



## Review

## Treatment of municipal sewage sludge in supercritical water: A review



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## ABSTRACT

With increasing construction of wastewater treatment plants and stricter policies, municipal sewage sludge (MSS) disposal has become a serious problem. Treatment of MSS in supercritical water (SCW) can avoid the pre-drying procedure and secondary pollution of conventional methods. SCW treatment methods can be divided into supercritical water gasification (SCWG), supercritical water partial oxidation (SCWPO) and supercritical water oxidation (SCWO) technologies with increasing amounts of oxidants. Hydrogen-rich gases can be generated from MSS by SCWG or SCWPO technology using oxidants less than stoichiometric ratio while organic compounds can be completely degraded by SCWO technology with using an oxidant excess. For SCWG and SCWPO technologies, this paper reviews the influences of different process variables (MSS properties, moisture content, temperature, oxidant amount and catalysts) on the production of gases. For SCWO technology, this paper reviews research regarding the removal of organics with or without hydrothermal flames and the changes in heavy metal speciation and risk. Finally, typical systems for handling MSS are summarized and research needs and challenges are proposed.

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## Nomenclature

AC	activated carbon, –
AS	activated sludge, –
COD	chemical oxygen demand, mg/L
DS	digested sludge, –
DSS	dewatered sewage sludge, –
$\epsilon_r$	relative dielectric constant
IPA	isopropanol, –
HM	heavy metal, –
MSS	Municipal sewage sludge, –
$n$	oxidant coefficient, –
NH <sub>3</sub> -N	ammonia nitrogen, mg/L

OM	organic matter, –
R <sup>2</sup>	coefficient of determination, –
P	pressure, MPa
PS	primary sludge, –
SCW	supercritical water, –
SCWG	supercritical water gasification, –
SCWO	supercritical oxidation, –
SCWPO	supercritical water partial oxidation, –
SS	secondary sludge, –
subCWL	subcritical water liquefaction, –
T	temperature, °C
TN	total nitrogen, mg/L
TOC	total organic carbon, mg/L

## 1. Introduction

Municipal sewage sludge (MSS) is a by-product of wastewater treatment, and the amount of MSS has increased with the construction and expansion of wastewater treatment plants, while stricter policies have limited its disposal (Jin et al., 2014). Compared with other organic wastes such as proteinaceous wastes, cellulosic wastes and plastic wastes (Quitain et al., 2002), MSS contains complex organic material mainly consisting of carbohydrates (~14%), proteins (~40%), lipids (~10%), lignin (~17%) and ash (30–50%) (Goto et al., 1999a; Youssef et al., 2011). It also contains heavy metals (HMs), viruses, bacteria and other microorganisms. The operation costs of MSS treatment are responsible for approximately 50% of those of a sewage treatment plant (Kroiss, 2004; Neyens and Baeyens, 2003).

Conventional MSS treatment methods include landfills, composting and incineration. All of these methods not only require a pre-drying procedure but can also generate secondary pollution (Zhang et al., 2014). However, treatment of MSS in supercritical water (SCW) can eliminate the pre-drying procedure of conventional treatments and stabilize the heavy metals (HMs) that it contains.

Oxidant coefficient ( $n$ ) is defined as the ratio between the practically added oxidant amount and theoretically required oxidant amount. According to the increasing value in the oxidant coefficient, treatment of MSS in SCW can be classified as supercritical water gasification (SCWG,  $n = 0$ ), supercritical water partial

oxidation (SCWPO,  $0 < n < 1$ ) or supercritical water oxidation (SCWO,  $n \geq 1$ ). SCWG and SCWPO aim to generate hydrogen-rich gases from MSS using oxidant less than stoichiometric ratio, whereas SCWO is an efficient and environmentally benign method for completely degrading organic compounds using an oxidant excess. The SCWO process can take place with or without

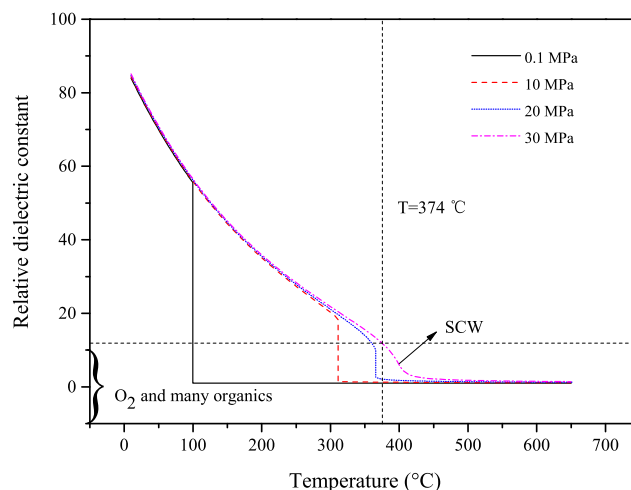


Fig. 1. Relative dielectric constant of water as a function of temperature at 0.1, 10, 20 and 30 MPa (NIST Database, 2013).

hydrothermal flames.

Given these advantages of and increasing interest in SCW treatment technologies of the disposal of MSS (Goto et al., 1997; Guo et al., 2010a; Sawai et al., 2014), it is useful to collect and compare the related data on resource utilization and degradation of MSS in SCW. This paper first discusses the influences of the process variables on the production of gases through SCWG or SCWPO of MSS. Then, the treatment of MSS via SCWO, regarding the decomposition of organics with or without hydrothermal flames and the risk of HMs in MSS, is extensively reviewed. Finally, typical experimental facilities, pilot units and commercial systems handling MSS using SCW technologies are presented.

## 2. Reactant and reaction media

### 2.1. Municipal sewage sludge

MSS can be produced by different processes such as the activated sludge (AS), aerobic-oxic, oxidation ditch, anaerobic-anoxic-oxic, up-flow anaerobic sludge bed and cyclic activated sludge technology processes (Gong et al., 2014a). In the case of an AS process, sewage can form primary sludge (PS) by settling in a primary clarifier. PS then flows into the secondary treatment system to produce secondary sludge (SS). After thickening, the PS and SS are dewatered directly or enter an aerobic or anaerobic digestion system to generate digested sludge (DS). PS, SS and DS usually have a moisture content higher than 95 wt.%. Finally, MSS is dehydrated to produce dewatered sewage sludge (DSS) with a moisture content of 30–85 wt.% (Appels et al., 2008). MSS is very complex and contains carbohydrates, proteins, fats and humic substances (Azadi et al., 2013). It can be viewed as a waste, but possibly also as a wet resource.

### 2.2. Supercritical water

SCW is water whose temperature and pressure both exceed the critical values ( $T_c > 374$  °C,  $P_c > 22.1$  MPa) (Savage, 1999). The physicochemical characteristics including the density, enthalpy and relative dielectric constant ( $\epsilon_r$ ) of high pressure water continuously change with temperature. Fig. 1 shows the  $\epsilon_r$  of water as a function of temperature at 0.1, 10, 20 and 30 MPa. Weaker hydrogen bonds result in a lower  $\epsilon_r$  of SCW than for liquid water. The  $\epsilon_r$  of SCW approaches that of  $O_2$  and many organics, which leads to a change in the dissolving capacity of water. As a result, SCW can become miscible with  $O_2$  and a majority of organics to form a homogeneous reaction system (Shaw et al., 1991).

## 3. Production of gases via SCWG or SCWPO

SCWG or SCWPO of MSS can produce  $H_2$ , CO,  $CO_2$ ,  $CH_4$  and a small amount of  $C_2$ – $C_4$  gas. Production of gases including  $H_2$ , CO and  $CH_4$  is of great interest due to their high heating values and wide range of applications (Elliott, 2008; Kruse, 2008). The compositions and yields of these gases are affected by the properties and moisture content of MSS, temperature, oxidant coefficient and catalyst. However, the influence of pressures that exceed the critical point of water (374 °C, 22.1 MPa) is not obvious (Castello and Fiori, 2011; Yan et al., 2006).

### 3.1. Influence of MSS properties

Different types of MSS have various moisture, alkali metal and organic matter (OM) contents; thus, the influence of the properties of MSS involves a combination of all of these factors. Gong et al. (2014a) studied the direct SCWG process of ten types of DSS

(S0–S9) produced by different sewage treatment technologies. Although DSS samples with different water (73.48–88.51 wt.%) and OM contents (29.25–73.02 wt.%) were tested, the components of the gaseous products were similar and exhibited no fundamental differences, demonstrating that the SCWG technology produces a common result in the treatment of MSS with various properties.

Fig. 2 summarizes several studies involving the influence of the OM content on gas yields through SCWG of MSS. Gong et al. (2014a) observed a linear increase in gas yields with increasing OM content for a given quantity of dry sludge, except for S2 at 400 °C, which produces a relatively lower gas yield. Zhang et al. (2010) compared the gas yields of MSS from different sources (PS, SS and DS) at 500 °C.  $H_2$  and  $CH_4$  were produced in the following order: PS > SS > DS, which is associated with the high OM content of PS, although PS has the lowest pH value and alkali metal content. As a result, using MSS with high OM content as the feed is more suitable for the production of gases.

### 3.2. Influence of the moisture content

Gas production refers to the amount of gas produced by a given amount of original MSS, while gas yield refers the quotient between the mole number of certain gas products and the mass of dry matter in MSS. Generally, an increase in water contents results in a decrease in total gas production due to the reduced OM content of MSS, but an increase in gas yield from inhibition of the formation of undesired char or coke, as well as from the enhancement of the production of  $H_2$  because SCW can act as a participant in gasification reactions by providing of hydrogen and free-radicals (Guo et al., 2010b).

Xu et al. (2012b) thoroughly investigated the effects of moisture (76.2–94.4 wt.%) content on the gas yields and composition and established a linear relationship equation between the gas yield and water content in DDS:

$$Y = 0.342X - 18.35, R^2 = 0.889 \quad (1)$$

where Y (mol/kg OM) is the gas yield, and X (%) is the water content in DDS. According to Eq. (1), high moisture content favours high gas yield.

Regarding the gas composition, the yields of  $CH_4$ , CO and  $H_2$  slightly decrease and that of  $CO_2$  dramatically decreases with reduced moisture contents because with low moisture content, a

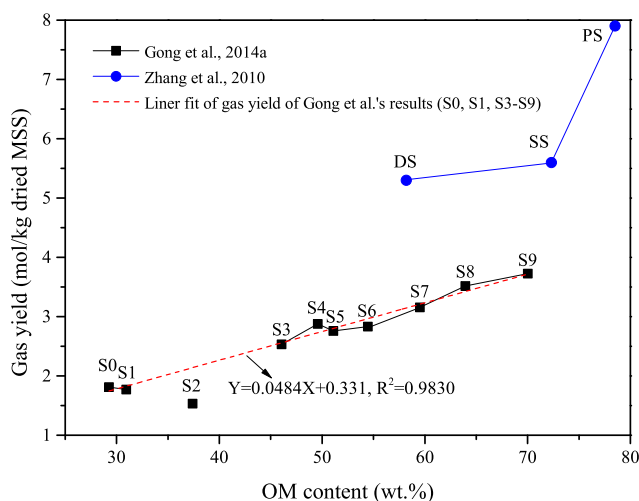


Fig. 2. Influence of the OM content on gas yields through SCWG of MSS in the published literature.

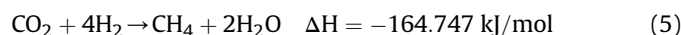
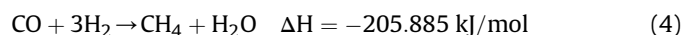
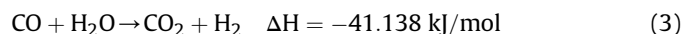
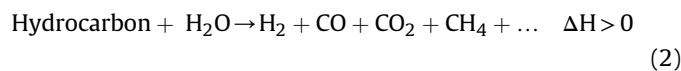
portion of carbon has forms char or tar before being gasified (Xu et al., 2012b). Therefore, regardless of the transport problem caused by high concentration of MSS and the plugging problem caused by char and tar, low moisture content is preferred because it improves the fraction and production of combustible gases.

For the sake of energetic self-sufficiency, sludge with low moisture content is needed to produce enough combustible gaseous products to produce the heat needed during the SCWG or SCWPO process. Fiori et al. (2012) calculated the lowest auto-thermal concentration of sludge with heat recovery using Aspen Plus™ and found a value of 22.9 wt.% with fuel cells used to generate power and 24.4 wt.% using both fuel cells and turbines. Without the utilization of H<sub>2</sub> and heat recovery, Wilkinson et al. (2012) found the lowest auto-thermal concentration to be 30.4 wt.%. However, if the heat of the effluent from the reactor was recovered to preheat the feed, the auto-thermal concentration was reduced to 27.4 wt.% or 24.4 wt.% with 10% or 20% heat recovery, respectively.

Considering the transportation of MSS, Qian et al. (2015) proposed that the viscosity of the feedstock should be lower than 8000 MPa s, corresponding to approximately 87 wt.% moisture content. Furthermore, Xu et al. (2012b) observed that the char and coke contents are greatly enhanced when the water content of DDS is lower than 81.7 wt%, which will likely cause plugging of the reactor. According to MSS commercial systems (Gidner and Stenmark, 2001; Griffith and Raymond, 2002; Sloan et al., 2009), MSS with a moisture content higher than 85 wt.% can be used as the feed and continuously transported.

### 3.3. Influence of temperature

Temperature plays the most significant role in the gasification of MSS. The SCWG process mainly involves the steam reforming (Eq. (2)), water–gas shift (Eq. (3)) and methanation reactions (Eqs. (4) and (5)) (Guo et al., 2007).



In general, the yields of H<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub> all increase with an increase in temperature because the steam reforming reaction is strongly endothermic. The yield of CO remains at a low level because of the water–gas shift reaction. Several studies on the influences of temperature without oxidants or catalysts are shown in Fig. 3. Among them, the results of Qian et al. (2015), Acelas et al. (2014) and Chen et al. (2013a, 2013b) show a good linear relationship between gas yield and temperature, although Chen et al. performed their experiments in two reactors, including a batch reactor (350–450 °C) (Chen et al., 2013a) and a fluidized bed reactor (480–540 °C) (Chen et al., 2013b). As presented in Fig. 3, gas yields obtained by Chen et al. are higher than those obtained by other researchers, especially at higher temperatures. This can be attributed to their application of the fluidized bed reactor with a high heating rate, which can suppress the formation of char or tar and achieve an increased gasification efficiency (Sinag et al., 2004).

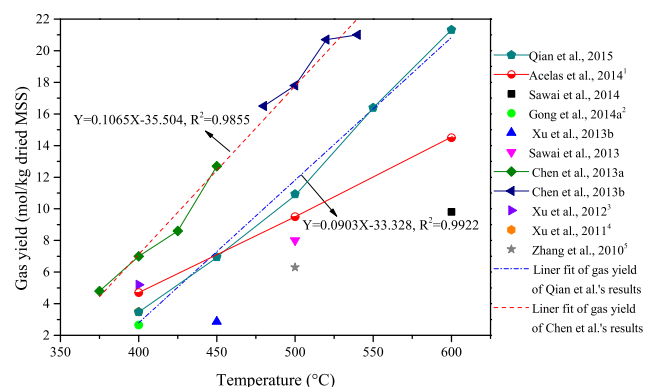
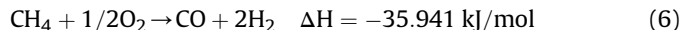


Fig. 3. Influence of temperature on gas yield through SCWG of MSS in the published literature. <sup>1</sup>Mean value of DSS with three different reaction times (Acelas et al., 2014). <sup>2</sup>Mean value of ten different types of DSS at 400 °C (Gong et al., 2014a). <sup>3</sup>Mean value of DSS with nine different moisture contents at 400 °C (Xu et al., 2012b). <sup>4</sup>Mean value of DSS with two different reaction times at 400 °C (Xu et al., 2011b). <sup>5</sup>Mean value of three different types of MSS (Zhang et al., 2010).

### 3.4. Influence of the oxidant coefficient

The oxidant coefficient ( $n$ ) dramatically influences the SCWPO process of MSS, and especially the gas composition. A large amount of oxidant can enhance the oxidation reaction and convert combustible gases to H<sub>2</sub>O and CO<sub>2</sub>. However, a small quantity of oxidant is preferred due to its inhibition of char or tar formation, production of hydrogen peroxide radicals and promotion of the steam reforming reaction (García Jarana et al., 2008; Jin et al., 2010; Xu et al., 2011a), as well as the following reaction:



Xu et al. (2013a) explored the influence of  $n$  on product properties at 400 °C and 450 °C in detail and found that gaseous products are only composed of CO<sub>2</sub> when  $n \geq 1.0$ . Their yields increase prominently and monotonously with an increasing value of  $n$  when  $n < 1.0$ . The maximum H<sub>2</sub> yield was obtained at  $n = 0.6$ . However, Guo et al. (2010a) observed that the mole fraction of H<sub>2</sub> peaks at  $n = 0.3$  with or without an activated carbon (AC) catalyst. Furthermore,  $n$  affects the operation costs and corrosion behaviours of reactors, therefore affecting the capital investment. Their results show that corrosion, including pitting and general corrosion, is more severe in the SCWPO environment than in the SCWG or SCWO environment. Therefore, a reasonable  $n$  should take into account not only gas yields but also operation and capital costs.

### 3.5. Influence of catalysts

Catalysts can reduce the high activation energy required by non-catalytic SCWG or SCWPO process. Thus, the reaction temperature and costs can be lowered. Table 1 summarizes studies on SCWG or SCWPO of MSS using catalysts. The related catalysts include activated carbon (AC), metal or metallic oxide and alkali salt catalysts.

#### 3.5.1. Activated carbon catalysts

AC is a potential heterogeneous catalyst. Unlike metal catalysts, secondary pollution by leaching of metal ions is avoided through the use of an AC catalyst.

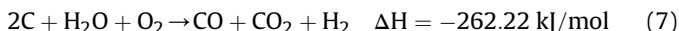
Xu et al. (1996) obtained a H<sub>2</sub> yield of 13.5 mol/kg of dry sewage sludge with a moisture content of 2.8 wt.% using coconut shell activated carbon as a catalyst. However, their feeding systems failed to provide a reproducible and steady flow of high concentration slurries with a “diaphragm” type pump. For better transportation of

**Table 1**  
Summary of investigations of SCWG or SCWPO of MSS using catalysts.

Feed	Catalyst	Reactor type	Reactor volume	Experiment conditions	Reference
MSS (2.8 wt.%)	Coconut shell activated carbon	Inconel 625 tubular reactor	9.53 mm OD × 4.75 mm ID × 0.41 m functional length	600 °C; 34.5 MPa; WHSV 10 h <sup>-1</sup>	Xu et al., 1996
DS (2.1 wt.%) / corn starch (5.1 wt.%) and DS (7.69 wt.%) / corn starch (7.69 wt.%)	Coconut shell activated carbon	Hastelloy C276 tubular reactor	9.53 mm OD × 6.22 mm ID × 1.016 m length	650 °C; 28 MPa; WHSV 1.48 h <sup>-1</sup> or 3.2 h <sup>-1</sup>	Xu and Antal, 1998
MSS (0.16 wt.%)	Activated carbon	316 stainless steel batch reactor	572 cm <sup>3</sup>	360–425 °C; 22.5–26 MPa; 30–60 min; n 0–0.8; catalyst 0 or 1.0 wt.%	Guo et al., 2010a
MSS (3.2 wt.%)	RuO <sub>2</sub>	Inconel 625 reaction vessel	10.8 cm <sup>3</sup>	450 °C; 47.1 MPa; 120 min; catalyst 0.2 g/g dry sludge	Yamamura et al., 2009
AS (3 wt.%)	Raney nickel	316 stainless steel batch reactor	50 mL	320–410 °C; 11.3–28.1 MPa; 0–120 min; catalyst 0–1.8 g/g dry sludge	Afif et al., 2011
AS model compounds (3 wt.%)	Raney nickel, Ni/α-Al <sub>2</sub> O <sub>3</sub> , Ru/C, Ru/γ-Al <sub>2</sub> O <sub>3</sub>	316 stainless steel batch reactor	50 mL	380 °C; 23 MPa; 15 min; catalyst 0.4 g Ni/g dry feed or 0.02 g Ru/g dry feed	Azadi et al., 2013
MSS (20 wt.%) with or without subCWL treatment	Nickel (65 wt.%) on silica/alumina (35 wt.%)	316 stainless steel batch reactor	20.1 mL (subCWL) and 26.4 mL (SCWG)	500 °C; 25 MPa; 5–30 min; catalyst 0–500% dry sludge mass	Sawai et al., 2013
MSS (2 wt.%)	Nickel (65 wt.%) on silica/alumina (35 wt.%)	316 stainless steel batch reactor with titanium insert	3000 mL	600 °C, 23 MPa; 60 min; catalyst 10 or 200 wt.% dry sludge mass	Sawai et al., 2014
MSS (TOC = 2300 mg/L)	K <sub>2</sub> CO <sub>3</sub>	Stainless steel batch reactor	1000 mL	450 °C; 33 MPa; 120 min; catalyst 1.7 × 10 <sup>-3</sup> mol/L	Schmieder et al., 2000
MSS (5 wt.%)	NaOH	Hastelloy C276 tubular reactor	12.3 mm ID × 1.8 m length	600 °C; 24–30 MPa; 3 min; catalyst 10 wt.%	Zhang et al., 2007
PS (2 wt.%)	NaOH	Hastelloy alloy batch reactor	75 mL	500 °C; 37 MPa; 50 min; pH from 5 to 9 after adding catalyst	Zhang et al., 2010
DSS (22.95 wt.%)	NaOH, Nickel	316L stainless steel batch reactor	100 mL	400 °C; 24 MPa; 10 min; catalyst 5 wt.% of DSS	Gong et al., 2014b
2 wt.% MSS and 2 wt.% CMC	KOH, K <sub>2</sub> CO <sub>3</sub> , NaOH, Na <sub>2</sub> CO <sub>3</sub>	316 stainless steel fluidized bed reactor	30 mm bed diameter, 40 mm freeboard diameter and 915 mm long	540 °C; 25 MPa; water flow rate 125 g/min, slurry flow rate 25 g/min; catalyst 0–0.9 wt.%	Chen et al., 2013b
DSS (16.96 wt.%)	NaOH, KOH, K <sub>2</sub> CO <sub>3</sub> , Na <sub>2</sub> CO <sub>3</sub> , Ca(OH) <sub>2</sub>	316L stainless steel batch reactor	100 mL	450 °C; >22.1 MPa; 30 min; catalyst 0–0.08 g/g DSS	Xu et al., 2013b
DS (10 wt.%)	K <sub>2</sub> CO <sub>3</sub>	321 stainless steel batch reactor	500 mL	400 °C, >25 MPa; 30 min; catalyst 1.5 wt.%	Zhai et al., 2013

sewage sludge, Xu and Antal (1998) mixed DS with corn starch paste, but the reactor plugged after 1–2 h due to the high ash content of DS. It has been found that different weight hourly space velocities do not have obvious effects on gasification products always, with H<sub>2</sub> and CO<sub>2</sub> always dominating.

Guo et al. (2010a) investigated the SCWPO process of MSS with or without an AC catalyst. AC can enhance the mole fraction of H<sub>2</sub> and suppress that of CO. However, by increasing the reaction time to 120 min, AC undergoes changes that decrease surface area and increase pore size and adsorbed oxide on the surface of catalyst. Because AC can be hydrolysed and oxidized after being exposed to SCW during long reaction times (see Eq. (7)), it may not be a stable catalyst.



### 3.5.2. Metal or metallic oxide catalysts

Studies of metal or metallic oxide catalysts on SCWG or SCWPO process of MSS mainly include on Ni and Ru catalysts. These catalysts play an important role in steam reforming and methanation reactions.

Yamamura et al. (2009) employed a RuO<sub>2</sub> catalyst for the SCWG of MSS. MSS are completely decomposed in SCW. The hydrogen gasification efficiency was only 23.1% and the carbon efficiency was only 11%, suggesting the deactivation of RuO<sub>2</sub> because sulphur in MSS can deactivate the RuO<sub>2</sub> catalyst.

Afif et al. (2011) used a Raney nickel catalyst to gasify AS. In the presence of the Raney nickel catalyst, the carbon gasification ratio

increased from 10% for catalyst-free conditions to approximately 70% whereas the hydrogen gasification ratio increased from 4% to 113% at 380 °C with a catalyst loading of 1.8 g/g and a reaction time of 15 min. However, Raney nickel significantly loses its activity after pre-exposure to water at 380 °C for 8 min. It causes an increase in the average nickel crystallite size via hydrothermal sintering. Sulphur and ash in AS can also cause poisoning of the Raney nickel catalyst, although alkali metals in ash can enhance the hydrogen yield by promoting the water–gas shift reaction. To better understand the reaction pathways, Azadi et al. (2013) studied catalytic reforming of AS model compounds, including glucose, glycine, glycerol, lauric acid and humic acid, separately representing carbohydrates, proteins, alcohols, fatty acids and humic substances with Raney nickel, Ni/Al<sub>2</sub>O<sub>3</sub>, Ru/C and Ru/Al<sub>2</sub>O<sub>3</sub> catalysts. Using the Raney nickel catalyst, the carbon gasification ratios decreased in the following order: glycerol > glucose > glycine > lauric acid ≈ AS > humic acid. Compared to Raney nickel, the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst showed a high catalytic activity for glycerol and glycine but a low activity for glucose and humic acid. With Ru/C and Ru/Al<sub>2</sub>O<sub>3</sub> catalysts, the carbon gasification ratios decreased in the following order: glycerol > glycine > glucose > lauric acid > humic acid.

Sawai et al. (2013) investigated the effects of subcritical water liquefaction (subCWL) pre-treatment on SCWG of MSS. SubCWL can significantly decrease the viscosity of MSS and better enable its transportation. In addition, subCWL can increase yields of H<sub>2</sub> and CH<sub>4</sub>, decrease that of CO<sub>2</sub> and subsequently produce gaseous products with high heating values. For MSS with or without subCWL treatment, carbon can be completely gasified when the nickel (65 wt.%) on silica/alumina (35 wt.%) catalyst loading reaches 400–500% dry sludge mass, representing a five-fold increase

compared with conditions without a catalyst. However, similar to the study of Azadi et al. (2013), no data related to the characterization and stability of the catalysts are available.

### 3.5.3. Alkali salt catalysts

Studies involving the catalytic effects of alkali salts on the SCWG or SCWPO of MSS focuses on KOH, Na<sub>2</sub>CO<sub>3</sub> and Ca(OH)<sub>2</sub>, but even more on NaOH and K<sub>2</sub>CO<sub>3</sub>. The primary role of these catalysts is to enhance the water–gas shift reaction (Kruse and Dinjus, 2005).

Schmieder et al. (2000) found that although K<sub>2</sub>CO<sub>3</sub> can improve the degradation efficiency of MSS from 0.552 to 0.853, the volume fractions of gaseous products including H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub> change little, indicating that the water–gas shift reaction is not greatly enhanced. However, Zhai et al. (2013) found that K<sub>2</sub>CO<sub>3</sub> can produce a much higher yield of CO<sub>2</sub> with a lower yield of CO than in conditions without catalysts, suggesting that the water–gas shift reaction is indeed intensified. Unfortunately, in Zhai et al.'s (2013) research, the gas yield of H<sub>2</sub> is not available because H<sub>2</sub> was employed as the carrier gas for a gas chromatography. The conflicting results obtained by them can likely be attributed to the different catalyst concentrations used. The K<sub>2</sub>CO<sub>3</sub> concentration used in the experiment by Zhai et al. (2013) was 0.12 mol/L, which is almost 71 times higher than that used in the experiments by Schmieder et al. (2000).

Zhang et al. (2007) observed that NaOH can significantly reduce the mole fraction of CO from approximately 40% to lower than 5% and increase the mole fractions of H<sub>2</sub> and CO<sub>2</sub>, indicating the promotion of the water–gas shift reaction by NaOH, which was also confirmed by Zhang et al. (2010) in the investigation of PS. Furthermore, combined addition of NaOH and a Ni catalyst mutually promotes the gasification of DSS. NaOH can not only promote the water–gas shift reaction but also capture CO<sub>2</sub>, thus driving the steam reforming and methanation reactions with Ni towards further H<sub>2</sub> generation (Gong et al., 2014b).

Chen et al. (2013b) studied the SCWG process of MSS using a fluidized bed reactor with various alkali salts. H<sub>2</sub> production occurred in the following order: KOH > K<sub>2</sub>CO<sub>3</sub> > NaOH > Na<sub>2</sub>CO<sub>3</sub> > none. The gasification and carbon gasification efficiencies exhibited in the following order: K<sub>2</sub>CO<sub>3</sub> > KOH ≈ NaOH > none > Na<sub>2</sub>CO<sub>3</sub>. However, the changes in gasification and carbon gasification efficiencies were small whereas the molar fraction and yield of H<sub>2</sub> were significantly enhanced with alkali salts, suggesting that alkali salts mainly catalyse the water–gas shift reaction rather than the steam reforming reaction. Xu et al. (2013b) also compared different catalysts for SCWG of DSS using a batch reactor. The gas yield and H<sub>2</sub> production exhibited in the following order: K<sub>2</sub>CO<sub>3</sub> > KOH > NaOH > Na<sub>2</sub>CO<sub>3</sub> > none > Ca(OH)<sub>2</sub>. Xu et al. (2013b) attributed the low gasification efficiencies found with the use of Na<sub>2</sub>CO<sub>3</sub> and Ca(OH)<sub>2</sub> to their low solubility in the SCW environment, while Chen et al. (2013b) proposed that Na<sub>2</sub>CO<sub>3</sub> has a positive effect on the SCWG of some types of organic matters but not on MSS. Nevertheless, in their results, the catalytic effects of K<sub>2</sub>CO<sub>3</sub> and KOH on H<sub>2</sub> production were opposite, which may be due to the differences in reactor types and reaction temperatures. In both experiments, the water–gas shift reaction was enhanced with alkali salts, presenting increased CO<sub>2</sub> and H<sub>2</sub> yields.

Regarding the catalytic mechanism, the primary role of these catalysts is to improve the water–gas shift reaction. The catalytic effect of alkali salts can be explained by the following reactions (Kruse and Dinjus, 2005; Sinag et al., 2003; Yanik et al., 2008):

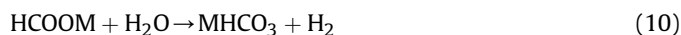
Carbonate reacts with water to produce bicarbonate and alkali



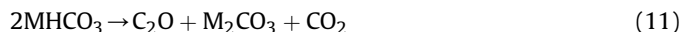
Alkali reacts with CO to form formate salt



Formate salt reacts with water to form H<sub>2</sub>



Decomposition of MHCO<sub>3</sub> to form CO<sub>2</sub>



The overall reaction is



## 4. Treatment efficiency of MSS via SCWO

Degradation of MSS can be achieved through SCWO technology with or without hydrothermal flames. During this process, the total organic carbon (TOC), chemical oxygen demand (COD) and ammonia nitrogen (NH<sub>3</sub>-N) of MSS can be reduced to produce qualified effluents. Moreover, during this process, HMs can be converted to stable states.

### 4.1. Decomposition of organics without hydrothermal flames

Although the traditional SCWO process without flames is performed at relatively low temperatures, normally lower than 600 °C, it can still achieve a high removal rate of organics due to the unique properties of SCW.

#### 4.1.1. Influence of the operation parameters on the removal rates of organics

The operation parameters significantly influence the removal rates of organics. Goto et al. (1997) studied the effects of reaction time, temperature, pressure and total solid content on the removal of TOC, organic acid and NH<sub>3</sub>-N from MSS. The TOC concentration decreased dramatically with increases in temperature and oxidant amount. The TOC concentration was less than 20 mg/L when the hydrogen peroxide concentration was higher than the stoichiometric demand in the supercritical water environment. All the organic carbons in the liquid product are organic acids when  $n > 0.8$ . In addition, it was found that NH<sub>3</sub>-N is an intermediate product of nitrogen-containing compounds. When  $n = 1.0$  or 1.5, NH<sub>3</sub>-N first increases at temperatures lower than 700 K and then decreases at higher temperatures, suggesting competitive reactions of hydrolysis and oxidation (Shanableh, 2000). Xu et al. (2013a) achieved COD, TOC and NH<sub>3</sub>-N removal ratios of 99.95%, 99.8% and 99.7%, respectively, using reaction conditions of 540 °C, 25 MPa,  $n = 2.0$  and 2.5 min. They also conducted SCWPO at 450 °C and 25 MPa with  $n = 0.6$  and a residence time of 1.5 min, and the liquid products were further treated by SCWO at 450 °C and 25 MPa with  $n = 1.5$  and residence time of 1.0 min. The total  $n$  was approximately 0.74, and the removal ratios of COD, TOC and NH<sub>3</sub>-N were even higher than those obtained at 450 °C and 25 MPa with  $n = 1.5$  using only SCWO. Therefore, the SCWPO–SCWG combined process can not only increase the production of H<sub>2</sub> or other combustible gases but also decrease oxidant consumption, which was analysed in detail by Qian et al. (2015).

Among all operation parameters, temperature and  $n$  are the most important operation parameters for the removal rates of organics, especially for NH<sub>3</sub>-N. NH<sub>3</sub>-N can be produced by the dissolution or hydrolysis of nitrogenous organic compounds in MSS (Benjamin and Savage, 2004). Once NH<sub>3</sub>-N is formed, it tends to be stable in SCW (Segond et al., 2002), especially at low temperatures

and values of  $n$ , causing an increasing tendency of  $\text{NH}_3\text{-N}$  formation with increasing temperature. Compared with  $\text{NH}_3\text{-N}$ , the content of TOC decreases with increasing temperature, even without oxidant (Chen et al., 2013a; Goto et al., 1997; Onwudili et al., 2013; Qian et al., 2015).

#### 4.1.2. Kinetic analysis

The SCWO process of MSS is very complex, but it can be simplified via a direct or an indirect path. In the direct path, MSS reacts with  $\text{O}_2$  to form  $\text{CO}_2$ , leading to a decrease of the TOC concentration; therefore, a first-order global rate kinetic model based on the change in the TOC concentration can be applied. In the indirect path, MSS first dissolves or hydrolyses to form refractory intermediates such as acetic acid, phenol and  $\text{NH}_3\text{-N}$ ; then, these intermediates are further oxidized to  $\text{CO}_2$ . In this path, a lumped kinetic model can be employed to include the reactions of these recalcitrant intermediates.

A first-order global rate kinetic model for MSS by Goto et al. (1999a, 1999b) is given in Eq. (13), which describes the changes in reactant concentrations over time. This model ignores the influence of  $n$ , and the reaction order of sludge is presumed to be 1.0. It can only be applied to situations with excess oxygen. Considering the influence of the oxidant, the reaction order of oxygen can be calculated through experimental results for various values of  $n$  using a Runge–Kutta algorithm or a multi-linear regression (Sánchez-Oneto et al., 2008). In a model proposed by Goto et al., the TOC and  $\text{NH}_3\text{-N}$  concentrations of sludge are used to express the concentration of  $A$ .  $k_0$  is  $1.91 \times 10^2\text{--}1.08 \times 10^4$  1/s,  $E_a$  is 53.2–76.3 kJ/mol and the temperature ranges from 673 to 773 K for the degradation of TOC, while  $k_0$  is  $3.16 \times 10^5$  1/s,  $E_a$  is 139 kJ/mol and the temperature ranges from 723 to 873 K for the degradation of  $\text{NH}_3\text{-N}$ .

$$\ln([A]/[A]_0) = -k_0 \exp(-E_a/RT)t \quad (13)$$

$[A]$  is the concentration of the reactant at the time  $t$ ,  $[A]_0$  is the concentration of the reactant at  $t = 0$ ,  $k_0$  is the pre-exponential factor for the rate of the reaction (1/s),  $E_a$  is the activation energy (kJ/mol),  $R$  is the ideal gas constant (8.3145 J/mol K), and  $T$  is the reaction temperature (K).

In addition, a four-lumped kinetic model for oily sludge by Cui et al. (2011) is presented in Fig. 4. Acetic acid and  $\text{CO}$  are commonly regarded as the main refractory intermediates (Portela et al., 2001), and  $\text{CO}_2$  is regarded as the end product in the SCWO process. The reaction orders of  $\text{CO}$ , acetic acid and  $\text{CO}_2$  are presumed to be 1.0. The reaction order and activation energy of the feedstock lump are 1.3 and 98.4 kJ/mol, respectively. The conversion of acetic acid to  $\text{CO}_2$  is the rate-limiting step with activation energy up to 219 kJ/mol.

#### 4.1.3. Mechanism analysis

Due to the complicated nature of MSS, it is unrealistic to obtain

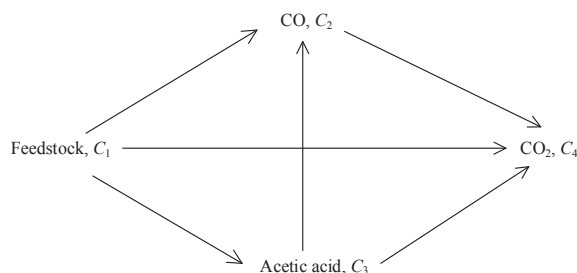


Fig. 4. Reaction network of a four lumped kinetics model (Cui et al., 2011).

an exhaustive reaction mechanism. Qian et al. (2015) found that long chain aliphatic acids originating from fats account for the highest proportion of compounds in MSS, which contributes to the high viscosity of MSS. These acids can be easily decomposed to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  by the abstraction of hydrogens near a  $-\text{COOH}$  group (Jin et al., 2003). However, after SCWO treatment at 823 K with  $n = 4.0$ , nearly all organics consisted of non-nitrogen aromatic and nitrogen aromatic compounds. Among these compounds, phenols and pyridines were dominant. Phenols can be generated by the cleavage of the aryl ether linkages in lignin (Wahyudiono et al., 2008) or by the condensation or cyclization of sugars (Sinag et al., 2003), while the amount of pyridines can be increased by the dissolution and hydrolysis of proteins or by the Maillard reaction between protein degradation products and cellulose splitting products (Kruse et al., 2007). By contrast, Goto et al. (1997) regarded  $\text{NH}_3\text{-N}$  and acetic acid as the stable intermediates. MSS is first converted to these products then to  $\text{N}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

#### 4.2. Decomposition of organics with hydrothermal flames using auxiliary fuel

SCWO with hydrothermal flames refers to an oxidation process occurring in a SCW environment at temperatures higher than the auto-ignition temperature of the feed, which produces a luminous flame (Augustine and Tester, 2009; Franck and Wiegand, 1996). The ignition temperature of the feed can decrease to 450–550 °C when the pressure increases to 25–30 MPa (Steinle and Franck, 1995). Besides the pressure, increasing the concentration of the feed also reduces the ignition temperature (Steeper et al., 1992; Wellig et al., 2009). Therefore, in the case of feed with a low reaction heat, auxiliary fuel is required to increase the concentration of mixtures to reduce the ignition temperature to sub-critical or even ambient temperatures.

Decomposition of organics in MSS with hydrothermal flames using auxiliary fuel can avoid or lessen the heating process; thus corrosion, salt deposition and tar formation problems encountered during this period can be circumvented or retarded (Abelleira et al., 2013; Cabeza et al., 2013). In addition, decomposition of organics with hydrothermal flames usually occurs at a higher temperature than the regular SCWO process; hence, complete decomposition of organics can be achieved with shorter residence times (Vadillo et al., 2013). However, to withstand this high temperature, specially designed hydrothermal reactors are needed. Due to the low flame front velocity of an empty vessel reactor, it is generally superior to a tubular reactor (Bermejo et al., 2011; Cabeza et al., 2011). Cabeza et al. (2013) employed an empty cooled wall reactor to treat MSS (1.3% mass of volatile solids) with hydrothermal flames using isopropanol (IPA) (a mass concentration of 11%) as auxiliary fuel. TOC removal rates higher than 99.82% were achieved at 553–512 °C and 21–25 s. The  $\text{NH}_3\text{-N}$  and nitrate concentrations in the effluent were below 36 and 11 ppm, respectively. For feed with a high concentration of  $\text{N-NH}_3$  such as MSS, the reaction temperature and oxidant coefficient should be lower than 650 °C and 2.5, respectively, to avoid the conversion of  $\text{N-NH}_3$  to nitrate and the production of  $\text{NO}_x$ .

#### 4.3. Speciation and risk of HMs in the effluent

Risk of heavy metals (HMs) depends on the toxicity of HMs in the products, especially in solid products, after treatment in SCW (Shi et al., 2013). The toxicity of HMs is determined by the leaching ability and speciations of HMs in MSS rather than their total concentrations.

Regarding the leaching ability of HMs, most HMs that remain in solid products are in non-leachable forms. Shanableh (1990) and

Tongdhamachart (1990) found that HM concentrations in solid products after SCWO increased by a three to five folds. Nevertheless, after SCWO, the HM concentrations in the leachate of solid products were all below regulatory limits. Similar to the SCWO process, Xu et al. (2011b) found that HMs (As, Cd, Cr, Cu, Ni, Pb and Zn) in solid products of MSS increased after subcritical water and supercritical water gasification, especially Cr and Ni, due to the corrosion of the autoclave, but all HMs were below the related limits. However, HMs in solid products after SCWG are more stable than those in original sludge, representing a much lower leaching toxicity, but after subcritical water treatment, the leaching toxicity of HMs, except for Cu and Zn, increases, showing that the SCW environment is essential for decreasing the risk of HMs.

Tessier et al. (1979) divided HMs into exchangeable (F1), bound to carbonates (F2), bound to iron and manganese oxides (F3), bound to organic matter (F4) and residual (F5) speciations. F1 and F2 speciations can migrate by acting with water, acids and organisms in soils and can be absorbed by plants; therefore, they possess direct toxicity. F3 and F4 speciations can change into F1 or F2 speciations in some circumstances; therefore, they own potential toxicity. Only the F5 speciation is stable because it can hold HMs within their crystal structure. Regarding the speciation of HMs, F1 and F2 speciations can convert into F3 and F4 speciations after SCW treatment. Li et al. (2012) distinguished different forms of heavy metals (HMs) in MSS, as well as solid products after gasification at 375 °C and 400 °C using Tessier's sequential extraction procedure. Comprehensive evaluation including the bioavailability and ecotoxicity of HMs, geo-accumulation index, potential ecological risk index, risk assessment code were applied to represent the toxicity of HMs. Although the total concentration of HMs increased, the bioavailability and eco-toxicity of HMs in solid products decreased because F1 and F2 speciations are dissolved in SCW and combine with Fe, Mn or other organics to form F3 or F4 speciations. Xu et al. (2011c) observed that As, Cr, Cu, and Pb dominate in F4 and F5 speciations, whereas Cd and Zn are mainly found in F3, F4 and F5 speciations after gasification at 375 °C and 400 °C. With increasing residence time, the F3 speciation of Ni sharply increases from 0 to 49.48% at 400 °C and 23.5 MPa, indicating that serious corrosion occurring in the SCW environment with extended reaction time. Above all, the F1 and F2 speciations can transform into other more stable speciations in the SCW environment because SCW has excellent solubility for organics but poor solubility for inorganics. The F1 and F2 speciations first dissolve in subcritical water during the heating period; then, they are bound to Fe, Mn or other organics and precipitate to form other speciations during the reaction period.

To lower the risk of HMs, sewage sludge-based activated carbon

and pyrolysis products of DSS can be added to DSS. It is conducive to lower the risk of Cd, Cu and Zn after SCWG at 400 °C (Zhai et al., 2014), and hydroxyapatite has the same effect due to its strong binding capacity of Cd after hydrothermal treatment (Shi et al., 2014).

## 5. Typical systems

Due to the remarkable advantages of treating MSS in SCW, several experimental facilities, pilot units and commercial systems have been designed or established.

### 5.1. Experimental facilities

Table 1 in section 3.5 summarizes experimental facilities used to treat MSS with catalysts. The main installations without catalysts are shown in Table 2. Due to the high viscosity of MSS, most facilities contain batch reactors. Despite of the slow heating process, these facilities can avoid the plugging problems of continuous facilities (Sawai et al., 2014). The volumes of batch reactors vary from 4 to 1000 mL. Batch reactors with volumes less than 10 mL can be heated quickly. However, for such a small volume, the amount of feed added to the reactor is limited, especially at high temperatures. Using a 4 mL batch reactor as example, only 0.28 mL of feed can be added to the reactor at 600 °C and 25 MPa. Therefore, these types of reactors are suited for reactions with catalysts due to the low temperature. With an increase in the volume of batch reactors, the heating time will be prolonged, which will have a negative effect on the gasification efficiencies or oxidation removal rates because tar or other refractory pyrolysis products may be generated. Consequently, on the premise that the products are sufficient for subsequent analyses, batch reactors with small volumes should be selected.

Compared with batch reactors, continuous reactors are better suited for practical applications. Continuous reactors for MSS can be classified as tubular reactors, fluidized bed reactors and tank reactors. Tubular reactors can be easily blocked using MSS with high solid contents (Xu et al., 1996; Xu and Antal, 1998). Chen et al. (2013b) successfully employed a fluidized bed reactor to treat MSS with a solid content of 12 wt.%. However, in their systems, their feedstock was preheated by water with a ratio of 1:5, which decreased the sludge concentration. In contrast, the transpiring wall reactor can form a protective film on the inner surface to prevent corrosion and plugging problems, but transpiring wall water will remove a large amount of heat. Chen et al. (2015) substituted air for water and developed a dynamic gas seal wall reactor. It uses three methods to prevent plugging. First, auxiliary

**Table 2**  
Experimental facilities used to treat MSS without catalysts.

Feed	Reaction type	Reactor type	Reactor volume (mL)	Reference
PS (3.84 or 21.3 wt.%)	SCWG	316 stainless steel batch reactor	9	Wilkinson et al., 2012
DSS (5.6–23.8 wt.%)	SCWG	316L stainless steel batch reactor	1000	Xu et al., 2012b
MSS (8.9 wt.%)	SCWG	316L stainless steel batch reactor	140	Chen et al., 2013a
DSS (15 wt.%)	SCWG	Inconel 600 batch reactor	45	Acelas et al., 2014
DSS (11.49–26.52 wt.%)	SCWG	316L stainless steel batch reactor	100	Gong et al., 2014a
MSS (13 wt.%)	SCWG, SCWPO and SCWO	316 stainless steel batch reactor	572	Qian et al., 2015
MSS (3.49 wt.%)	SCWO	stainless steel batch reactor	4	Goto et al., 1997; Goto et al., 1999a; Goto et al., 1999b
MSS (3.01 wt.%)	SCWO	Hastelloy alloy batch reactor	75	Onwudili et al., 2013
MSS (2.62–11.78 wt.%)	SCWO	316L stainless steel dynamic gas seal wall reactor	Not available	Chen et al., 2015



fuels are applied to reduce the preheating temperature to less than 350 °C. Second, the bottom of the reactor contains a solid collector. The mixture of salts and solids can be settled by gravity and stored in this collector during the upward flow process. Third, products flow through a condenser after leaving the reactor. Sticky salts will re-dissolve in the quench water, while non-sticky solid particles will be stored in the condenser. As a result, MSS with a solid content of 11.78 wt.% can be treated without plugging problems.

## 5.2. Pilot units

### 5.2.1. Duke University

At Duke University, a SCWO system for the treatment of fecal sludge was designed, built and placed in operation in December, 2014 with a target capacity of ~1000 kgwet/day flow rate with 10–20% solids (Deshusses and Jacoby, 2015). This unit is housed in a standard 20 ft shipping container and can be conveniently transported. The waste slurry is mixed with supercritical water and air at approximately 600 °C to reach supercritical conditions at approximately 400 °C and 24 MPa. After the reaction, heat recovery is achieved in a 40 m long heat exchanger. Then, the effluent passes through a high-pressure gas–liquid–solid separator and the liquid is depressurized in a series of capillary tubes. In the process, organic matter is converted to CO<sub>2</sub> and clean water. This system has been tested with liquid fuel and with secondary sludge at supercritical conditions for over 200 h. The research is ongoing.

### 5.2.2. University of Missouri

A continuous reaction system was designed and fabricated at the University of Missouri (Miller et al., 2015). A simulant fecal sludge is mixed with a preheated supercritical fluid of mixture of water and air, which then enters in a 305 cm length of 316 stainless steel tubing. Although the reactor is not heated externally, the temperature in the reactor is higher than that at the mixing point, with an average temperature gain of 87 °C due to the exothermic nature of the SCWO reaction. Finally, the effluent is depressurized by back-pressure regulators.

The results from this bench-scale system show that the concentration of the feed significantly influences the temperature gain in the reactor while the stoichiometric excess of oxygen,  $n$  and pressure affect the efficiency of heat transfer. Although nearly full conversion of organics can be obtained when  $n$  is as low as 1.1, further increasing  $n$  to about 1.5 results in maximum temperature

gains.

### 5.2.3. University of Valladolid

A pilot plant treating 24 L/h of feed was designed by the High Pressure Process Group of the University of Valladolid (Cabeza et al., 2013). A cooled wall reactor is operated at  $T = 400\text{--}700$  °C and  $P < 30$  MPa. Feed containing sludge and IPA (which serves as auxiliary fuel) is pumped by a membrane pump, which can resist some small particles in the sludge. After heating by electrical pre-heaters when necessary, the feed and preheated air produced by a four-stage reciprocated compressor are mixed and injected into a tubular injector from the bottom of the sludge. The feed and the oxidant then enter into an empty vessel at the top of the reactor and flow in reverse to mix with the cooling water between the walls of the vessels. In this manner, a cold pool in the bottom of the reactor can be generated to dissolve the precipitated salts in the sludge.

### 5.2.4. Xi'an Jiaotong University

Xi'an Jiaotong University has constructed the first SCWO pilot scale plant in China with a transpiring wall combined with a Modar reactor made of 316 stainless steel to treat MSS with a solid content lower than 10 wt.%. This system has a treatment capacity of 3 t/d and is composed of six skidded modules. It can reach a COD removal rate higher than 99.5% and surplus heat utilization efficiency higher than 80%. A brine pool is formed in the bottom of the reactor. Fluid in the pool with a high concentration of salts then enters the salt-removing device and is heated to a supercritical state. The salts are precipitated again and finally stored in the salt-collecting tank. The equipment investment is 0.58 million USD, and the operating cost is 76.56 USD/dry ton for MSS with a moisture content of 92 wt.%, which is much lower than the cost of incineration (Xu et al., 2010, 2012a).

## 5.3. Commercial systems

For SCWG, Gasafi et al. (2008) designed a 5 t/h (80 wt.% water content) SCWG process and demonstrated that SCWG is a cost-effective process. The equipment cost is 2915 million EUR, which accounts for 39% of the total cost. The levelized annual costs including inflation are 2953 million EUR and 2833 million EUR for 10 and 20 years, respectively.

For SCWO, Table 3 summarizes the operation and economic

**Table 3**  
Operation and economic parameters of three commercial SCWO systems of MSS.

Company	HydroProcessing	Chematur Engineering AB	SuperWater solutions
Country	USA	Sweden	USA
Capacity	150 t/d	168 m <sup>3</sup> /d	35 dry ton/d
Solid content (wt.%)	6–9	15	10
COD (mg/L)	80,000–120,000	110,000	n/a <sup>a</sup>
Temperature (°C)	592	510–580	600
Pressure (MPa)	23.47	25	26
Residence time (s)	20–90	30–90	30–60
Oxidant consumption (kg/kg dried sludge)	1.5	1.05	n/a
Oxidation coefficient	1.125	1.43	n/a
Oxygen recovery	No	No	Yes
CO <sub>2</sub> recovery	Yes	No	Yes
Reactor	Tubular	Tubular	Tubular
Capital cost	3 million USD	5 million GBP	33.7 million USD
Operation cost	100 USD/dry ton	105 USD/dry ton	268 USD/dry ton
Depreciation cost	80 USD/dry ton	119 USD/dry ton	n/a
Reference	Griffith and Raymond, 2002; Svanstrom et al., 2004	Gidner and Stenmark, 2001; Patterson et al., 2001	Sloan et al., 2008; Oyler, 2011

<sup>a</sup> n/a, not available.

parameters of three commercial systems, which will be discussed later.

### 5.3.1. HydroProcessing

HydroProcessing constructed the first commercial SCWO sludge processing equipment for the Harlingen Wastewater Treatment Plant, in Texas, USA (Griffith and Raymond, 2002). It was built in 2001 and stopped operation in 2002 due to corrosion in the heat exchanger (Marrone, 2013). Its flow sheet is shown in Fig. 5.

As shown in Fig. 5, in the HydroProcessing system, a hydrocyclone is applied to separate the flow after the reactor and to maintain the solids in the underflow. The overflow and subsequent underflow are used to heat the feed. The heated feed mixes with oxygen and they enter the gas-fired heater together for further heating; then, they enter a tubular reactor. It is interesting that the underflow with solids is depressurized by a capillary pressure reduction device using its frictional resistance.

The results from early operation show that the destruction efficiencies of sludge are 99.93–99.96%, 49.6–84.1% and 92.89–98.90% for COD, ammonia and total solid in the overflow, respectively. The destruction efficiencies of sludge are 99.92–99.93%, 49.6–86.4% and 62.72–88.94% for COD, ammonia and total solid in the underflow, respectively (Griffith and Raymond, 2002). However, effluent ammonia ranges from 410 to 2075 mg/L, which is much higher than the related discharge standards, indicating the recalcitrant nature of ammonia (Segond et al., 2002; Webley et al., 1991). Due to the high ammonia concentration of the effluent, it can be sent to municipal wastewater plants or to industrial plants as a nutrient. The heat from the gas-fired heater is approximately 4100 kWh/dry ton sludge, the oxygen consumption is 1500 kg/dry ton sludge, and the electricity consumed by the pumps is 550 kWh/dry ton sludge, producing a net operation and maintenance cost of approximately 100 USD/dry ton sludge (Svanstrom et al., 2004).

### 5.3.2. Chematur AB and SCFI

For demonstration purposes, Chematur AB has built a 6 t/d unit in Karlskoga, Sweden for the treatment of both undigested and

digested sludge, which has been in operation since 1998 (Patterson et al., 2001). Chematur AB licenced the SCWO process to the Shinko Pantec Co. of Japan, and they have built a pilot SCWO unit with a capacity of approximately 26.4 t/d for the treatment of MSS in Kobe, Japan (Gidner and Stenmark, 2001). They also evaluated the economic value of a unit treating 168 m<sup>3</sup> of sludge per day (see Table 3). Its flow sheet, called the Aqua Critox process, is presented in Fig. 6.

As depicted in Fig. 6, this system consists of a series of sludge homogeneous equipment including a feed tank with a paddle mixer, a macerator, an ultra turrax and a grinder. The first three facilities along with a mono pump constitute a recirculation loop, which provides size reduction and homogenisation during a batch operation. After homogenisation, sludge enters a hose diaphragm piston pump pressurised to approximately 25 MPa and is pumped to a double-pipe economiser heated by the reactor effluent. Fouling problems in the economiser are avoided due to the high velocity and reduced feed particle size. After heat exchange, sludge enters a heater for a further temperature increase. Preheated sludge and oxygen subsequently enter the reactor. To accurately control the reaction temperature with high concentration sludge, quench water is added, and oxygen is injected in two stages. Similar to the HydroProcessing system, the effluent is depressurized by capillaries in parallel. Many capillaries are applied instead of a single one to minimize the erosion and control the velocity in the capillaries. To accurately control the pressure drop, choke water is added before reaching capillaries to change the flux and thus the frictional drag in the capillaries (Suzuki and Oonobu, 2000).

The tests show that all organics can be easily destroyed. The removal rate of COD is greater than 99.99% when  $T > 520$  °C. A temperature higher than 540 °C is needed to completely destroy total nitrogen (TN). For a 168 m<sup>3</sup>/d system, the natural gas consumed by the gas-fired heater is approximately 21.9 Nm<sup>3</sup>/dry ton sludge, the oxygen consumption is 1048 kg/dry ton sludge, the electricity consumption is 229 kWh/dry ton sludge, the process water consumption is 1.7 m<sup>3</sup>/dry ton sludge, the cooling water consumption is 100 m<sup>3</sup>/dry ton sludge, and the steam generated by the heat of the reaction is 4200 kg/dry ton sludge, producing a net

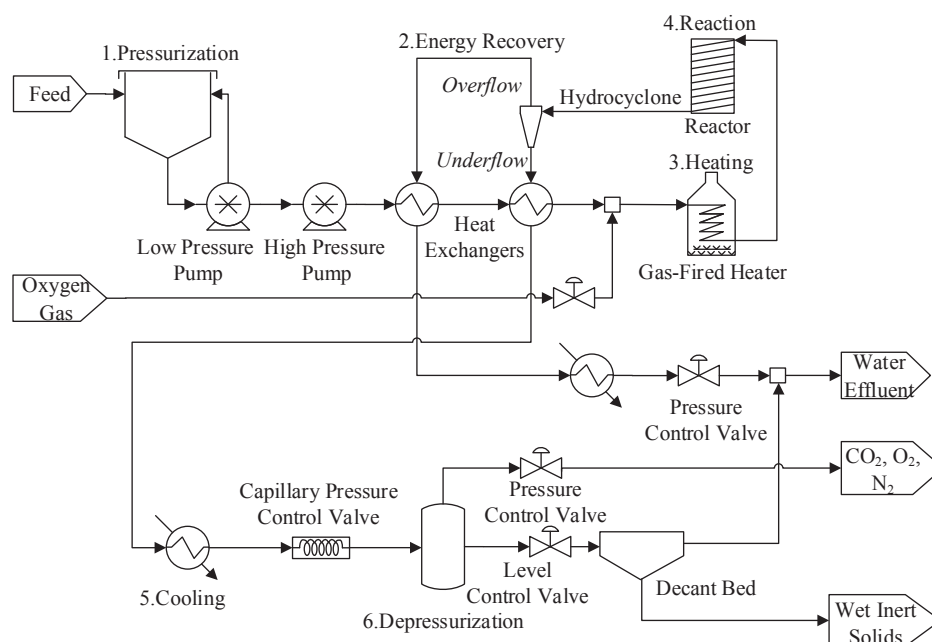


Fig. 5. Flow sheet of the HydroProcessing system (Griffith and Raymond, 2002).

operation and maintenance cost of approximately 105 USD/dry ton sludge (Gidner and Stenmark, 2001).

In 2007, the SCFI Group acquired patented supercritical water oxidation technology (Aqua Critox<sup>®</sup>) from Chematur Engineering AB of Sweden; therefore, Chematur AB is now SCFI (Regan et al., 2010). Further work directed by the SCFI group has emphasized the reduction of costs. The residual inorganic fraction of the sludge can be recovered as phosphoric acid and an iron coagulant if required. The ortho-phosphates from the supernatant, representing 78% of the total influent phosphorus, can also be recovered using fluidized bed crystallization technologies (Callaghan and Regan, 2010).

### 5.3.3. SuperWater solution

From 2009 to 2011, SuperWater Solution installed and successfully tested a 5 dry t/d SCWO system for the Iron Bridge Regional Water Reclamation Facility in Orlando, FL, USA (Sloan et al., 2008, 2009). They also assessed the economic value of a unit that treats 35 dry tons of sludge per day (see Table 3) (Oyler, 2011). The flow sheet is illustrated in Fig. 7.

As presented in Fig. 7, the sludge and oxygen mix and together enter a tubular system with a constant pipe diameter that includes a preheater, reactor and cool-down heat exchanger. Pressurized pure water is applied to carry heat from the reactor effluent to the preheater. This structure can minimize solid and scale deposition. It is interesting that the SuperWater Solution system has an oxygen recycling process based on the difference in liquefaction temperatures between O<sub>2</sub> and CO<sub>2</sub>. Through the oxygen recycling process, sludge can be oxidized at a high  $n$  value with low oxygen consumption, thus increasing the effluent quality and decreasing operation costs.

## 6. Research needs and challenges

From the perspective of producing gases via SCWG or SCWPO, the selection of a catalyst is highly important because complete gasification of MSS requires a temperature as high as 800 °C (Wilkinson et al., 2012). A heterogeneous catalyst is superior to a homogenous catalyst due to its high recyclability. However, most experiments with catalysts only focus on the gas yield and the gasification efficiency; therefore, the screening and stability of heterogeneous catalysts should be further investigated to test their long-term catalytic activity.

From the perspective of decomposition of organics without hydrothermal flames, studies on corrosion, tar formation and solid deposition of MSS are not sufficient. Regarding corrosion, Tang et al. (2011) investigated the corrosive behaviours of 316L stainless steel

bulk and mesh samples (representing the pressure bearing wall and transpiring wall, respectively) in an SCWO environment with MSS. They found that the corrosive behaviours of mesh samples were superior to those of the bulk samples, especially in acid environments. Besides the corrosion behaviour in the reaction conditions, corrosion problems should also be studied in the preheating process. Although the preheating process occurs at a lower temperature than the reaction, the preheating process is usually performed under a reducing atmosphere, causing difficulty in the formation of a stable oxide film (D'Jesús et al., 2006; Kritzer et al., 1999), especially near the critical point of water (Kritzer, 2004).

Furthermore, tar formation and solid deposition may cause plugging of the SCW system and the deactivation of catalysts. Karayildirim et al. (2008) proposed two possible reaction pathways including degradation-polymerization and solid–solid conversion to form coke and char, respectively. Additionally, the fundamental research and their inhibition methods including the use of an additive, feed pre-treatment and adjustment of operating conditions have been reviewed in detail (Hodes et al., 2004; Marrone et al., 2004). However, these studies do not focus on MSS. Considering the complex nature of MSS, tar formation and solid deposition problems, when using MSS as the feed, need future experiment and analysis.

Regarding the decomposition of organics with hydrothermal flames using auxiliary fuel, this has only been investigated using low concentration sludge (volatile solids of only 1.3%) with IPA. If higher concentrations of sludge can be applied, the auxiliary fuel consumption will be lower, and the injection temperature of the sludge into the reactor can be lowered. For example, if the solid content of sludge can be concentrated to 17.4 wt.%, sludge can be injected at ambient temperature (approximately 25 °C) (Cabeza et al., 2013); thus, the preheating process can be completely avoided. However, high-concentration sludge has high viscosity (Eshtiaghi et al., 2013), which may affect the feed velocity in the reactor and subsequently influence the production of a hydrothermal flame. Moreover, high-concentration sludge may cause plugging of the reactor; therefore, an appropriate concentration, as well as reasonable reactor configurations (e.g., cooled wall reactor or transpiring wall reactor), should be determined.

In addition, although studies on the use of co-fuels are limited to IPA for MSS, for some refractory compounds such as acetic acid, ammonia, dioxins and naphthalene, the use of IPA as well as other auxiliary fuels or co-fuels to produce a hydrothermal flame has been investigated (Queiroz et al., 2015; Reddy et al., 2015). For acetic acid, it has been found that 99% elimination of TOC is achieved using IPA as a co-fuel in a tubular reactor with a residence

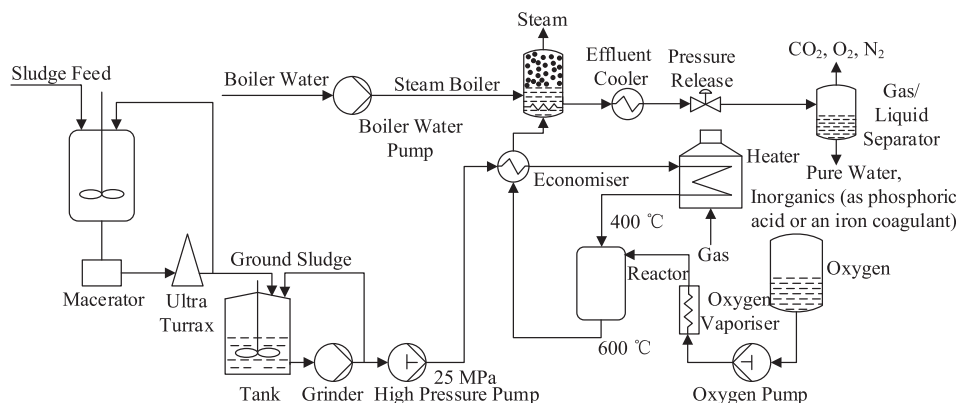


Fig. 6. Flow sheet of the Chematur AB system (Patterson et al., 2001).

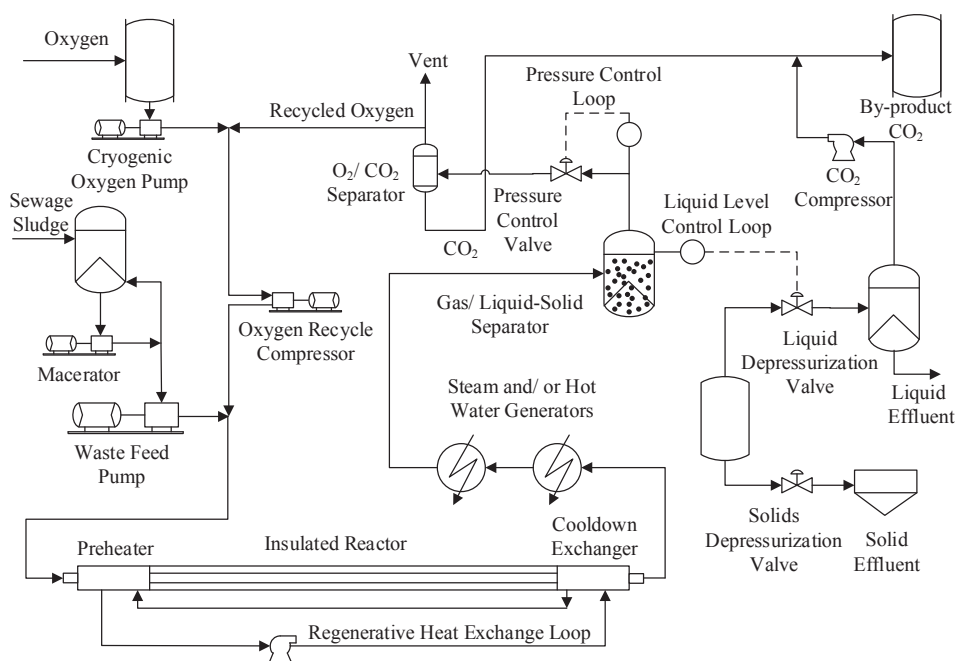


Fig. 7. Flow sheet of the SuperWater Solution system (Sloan et al., 2008).

time of 0.7 s (Cabeza et al., 2011). For ammonia, similar to acetic acid, IPA is used as a co-fuel to produce a hydrothermal flame. However, it is essential to maintain the reaction temperature below 650 °C and the air excess below 2.5% to prevent the formation of NO<sub>x</sub> (Cabeza et al., 2013). For dioxins, the decomposition rate was higher than 99.9% for all isomers when hexane was used as a fuel (Serikawa et al., 2002). Moreover, a concentration of 75 mg/L naphthalene can be degraded by 99.9% using a 25% methanol solution as fuel at a 400 °C air temperature and pressure of 24 MPa (Sobhy et al., 2009). For MSS, auxiliary fuel is not limited to IPA. Different types of auxiliary fuels possess various heating values and have co-oxidation effects on MSS (Zhang et al., 2013), which affect the ignition, combustion and extinction processes of sludge. Accordingly, decomposition of high content sludge with hydrothermal flames in both cooled wall and transpiring wall reactors using various auxiliary fuels requires further study.

## 7. Conclusions

In this work, SCW treatment technologies including, SCWG, SCWPO and SCWO, have been discussed as potential methods for handling MSS due to the conversion of MSS to combustible gases by SCWG or SCWPO, the complete degradation of organics by SCWO and the reduced risk of HMs. With respect to the SCWG and SCWPO technologies, increasing the temperature, adding a small amount oxidant ( $n < 0.6$ ) and using activated carbon, metal or alkali catalysts can promote the gasification of MSS. Although MSS with low moisture content is preferred to reach an auto-thermal status, transport and char formation problems require further study. In contrast, SCWO technology aims to degrade organic compounds in MSS. Removal rates of COD, TOC and NH<sub>3</sub>-N removal ratios higher than 99% can be achieved, and several systems have been designed or constructed to verify this technology. However, corrosion or plugging problems, especially during the preheating period, restrict this technology. Therefore, decomposition of organics with hydrothermal flames using auxiliary fuel instead of preheating may be an alternative, and a better understanding of this process using high concentration sludge and reasonable reactor configurations is essential.

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