# Partial oxidation of municipal sludge with activited carbon catalyst in supercritical water

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## ABSTRACT

The partial oxidation (POX) characteristics of municipal sludge in supercritical water (SCW) were investigated by using batch reactor. Effects of reaction parameters such as oxidant equivalent ratio (OER), reaction time and temperature were investigated. Activated carbon (AC) could effectively improve the mole fraction of $H_2$ in gas product at low OER. However, high OER (greater than 0.3) not only led to the combustion reaction of CO and $H_2$, but also caused corrosion of reactor inner wall. Hydrogenation and polymerization of the intermediate products are possible reasons for the relative low COD removal rate in our tests. Metal oxide leached from the reactor inner wall and the main components of the granular sludge were deposited in the AC catalyst. Reaction time had more significant effect on BET surface area of AC than OER had. Long reaction time led to the methanation reaction following hydrolysis and oxidation reaction of AC in SCW in the presence of oxygen. Correspondingly, the possible reaction mechanisms were proposed.

## 1. Introduction

It is known that municipal sludge is the byproduct of sewage disposal, which contains organic matter, heavy metal and a large number of pathogen. If not be handled properly, it is possible to cause secondary pollution to the environment. Treatment of sludge can be very intricate by conventional treatment methods. Nevertheless, the hydrocarbon in sludge, if utilized wisely, would be a renewable source of energy to produce hydrogen. The topic of municipal sludge reforming for hydrogen production has received some attention [1,2].

Supercritical water ($T_c$ = 647 K and $P_c$ = 22.1 MPa), as one of the most suitable and effective reaction medium for biomass feedstock with high moisture content, has attracted wide attention due to its unique physicochemical properties and environmentally benign nature [3]. Supercritical water oxidation (complete oxidation, SCWO) is mainly applied to the destruction of harmful organics, whose primary target is to convert organics to $CO_2$ and $H_2O$ as much as possible without any consideration of chemicals recovery or production selectivity. Much work has been done in this research field [4–6].

SCW can also provide a favorable environment for partial oxidation (POX) reaction. Previous study demonstrated that hydrogenation of hydrocarbons through POX and water–gas shift reaction occurs in SCW without addition of hydrogen [7]. Oxidant can play a key role in improving the gasification efficiency and meanwhile decrease the production of char and tar so that the continuous operation of the system can be guaranteed [8]. Different from complete oxidation, CO produced by POX reaction can be consumed by water–gas shift reaction and therefore leads to $H_2$ production. Adschiri et al. [9] reported that, in the presence of oxygen, effective hydrogenation reaction took place in SCW. Hydrogenation occurs faster in CO-SCW and $H_2$-$CO_2$-SCW than in $H_2$-SCW and the CO selectivity in POX process increased with water density [7]. Water density has influence on the distribution of POX products, and formaldehyde was found to play an important role in the product selectivity and the POX chemistry [10,11]. The POX reaction pathway of p-Xylene has been examined by Kim et al. [12]. In addition, partial oxidation reaction concerning catalysts in SCW has been explored by some researchers [13,14]. Supercritical water gasification (SCWG) is an endothermic process, but POX technology can integrate the endothermic gasification reaction with the exothermic oxidation reaction in one reactor to realize the internal coupling of the heat transfer and the reaction process [8]. Smith and Adschiri [15] provided a systematic investigation on energy integration of methane's POX in SCW and exergy analysis. They held the view that conversion of methane to methanol and carbon monoxide in SCW can be accomplished by supplying only chemical exergy.

Activated carbon is a catalyst with great potential for hydrothermal reaction due to its low-cost, abundant availability and non-toxicity. AC such as spruce wood charcoal, macadamia shell

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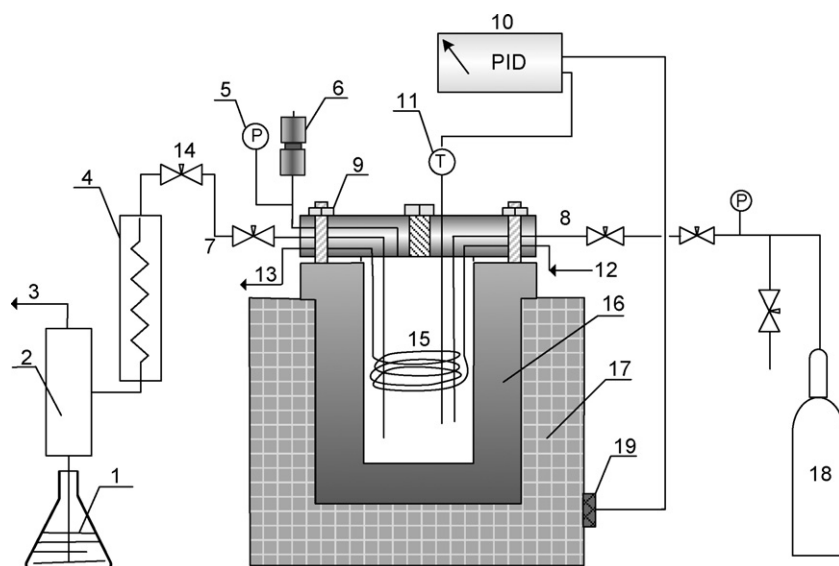*E-mail address:* s_z_wang@yahoo.cn (S.Z. Wang).

**Fig. 1.** Schematic presentation of the experimental setup.

charcoal, coal activated carbon and coconut shell for SCWG process of organic feedstock was probably the first evaluated by Matsumura and co-workers [16]. They suggested that the reaction pathway should include adsorption of a reactant or an intermediate onto the carbon surface, which is likely to have a significant effect on the catalytic performance of the AC [17]. Antal et al. [18] found that biomass laden gel can be steam reformed over a packed bed of carbon catalyst into a gas composed of hydrogen, carbon dioxide, methane, carbon monoxide, and traces of ethane. Although the presence of oxygen may result in the drawback of its combustion, carbonaceous materials can be utilized as a fuel to promote the destruction of the target materials rather than as a catalyst [19]. It can also compensate for the heat needed in SCWG process.

Most of the above studies mainly focused on the hydrogenation of organic compound. Besides, AC catalyst was used in SCWG reaction, while it is noted that little of published literature concerning AC catalyst used in supercritical water partial oxidation has been available so far. The aim of this study is to characterize the catalytic effect of activated carbon on production distributions in supercritical water partial oxidation. We also investigated the effects of the process variables such as temperature, reaction time, and oxidant equivalent ratio on the whole reaction process. Besides, the corresponding reaction pathways were also discussed.

## 2. Experimental

### 2.1. Experimental apparatus and procedure

The experimental set-up of the batch reactor system is illustrated in Fig. 1. The reactor was made of stainless steel 316, which was designed to a maximum temperature and pressure of 773 K and 35 MPa, respectively. The volume capacity of the reactor was 572 cm$^3$ and the inside temperature was controlled by the PID temperature controller unit using Pt100 as the temperature sensor (temperature-controlled precision is ±1 K). A cooling coil was fixed in the reactor and to be used in cooling the reactor fairly rapidly with water to ambient temperature at the end of each experiment. The sludge slurry sample was collected from WuXi sewage treatment plant with water content of 99.84%. Besides, the results of proximate and elementary analysis are shown in Table 1. H$_2$O$_2$, which was obtained from TianJin FuChen chemical agent company as a 30 wt% solution, served as the oxygen source.

According to the temperature and pressure required in this experiment, a known volume of sludge slurry and quantitative AC catalyst were loaded in the reactor. This was followed by the addition of a known volume of hydrogen peroxide to bring the total volume of liquid to desired volume (calculated by water physics properties software when desired reaction temperature and pressure were given). The amount of hydrogen peroxide was less than the stoichiometric requirements for complete oxidation. Before heating, purge whole system with nitrogen for 10 min in order to reduce the influence of residue oxygen in the air and sludge particles on the experimental result as much as possible. After purging, the reactor was heated at 4.07 °C min$^{-1}$ (average value) to the final temperature. As soon as the set temperature was reached, the reactor was held for a specified time. At the end of each experiment, the heating was stopped and mixture of products exited the reactor. The products were quickly cooled and depressurized. Then the cooled effluent was separated into the gas and liquid phases. The gas and liquid products were collected by airbag and conical beaker, respectively. The airbag used in our study is made of rubber, which was vacuous and connected to the vent of pipeline 3 before the gas collection after each run. The catalyst and corrosive samples were obtained after opening the end closure of the reactor under ambient condition.

### 2.2. Analysis

The gas composition was determined by using a gas chromatograph (Shanghai, GC-112A) equipped with a thermal conductivity detector (TCD) and a 3 m × 3 mm TDX-01 packed column; helium served as the carrier gas and the flow rate and the pressure were 18.5 mL/min and 0.42 MPa respectively; the column temperature was maintained at 353 K and the TCD detector temperature was maintained at 373 K. The method of analysis is simple and effective for the detections of H$_2$, CO$_2$, CO, CH$_4$, N$_2$ and other light organic gases. Measurements of chemical oxygen demand (COD) and ammonia–nitrogen (NH$_4$–N) in the liquid product were conducted by individual Merck cell test via the Spectroquant NOVA 60 minpectrophotometer. The analysis of the corrosion sample and AC catalysts was performed by scanning electron microscopy (SEM, HITACHI S-2700) equipped with energy-dispersive X-ray analysis (EDX, EDAX) system. Surface areas and average pore size of AC catalysts were measured by N$_2$ adsorption at the temperature of

**Table 1**
The proximate and elementary analysis[a] of the sludge sample[b].

| Oxide percentage composition (%) | | Metal element content (mg/kg) | | Nonmetallic element composition (%) | |
|---|---|---|---|---|---|
| $SiO_2$ | 15.63 | Cr | 220.70 | C | 33.88 |
| $Al_2O_3$ | 4.18 | Pb | 43.75 | H | 3.02 |
| $Fe_2O_3$ | 2.04 | Ni | 99.10 | O | 21.05 |
| CaO | 4.19 | Cu | 170.30 | N | 4.14 |
| MgO | 1.99 | Zn | 210.52 | S | 0.93 |
| $K_2O$ | 0.93 | Hg | 2.50 | | |
| $Na_2O$ | 0.52 | Cd | 7.86 | | |
| $P_2O_5$ | 1.87 | | | | |

[a] The data is obtained from testing report of laboratory in Coal Geological Bureau in Shaanxi province.
[b] After drying sample

**Table 2**
Summary of the experiments in this investigation.

| $T$ (K) | $P$ (MPa) | OER | Reaction time (min) | Addition of AC (wt%) | Initial COD (mg/L) | Final COD (mg/L) |
|---|---|---|---|---|---|---|
| 633 | 22.5 | 0.5 | 30 | 0 | 4470 | 451.5 |
| 653 | 22.5 | 0.5 | 30 | 0 | 4360 | 381.5 |
| 673 | 22.5 | 0.5 | 30 | 0 | 4575 | 234.2 |
| 698 | 26 | 0.5 | 30 | 0 | 4520 | 212.4 |
| 633 | 23 | 0.5 | 30 | 1.0 | 4320 | 331.3 |
| 653 | 23 | 0.5 | 30 | 1.0 | 4375 | 341.7 |
| 673 | 23 | 0.5 | 30 | 1.0 | 4460 | 223.4 |
| 698 | 23 | 0.5 | 30 | 1.0 | 4315 | 152.3 |
| 683 | 26 | 0 | 30 | 0 | 4450 | 906.0 |
| 683 | 26 | 0.3 | 30 | 0 | 4295 | 607.3 |
| 683 | 26 | 0.5 | 30 | 0 | 4110 | 392.5 |
| 683 | 26 | 0.8 | 30 | 0 | 4060 | 356.9 |
| 683 | 26 | 0 | 30 | 1.0 | 4335 | 529.3 |
| 683 | 26 | 0.3 | 30 | 1.0 | 4395 | 485.6 |
| 683 | 26 | 0.5 | 30 | 1.0 | 4430 | 462.0 |
| 683 | 26 | 0.8 | 30 | 1.0 | 4355 | 371.0 |
| 673 | 23.5 | 0.5 | 30 | 1.0 | 3590 | 179.9 |
| 673 | 23.5 | 0.5 | 60 | 1.0 | 3560 | 119.6 |
| 673 | 23.5 | 0.5 | 90 | 1.0 | 3615 | 296.8 |
| 673 | 23.5 | 0.5 | 120 | 1.0 | 3410 | 207.7 |

77 K using a surface and porosity analyzer (BET, Quantachrome Autosorb-1) using BET method.

### 2.3. Data interpretation

The chemical oxygen demand (COD) removal rate and oxidant equivalent ratio (OER) are defined as follows:

$$COD\,removal\,rate(\%) = \frac{COD_{sludge} - COD_{product}}{COD_{sludge}} \times 100\% \neq \qquad (1)$$

where $COD_{slugde}$ and $COD_{product}$ are chemical oxygen demand of sludge sample and product, respectively (mg/L).

$$OER = \frac{O_{2,add}}{COD_{sludge}} \qquad (2)$$
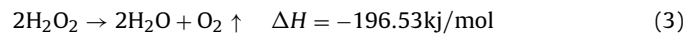
where, $O_{2,add}$ is calculated by the stoichiometric equation (Eq. (3)) and the $COD_{sludge}$ is initial COD of sludge sample.

$$2H_2O_2 \rightarrow 2H_2O + O_2 \uparrow \quad \Delta H = -196.53 kj/mol \qquad (3)$$

It is assumed that the gaseous product would not be dissolved into the liquid effluent.

### 3. Results and discussion

In this paper, the influences of temperature, OER and reaction time were investigated by single factor experiments. Table 2 summarizes the experimental conditions employed in this study along with the COD testing results we obtained.
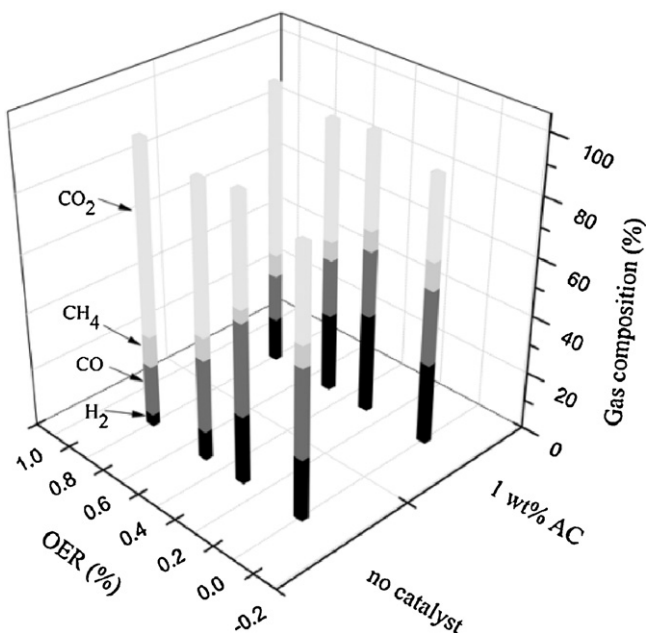
**Table 3**
Testing results with different temperature.

| Entry[*] | $T$ (K) | Addition of AC (wt%) | Mole % of gaseous products (%) | | | | COD removal rate (%) |
|---|---|---|---|---|---|---|---|
| | | | $H_2$ | CO | $CH_4$ | $CO_2$ | |
| 1 | 633 | 0 | 7.6 | 40.6 | 12.3 | 30.5 | 89.9 |
| 2 | 653 | 0 | 9.4 | 37.6 | 9.2 | 37.0 | 91.3 |
| 3 | 673 | 0 | 10.2 | 26.5 | 8.5 | 49.0 | 94.9 |
| 4 | 698 | 0 | 12.2 | 27.0 | 6.5 | 50.0 | 95.3 |
| 5 | 633 | 1.0 | 13.2 | 38.6 | 10.5 | 30.6 | 92.3 |
| 6 | 653 | 1.0 | 17.6 | 32.2 | 8.7 | 32.6 | 92.3 |
| 7 | 673 | 1.0 | 27.0 | 20.2 | 7.5 | 37.0 | 95.0 |
| 8 | 698 | 1.0 | 33.1 | 17.6 | 6.7 | 40.1 | 96.5 |

[*] The same order in Table 2.

**Fig. 2.** Gas production distribution of sludge POX in SCW under different OER conditions.



**Fig. 3.** SEM images of surface morphologies of SS316 tested at: 673 K and 25 MPa for 4 h. (A) and (C) OER = 0; (B) and (D) OER = 0.3.

### 3.1. Effects of temperature

Table 3 shows the molar % of gaseous effluents and COD removal rate with different operating temperature. The experiments were conducted at 0.5 OER with the reaction time of 30 min. Increasing temperature in the system from subcritical to supercritical conditions resulted in a decrease in the CO mole %. However, the mole % of $H_2$ and $CO_2$ increased with increasing temperature. The variation was insignificant above certain temperature point without AC addition. Lower viscosity can provide a high diffusion coefficient for SCW, which in turn can create a perfect reaction condition for high reaction rate. It indicates that chemical reaction equilibrium could be easily reached, which would lead to the further slower variation of mole % of gas products in this case.
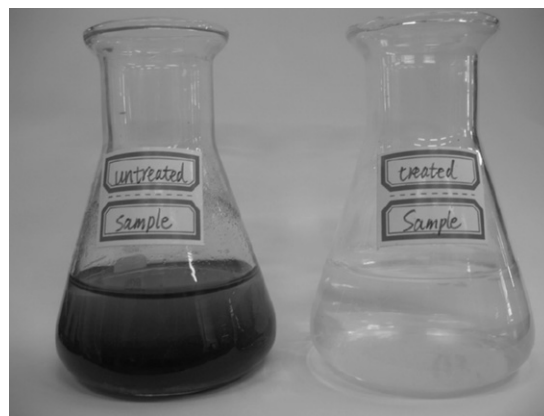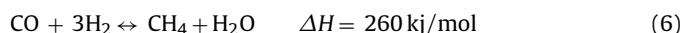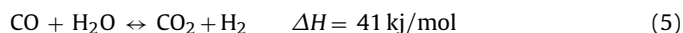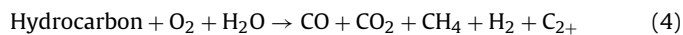
The experiments with AC catalyst (1 wt%) under the same base case condition were also conducted. As shown in Table 3 (entry 5–8), increment of $H_2$ mole % was more significant than that without AC addition. It is clear that the mole % of $H_2$ could be effectively improved by adding AC catalyst. The possible reaction pathways can be explained by Eqs. (4)–(7). Hydrocarbon in sludge can produce CO via POX reaction in SCW (Eq. (4)). Then, two competing reactions (Eqs. (5) and (6)) for CO may have crucial influence on the product distribution.

$$Hydrocarbon + O_2 + H_2O \rightarrow CO + CO_2 + CH_4 + H_2 + C_{2+} \qquad (4)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H = 41\ kj/mol \qquad (5)$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad \Delta H = 260\ kj/mol \qquad (6)$$

The Eq. (5) would be favored in the presence of AC catalyst reflected in the high $H_2$ mole % in the gaseous products. On the contrary, the mole fraction of methane was negatively correlated with increasing temperature. Corresponding to the Le Chatelier principle, the heat release of Eq. (5) is lower than that of Eq. (6), which indicates that the water–gas shift reaction is thermodynamically more preferred at higher temperature conditions. The presence of the AC catalyst may lead to a preferential adsorption of CO and $H_2$
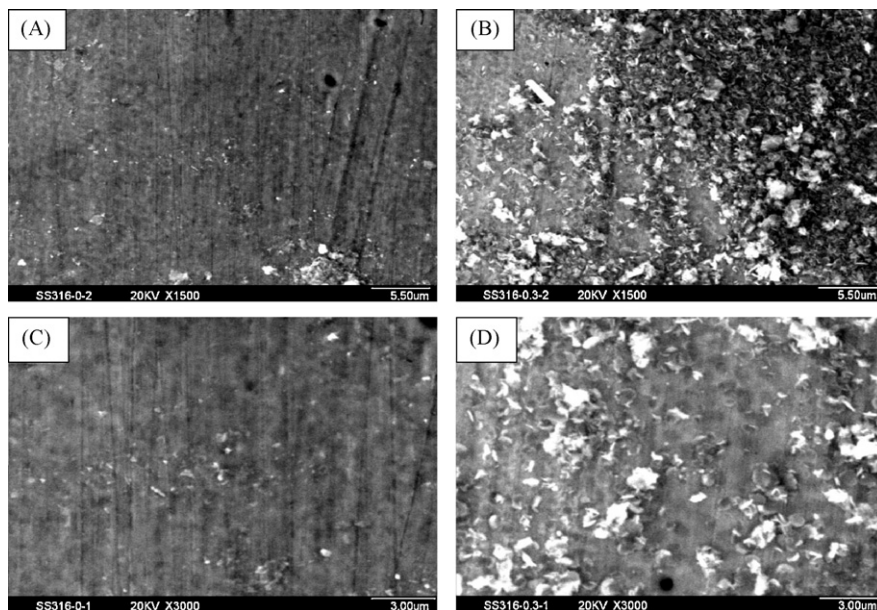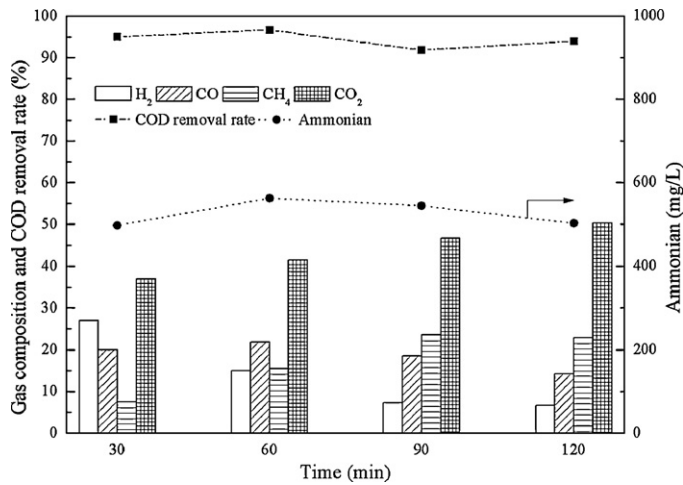


**Fig. 4.** Photo of untreated sludge sample (left) and liquid product after being treated (right, 0.5 OER with 1 wt% AC).

**Fig. 5.** Gas composition, COD removal rate and ammonian in the product of sludge POX in SCW at different reaction time with 1 wt% AC catalyst (0.5 OER, 673 K and 23.5 MPa).

on AC surface for yield of $CH_4$ [16]. But an oxidation reaction may be involved in the process for a further $H_2$ regeneration (Eq. (7)).

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \quad \Delta H = 36 \text{kJ/mol} \tag{7}$$
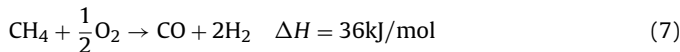
The variations of COD removal rate (<96.5%) were almost unaffected at different operating temperatures. We noted that it is obviously lower than the experimental value of our previous article (>99.2%) about SCWG of glycine and glycerol (model compounds of protein and fattiness in municipal sludge) [20]. This phenomenon could be explained by a wide number of unknown intermediate products as a result of hydrogenation reaction following the POX reaction in SCW [7]. It also may be attributed to the complex components of sludge and relatively lower operating temperatures in our tests.

### 3.2. Effects of OER

Fig. 2 shows the mole fraction of $H_2$, $CH_4$, CO and $CO_2$ with different OER for sludge POX in SCW with and without AC catalyst. The experiments were conducted at 683 K, 25 MPa with a 30 min reaction time. The mole % of $H_2$ went through a maximum at 0.3 OER, and further decreased as OER increased in all experiments with and without AC catalyst. There was a similar tendency of mole % of CO toward that of $H_2$. It indicates that small amount of oxidant can accelerate the production of $H_2$, but too much oxidant may lead to the combustion reaction of $H_2$ and CO to produce $CO_2$ and $H_2O$. In SCW reaction in which a small amount of oxygen is present, there are two competing pathways: gasification and oxidation reaction. For low levels of oxygen, the steam reforming reaction to hydrogen is more important than oxidation. However, when the oxygen coefficient values are above a definite value, the hydrogen levels drop because oxidation reaction becomes predominant [21]. It means that the oxidant concentration is an important parameter for the optimization of the hydrogen production process. By contrast, the $CH_4$ mole fraction was not much affected by variation of OER in our tests. This result agrees with the conclusion of other previous researches [22,23].

Oily substance was produced when the OER was low. However, liquid effluent became colorless as the reaction proceeded from OER of 0–0.8 in our experiments. The photo of untreated sludge slurry sample and liquid effluent after treated with 0.5 OER is shown in Fig. 3. Our findings are in substantial agreement with those of Williams and Onwudili [22]. They suggested, in the SCWG experi-
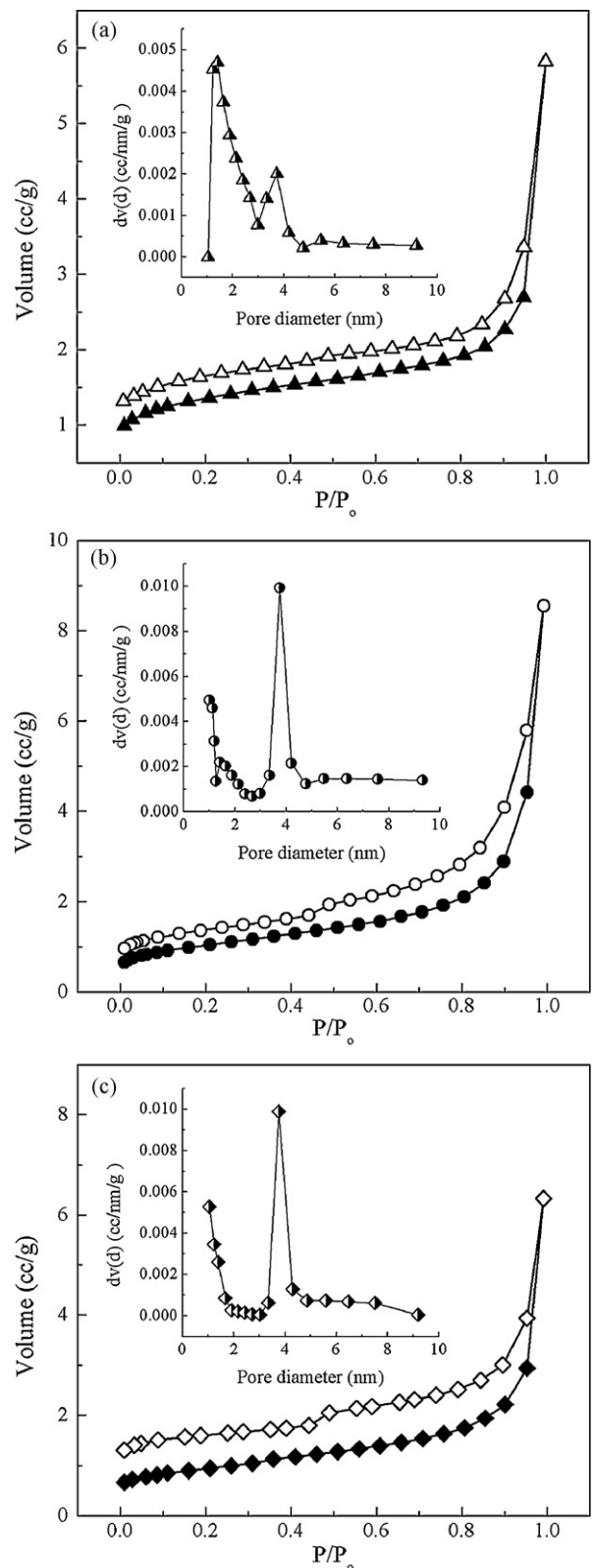


**Fig. 6.** $N_2$ adsorption–desorption isotherms and BJH pro size distributions (inset) of the AC catalysts. (A) The fresh sample. (B) The sample collected after reaction of 0.5 OER and 673 K within 30 min reaction time (C) The sample collected after reaction of 0.5 OER and 673 K within 120 min reaction time. adsorption (▲ ● ◆), desorption (△ ○ ◇).
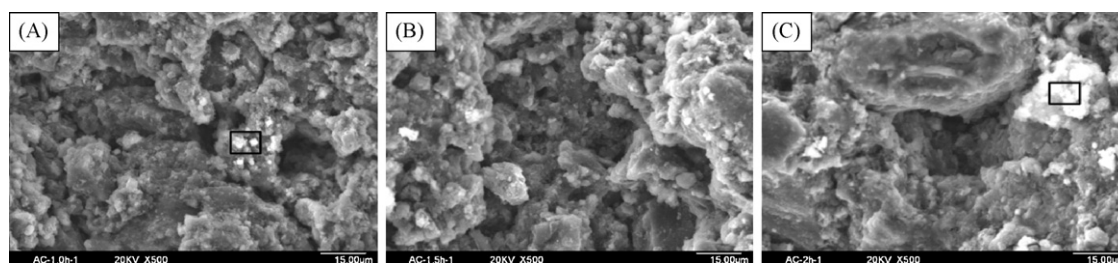
**Fig. 7.** SEM images of surface morphologies of used AC catalyst tested at: 673 K, 25 MPa and OER of 0.5. (A) 60 min; (B) 90 min; (C) 120 min.

ments of glucose, a large amount of carbonization reflected in the high production of char and oil in the absence of any hydrogen peroxide. High concentration of $H_2O_2$ was not only helpful to decrease the amount of char or oil but also result in the increasing yields of water and gas. As also reported by Lee and Foster [23], in the process of SCWO of methane, the main products were $H_2O$, CO and $CO_2$ with sufficient oxygen. However, high selectivity of intermediate product was observed at lower conversions of oxygen.

Fig. 4 shows SEM images of surface morphologies of SS316 tested at 673 K and 25 MPa for 4 h (OER of 0 and 0.3). As Fig. 4 shows, most of the metal surface is covered by metallic oxide in the case of 0.3 OER after test, which, however, is little produced under the condition without addition of $H_2O_2$. It indicates that partial oxygen in the reaction system can be consumed by reactor inner wall to form oxide films. But this iron-rich film was unstable and covering thinly on the metal surface and very likely to flake off under oxidation condition. Gao et al. [24] also found that the oxide films formed on SS 316 exposed to $H_2O_2$-containing SCW showed poor protection against corrosion in SCWO environment. But this part of oxygen was undetectable and not taken into account in this investigation.

### 3.3. Effects of reaction time

The gas compositions, COD removal rate and ammonia–nitrogen content in the product for POX of sludge in SCW at different reaction time with AC catalyst are depicted in Fig. 5. It is observed that the mole fraction of $H_2$ decreased from 27% to 6.6% when reaction time increased from 30 to 120 min. Mole % of CO reaches a maximum value of 21.9% at 60 min and then fall to 14.2% as the reaction time increased. The mole % of $CH_4$ increased from 7.5% to 22.9% as the reaction time increased from 30 to 120 min. Methanation reaction (Eq. (7)) may be a possible explanation for this phenomenon.

Activated carbon is easily subject to hydrolysis in SCW. Our experimental results support the suggestion that methane formation is due to pyrolysis of the activated carbon itself via Eq. (8) to produce CO and $H_2$ in high temperature water [17]. Besides, an irreversible adsorption of hydrogen atoms onto the carbon surface react with dangling carbon atoms and then methane is formed [25].

$$C + H_2O \rightarrow CO + H_2 \quad \Delta H = 131.4 kJ/mol \quad (8)$$
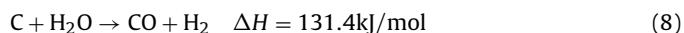
In contrast, previous researchers reported that the gas product distribution was almost constant at different reaction time in the SCWG of glucose [26]. This inconsistency may be caused by the polymerization of the intermediate product, which is easier to occur in SCWG reaction without addition of oxidant. However, in the presence of oxidant, the polymerization can be inhibited to

some extent, consequently lead to the change of the gas product distribution. Besides, AC as a carbon source may have an effect to the chemical equilibrium.

In our experiments, COD removal rate and ammonia–nitrogen content had no evident variation with increasing reaction time. The complete conversion or removal of nitrogen-containing organic compounds is difficult in hydrothermal oxidation condition, because it can produce $NH_3$ in subcritical water [27], which is still stable in SCWO environment with high OER even above 873 K [28–30]. As can be observed in our experiment results, AC had no promoting effect on the conversion of ammonia–nitrogen.

### 3.4. Performance of catalyst

BET surface area of the present AC catalyst decreased from 24.92 to 23.72 $m^2/g$ after reaction of 673 K and 0.5 OER within 30 min, and decreased drastically to 18 $m^2/g$ within 120 min. It is evident that reaction time had more significant influence on surface area of AC catalyst compared with OER. The $N_2$ adsorption–desorption isotherms and BJH pro size distributions (inset) of the AC catalysts are shown in Fig. 6. The fresh catalyst has an average pore size of 1.407 nm, and that of the catalysts collected after the reaction (0.5 OER, 673 K) within 30 and 120 min were 3.745 and 3.750 nm, respectively. There were similar changes in pore size of the both fresh and reacted catalysts under two different reaction conditions, which suggested that the pore size of AC catalyst was vulnerable to SCW condition in the presence of oxygen even within short reaction time.

SEM images of surface morphologies of reacted AC catalyst tested at different reaction time are demonstrated in Fig. 7. It can also be found that the surface morphology of AC catalyst was modified to a great extent as reaction time increased, and some oxide adsorbed on the AC catalyst (the white substance in the photos) increased with the increasing reaction time as well. This change of surface morphologies indicates that hydrolysis and oxidation reaction of AC catalyst occurred after being exposed to SCW for long reaction time in the presence of oxygen (Eq. (9)).

$$2C + H_2O + O_2 \rightarrow CO + CO_2 + H_2 \qquad exothermic \quad (9)$$
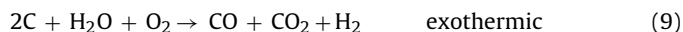
However, according to the results of BET analysis, it seems that Eq. (9) was not favored under the condition of low OER and short reaction time, because most of the oxygen was consumed by POX reaction of hydrocarbons in sludge within a short period of reaction time.

Our results showed that AC catalyst had a positive effect on hydrogen production. It is hypothesized that surface of AC catalyst

**Table 4**
Compositions[a] of the AC catalyst surface with different reaction time after experiments.

| Reaction time | O | Mg | Al | Si | P | Mo | K | Ca | Ti | Fe |
|---|---|---|---|---|---|---|---|---|---|---|
| 60 min | 30.16 | <0.01 | 22.99 | 32.07 | 2.08 | 3.54 | 1.63 | 1.46 | <0.01 | 6.07 |
| 120 min | 27.06 | 2.41 | 19.65 | 32.80 | 2.08 | 9.21 | <0.01 | <0.01 | 1.72 | 5.06 |

[a] Scan area of EDX point analysis (results in wt%) on the catalyst surface is shown in the Fig. 7.

may have a selective adsorption ability of CO and $H_2$. More detailed discussion is presented in Section 3.1. Xu et al. [16] reported that activated carbon cannot only improve the water–gas shift reaction, but also accelerate the methanation reaction to produce huge amount of methane. This phenomenon is consistent with our experimental result. But we believe that it mainly occurs under the condition of relatively long reaction time.

The adsorption capacity of AC catalyst was testified by EDX analysis. Some traces of elements, as can be seen from Table 4, were deposited in AC catalyst. These substances were mainly supposed to be the siallite residue in sludge and dissolved metal oxide leaching from reactor inner wall. Previous researchers [18] also reported that nickel and other metal were leached from the reactor inner wall (made of Inconel C-276) and deposited in the AC catalyst. Catalytic effect of Ni has been proved by numerous studies [31–34]. However, in our tests, we did not find Ni element in the used AC catalyst. It may be due to the relatively low Ni content in SS 316 material employed in our experimental equipment.

## 4. Conclusions

Our experiments of sludge partial oxidation in supercritical water were conducted in batch type reactor and the following results were obtained:

(1) The mole % of $H_2$ in gaseous production was enhanced with the increased temperature at OER of 0.3 and 25 MPa. The production of $H_2$ can be effectively improved by adding AC catalyst. Mole fraction of methane is negatively correlated with increasing temperature. The COD removal rate was unaffected by increasing temperature, which suggested that intermediate products were formed via hydrogenation reaction after POX reaction in SCW.
(2) The maximum level of hydrogen fraction was reached at OER of 0.3. High concentration of $H_2O_2$ was helpful to decrease the amount of oily production, while excessive OER would lead to the combustion reaction of CO and $H_2$, and caused the corrosion of the reactor inner wall made of SS 316.
(3) Long reaction time resulted in the reduction of BET surface area of activated carbon used in our investigation. Hydrolysis and oxidation reaction of AC catalyst occurred at the conditions investigated, then methanation reaction proceeded as reaction time increased. According to the analysis of the EDX test, it was found that the metal oxide leached from the reactor inner wall and main components of granular sludge were deposited in AC catalyst. Ammonia–nitrogen content was unaffected by the reaction time.

As illustrated by the results, activated carbon not only acts as a catalyst but also as a source of carbon can improve the partial oxidation reaction in SCW, which could be utilized for recycling and harmless treatment of municipal sludge. However, the evaluation of the potential gas yield still need to be made in continuous type experimental equipment and the chemistry of sludge POX reaction in SCW will be studied in more detail by subsequent investigations.

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