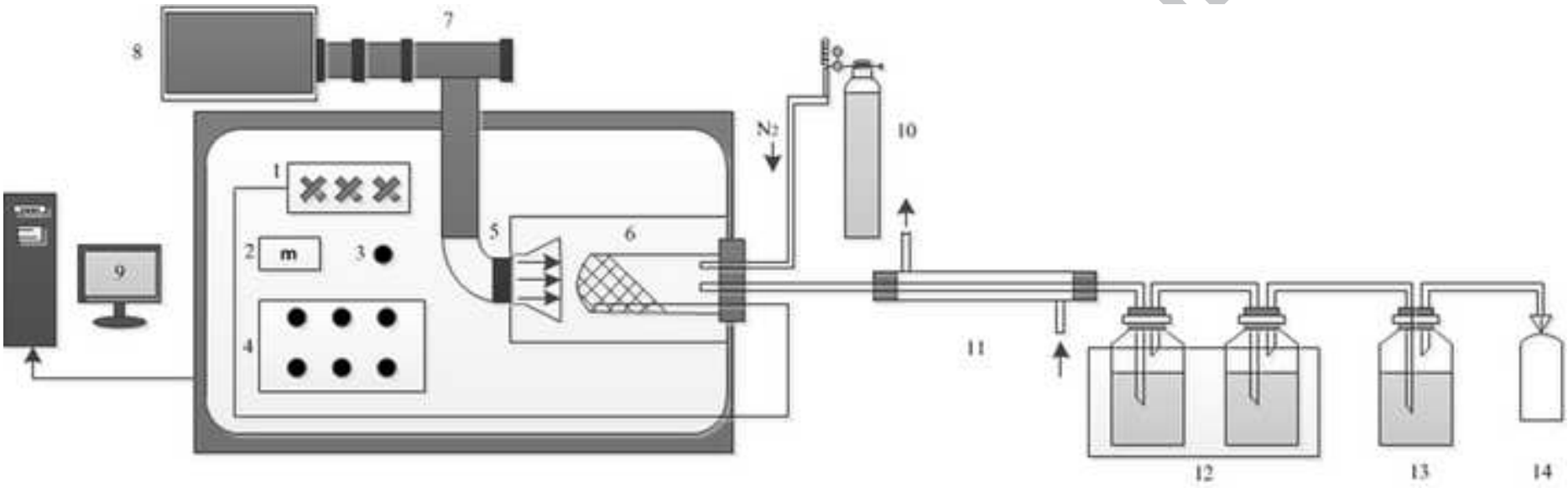

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Figure2

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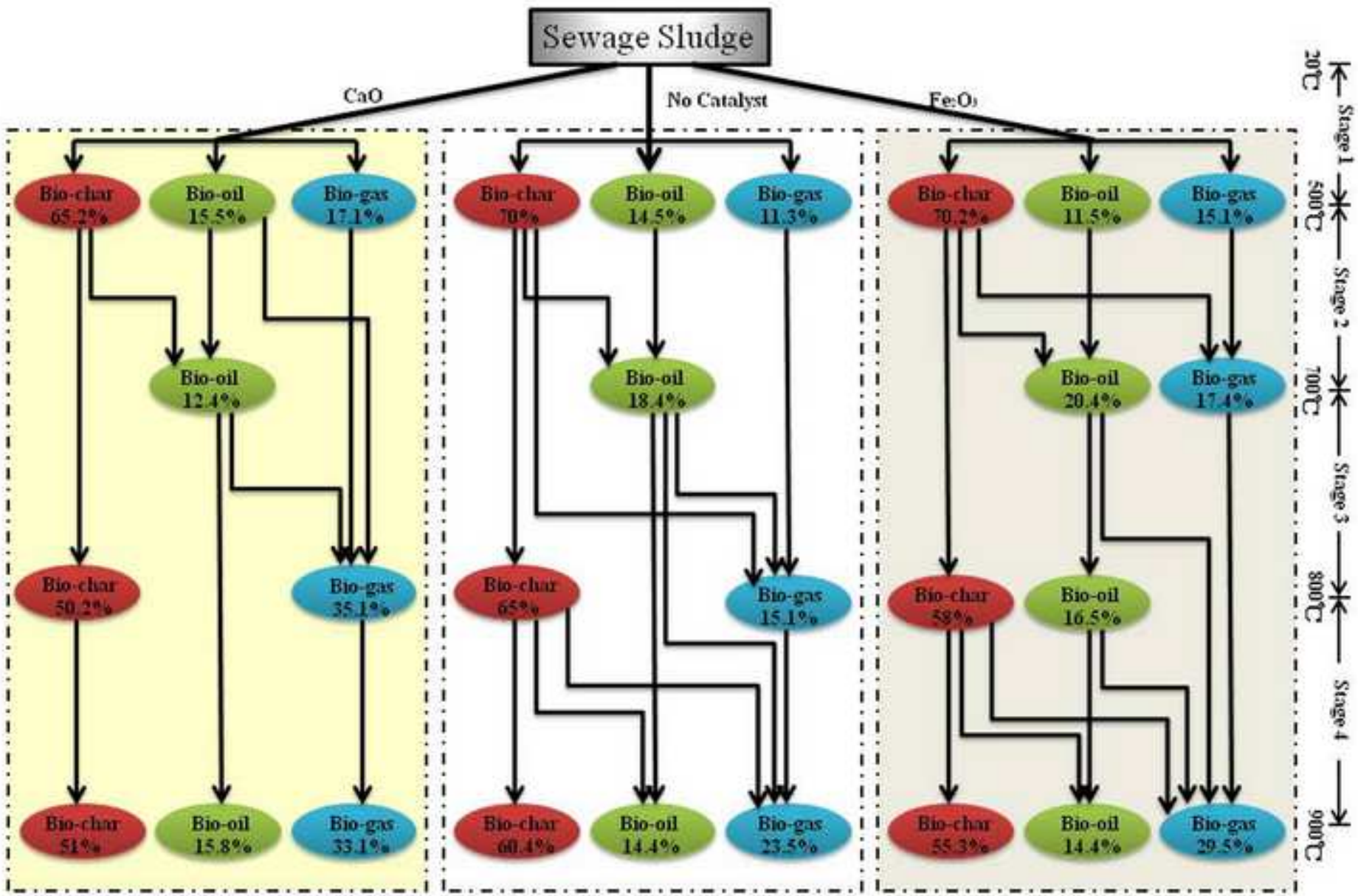

Figure3

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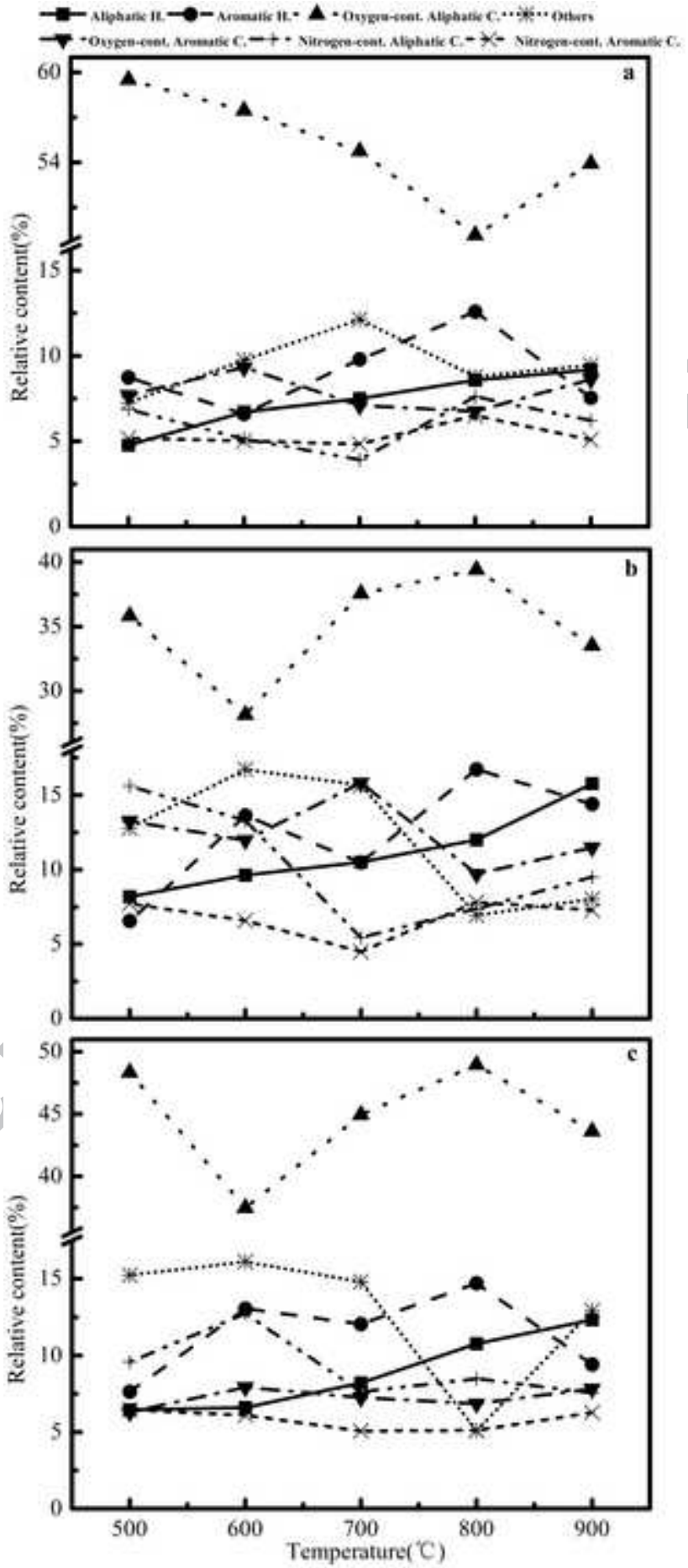

Figure4

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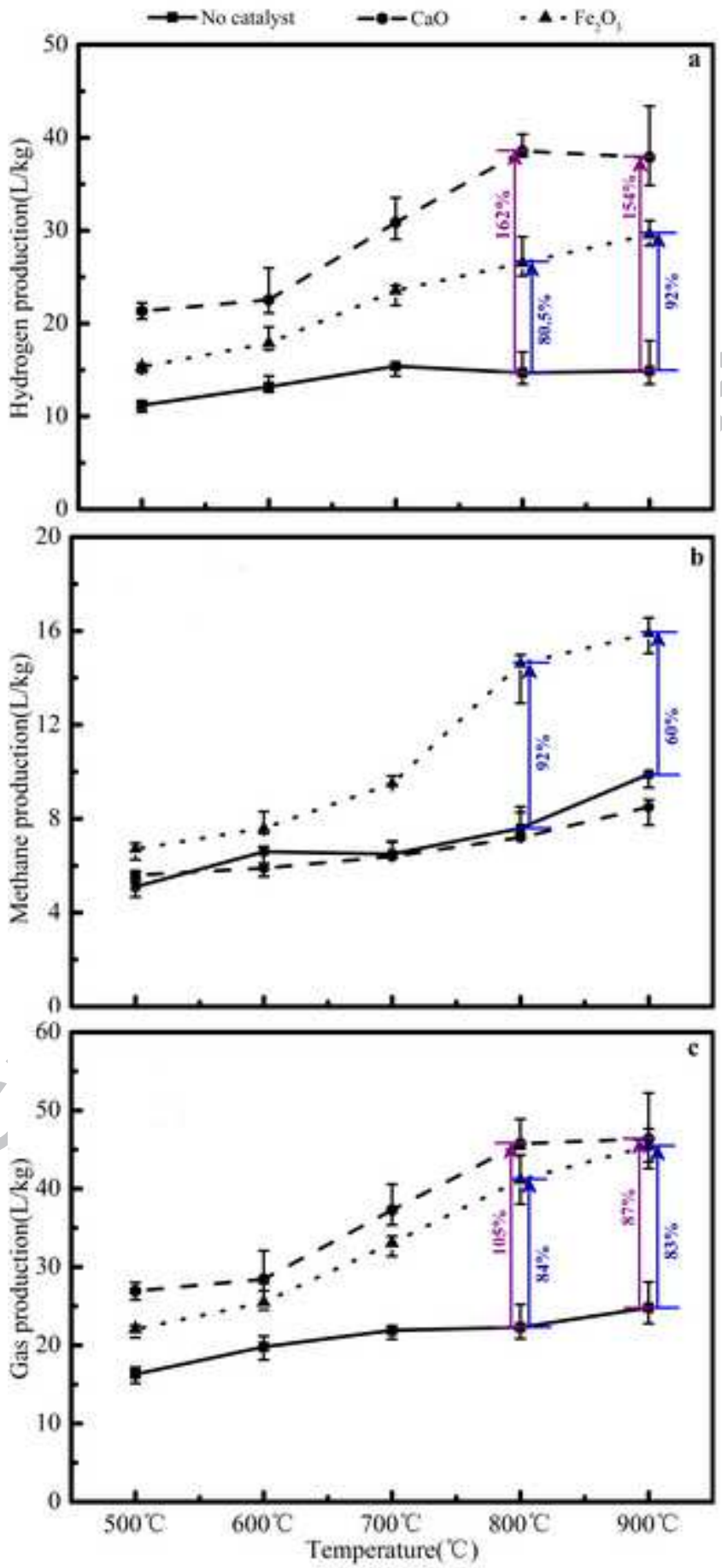

Figure5

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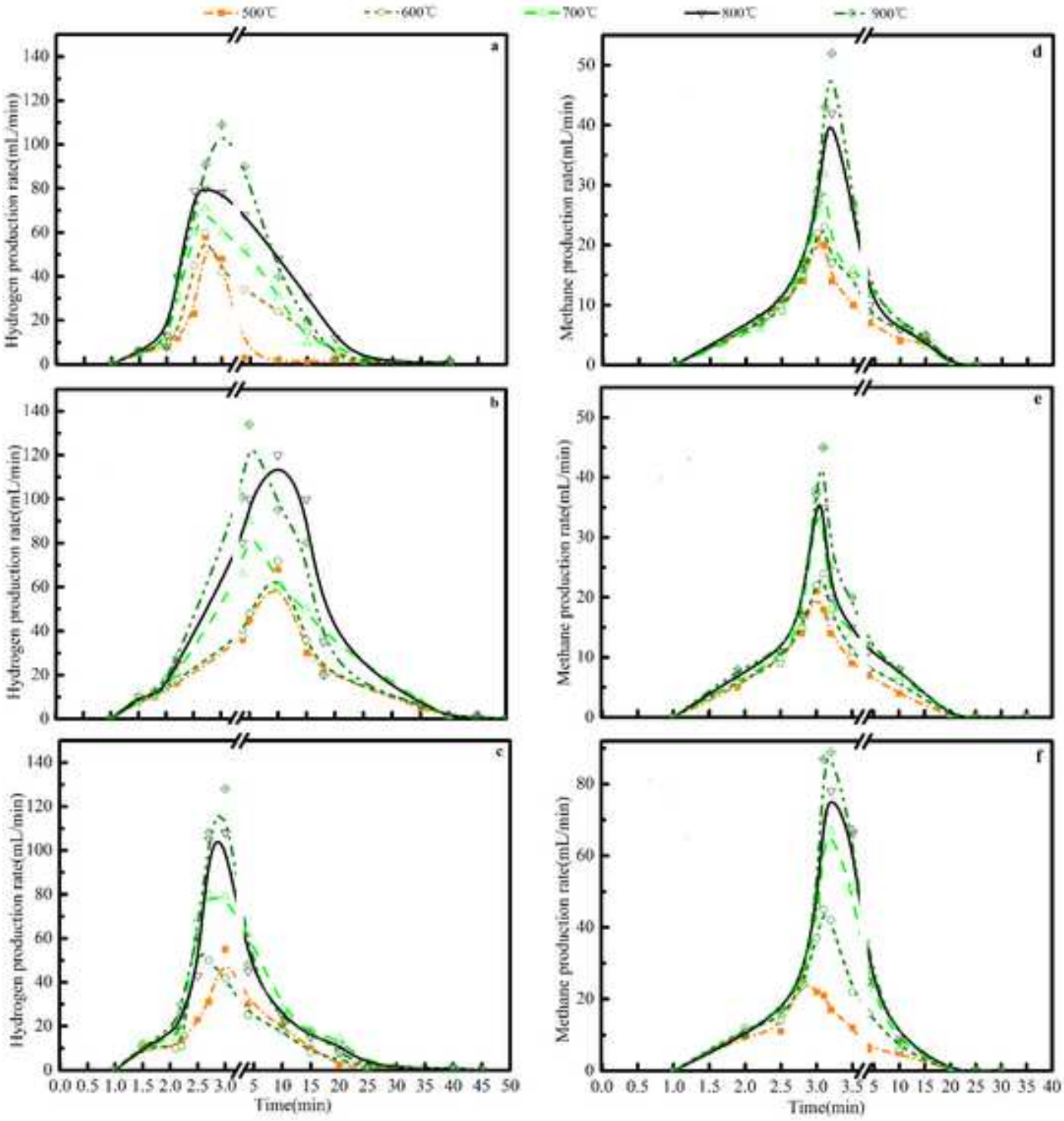

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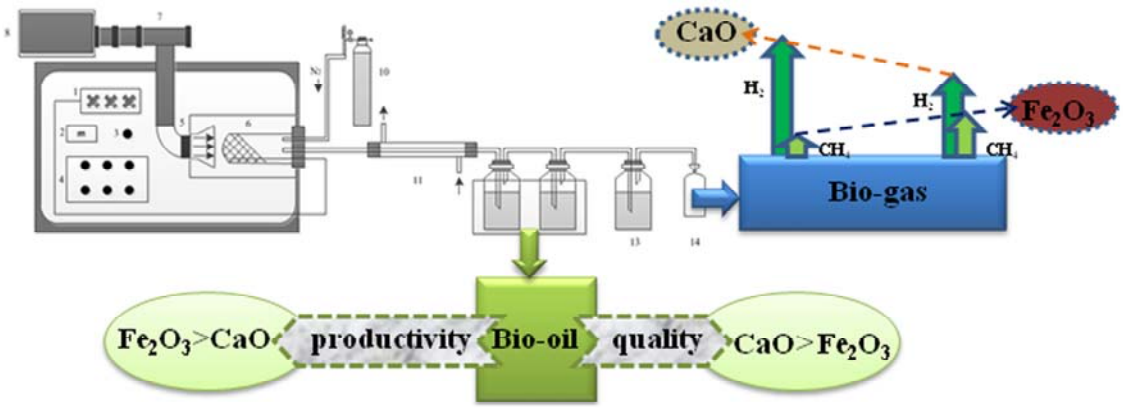

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