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Catalytic gasification of glycine and glycerol in supercritical water

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ABSTRACT

Glycine and glycerol were used as the model compounds of protein and fattiness, respectively. A continuous tubular-flow reactor was used for the gasification experiments operated at 380–500 °C and 25 MPa with or without Na_2CO_3 catalyst. Compared with a negative effect on glycerol gasification, Na_2CO_3 could increase hydrogen yield and Chemical Oxygen Demand (COD) destruction efficiency, and the catalytic performance of 0.1 wt% Na_2CO_3 was better than that of 0.2 wt% for glycine gasification. When 1 wt% glycine solution with 0.1 wt% Na_2CO_3, or 1 wt% glycerol solution without Na_2CO_3 was gasified at 500 °C with the residence time of 0.98 min, their corresponding gasification efficiencies were up to 95.8% and 98%, and hydrogen yields could reach 4.14 and 5.08 mol/mol, respectively. Hydrogen molar fraction in gaseous product was about 60% and liquid effluents could be reutilized. Correspondingly, the ideal overall reaction equations for glycine and glycerol gasification were proposed.

1. Introduction

Supercritical water gasification (SCWG), which has a promising future for using biomass to produce hydrogen [1–3], has received more attention because large amount of hydrogen will be required significantly for engine application in future. Compared with conventional gasification processes, SCWG can gasify wet biomass with high moisture content up to 90% without drying at lower gasification temperatures, and can obtain higher gasification efficiency as well as cleaner products [4]. However, tar and char formation is a critical technology problem for its commercial applications, because it may not only decrease gasification efficiency of biomass, energy efficiency of system and running cost, but also plug reactor or pipe line [5,6]. This problem can be solved by different ways such as selecting proper preheating temperature [5,7], rapid heating rate [8–10], partial oxidation [11–14], and adding catalyst [12,15–18].

It is known that adding catalyst has a positive effect on hydrogen production by biomass SCWG. On the one hand, adding catalyst will reduce tar and char formation, and organic matter gasification efficiency can reach up to 98%. On the other hand, it can increase hydrogen yield, and hydrogen molar fraction even reaches more than 50% [1,6]. Therefore, selecting a cheap, effective, stable catalyst is a key problem for biomass SCWG. Nowadays, there are a series of catalysts such as alkali compound, metal, metal oxide, carbon and ore for converting biomass to product hydrogen in supercritical water, in which alkali compound is the most active catalyst [19]. Alkali compounds, such as KOH, NaOH, LiOH, K_2CO_3 and Na_2CO_3, commonly promote the splitting of C–C bonds [20] and increase gasification efficiency and hydrogen yield by

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enhancing the water–gas shift reaction via forming formate, meanwhile retard tar and char formation [7,9,12,20–23]. However, alkali compound acted as a homogeneous catalyst may result in a pollution problem because it is difficult to recover from the reactor's effluent, and there is no doubt that SCWG running cost and technology complexity will increase evidently if it is recovered. Secondly, alkali compound may also plug reactor because its solubility in supercritical water is so low [24] that it will precipitate on pipe reactor wall. In addition, alkali compound solution of high pH will severely corrode reactor under supercritical water condition. These factors above have limited SCWG commercial processes if alkali compound is utilized as the catalyst for hydrogen production, thus the catalytic mechanisms and precipitation properties of alkali compound should be investigated in more detail on the basis of previous studies [20,25].

Sewage sludge, which usually contains plenty of water and organics such as carbohydrate, protein, and fattiness, is suitable to be gasified for hydrogen production under supercritical water condition. In this work, glycine and glycerol were chosen as the model compounds of protein and fattiness to be gasified for hydrogen production in supercritical water, respectively. Their SCWG properties were investigated with or without Na_2CO_3 representing an alkali compound catalyst, and the corresponding catalytic reaction mechanism was also discussed.

2. Experimental

2.1. Feedstock

Glycine (99.5% purity) or glycerol (99.0% purity) was gasified with or without Na_2CO_3 catalyst (99.8% purity) in supercritical water. Aqueous solution of 1 wt% glycine or glycerol was prepared by resolving appropriate amount of reagent into deionized water. Some amount of Na_2CO_3 was added into the above solution to form proper catalyst concentration needed for investigation.

2.2. Apparatus and experimental procedures

Glycine and glycerol SCWG experiments were performed in the experimental apparatus schematically illustrated in Fig. 1. At the beginning of each run, the preheater (1 m length and 15 mm i.d.) and the reactor (1.7 m length and 12.3 mm i.d.) were heated up to the desired temperatures without any feedstock in order to save preheating time and to reduce energy consumed. Then, the residues from previous experiments were rinsed by deionized water to minimize their effects on the following gasification process. Glycine or glycerol solution in feed tank was introduced into the reaction system from preheater to reactor by high-pressure metering pump whose flow rate was controlled by transducer. Reaction products were cooled down to ambient temperature in a water-cooled heat exchanger rapidly and depressurized to atmospheric pressure through a back pressure regulator, then released into a glass gas–liquid separator. Before gaseous product was collected, its volumetric flow rate was determined by a wet test meter.

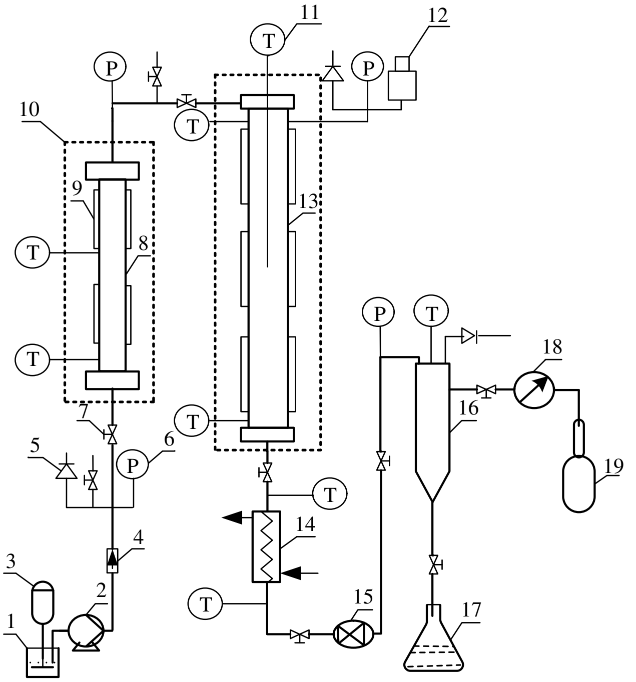

Fig. 1 – Schematic diagram of tubular-flow reactor system. (1) Feed tank, (2) high-pressure metering pump, (3) homogenizer, (4) check valve, (5) safety valve, (6) pressure gauge, (7) pin valve, (8) preheater, (9) heat wiring, (10) safeguarding structure, (11) thermocouple, (12) explosion valve, (13) reactor, (14) cooler, (15) back pressure valve, (16) gas–liquid separator, (17) effluent tank, (18) wet test meter, (19) gas bag.

The tubular reactor was made of Hastelloy C276, which was designed for temperature of 600 °C and pressure of 40 Mpa. It was heated to the set-point temperature by electrical heating wires coiled around the outer wall of the reactor tube. Temperatures of the outside wall and the inside fluid of the reactor were measured at the locations shown in Fig. 1, and their averaged value was used as reaction temperature. Pressure measurement was determined by pressure gauges.

2.3. Experimental conditions

In this work, reaction temperature and residence time were the main experimental variables. The feedstock concentration and reaction pressure were fixed at 1 wt% and 25 MPa, respectively. Similar to our previous work, residence time (t) was calculated from Eq. (1) displayed as follow [26]:

$$t = (V/Q_0) \times (V_0/V_r) \quad (1)$$

where V (0.2 L) is reactor volume, Q_0 ($1.83 \times 10^{-2}\ L\ min^{-1}$) and V_0 (about $0.001\ m^3\ kg^{-1}$) are the volumetric flow rate and specific volume of liquid effluent under room temperature and atmospheric pressure conditions, respectively. V_r is the specific volume of feedstock under reaction conditions, which is determined with a common calculation software of water physics properties when reaction temperature and pressure are given. Because organic matter mass concentration in feedstock was very low, feedstock properties were similar to those of water.

Fig. 2 indicates the change trends of feedstock density and residence time with increasing the reaction temperature. Residence times were 4.94, 1.58, 1.25, 1.09, and 0.98 min when reaction temperatures were at 30 °C intervals from 380 °C to 500 °C, respectively. Feedstock density and residence time had a similar change trend, indicating the high correlation between them. The heating rate and preheating temperature were 1.7 K/s and 200 °C, respectively. Experiments were conducted twice, and the sample was collected when experimental conditions were stable enough and then measured twice, the averaged value was utilized as the final data for plotting. The experimental errors of volumetric flow rate, pressure, and temperature were $\pm 0.02\ \mathrm{L\,h^{-1}}$, ± 0.1 MPa, and ± 2 °C, respectively.

2.4. Analytical

The identification and quantification of gaseous product were analyzed with a gas chromatography–thermal conductivity detector (Shanghai, GC-112A) based on the peak area of a standard gas mixture (Bought from Beijing Haipu Beifen Gases Industry Limited Company) utilized for day-to-day calibration with helium as the carrier gas. A 3 m × 3 mm TDX-01 packed column was used and operated at 100 °C, and the other constant temperature conditions were as follows: thermal conductivity detector temperature and electric current of 100 °C and 120 mA, carrier gas pressure and flow rate of 0.42 MPa and 18.5 ml/min, injector temperature of 70 °C. The method of analysis is simple and effective for the detections of H_2, CO_2, CO, CH_4, N_2 and other light organic gases. Liquid products were identified by a high-performance liquid chromatography (Model LC-3000) with an ultraviolet detector (Model UV3000). The COD concentration, pH and salt content of liquid product entering into effluent tank were monitored by HH-5 Chemical Oxygen-consuming Measurer, Professional Meter Model PP-50 and Salinometer Model 55, respectively.

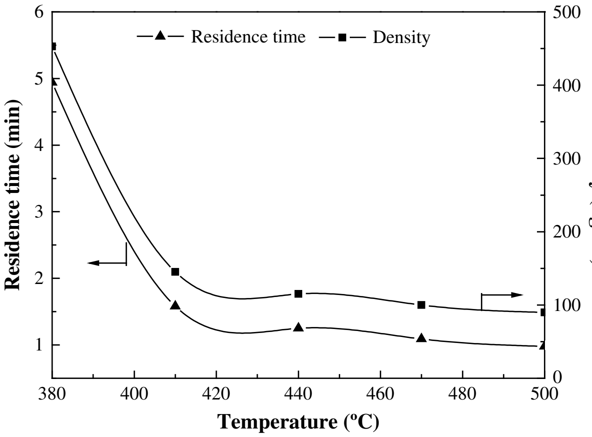

Fig. 2 – Temperature dependence of feedstock density and thereby variations in reactor residence time.

Gasification efficiencies (GE) were defined as follows:

$$H_{GE} = \frac{\text{the number of hydrogen atom in } H_2 \text{ produced}}{\text{the number of H in the reactant}} \times 100\% \quad (2)$$

$$N_{GE} = \frac{\text{the number of nitrogen atom in } N_2 \text{ produced}}{\text{the number of N in the reactant}} \times 100\% \quad (3)$$

$$C_{GE} = \frac{\text{the number of carbon atom in } CO_2,\ CO \text{ and } CH_4 \text{ produced}}{\text{the number of C in the reactant}} \times 100\% \quad (4)$$

In Eqs. (2)–(4), the reactant was glycine or glycerol, excluding water, catalyst and other impurities. Moreover, it was assumed that gaseous product would not be dissolved into the liquid collected in the effluent tank.

3. Results and discussion

3.1. Study of glycine

Fig. 3 indicates the influences of different concentrations of Na_2CO_3 on hydrogen yield and COD destruction efficiency for glycine SCWG. Hydrogen yield had a very complex change trend with Na_2CO_3 concentration increasing, which reached the maximum value when about 0.1 wt% Na_2CO_3 was added at 400 or 450 °C. COD destruction efficiency had no evident variation with increasing Na_2CO_3 concentration. Increasing reaction temperature was helpful to increase hydrogen yield and COD destruction efficiency. 0.5 wt% Na_2CO_3 would result in reactor plugging after 8 h run in our experiments. Additionally, as shown in Fig. 3, compared with 0.1 wt% Na_2CO_3, high concentrations (>0.2 wt%) of Na_2CO_3 had not shown better catalytic performance for glycine SCWG, which were not necessary to be further investigated. In this work, 0–0.2 wt% Na_2CO_3 concentrations will be chosen for further study and catalytic mechanism discussion.

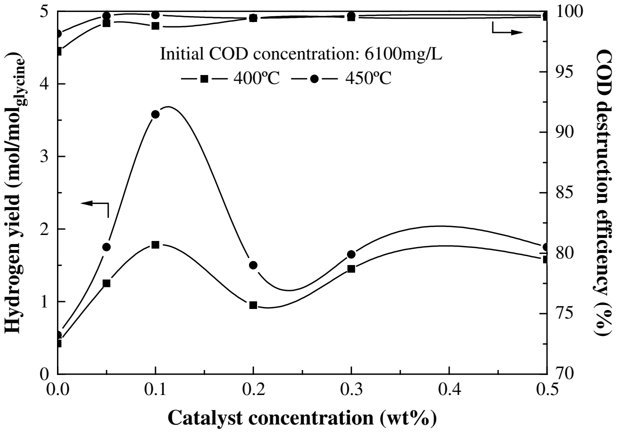

Fig. 3 – Different concentrations of Na_2CO_3 dependences on hydrogen yield and COD destruction efficiency for glycine SCWG at different reaction temperatures.

Fig. 4 also shows the influence of Na_2CO_3 on hydrogen yield of glycine SCWG. It can be seen that hydrogen yield was considerably low and hardly changed without Na_2CO_3 catalyst, but increased sharply with Na_2CO_3 with increasing reaction temperature. The catalytic performance of 0.1 wt% Na_2CO_3 for hydrogen yield was much better than that of 0.2 wt%. Hydrogen yield could reach up to 4.14 mol/mol at 500 °C with 0.1 wt% Na_2CO_3. As shown in Fig. 5, COD destruction efficiency (>99.2%) of liquid product of glycine SCWG with Na_2CO_3 was higher than the value when no Na_2CO_3 was added. Moreover, COD destruction efficiency slightly increased and pH varied in a small range of 6.5–7.5 with increasing reactor temperature. The detailed catalytic mechanism will be discussed in the following sections.

From Figs 3 to 5, it is observed that 0.1 wt% Na_2CO_3 had a positive effect on glycine SCWG products. Therefore, hydrogen yield and molar fraction of glycine SCWG with 0.1 wt% Na_2CO_3 is given in Fig. 6 for further discussion. The gaseous product was composed of H_2, CO_2, CH_4, C_{2+} and N_2, in which H_2 and CO_2 were two main components. The yields of H_2, CO_2 and N_2 increased with increasing reaction temperature. Opposite to CO_2 yield, H_2 yield increased rapidly below 440 °C and raised slightly above 440 °C. Especially, no CO was detected during the glycine SCWG process. Thus, it can be concluded that water–gas shift reaction is not the main reaction pathway for hydrogen production by glycine SCWG. Low temperature and alkali reaction environment are not favorable to CH_4 formation; therefore, CH_4 yield was very low and changed slightly, as shown in Fig. 6. The fact that C_{2+} yield decreased slightly is due to increasing CO_2 increasing with reaction temperature. Additionally, hydrogen molar fraction, which could be more than 60%, increased evidently below 440 °C and then decreased slowly at 440–470 °C, and finally was stable above 470 °C with increasing reaction temperature. Changing different gas composition yields at different rates lead to varying hydrogen molar fraction as shown in Fig. 6.

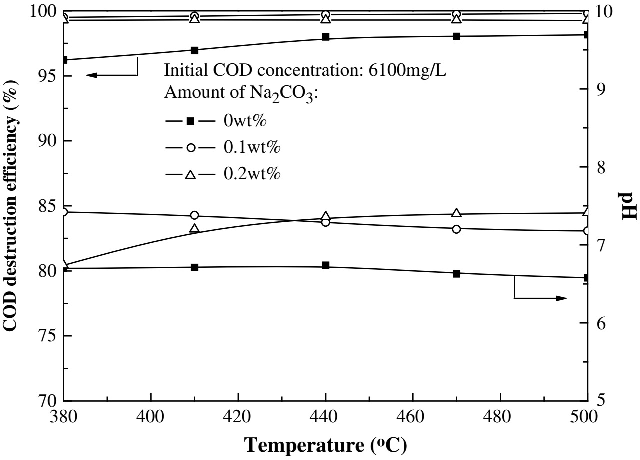

Fig. 5 – Different amounts of Na_2CO_3 dependences on COD destruction efficiency and pH of liquid product for glycine SCWG.

Based on the above experimental results, as a homogenous catalyst, Na_2CO_3 played a significant role not only on hydrogen yield of gaseous product but also on COD destruction efficiency of liquid product when glycine was gasified in supercritical water. Adding 0.1 wt% or 0.2 wt% Na_2CO_3 did not cause drastic variety of liquid pH during whole process, thus its influence on corrosion of reactor can be ignored.

In addition, a small amount of Na_2CO_3 mentioned above would not result in reactor plugging because of its little depositing on reactor wall, which was concluded by the measurement of salt content at the two ends of reactor. Meanwhile, the catalytic performance of 0.1 wt% Na_2CO_3 was better than that of 0.2 wt%. Therefore, 0.1 wt% Na_2CO_3 is an ideal catalyst or additive for glycine SCWG process under tested conditions.

Many studies [7,20,27–29] report that gaseous product is formed by free radical reaction in supercritical water. The catalytic mechanism of K_2CO_3 on hydrogen and carbon dioxide yields for carbohydrate SCWG is that K_2CO_3 promotes the water–gas shift reaction via forming formate reacting with water to form hydrogen, then achieves the recycle by producing CO_2 and K_2CO_3 [25]. Formic acid is considered as the

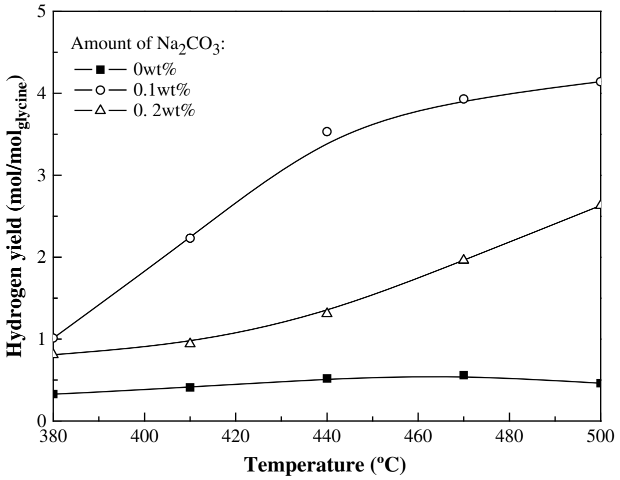

Fig. 4 – Influences of different amounts of Na_2CO_3 on hydrogen yield of glycine SCWG.

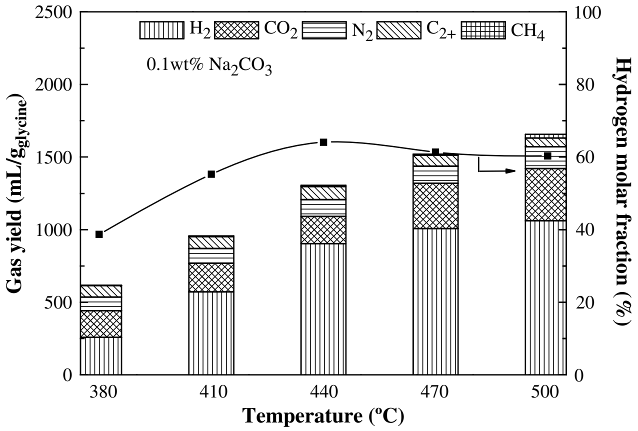

Fig. 6 – Yields of different gas products and molar fraction of hydrogen measured at atmospheric pressure and 20 °C for glycine SCWG with 0.1 wt% Na_2CO_3.

intermediate product of the water–gas shift reaction [16], and its decomposition has two approaches which are decarboxylation and dehydration reactions [22], as shown in Eqs. (5) and (6).

$$HCOOH \rightarrow CO_2 + H_2 \quad (5)$$

$$HCOOH \rightarrow CO + H_2O \quad (6)$$

Considering no CO was discovered in our experiments, if we assume formic acid is formed indeed as the intermediate product of glycine SCWG, so its decomposition approach is the former (Eq. (5)), which has been verified through an added experiment under the same reaction conditions. It may be achieved by accelerating the decarboxylation reaction of formic acid but not by promoting the water–gas shift reaction that Na_2CO_3 increases hydrogen yield of glycine SCWG. Na_2CO_3 increasing hydrogen yield is not to achieve by promoting the water–gas shift reaction but probably by accelerating the decarboxylation reaction of formic acid. As shown in Eq. (8), formic acid may be a hydrolysate and be produced by decarboxylation reaction of glycine. This paper gives a probable explanation about the catalytic mechanism of Na_2CO_3 for glycine SCWG process as follows:

$$C_2H_5NO_2 + H_2O \rightarrow H_2 + CH_4 + CO_2 + N_2 + C_{2+} \quad (7)$$

$$NH_2CH_2COOH + H_2O \rightarrow NH_2CH_2OH + HCOOH \quad (8)$$

$$NH_2CH_2OH \rightarrow H_2 + CH_4 + N_2 + CO_2 + C_{2+} \quad (9)$$

$$HCOOH + N_2CO_3 \rightarrow NaHCO_3 + HCOONa \quad (10)$$

$$HCOONa + H_2O \rightarrow NaHCO_3 + H_2 \quad (11)$$

$$2NaHCO_3 \rightarrow CO_2 + Na_2CO_3 + H_2O \quad (12)$$

$$Na_2CO_3 + H_2O \rightarrow NaHCO_3 + NaOH \quad (13)$$

According to Figs. 5 and 6, we can make a reasonable assumption that glycine was gasified completely and the products only included H_2, CO_2, CH_4, CO, N_2, and C_{2+}. It was also proved in the following section that water participated in glycine SCWG reaction, see Fig. 11. Thus Eq. (7) can be obtained based on the above analysis. If Eq. (7) is constructed of Eqs. (8) and (9), it is known that adding Na_2CO_3 will accelerate the reaction equilibrium of Eq. (10) to move towards the right, and then the reaction equilibriums of Eqs. (8), (9), (11) and (12) are promoted to shift towards the right. Meanwhile, increasing reaction temperature is favorable to these changes. These reasons may lead to the increases of hydrogen yield and COD destruction efficiency, as shown in Figs. 4 and 5.

It has been proved that Na_2CO_3 has a positive catalytic performance on glycine SCWG process. Sodium carbonate particles precipitated can provide a larger surface, which is helpful for catalytic reaction [24]. Additionally, alkalescent Na_2CO_3 has a solubility lower than 100 ppm in supercritical water, and it played an important role on reducing corrosion of reactor. It is attributed to that its deposit can provide a larger surface than reactor inner wall to possibly absorb corrosive compounds produced [24]. However, excess Na_2CO_3 is not advocated because it may plug reactor due to its depositing under supercritical water conditions, meanwhile it is also not beneficial to the selectivity of hydrogen. The reason is proposed that excess Na_2CO_3 promotes the reaction equilibrium of Eq. (13) to move towards the right, and a large amount of $NaHCO_3$ produced inhibits hydrogen formation (Eq. (11)). On the other hand, it has been summarized that adding Na_2CO_3 will also promote hydrogen production by Eqs. (10) and (11). Therefore, the two opposite effects on promoting and inhibiting hydrogen formation counteract with each other, and the former is much larger than the latter with an appropriate amount of Na_2CO_3 such as 0.1 wt%. That is why the catalytic performance of 0.1 wt% Na_2CO_3 was better than that of 0.2 wt%.

3.2. *Study of glycerol*

Fig. 7 indicates the influences of different concentrations of Na_2CO_3 on hydrogen yield and COD destruction efficiency for glycerol SCWG. Hydrogen yield decreased rapidly and then slowly, and COD destruction efficiency changed from decreasing to increasing at the range of 0–0.2 wt% at 500 °C. The maximum values of hydrogen yield and COD destruction efficiency were obtained when no Na_2CO_3 was added at 450 or 500 °C. As shown in Fig. 7, it was difficult to describe the effect of reaction temperature on hydrogen yield. It seemed that Na_2CO_3 had a negative effect for glycerol SCWG process. Additionally, based on the disadvantages of high concentrations of Na_2CO_3 and the complicated effects of low concentrations of Na_2CO_3 on glycerol SCWG, as done in the study of glycine, only 0–0.2 wt% Na_2CO_3 concentrations will be further studied in the following.

Fig. 8 shows Na_2CO_3 influence on glycerol SCWG process. Without Na_2CO_3 additive, hydrogen yield increased gradually below 430 °C and raised sharply above 430 °C, which could

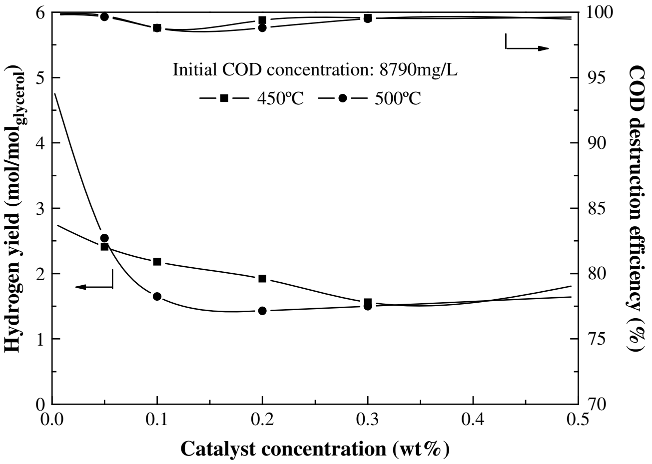

Fig. 7 – Different concentrations of Na_2CO_3 dependences on hydrogen yield and COD destruction efficiency for glycerol SCWG at different reaction temperatures.

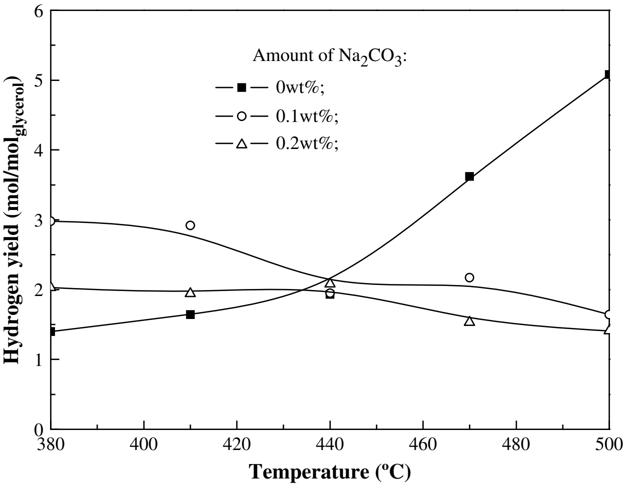

Fig. 8 – Influences of different amounts of Na_2CO_3 on hydrogen yield of glycerol SCWG.

reach up to 5.08 mol/mol at 500 °C. However, hydrogen yield decreased gradually in the presence of Na_2CO_3 with increasing reaction temperature. Compared with 0.1 wt% Na_2CO_3 additive, 0.2 wt% Na_2CO_3 had a more negative effect on hydrogen yield. Therefore, it is believed that adding Na_2CO_3 would inhibit the increase of hydrogen yield of glycerol SCWG process. In addition, Na_2CO_3 similarly had a negative pole on COD destruction efficiency of liquid product (Fig. 9). The detailed reasons are not clear and further investigations are required.

The variations of liquid color in the whole glycerol SCWG process were as follows: first, the glycerol solution with Na_2CO_3 additive was clear and transparent, then became black when preheated up to 200 °C, and finally became clear and transparent again after reaction. It is due to glycerol's decomposition and/or polymerization in the preheater and gasification in the reactor. The intermediate product of glycerol's decomposition and/or polymerization was a complicated mixture, which included a little amount of polyglycerin and other unknown organics. These compounds were probably difficult to be gasified, which resulted in a much lower gasification efficiency of glycerol. In fact, experimental results indicated that glycerol gasification efficiency only reached up to 60% in the presence of Na_2CO_3.

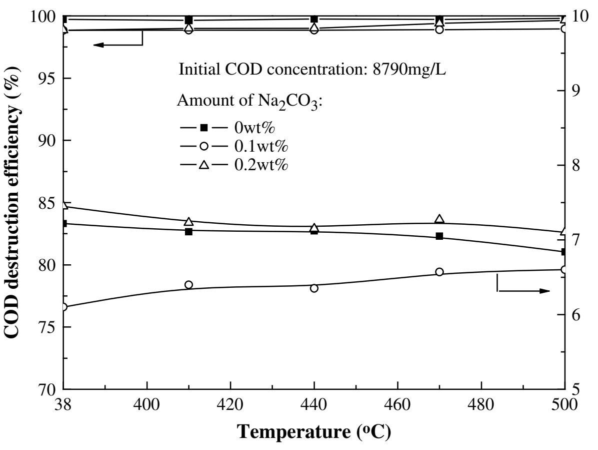

Fig. 9 – Different amounts of Na_2CO_3 dependences on COD destruction efficiency and pH of liquid product for glycerol SCWG.

Since Na_2CO_3 has a negative effect on glycerol SCWG process, Fig. 10 indicates hydrogen yield and molar fraction of glycerol SCWG process in the absence of Na_2CO_3. Glycerol SCWG gaseous product included H_2, CO_2, CH_4, C_{2+}, CO, in which H_2 and CO_2 were also main components. With increasing reaction temperature, the yields of H_2, CH_4 and CO_2 increased slowly below 440 °C but increased rapidly above that, C_{2+} yield decreased gradually owing to the same reason for glycine gasification, and CO yield was very low and changed slightly. Additionally, hydrogen molar fraction increased gradually below 440 °C and increased evidently above that with reaction temperature increasing from 380 to 500 °C, and it could be near to 60% at 500 °C.

Similar to Eq. (7), Eq. (14) is obtained from Figs. 9–11. It is confirmed that formaldehyde usually is an intermediate product in biomass SCWG process [12,17,30,31]. Therefore, it can be assumed that glycerol is decomposed into glycol and formaldehyde via fragmentation reaction (Eq. (15)) in our experiments. Additionally, the low concentration of formaldehyde can thermally decompose into H_2 and CO in the absence of O_2 in supercritical water, according to Eq. (16) [32]. Thus hydrogen may be mainly produced via Eqs. (16) and (17), and the increase of CO_2 and CH_4 yields in Fig. 10 is possibly accomplished by Eqs. (18) and (19).

$$C_3H_8O_3 + H_2O \rightarrow H_2 + CO_2 + CH_4 + CO + C_{2+} \tag{14}$$

$$CH_2OHCHOHCH_2OH \rightarrow CH_2OHCH_2OH + HCOH \tag{15}$$

$$HCOH \rightarrow CO + H_2 \tag{16}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{17}$$

$$CO_2 + 3H_2 \rightarrow CH_4 + H_2O \tag{18}$$

$$2CO + 2H_2 \rightarrow CH_4 + CO_2 \tag{19}$$

3.3. *Overall reaction processes*

The change trends of gasification efficiencies of hydrogen element, glycine and glycerol in SCWG process are elucidated in Fig. 11. In this paper, gasification efficiencies of glycine and glycerol were determined by those of nitrogen and carbon element, respectively. As shown in Fig. 11, glycine or glycerol gasification efficiency increased with increasing temperature. For glycine gasification with 0.1 wt% Na_2CO_3, nitrogen element whose gasification efficiency could reach up to 95.8% at 500 °C, and mainly converted to nitrogen but not ammonia [16]. H_{GE} increased drastically below 440 °C and slowly above that with increasing reaction temperature, which could reach up to 165.6% at 500 °C. On the other hand, for glycerol gasification, the gasification efficiency of carbon element mainly converted to CO_2 could reach 98% and H_{GE} could reach up to

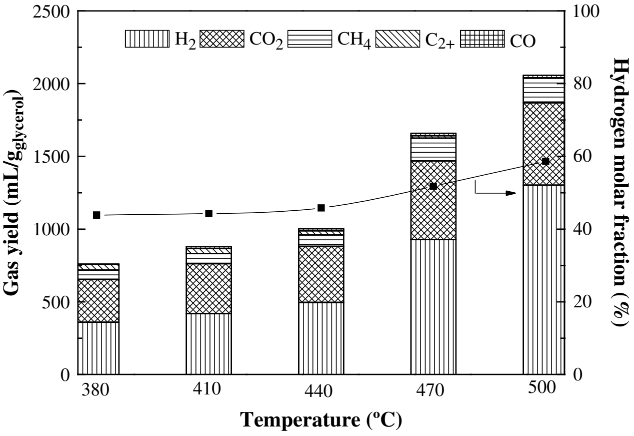

Fig. 10 – Yields of different gaseous products and molar fraction of hydrogen measured at atmospheric pressure and 20 °C for glycerol SCWG.

127.1% at 500 °C. Therefore, more than one third of hydrogen produced in glycine gasification process and more than at least 150 of hydrogen produced in glycerol gasification process originated from water, and it testified the conclusion of Kruse et al. [9] that water is a hydrogen source as well as a benign solvent for reaction.

Meanwhile, experiment results also showed that 1 wt% glycine with 0.1 wt% Na_2CO_3 or 1 wt% glycerol without Na_2CO_3 was nearly completely gasified at 500 °C. COD destruction efficiency and pH, these two indexes were completely in agreement with the quality standard of domestic water for miscellaneous use. In addition, liquid effluents were clear and transparent, and no tar and char were discovered.

Hydrogen formation mechanism is very complex in SCWG process and cannot be easily summarized. Except possible approaches introduced above, it may include a series of hydrolyzation, pyrolysis, isomerization, dehydration, condensation, and steam reforming reactions [5,6,17,33,34].

In view of experiment results shown in Figs. 5, 6, 9–11, the overall reaction processes of glycine and glycerol SCWG at 500 °C can be expressed by Eqs. (20) and (21), respectively.

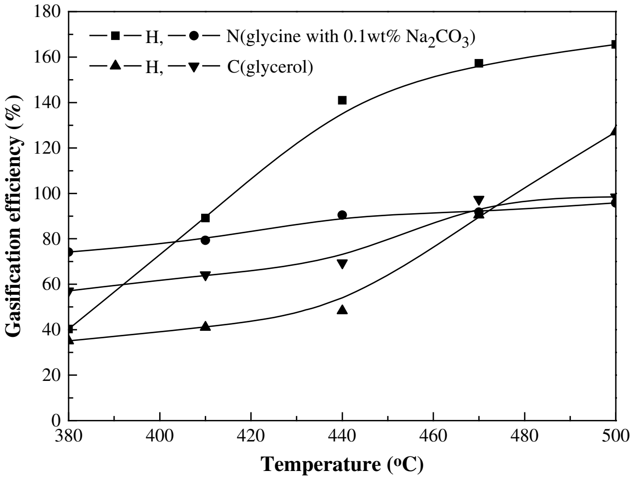

Fig. 11 – Gasification efficiencies of glycine, glycerol and hydrogen element.

$$C_2H_5NO_2 + H_2O \rightarrow 3.33H_2 + 1.12CO_2 + 0.48N_2 + \text{other small amount of gas} \quad (20)$$

$$C_3H_8O_3 + H_2O \rightarrow 4.98H_2 + 2.16CO_2 + 0.60CH_4 + \text{other small amount of gas} \quad (21)$$

According to Fig. 11, gasification efficiencies of glycine and glycerol were 165.6 and 127.1% at 500 °C, respectively. Under ideal conditions, provided that hydrogen element in glycine or glycerol completely converted into hydrogen and the other small amount of gases produced were neglected, the theoretically ideal equations at 500 °C can be proposed as Eqs. (22) and (23):

$$C_2H_5NO_2 + 2H_2O = 4.5H_2 + 2CO_2 + 0.5N_2 \quad (22)$$

$$C_3H_8O_3 + 2H_2O = 5H_2 + 2.5CO_2 + 0.5CH_4 \quad (23)$$

As shown in Eqs. (22) and (23), hydrogen gasification efficiencies are 180 and 125%, respectively. Therefore, the correspondingly maximum experiment errors are 8 and 1.68% for glycine and glycerol, respectively. Moreover, if calculated by the CO_2 stoichiometric number, the maximum experiment errors are 43.5 and 13.6%, respectively. It is considered that the small amount of gases neglected and experimental conditions not optimized made the maximum errors much bigger for glycine SCWG.

4. Conclusions

Na_2CO_3 could increase hydrogen yield and COD destruction efficiency of glycine SCWG products, and the catalytic performance of 0.1 wt% Na_2CO_3 was better than that of 0.2 wt%. However, Na_2CO_3 had a negative effect on glycerol gasification. Therefore, as a catalyst or additive, Na_2CO_3 only had a positive effect on some types of organic matters SCWG processes. A catalyst combined may be utilized as the catalyst for complex wet biomass such as sewage sludge SCWG in future.

When 1 wt% glycine solution with 0.1 wt% Na_2CO_3, or 1 wt% glycerol solution without Na_2CO_3 SCWG were conducted using a continuous tubular-flow reactor at 500 °C, 25 MPa, and residence time of 0.98 min, both of them could be gasified nearly completely (95.8% and 98%, respectively) and hydrogen yields were 4.14 and 5.08 mol/mol, respectively. Additionally, hydrogen molar fraction was about 60% and the liquid effluents could be recycled into the reactor. Water participated in SCWG processes and was an important resource of hydrogen. Correspondingly, the ideal overall reaction equations were proposed. Presentation above indicated that SCWG is feasible for converting biomass or organic pollution matter contenting protein or fattiness to produce hydrogen.

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