Effect of Fe/Ca-based composite conditioners on syngas production during different sludge gasification stages: Devolatilization, volatiles homogeneous reforming and heterogeneous catalyzing

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Abstract

The process of sewage sludge steam gasification can be divided into three stages: devolatilization, volatiles homogeneous reforming and heterogeneous catalyzing. This study investigated the direct and indirect impacts of Fe/Ca-based conditioners on syngas generation at different stages using a special decoupling reactor. The results show that the highest \( \text{H}_2 \) production for raw sludge gasification was 190 mL/g at 1273 K. The maximum promotion of \( \text{H}_2 \) yield was 51.2% for Fenton's reagent (\( \text{Fe}^{2+} + \text{H}_2\text{O}_2 \)) addition at 1273 K and 132.5% for CaO addition at 1073 K. Among that, 52.8% and 62.9% of \( \text{H}_2 \) increment was attributed to the catalytic effect on devolatilization stage respectively. Fenton oxidation was conducive to the conversion and fixation of protein structure while the corresponding organic matter in CaO-conditioned sludge was aromatics. The catalysis of volatile reforming was proven an important process, thus reusing char/ash as bed material or cracking catalysts maybe a promising method for hydrogen energy production.

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Introduction

With the development of society, the consumption of fuel is increasing rapidly in recent years. Because of non-renewable energy sources, keeping the trend of decrease and difficult to meet the large demands of energy in the developing countries [1]. Compared with the heavily polluting coal, the development of renewable and clean biofuel becomes necessary and has attracted widespread attention [2,3]. Sewage sludge, a kind of municipal solid waste with large amounts of microorganisms and organics, can be converted to clean H₂ via thermal treatment [4,5]. In this way, sludge is a potential renewable resource for hydrogen energy production [6].

Among all the thermochemical technology, steam gasification provides the highest stoichiometric yield of hydrogen [7]. Nipattummakul et al. [8] found that the hydrogen yield during sludge steam gasification was three times as compared to air atmosphere. Gai et al. [9] obtained 16–28% hydrogen production from sludge steam gasification at 973–1273 K, and the lower heating values reached from 3.54 to 6.36 MJ/m³. However, sludge contained abundant heavy aromatic compounds, which would volatilize and condense to tar in case of insufficient decomposition [10]. The generation of tar not only caused the serious operational interruptions, but also influenced the yield and quality of syngas so that the use was limited [11]. Schweitzer et al. [12] detected a high tar yield of 80 g/kg dry sludge in the process of sludge steam gasification, and only 51 mol.% of the carbon was converted to gas product. Roche et al. [13] also found that the tar concentration was 4.1–9.8 g/m³ at different throughput during sludge pyrolysis, and the tar removal was only 17–24% in condition of steam supply. Relatively high concentration of tar and low conversion efficiency of syngas seriously hindered the application and development of sludge steam gasification technique. To solve these difficulties, catalyst was introduced into gasification technology [14,15].

Considerable research efforts have been devoted to develop the different types of catalyst acting on the process of fuel thermal conversion, such as alkalis, transition metals and minerals [3,16,17]. Among them, Ca-based and Fe-based catalysts were widely used because they were cheap, available and efficient [18,19]. Chiang et al. [20] mixed CaO with bamboo chopsticks during gasification, resulting in high hydrogen production and syngas heating values. Virginie et al. [21] found that the yield of tar reduced by up to 65% at 1123 K with the addition of Fe/olivine during pine wood gasification. The synergistic effect was observed on H₂ promotion when CaO was impregnated with Fe, and the activity of nascent Fe/ CaO catalyst was determined by species and ratio of synthetic precursors [22,23]. Except directly mixed with fuel to preliminarily catalyze the cracking of volatile, Ca-based and Fe-based catalysts could be also loaded in a separate reactor in downstream of the gasifier to carry out secondary catalysis [24]. In this case, condensable gas was further reformed with steam to reduce tar content as well as improve H₂ production [25]. For sludge treatment, Fe/Ca-based minerals were usually added as conditioner instead of physical additive during conditioning for sludge deep dewatering [26]. Our previous studies indicated that the residual Fe/Ca in sludge matrix distributed evenly and existed in different form. They were found to catalyze the gasification reaction, and the H₂ production was higher than that under condition of Fe/Ca-based minerals physically mixing with dry sludge [27–29].

Because of relative high Fe/Ca content in sludge after deep dewatering, it is worthwhile that the two catalytic processes mentioned above may be presented simultaneously in a fluidized bed reactor. As the rate of devolatilization was faster than char steam gasification, the volatiles from the continuously fuel feeding would be reformed in steam atmosphere with the gasifying char [30]. Thus, the conditioner Ca/Fe in sludge could firstly enhance the process of devolatilization, and then remain in char to catalyze the reforming of tar. However, it is doubt that which catalytic process is more important for Fe/Ca-conditioned sludge gasification. The understanding of related mechanism is helpful to strengthen the route of H₂ production. In this study, a special decoupling gasification reactor was designed to quantify the effect and clarify the catalytic mechanism of conditioner Fe/Ca on different catalytic process.

Experimental

Sample preparing

Raw sludge (named RS) was received from a municipal wastewater treatment plant in Wuhan, China. The initial moisture content was about 80%. Firstly the RS was mixed with water to form slurry (moisture content was 93%), and was subsequently conditioned respectively with Fenton’s reagent (Fe²⁺ + H₂O₂), CaO and Fenton/CaO addition (named S-Fenton, S-CaO and S-Fenton-CaO). The dosage and procedure can be seen in Ref. [31]. Four samples in 180–250 μm were prepared through drying, crushing and screening. The basic characteristics of sludge samples were listed in Fig. 1 and Table 2 [31]. After conditioning and dewatering, the content of C and H decreased and most of Ca and Fe were remained in the sludge matrix.

Sludge decoupling gasification

The different stages of gasification were performed using a special decoupling gasification reactor (Fig. 1). The reactor consisted of three parts: (1) The injector, which provided water-cooling to prevent samples reacting before the constant temperature zone; (2) The intermediate reaction tube with 420 mm length of reaction zone (from the bottom of injector to that of the intermediate reaction tube) and 25 mm inner diameter. Around the bottom of this reactor, sintered quartz filter was inlaid to separate volatile from sample particles in the process of devolatilization; (3) The outer tube with 2000 mm length and 74 mm inner diameter. Two symmetrical steam inlet tubes were designed on the top the outer tube, and outlet ones were 100 mm below the intermediate reaction tube to carry out the individual steam reforming of the volatile. In order to explore the catalytic role of dewatered sludge char on the steam reforming of the volatile, a ring support about 400 mm below the intermediate reaction tube was...
designed to keep quartz basket (quartz filter bottom) with char loading. The reactor contained two “air” inlets and an “air steam” inlet. The two “air” inlets provided the carrier gas of intermediate reaction tube and outer tube, and the “air steam” provided the carrier gas for steam injection.

The effect of conditioners on different gasification stage was distinguished by comparing three experiments: (a) Devolatilization experiment, with pure argon atmosphere; (b) Volatiles steam reforming experiment. On the basis of experiment a, the steam was injected through steam inlet tubes at the 1.5 M ratio of $H_2O/C$; (c) Volatiles catalytic reforming experiment. On the basis of experiment b, a certain amount of char (collected from experiment a according to the char yield at different devolatilization temperatures) was loaded in quartz basket to provide catalytic medium. In each experiment, 0.2 g/min sludge sample was fed continuously along with 1.8 L/min carrier gas at different temperatures (873 K, 1073 K and 1273 K). U-shape tubes were used for gas

Table 1 – Proximate and ultimate analysis of four sludge samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Volatile matter (wt%)</th>
<th>Ash (wt%)</th>
<th>Fixed carbon (wt%)</th>
<th>Ultimate analysis (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>RS</td>
<td>52.10</td>
<td>41.94</td>
<td>5.96</td>
<td>28.27</td>
</tr>
<tr>
<td>S-Fenton</td>
<td>56.38</td>
<td>42.26</td>
<td>1.36</td>
<td>26.72</td>
</tr>
<tr>
<td>S-CaO</td>
<td>46.04</td>
<td>53.70</td>
<td>0.26</td>
<td>20.73</td>
</tr>
<tr>
<td>S-Fenton-CaO</td>
<td>46.13</td>
<td>53.69</td>
<td>0.18</td>
<td>19.60</td>
</tr>
</tbody>
</table>

* Dry basis.

* Calculated by difference.

Table 2 – Mineral compositions (wt. %) of four sludge ashes.

<table>
<thead>
<tr>
<th>Materials</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>SO₃</th>
<th>P₂O₅</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>RS</td>
<td>39.74</td>
<td>15.17</td>
<td>8.49</td>
<td>6.18</td>
<td>2.01</td>
<td>2.74</td>
<td>0.49</td>
<td>5.69</td>
<td>16.61</td>
<td>2.88</td>
</tr>
<tr>
<td>S-Fenton</td>
<td>35.27</td>
<td>13.57</td>
<td>20.42</td>
<td>2.36</td>
<td>1.01</td>
<td>1.58</td>
<td>0.34</td>
<td>9.26</td>
<td>14.55</td>
<td>1.62</td>
</tr>
<tr>
<td>S-CaO</td>
<td>21.43</td>
<td>7.72</td>
<td>5.80</td>
<td>48.84</td>
<td>1.53</td>
<td>1.10</td>
<td>0.22</td>
<td>3.07</td>
<td>8.42</td>
<td>1.87</td>
</tr>
<tr>
<td>S-Fenton-CaO</td>
<td>19.95</td>
<td>7.35</td>
<td>13.51</td>
<td>37.26</td>
<td>1.60</td>
<td>0.93</td>
<td>0.20</td>
<td>9.51</td>
<td>8.07</td>
<td>1.61</td>
</tr>
</tbody>
</table>
collection with ice-water bath and tar collection with liquid nitrogen condensation. The gas products were analyzed by GC (Agilent 7980B) and tar compositions were identified using GC-MS (Agilent 7980A/5975C). The characteristics of char and ash products were decided by elemental analyzer (Vario Micro cube, Germany), XPS (Axis-ultra dld-600W, Japan) and FTIR (Vertex 70, Germany). After each run, the reactor was washed and burned to eliminate the soot, which was less than 0.1 wt %. Each experiment was repeated more than three times.

In order to quantify the effect of conditioners on different gasification stages, the effect value of conditioners on final H₂ promotion (Vfp) and the contribution rate of devolatilization process influenced by conditioners on the final H₂ yield (Rd) were calculated using Eqs. (1) and (2). Where A values are the H₂ yields during volatile catalytic reforming and B values are the H₂ yields during volatile steam reforming.

\[
V_{fp}(\%) = \left( \frac{A_{\text{conditioners}} - A_{\text{RS}}}{A_{\text{RS}}} \right) \times 100
\]

\[
R_d(\%) = \left( \frac{B_{\text{conditioners}} - B_{\text{RS}}}{A_{\text{conditioners}} - A_{\text{RS}}} \right) \times 100
\]

**Results and discussion**

**Syngas products**

The syngas yields including H₂, CH₄ and CO in three experiments were showed in Fig. 2. At 873 K, only 14.5 mL/g CH₄, 15.5 mL/g H₂ and less than 5 mL/g CO were generated during RS devolatilization. When temperature reached 1073 K, the production of syngas especially CO substantially increased, owing to the decomposition of oxygen-containing organics such as lipids, carboxyls and aldehydes. Furthermore, partial small hydrocarbon gases (C₂H₆, C₂H₄, C₃H₈, etc.) maybe also reduced to generate CH₄ and H₂ (Eqs. (3) and (4)) [32]. CH₄ would decompose at higher temperatures according to Eq. (5), resulting in abundant H₂ production. Fenton’s reagent pretreatment reduced CH₄ yield by 8.2 mL/g at 1073 K, and the corresponding H₂ yield increased by 15 mL/g. The ratio of H₂ increment to CH₄ decrement approached to the equivalent coefficient of Eq. (5), suggesting that the H₂ yield promoted by Fenton’s reagent was mainly from the catalytic decomposition of CH₄. However in the case of CaO addition alone, CH₄ production almost unchanged while H₂ yield increased even far more than that from S-Fenton devolatilization. Without a doubt, CaO has been proven to catalyze CH₄ decomposition [33]. The results demonstrated that conditioner CaO also had a well performance on hydrocarbons cracking to CH₄. The integrated effect kept the CH₄ production stable. When both Fenton’s reagent and CaO were used for sludge conditioning, all the syngas would be obtained within a high output because the decrement of CH₄ yield caused by Fenton’s reagent was mitigated with the effect of CaO.

\[
\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 \quad (3)
\]

\[
\text{C}_2\text{H}_4 \rightarrow \text{CH}_4 + \text{C} \quad (4)
\]

Volatiles reforming were a homogeneous process for volatile reacting with steam, including the reforming of non-condensable gas and condensable tar. In this stage, the homogeneous reaction mechanism was almost the same for four kinds of sludge because the conditioners did not participate in the reactions directly. At 873 K, all the syngas yields increased slightly due to the reforming of tar (Eq. (6)). The methane

\[
\text{CH}_4 \rightarrow 2\text{H}_2 + \text{C} \quad (5)
\]
reforming reaction (Eq. (7)) and water gas shift reaction (Eq. (8)) occurred at above 1073 K, as the decrease of CH₄ and CO and significant increase of H₂ yield. After homogeneous reforming, the H₂ yield of RS reached 119 mL/g at 1273 K, but less than that of other dewatered sludge which were 165 mL/g (S-Fenton), 207 mL/g (S-CaO) and 212 mL/g (S-Fenton-CaO) respectively. The volatile generated from dewatered sludge especially via CaO conditioning may contain high CH₄, CO and hydrocarbon gases concentration, enhancing the reforming reactions to release H₂. Thus the conditioners could indirectly influence syngas yield via changing the composition of precursors in the volatile during devolatilization.

\[
\text{Tar} + 2\text{H}_2\text{O} \rightarrow C_n\text{H}_m + \text{CO} + \text{CH}_4 + \text{H}_2 \quad (6)
\]

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad (7)
\]

\[
\text{CO} + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad (8)
\]

The volatiles steam reforming would turn to a heterogeneous process in the presence of char. The minerals in the char could catalyze the hydrolysis of volatiles, and in this period carbon was also gasified to CO and H₂ (Eq. (9)) [34]. The effect of char on volatiles steam reforming became more remarkable with the increasing temperature, leading to more syngas generation. The H₂, CO and CH₄ yield increased in sequence by 51 mL/g, 56 mL/g and 5.5 mL/g at 1273 K during volatiles heterogeneous catalyzing of RS. The increment of H₂ in this step accounted for 30% of the total H₂ yield in the process of RS steam gasification even though the minerals content (seen in Table 2) was relatively low in RS ash, indicating that the gasification of char was an unnegligible step for H₂ production at 873 K, but the change of syngas yield was slight for the same sludge during different gasification stages. Hence the effect of conditioners on syngas at 873 K was mostly on devolatilization process. The effects on other gasification stages may be reflected in the compositions of tar.

**Tar compositions identification**

The methane reforming reaction and water gas shift reaction was endothermic and significant in the process of volatiles steam reforming, but in Fig. 2 the reactions were not of importance at 873 K without enough heat supplying. Thus the condensable tar in volatiles was important and the related compositions were detected and classified in Table 3.

Compared with previous study [31], the construction of tar may be relatively simple for 1 to 4 rings in this experiment. Perhaps the reactor was long enough and caused the secondary cracking of tar. In RS pyrolysis tar, 2-rings structure accounted for 58.9%, including stable naphthalene class and unstable heterocycles. The proportion of branch-containing compounds such as methyl, ethyl and nitrile was the minimum 7.7%. The phenols, benzofuran and acids were the main oxygen-containing compounds in tar and accounted for 7.2%. As a carrier of oxygen, Fenton’s reagent was able to facilitate the oxidation and cracking of 4-rings (fluoranthene, chrysene) to 3-rings and 1-ring phenol, along with the abundant CO emission, which was in accordance with the CO increment in Fig. 2. Zhang et al. [35] found that iron could convert other heavy oxygen-containing tar to light phenols during fast pyrolysis. Conditioner CaO was likely to promote 4-rings and 3-rings further decomposition to benzene homologs and derivates. The high degree of rings opening led to more branch chain formation and H₂ generation. At the same time, the oxygen-containing compounds were only 1.1% in S-CaO pyrolysis tar. CaO had a catalytic cracking ability on acids and aldehydes elimination [36]. The synergistic effect of Fenton’s reagent combined with CaO may be embodied in the deep decomposition of 1-ring compounds. A great amount of toluene, ethylbenzene and styrene were broken down for small molecule hydrocarbon and H₂ generation. Therefore after Fenton’s reagent and CaO conditioning, more unstable small molecule compounds would appear in pyrolysis tar, which were easier to be decomposed for syngas generation at higher temperatures.

With steam supplying, the multiple rings would be hydrolyzed to one-loop and double-loop structure. In the homogeneous system, the reactions largely depended on the different compositions of various sludge tar. Compared with S-CaO, the 3-ring structure in S-Fenton pyrolysis tar was prone to react with steam. The 3-ring structure was stable and saturated phenanthrene and anthracene in S-CaO tar. But after Fenton’s reagent conditioning, more 3-ring compounds containing unstable heterocycles such as pyridine, thiophene and quinoline structure were formed. The hydrolysis of heterocycles also caused the increase of monomicyclic compounds. Partial monomycyclic compounds were hydrolyzed in RS and S-CaO tar, thereby increasing the relative proportion of double-loops in a certain extent. At the same time, benzo[b]furan and a part of phenols reacted with steam as the oxygen-containing compounds decreased. But the yields of syngas almost kept the same. It was speculated that small molecular gaseous
hydrocarbons, aldehydes, ethers and so on may generate during the volatile steam reforming.

With the catalysis of char, the compounds in tar were further composed to simpler ones. More benzene homologs and derivates appeared in RS tar. Iron in S-Fenton char further oxidized tar to form CO and phenols. Different with improving 1-rings during devolatilization, CaO remained in S-CaO char instead enhanced the cracking of benzenes to release H₂. Jordan et al. [37] found that both 3-rings and 1-rings in tar decreased during secondary catalytic gasification with CaO at air atmosphere. Besides, not only conditioners but also carbon structure in char also did work in the process of volatile catalytic reforming. The related conclusions would be discussed later in the section of solid products analysis.

When temperature reached to 1073 K, the branch chains and oxygen-containing structures were only detected in RS tar and the contents were nearly zero in dewatered sludge tar. Hence Table 4 only listed the contents of branch chains and oxygen-containing structures at different gasification stages of raw sludge. High temperature would enhance the decomposition of tar to stable and saturated compounds without branches, oxygen-groups and heterocycles, which may be the reason why the syngas yields especially CH₄ increased rapidly at this temperature. At the moment, the reactions of condensable tar gradually turned to that of non-condensable gas. When up to 1273 K, the yield of tar could be ignored and the conversion of non-condensable gas became the main reactions.

**Solid products characteristic**

As mentioned above, the content of C and H in Table 1 decreased after conditioners addition. In order to understand the transformation of organics in solid during gasification, the contents of C and H on the char after devolatilization stage and the ash after volatiles heterogeneous catalyzing stage were detected and showed in Table 4. For a clear comparison, the solid yields were taken into consideration and the values in Table 4 were the percentage accounting for each sludge sample. Thus the initial values of C and H content in each sludge sample were 100%.

The RS presented the highest C and H releasing rate, but on the contrary obtaining the least syngas production during devolatilization. Thus a great number of C and H were released in the form of tar. The contents of C and H in ash decreased but the syngas yields increased slightly at 873 K, indicating that the reactions between organics in char and volatile occurred accompanied by the char steam gasification during the volatiles heterogeneous catalyzing. The similar view was also believed by El-Rub et al. [38]. Compared with RS, iron salts in sludge could fixed carbon in the char and then oxidized to CO. CaO showed a better adsorption on organics and increased both C and H content in char. In the later process of volatiles heterogeneous catalyzing, the organics largely reacted with steam and volatiles to generate syngas by CaO catalysis as the steepest slopes of C and H decrement. S-Fenton-CaO also had the similar slopes, but the contents of C and H in solid products were lower than that of S-CaO, resulting in more organics conversion to syngas.

| Table 3 – Compositions (Peak areas %) of tar at 873 K in different experiments. |
|-------------------|-------------------|-------------------|
| Samples           | Number of rings | Branch-containing | Oxygen-containing |
|                   | 1    | 2    | 3    | 4    | 1    | 2    | 3    | 4    | 1    | 2    | 3    | 4    |
| RS-a¹             | 19.8 | 58.9 | 11.1 | 10.2 | 37.7 | 7.2  |      |      |      |      |      |      |
| RS-b²             | 15.0 | 69.2 | 13.6 | 2.2  | 38.4 | 4.9  |      |      |      |      |      |      |
| RS-c³             | 21.0 | 67.7 | 10.5 | 0.8  | 40.6 | 2.5  |      |      |      |      |      |      |
| S-Fenton-a        | 23.9 | 56.0 | 19.4 | 0.7  | 46.2 | 9.5  |      |      |      |      |      |      |
| S-Fenton-b        | 27.2 | 56.9 | 14.7 | 1.2  | 41.3 | 7.8  |      |      |      |      |      |      |
| S-Fenton-c        | 26.5 | 58.1 | 15.4 | 0    | 49.3 | 11.6 |      |      |      |      |      |      |
| S-CaO-a           | 33.9 | 58.1 | 6.6  | 1.4  | 49.1 | 1.1  |      |      |      |      |      |      |
| S-CaO-b           | 25.9 | 66.6 | 5.7  | 1.8  | 43.0 | 2.4  |      |      |      |      |      |      |
| S-CaO-c           | 14.5 | 75.6 | 8.2  | 1.7  | 44.5 | 2.5  |      |      |      |      |      |      |
| S-Fenton-CaO-a    | 13.3 | 74.6 | 11.3 | 0.8  | 45.8 | 11.7 |      |      |      |      |      |      |
| S-Fenton-CaO-b    | 24.2 | 63.8 | 12.0 | 0    | 53.6 | 5.7  |      |      |      |      |      |      |
| S-Fenton-CaO-c    | 32.3 | 58.0 | 9.7  | 0    | 52.9 | 9.1  |      |      |      |      |      |      |

¹ devolatilization experiment. ² Volatile steam reforming experiment. ³ Volatile catalytic reforming experiment.

| Table 4 – Compositions (Peak areas %) of tar at 1073 K at different gasification stages of RS. |
|---------------------------------|-------------------|-------------------|
|                                 | Devolatilization | Volatile steam reforming | Volatile catalytic reforming |
| Branch-containing               | 9.51             | 5.59              | 5.41             |
| Oxygen-containing               | 0.26             | 0.33              | 0                |
with steam and tar to produce uronic acids and carboxylates. Compared with RS, the relative ratios of C-(O, N) and C=O were less in S-Fenton sample. Proteins and acetals were converted to hydrocarbons with the strong oxidation of Fenton's reagent during dewatering. The relative content of C-(O, N) was high in S-Fenton char. In accordance with the C content in Fig. 3, Fenton's reagent could decompose proteins the fixed smaller ones or amino acid structures in char. Then the C-(O, N) species was oxidized to uronic acids and hydrocarbons during the volatile catalytic reforming. The increment of oxygen-containing compounds in tar (Table 3) also proved the catalytic oxidation performance of Fenton's reagent. Similar to Fenton's reagent, CaO converted organics in sludge to simple hydrocarbons during dewatering. The relative ratios of C-containing species were approximate before and after devolatilization, but C-H and C-C decreased in S-CaO ash. Combined with the tar compositions in Table 3, CaO may trend to adsorb 1-ring hydrocarbons for decomposition to CH₄ and H₂.

Fig. 3 – Element content of solid products from different stage on each sludge (a) carbon (b) hydrogen.

Fig. 4 – Relative content of C-species in different solid products from four kinds of sludge at 873 K.

Fig. 5 – FTIR spectra of different solid products from four kinds of sludge at 873 K.

during devolatilization and volatiles heterogeneous catalyzing. The interactions between char and tar decreased the small aromatic rings [41]. The adsorption of S-Fenton char was better than RS char as the S-Fenton ash contained some C=C and CH₂=CH₂ bonds. This phenomenon was more notable after CaO conditioning. The peak at 1649 cm⁻¹ belonging to conjugated C=O bond was obvious in CaO conditioned samples, indicating that CaO was beneficial to the deep cracking of benzene ring. Other than the aldehydes and esters at 1032 cm⁻¹ in S-Fenton and RS ash, the oxygen-containing
bond in S-CaO and S-Fenton-CaO was simple phenols and alcohol, which decomposed easily at steam atmosphere or higher temperature.

Combined with the above discussions, the main mechanism of Fenton’s reagent and CaO conditions on different sludge gasification stages could be simply described in Fig. 6. During devolatilization, Fenton’s reagent mainly improved the yields of H2 and CO in gas products, the relative content of protein structure in char and the ratio of heterocycles in tar. The changes on volatile led to more small ring compounds and H2 generation when steam was supplied. The interactions between S-Fenton char and volatile were revealed in two ways: (1) Catalyzing the reactions of methane reforming and water gas shift and (2) Catalyzing the organics in tar and char decomposition to hydrocarbons, phenols, CO and CH4. Different with Fenton’s reagent, CaO preferred to promote the extra yield of CH4 in gas products, the relative content of aromatics in char and the ratio of mono-ring compounds in tar. The increments of CH4 and mono-rings in volatile were conducive to gaseous hydrocarbons and H2 generation during steam homogeneous reforming. The catalytic ability of CaO was better than that of Fenton’s reagent addition, for the final syngas yields increasing sharply. The advantages of Fenton’s reagent and CaO would be reflected simultaneously on S-Fenton-CaO.

Conclusions

Both Fenton’s reagent and CaO can increase the yield of syngas especially H2 during sludge gasification. At 873 K the multi-ring compounds in tar was converted to smaller rings and slight syngas by hydrolysis and catalysis. With temperature increasing, the methane reforming, water gas shift and char gasification gradually played a dominant role and the H2 yield increased sharply. Fenton’s reagent can enhance the cracking of stable 4-ring structures in tar to 2-3-ring heterocycles and fix small protein structure in char. CaO showed a better catalytic ability as more mono-benzene ring structures and CH3—chains appeared in tar and solid products. The deep decomposition of tar and organics in char led to more syngas generation. The conditioners as well as changes of organics in char improved the adsorption and decomposition of tar, resulting more H2 generation. Compared with RS, the final H2 yield was improved by 51.2% for S-Fenton and 76.5% for S-CaO at 1273 K. And the contribution rate of conditioners acted on devolatilization stage was 52.8% (S-Fenton) and 67.7% (S-CaO). It shows that the catalysis of iron on volatile steam reforming is very important during sludge gasification. Thus in the actual industry, reusing conditioned sludge char/ash as fluidized bed material or catalysts on volatile reforming reactor may be a potential method for hydrogen energy production.

Acknowledgements

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References


