Original Research

Petrochemical Wastewater Gasification with Na$_2$CO$_3$ and K$_2$CO$_3$

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Abstract

Gasification of petrochemical wastewater for hydrogen production in supercritical water was studied in a fluidization bed system with the presence of Na$_2$CO$_3$ and K$_2$CO$_3$. The influences of the main parameters, including temperature, pressure, feedstock concentration, and catalyst addition, on the gasification process were discussed. Experiment results show that temperature is the key factor and pressure has a minor effect on petrochemical wastewater gasification. Higher temperature and pressure favors petrochemical wastewater gasification. Gasification performance of petrochemical wastewater decreases with increasing concentration. Gasification efficiency increases and molar fraction of CO decreases with Na$_2$CO$_3$ and K$_2$CO$_3$ addition. It is implied that the supercritical water fluidization bed system is effective for hydrogen production by biomass gasification.

Keywords: petrochemical wastewater, supercritical water gasification, fluidization bed, hydrogen

Introduction

A petrochemical refinery produces large amounts of wastewater [1] originating from a variety of processes, including desalting, hydrocracking, hydroskimming, and vapour condensates [2]. In consequence, a wide variety of pollutants are present in petrochemical wastewater. Such wastewater is characterized by high chemical and biological oxygen demands (COD and BOD), and contains large amounts of suspended particulate matter, oil and grease, sulphides, ammonia, phenols [3], benzene, toluene, ethylbenzene and xylenes (BTEXs), polycyclic aromatic hydrocarbons (PAHs), and heavy metals [4]. The treatment of petrochemical wastewater is a challenging issue [5].

Supercritical water gasification (SCWG) is a promising technology since it can produce hydrogen by complete gasification of organic matter in water without the drying procedure, which is an energy-intensive process required as a pretreatment of aqueous feedstock in conventional gasifi-

cation processes. Furthermore, supercritical water has an extraordinary ability to suppress char formation during the decomposition of organic compounds [6]. Char is known to be a refractory byproduct formed in a significant amount during steam gasification of biomass at atmosphere [7], or hydrothermal treatments of glucose [8] and cellulose [9] in hot liquid water at temperatures up to 350ºC (subcritical water conditions) unless appropriate catalysts are used. These impressive abilities of supercritical water to treat organic materials are based on its unique thermo physical properties [10, 11]. Under SCWG conditions, water is not only a solvent, but also an active reactant contributing to gasification chemistry [12-19].

In the last three decades, SCWG technology has rapidly developed, and domestic and foreign scholars have done a lot of theoretical and experimental studies [20-24]. However, when design and operating conditions are unreasonable, the tube is flowed, the transfer is not coupled with the reaction conditions, resulting in incomplete reaction, so a tubular reactor is prone to clog and slag in the wall, thereby resulting in failure of continuous gasification.

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This paper intends to solve the problem of reactor slagging blocked by supercritical water fluidized bed gasification system. In the newly developed system, gasification characteristics of glycerol were studied. Gasification results affected by the process parameter supercritical water fluidized bed system were gained. Long and stable gasification of high concentration feedstock was achieved. This will provide a useful basis of experimental data for industrialization of a supercritical water gasification technology.

Experiments

The experiments were carried out on a supercritical water fluidized-bed reactor. In this reacting system, the feedstock was fed into the reactor and mixed with the preheated water when the temperature in the reactor was heated to the set point. This can realize fast heating of the feedstock to suppress the side reactions that occurred at the lower temperature, which is unfavorable for the gasification process. A feeding system constructed of two feeders can realize the switching of the feedstock in the two separated feeders smoothly without changing the temperature and pressure in the reactor. The inside diameters of the fluidization part and suspension part of the fluidized-bed reactor are 40 and 50 mm, respectively. The whole length of the fluidized-bed reactor is 940 mm. The temperature mentioned in this paper refers to the fluid temperature in the reactor detected by K-type thermocouples inserted in the center of the reactor. Firstly, 120 mL petrochemical wastewater and 1.0 g catalyst is added to the reactor for these experiments. After gasification reaction, the reactor is cooled down. The product stream was then separated into liquid and vapor phases. The liquid products were collected in a graduated cylinder. Gaseous samples were collected with sample tubes.

The gas yield was measured by a wet-type flow meter. The composition of the gas product was analyzed by gas chromatography (Perkinelmer Clarus 680) with a thermal conductivity detector (TCD). High-purity helium is used as the carrier gas (purity >99.999%). A carbon molecular sieve
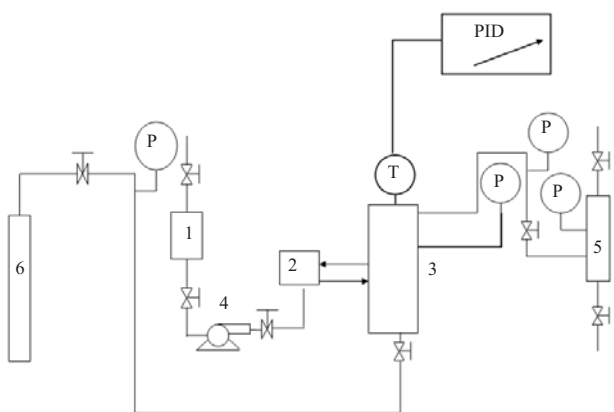

Fig. 1. Schematic diagram of the experimental setup
1. Oxidant container 2. Heater 3. Fluidized bed 4. High-pressure pump 5. Gas-liquid separator 6. Nitrogen cylinder.

a)

Gas yield

b)

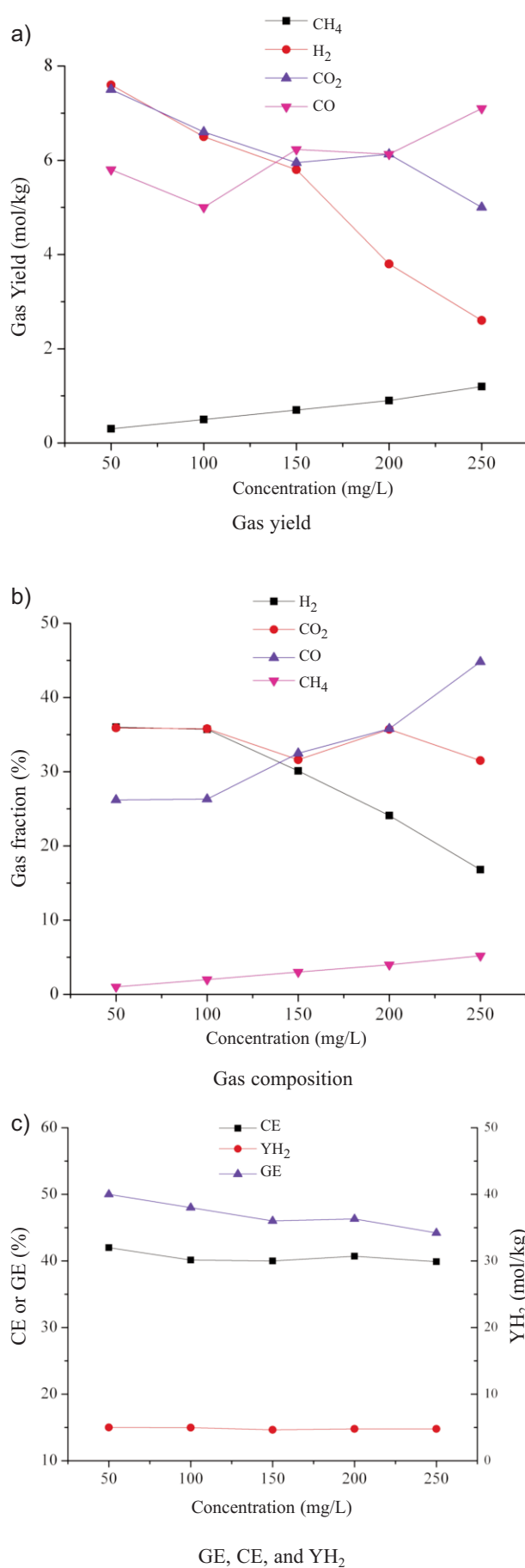Gas composition

c)

GE, CE, and YH_2

Fig. 2. Effect of feedstock concentration on SCWG of petrochemical wastewater.

column (TDX-01) purchased from Zhejiang Wanxin Analytic Instrument Co. in China was used, operating at 75ºC for 6 min, heating at 55ºC/min ramp to 145ºC and holding for 15 min.

$$CE = \frac{\text{the mass of carbon in gaseous product}}{\text{the mass of carbon in glycerol(ad)}} \times 100\ ,\% \quad (1)$$

$$GE = \frac{\text{the mass of gaseous product}}{\text{the mass of carbon in glycerol(ad)}} \times 100\ ,\% \quad (2)$$

$$YH_2 = \frac{\text{the molar number of produced hydrogen}}{\text{the mass of glycerol(ad)}} \times 100\ , \text{mol/kg} \quad (3)$$

Results and Discussion

Effect of Feedstock Concentration on SCWG of Petrochemical Wastewater

Petrochemical wastewater was gasified without catalyst addition at 610ºC and 25 MPa with feedstock flow 30 mL/min, preheat water flow 130 mL/min in the reactor for a long reaction time. It can be seen that hydrogen production decreased from 7.58 to 2.48 mol/kg when feedstock concentration decreased from 250 mg/L to 50 mg/L (Fig. 2). But CO and CH_4 production increased. CE, GE, and YH_2 decreased with feedstock concentration increasing. H_2 fraction decreased from 35.95% to 16.68% and CO fraction increased from 26.3% to 44.9% with feedstock concentration decreasing. But CH_2 fraction increased. It can be seen from Fig. 2 that the maximum concentration of petrochemical wastewater gasification reached 250 mg/L. Although in this case the YH_2 decreased more than relatively low concentration. But gasification of feedstock in supercritical fluid bed system is still continuous and stable; the reactor was found without clogging.

Effect of Temperature on SCWG of Petrochemical Wastewater

Fig. 3 presents results of petrochemical wastewater gasification determined by temperature at 25 MPa with feedstock flow 30 mL/min and preheat water flow 130 mL/min. It can be seen that CE, GE, and YH_2 significantly increased with temperature, increasing from 510 to 610ºC. Hydrogen production increased from 2.02 to 6.91 mol/kg. CO, CH_4, and CO_2 production increased with temperature increasing from 510 to 610ºC. H_2 fraction in gas product increased with temperature increasing and CO fraction in gas product decreased. CH_4 fraction is 2.01% to 3.03% and it showed a rising trend with temperature increasing. Temperature is one of the most critical factors affecting SCWG of glycerol. High temperatures accelerate the gasification reaction rate, and elevated temperatures favor the free radical reaction (e.g., ther-

mal decomposition reaction). It inhibits the ionic reactions (e.g., hydrolysis reaction) [25], resulting in gas production increase. The results also showed that the CO_2 production in gas product is high (25.1%-35.04%) without catalyst.
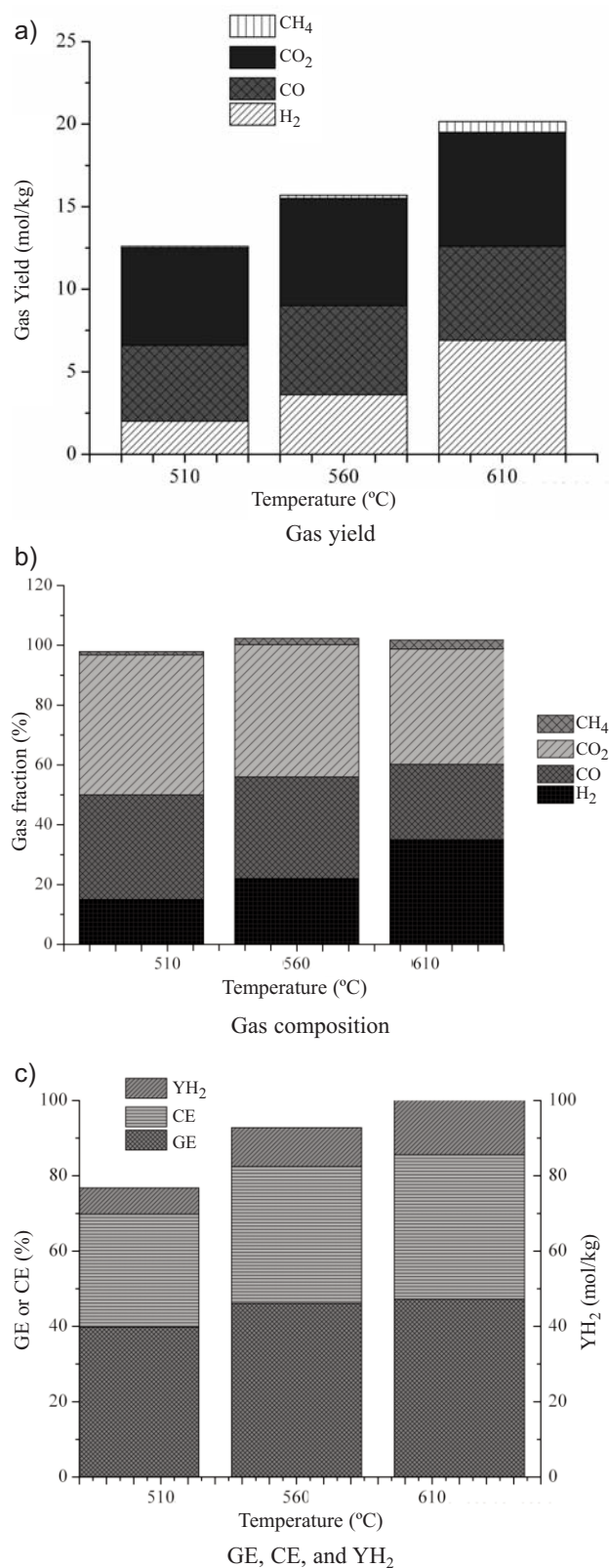

Gas yield

Gas composition

GE, CE, and YH_2

Fig. 3. Effect of temperature on petrochemical wastewater gasification.

Effect of Pressure on SCWG of Petrochemical Wastewater

Fig. 4 presents results of petrochemical wastewater gasification determined by pressure at 610ºC with feedstock flow 30 mL/min and preheat water flow 130 mL /min. It can be seen that the effect of pressure is much less than temper-
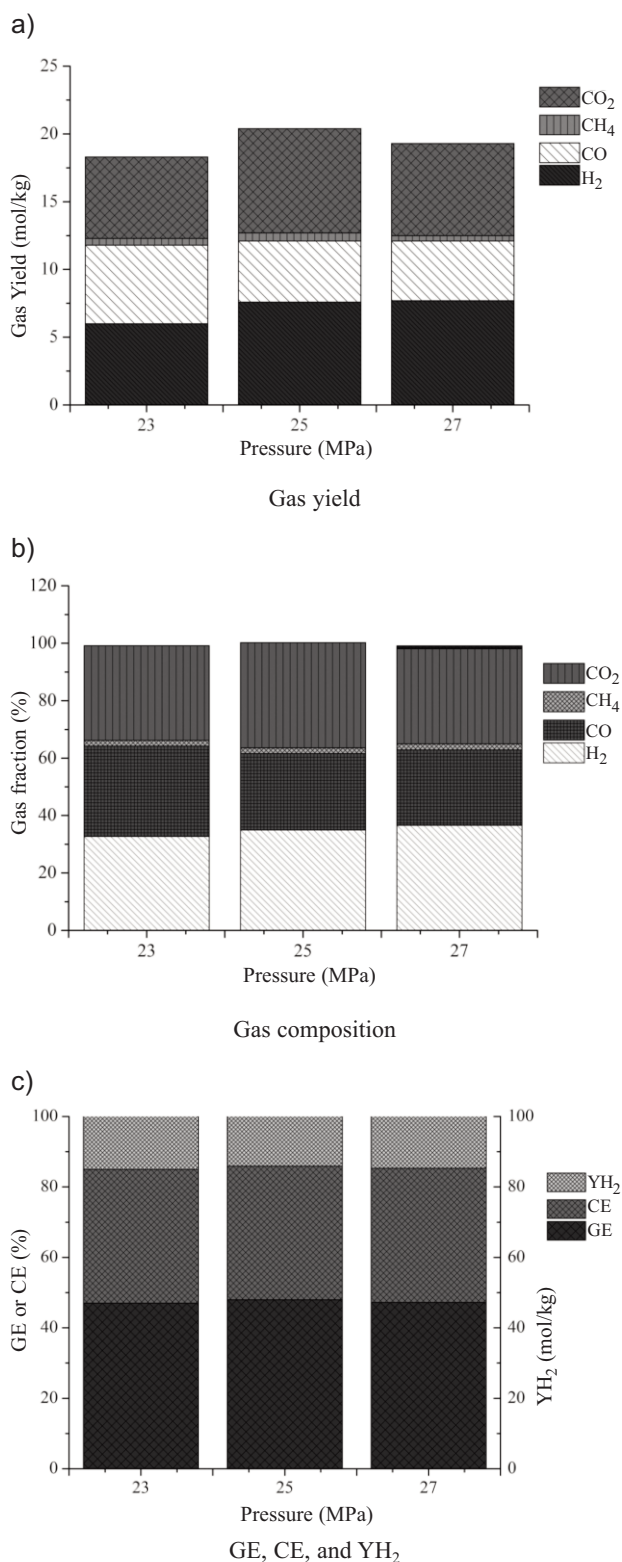
a)

Gas yield

b)

Gas composition

c)

GE, CE, and YH$_2$

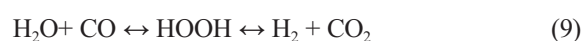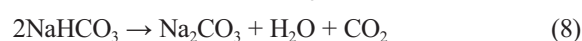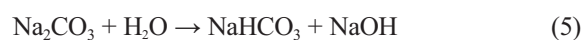Fig. 4. Effects of pressure on petrochemical wastewater gasification.

ature. With increasing pressure, GE and CE did not change significantly and YH$_2$ increased to a certain degree. H$_2$ production presented an increasing trend, while CO production decreased. H$_2$ fraction increased from 32.72% to 36.61% and CO fraction decreased from 31.51% to 26.32% with increasing pressure from 23 MPa to 27 MPa. Increasing pressure is in favor of hydrogen production. Increasing pressure raised "cage" effect of water as a sreaction solvent, which facilitates the reaction between the water molecules and the solvent, such as water gas shift reaction:

$$CO + H_2O = CO_2 + H_2 \qquad (4)$$
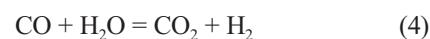
At the same time, increasing pressure favored the free radical reaction and it is conducive to the ionic reaction, which leads to the positive and negative effects of various factors on the impact of gasification canceled for each other. Thus it is shown that pressure has little effect on the overall effect of gasification. But below the critical pressure, special physical and chemical properties in favor of a chemical reaction for the water will disappear, and gasification effect will be significantly decreased compared with supercritical gasification. Experimental results showed that the pressure at about 25 MPa is more appropriate.

Effect of Catalysts on SCWG of Petrochemical Wastewater

Fig. 5 presents results of petrochemical wastewater gasification determined by catalysts at 610ºC with feedstock flow 30 mL/min and preheat water flow 130 mL/min. It can be seen that CE, GE, and YH$_2$ significantly increased with Na$_2$CO$_3$ and K$_2$CO$_3$ additions. H$_2$ production increased by 25.13% and 16.15% more than without Na$_2$CO$_3$ and K$_2$CO$_3$ additions, respectively. CO production decreased after the catalysts addition. CO fraction in gas product is highest, which reached 25.45%. When Na$_2$CO$_3$ is added, CO fraction in gas product declined to 10.52%. But H$_2$ fraction in gas product increased from 35.03% to 38.1%. When K$_2$CO$_3$ is added, CO fraction in gas product declined to 16.1%. But H$_2$ fraction in gas product increased to 39.02%. The effect of K$_2$CO$_3$ on the gas composition is relatively large, and it has little influence on GE and CE. Na$_2$CO$_3$ addition not only can improve H$_2$ fraction in the gaseous products, but also GE and CE. Na$_2$CO$_3$ mainly played a strong catalytic role in water gas shift reaction of the gasification process, which increased H$_2$ production and decreased CO production. Sinag et al. [26] showed Na$_2$CO$_3$ catalytic reaction mechanism of water gas shift reaction:

$$Na_2CO_3 + H_2O \rightarrow NaHCO_3 + NaOH \qquad (5)$$

$$NaOH + CO \rightarrow HCOONa \qquad (6)$$

$$HCOONa + H_2O \rightarrow NaHCO_3 + H_2 \qquad (7)$$

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2 \qquad (8)$$

$$H_2O + CO \leftrightarrow HOOH \leftrightarrow H_2 + CO_2 \qquad (9)$$

Conclusions

In this paper, gasification of petrochemical wastewater for hydrogen production in supercritical water was investigated in a fluidization bed system with the presence of Na_2CO_3 and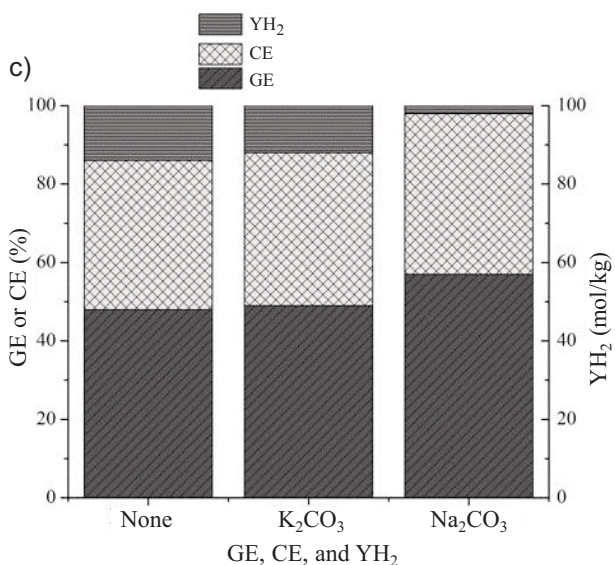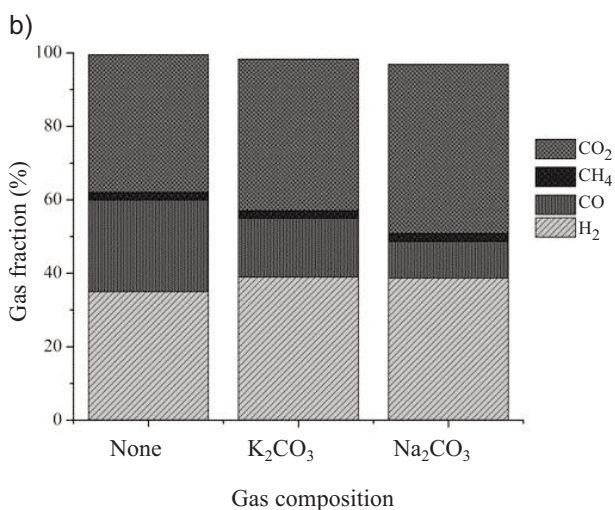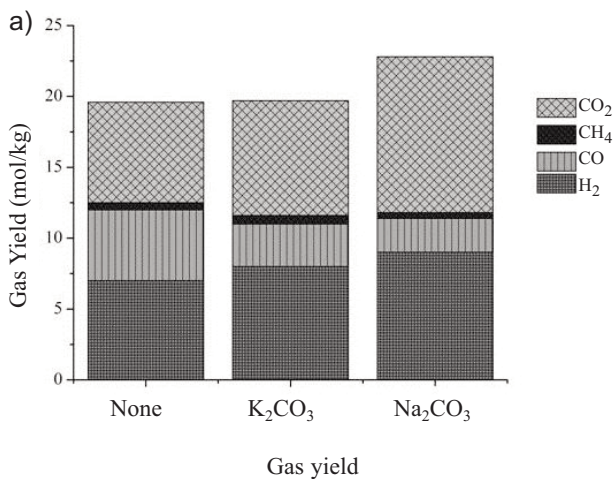 K_2CO_3. The influences of main parameters, including temperature, pressure, feedstock concentration, and catalysts addition on the gasification process were discussed.

The results showed that:

1. Temperature is one of the most critical factors affecting SCWG of petrochemical wastewater. Effect of pressure is much less than temperature. Increasing temperature favors hydrogen production. Increasing pressure is in favor of hydrogen production.

2. Hydrogen production decreased from 7.58 to 2.48 mol/kg, when feedstock concentration decreased from 250 mg/L to 50 mg/L. High concentrations of raw biomass gasification is more difficult.

3. Na_2CO_3 addition not only can improve H_2 fraction in the gaseous products, but also GE and CE. The effect of K_2CO_3 on gas composition is relatively large, and it has little influence on GE and CE.

Fig. 5. Effects of catalyst on petrochemical wastewater gasification.

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