



Supercritical water gasification of microalgae over a two-component catalyst mixture



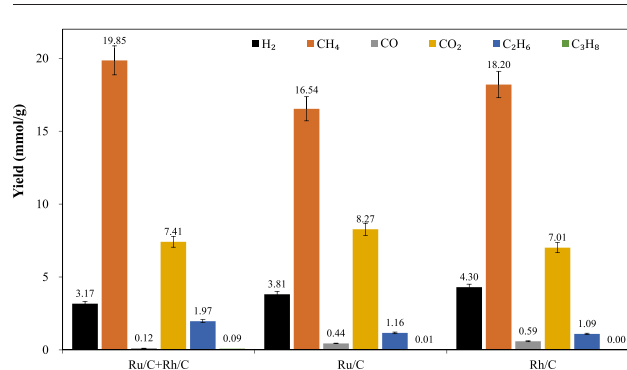
Pei-Gao Duan, Shi-Chang Li, Jia-Li Jiao, Feng Wang, Yu-Ping Xu *

College of Chemistry and Chemical Engineering, Department of Energy Chemical Engineering, Henan Polytechnic University, Jiaozuo, Henan 454003, PR China

HIGHLIGHTS

- Mixture of Ru/C-Rh/C achieved higher gasification efficiency than their separate alone.
- The roles of the catalyst mixture were weakened with increasing temperature.
- HGE was much higher than CGE due to the transfer of H atoms from H₂O to the gas.
- The nitrogen-containing compounds are potential poisons to the catalyst mixture.
- CH₄ made up half of the mole fraction of the gaseous products.

GRAPHICAL ABSTRACT



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ABSTRACT

Supercritical water gasification (SCWG) of the microalga *Chlorella pyrenoidosa* was examined with a catalyst mixture of Ru/C and Rh/C in a mass ratio of 1:1. The influences of temperature (380–600 °C), water density (0–0.197 g/cm³), and catalyst loading (0–20 wt%) on the yields and composition of the gaseous products and the gasification efficiency were examined. The temperature and water density significantly affected the SCWG of the microalgae. The hydrogen gasification efficiency was more dependent on the temperature, while the carbon gasification efficiency was more dependent on the water density. The gaseous products mainly consisted of CH₄, H₂, CO, and CO₂, with smaller amounts of C₂–C₃ hydrocarbons. CH₄ made up half of the mole fraction of the gaseous products under most reaction conditions. A synergistic effect between Ru/C and Rh/C existed during the SCWG of the microalgae, and this effect favored the production of CH₄. The role of the catalyst mixture became indistinct at higher temperatures. Hydrogen atoms from the water were transferred to the gaseous products during the SCWG, leading to hydrogen gasification efficiencies that exceeded 100%. The main components of the bio-oil were aromatics and nitrogen-containing compounds, and the main aromatics consisted of azulene and anthracene. The nitrogen-containing compounds are potential poisons to the catalyst mixture.

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1. Introduction

Microalgae are emerging as one of the most attractive feedstocks for the production of biofuel, which is a promising and environmentally

friendly alternative to fossil fuels (Mata et al., 2010; Rugini et al., 2017). Microalgae typically contain significant amounts of moisture (i.e., up to 85 wt%) after harvesting. Therefore, aqueous-phase processing (e.g., hydrothermal liquefaction or hydrothermal gasification) of such biomass feedstocks is attractive from an energy consumption perspective because it eliminates the need for a dewatering process (Savage, 2012; Patel et al., 2016). Hydrothermal liquefaction is a

* Corresponding author.

E-mail address: xuyuping@hpu.edu.cn (Y.-P. Xu).

thermal depolymerization process used to convert microalgae to crude-like oil, bio-oil or biocrude under moderate temperatures and high pressures. In contrast, hydrothermal gasification, also known as supercritical water gasification (SCWG), has the potential to produce high-quality gaseous biofuels in high yields under severe temperatures and pressures, especially from very wet biomass feedstocks, such as microalgae. The gaseous products produced from the SCWG of microalgae mainly consist of H₂, CH₄, and CO₂ along with small amounts of CO and C_xH_y (2 ≤ x ≤ 5). Both hydrogen and methane are regarded as clean energy sources and as important components of the future global energy portfolio (Onwudili and Williams, 2013).

Catalysts are often used for the SCWG of microalgae to decrease the reaction temperature and increase the gasification efficiency and selectivity of the targeted products. Noble metals are commonly employed in the SCWG of microalgae, as they can enhance the gasification of tar and char, thereby increasing the gasification efficiency and improving the selectivity for H₂ and CH₄ (Onwudili and Williams, 2013; Cherad et al., 2014; Deniz et al., 2015). Of the noble metals examined, ruthenium (Ru) is one of the most popular catalysts for the SCWG of microalgae (Stucki et al., 2009; Guan et al., 2012a; Guan et al., 2012b; Jiao et al., 2017). The researchers from the authors' group examined the SCWG of the microalga *Chlorella pyrenoidosa* (CP) in the presence of five noble metals supported on activated carbon (Pt/C, Pd/C, Ru/C, Rh/C, and Ir/C) in supercritical water (SCW) at 430 °C for 1 h (Jiao et al., 2017). The results suggested that Ru/C, Pt/C, and Ir/C preferentially catalyzed the water-gas shift and the steam reforming reactions, and Pd/C and Rh/C preferentially catalyzed the methanation reaction, particularly under conditions of high water densities. Ru/C produced the highest H₂ yield of 5.97 mmol/g, and Rh/C produced the highest CH₄ yield of 7.19 mmol/g. Thus, the authors expect that a mixture of these two catalysts will exhibit higher performance with respect to H₂ and CH₄ production than each catalyst alone.

Therefore, the objective of the present work was to screen the activity of a catalyst mixture of Ru/C and Rh/C in the SCWG of microalgae. This is the first study to examine the SCWG in the presence of a two-component catalyst mixture. The two-component catalyst mixture was prepared by mechanically mixing 5 wt% Ru/C with 5 wt% Rh/C in a mass ratio of 1:1. Using the Ru/C and Rh/C mixture in the SCWG of microalgae, the effects of the reaction temperature (380–600 °C), water density (0–0.197 g/cm³), and catalyst loading (0–20 wt%) on the compositions and the yields of gaseous products and the carbon and hydrogen gasification efficiencies were examined.

2. Experimental

2.1. Materials

Commercial CP was purchased as a dry powder from Shandong Binzhou Tianjian Biotechnology Co., Ltd. (Binzhou, Shandong, North China). The microalga was dried at 110 °C for 12 h to remove residual moisture from the cells prior to use. The proximate and ultimate analyses of the microalga are shown in Table 1. The two noble metal catalysts (Ru/C and Rh/C) used as the SCWG catalysts were prepared by the impregnation method, and they had an average particle size of 25 μm. They were obtained from Zhengzhou Alfa Chem Co., Ltd. (Zhengzhou, Henan, China). The catalysts were directly used without pre-reduction under H₂. The relevant properties of the catalysts are reported in Table 2. Gas standards were purchased from Changzhou Jinghua Industrial Gases Co., Ltd. (Changhong Rd., Wujin, Changzhou, Jiangsu, China).

Table 1
Proximate and ultimate analyses (wt%, dry basis) of *C. pyrenoidosa*.

Algae	C	H	N	O	S	Lipid	Ash	Fixed carbon
CP	51.88	7.51	8.49	27.31	0.62	10.78	4.62	19.92

Table 2
Characteristics of the catalysts.

Catalyst	Metal content (wt%)	BET(m ² /g)	Dispersion (%)
Ru/C	5	966 ± 19	23.2
Rh/C	5	980 ± 20	21.0

A custom-built high-pressure stainless-steel batch reactor with a total internal volume of 127 mL was used for the SCWG experiments. Prior to its use, the reactor was loaded with water and heated at 400 °C for 4 h to reduce the potential effects from the catalytic reactor walls. However, these effects may still have been strong enough to influence the results.

2.2. Procedure

In a typical experiment, 10 g of microalgae, a certain amount of water, and the catalyst mixture (Ru/C:Rh/C = 1:1) were loaded into the reactor. The water density was changed by varying the water loading amount. The water loading was 0, 10, 20, and 25 mL, which corresponds to water densities of 0, 0.079, 0.157, and 0.197 g/cm³ under supercritical water conditions, respectively. The biomass loading used in the present study was much higher than those of previous studies, as we sought to improve the energy efficiency. Residual air was removed from the sealed reactor by pressurizing it with helium for approximately 15 min. The purged reactor was then pressurized to 0.01 MPa with helium, which served as a standard in the quantification of the gas yields. After pressurization, the reactor valve was closed, and the reactor assembly was disconnected from the helium cylinder.

After the reactor was loaded and pressurized with helium, the reaction inside the reactor was initiated by switching on the electrical heater. Once the temperature inside the reactor reached the desired temperature, the reaction time was set to zero. The reaction temperature was maintained within ±5 °C of the desired temperature using a temperature controller. The pressure inside the reactor varied from 22 to 55 MPa depending on the reaction conditions. After a reaction time of 1 h, the reaction was stopped by switching off the electrical heater and immediately quenching the reactor in a cool water bath for approximately 1 h. The reactor was then removed from the cool water bath and left under ambient conditions for 12 h to allow the liquid-gas system to reach equilibrium. Finally, the gaseous products were analyzed with a gas chromatograph (GC).

After analyzing the gas fraction, the reactor was opened to recover the liquid fraction. Approximately 15 mL of dichloromethane was added, after which the reactor was resealed and shaken by hand. The reactor contents were then transferred to a glass separatory funnel. This washing procedure was repeated two more times to ensure that all the reactor contents were recovered and transferred to the separatory funnel. Upon standing, the aqueous and organic phases equilibrated and separated. The organic phase contained a flaky solid residue, which was removed by filtering the solution. The liquid phase was then carefully transferred to a round-bottom flask via a pipette. The dichloromethane solvent was evaporated under vacuum at 35 °C. The material remaining in the flask was the crude bio-oil, and its amount was determined gravimetrically. The bio-oil was redissolved in approximately 10 mL of dichloromethane and stored in a refrigerator while awaiting gas chromatography-mass spectrometry (GC-MS) analysis.

2.3. Analysis

The elemental analysis, including carbon, hydrogen, and oxygen, was performed using a Thermo Fisher Flash 2000 auto-analyzer, based on the principle of "Dumas method" which involves the complete and instantaneous oxidation of the sample by "flash combustion". The combustion products are separated by a chromatographic column and detected by the thermal conductivity detector (TCD), which gives an

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