Subcritical water gasification of beet-based distillery wastewater for hydrogen production

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A B S T R A C T

In the current study, subcritical water gasification of distillery wastewater (DWW) was conducted in a batch reactor at various temperatures (300, 325, 350 and 375 °C) for different reaction times (15, 30 and 45 min) and with three feedstock concentrations (20, 30 and 40 wt%). The gaseous product mainly contained H_2 and CO_2 with less amounts of CH_4 and CO. The results revealed that gasification efficiency and hydrogen selectivity are highly enhanced by temperature increment near critical point of water. H_2 mole fraction in gaseous product reached the enormous value of 48.8% at 375 °C after 45 min residence time with middle point concentration. It was observed that the rate of improvement in gasification efficiency over time was higher at low temperatures compared to that of near critical point. Gradual increase in hydrogen fraction of gas over reaction time was accompanied by a moderate decrease in CO_2 and CO fractions, offering that water–gas shift reaction tends to reach equilibrium at longer reaction time. Biomass loading had no considerable effect on gas composition; however, it had counteractive impacts on gasification characteristics: favoring gas product amount and suppressing gasification efficiency.

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1. Introduction

Hydrogen is a versatile fuel and a strategic clean energy carrier. Hydrogen has the highest energy content (120 MJ/Kg) compared to conventional fuels [1]. The major obstacle in utilization of hydrogen energy is that it's unavailable in molecular form in nature and has to be produced from main sources, namely biomass, water and hydrocarbons like natural gas, naphtha and coal [2,3]. Among these sources, hydrogen production from biomass is recently considered as a potential alternative to meet the energy demand of near future. It has a near zero emission cycle, because carbon dioxide released from the process will be theoretically captured during photosynthesis of plants [4,5]. Independency on finishing fossils, renewable, widespread and inexpensive feedstock and being environmentally benign are other advantages of this route. Political, economic and environmental impacts of biomass-based hydrogen are attractively discussed by Mustafa Balat and Mehmet Balat [6].

Hydrothermal gasification of wet biomass wastes and industrial effluents is a promising solution among various conversion technologies. The term "hydrothermal" refers to water at elevated temperature and pressure, around its critical point (T_c = 374.1 °C, P_c = 22.1 MPa), and covers two regions of sub- and supercritical water [7]. Sub- and supercritical water gasification (SCWG) is a novel process to transform biomass into hydrogen and methane-rich gas, with reduced tar and char formation [8], efficiently for biomass with high moisture content [9].

Applications of SCWG lie in two broad areas, including gas product utilization and aqueous effluent management. Various downstream processes are introduced for SCWG that depend on separation technologies and process intention. Gas product mainly contains H_2, CH_4, CO_2, and CO; with varying contributions depending on feed and operating conditions. High pressure hydrogen and syngas (H_2 + CO) are transmissible to petrochemical complexes with no need to further compression. Hydrogen could be also utilized in mobile and stationary fuel cells after depressurization. A novel process design is proposed by Fiori et al. [10]. Moreover, methane produced in SCWG is an alternative to substitute for in-plant usage of natural gas. Finally, compressed CO_2 obtained in process may be applicable for underground storage, deep-sea sequestration and reuse in chemical processes. Useful reviews on hydrothermal biomass gasification and its prospects are proponed by Kruse [11] and Matsumura et al. [12]. On the other hand, SCWG has the advantage of using wastewater streams as feed and delivering treated effluent with efficiently reduced TOC and COD levels. Depending on feed characteristics and operating conditions,

Nomenclature

AC	Activated carbon
CGE	Carbon gasification efficiency
COD	Chemical oxygen demand
DWW	Distillery wastewater
GE	Gasification efficiency
GP	Gas product
HID	Helium ion detector
HS	Hydrogen selectivity
P_c	Critical pressure
SCW	Supercritical water
SCWG	Supercritical water gasification
T_c	Critical temperature
TGA	Thermogravimetric analysis
TOC	Total organic compounds
WGS	Water–gas sift

aqueous effluent may be admissible to be discharged according to environmental regulations or could be recycled after removing the minerals in desalination unit. Hydrothermal process has been widely investigated as a novel alternative to conventional wastewater treatment routines [13].

Considerable progressive efforts have been made during past two decades to assess the reliability and feasibility of SCWG of various biomass types at different operating conditions. Choosing DWW as a proper feed to SCWG is of great interest, due to its high COD level, high organic solid matters and large volumes produced annually [14]. Since this study has exploited subcritical water to gasify DWW without catalyst, literature review focuses on non-catalytic, subcritical water and industrial waste stream studies.

There are several reports for hydrothermal gasification of industrial effluents, such as polyvinyl alcohol-contaminated wastewater [15], polyethylene glycol-contaminated wastewater [16], tannery waste [17], ethanol production waste [18] olive mill [9,19], domestic [8], and oily [19] wastewaters. A summary of previous studies and comparison to this work is presented in Table 1.
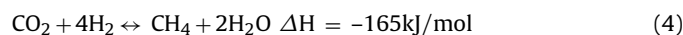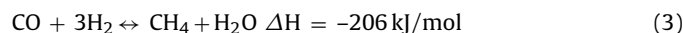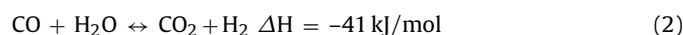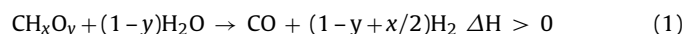
Several studies have been recently performed concerning non-catalytic hydrogen production from crude glycerol [21], sewage sludge [22] and willow [23] in hot compressed water; and from long-chain alkanes [24], carboxylic acids alcohols [25] and pulp/paper-mill sludge [26] in SCW.

Extensive investigations have been also conducted in subcritical water conditions. Gasification of cellulose as a model compound at low temperatures (200–350 °C) was reported in a series of articles by Minowa et al. [27–29]. They carried out the experiments

with and without presence of reduced nickel as catalyst. Azadi et al. conducted near-critical water gasification of glucose using metal [30] and homogeneous organometallic catalysts [31]. More recently, Muangrat et al. examined gasification of food waste components [17], model food waste [32] and food models [33] at 330 °C and 13.5 MPa, using NaOH, H_2O_2 and nickel catalysts. They also discussed about reaction products in liquid phase and proposed a comprehensive decomposition pathway.

In this work, we investigated subcritical water gasification of beet-based DWW in batch reactor system with residence times between 15 and 45 min and temperatures and pressures ranging from 300 to 375 °C and from 89 to 210 bar, respectively. In addition, influence of biomass loading in reaction mixture was studied with 20, 30 and 40 wt% solutions.

Although a comprehensive reaction mechanism has not been determined for hydrothermal gasification of biomass to date, many researchers have adopted reforming, water-gas shift (WGS) and methanation as three main pathways, presented by Eqs. (1)–(3), respectively [3,34,35]. In parallel with CO methanation (Eq. (3)), some researchers have also considered CO_2 methanation (Eq. (4)) as well [19].

$$CH_xO_y + (1-y)H_2O \rightarrow CO + (1-y+x/2)H_2 \; \Delta H > 0 \qquad (1)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \; \Delta H = -41 \, kJ/mol \qquad (2)$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \; \Delta H = -206 \, kJ/mol \qquad (3)$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \; \Delta H = -165 kJ/mol \qquad (4)$$

2. Materials and methods

2.1. Materials

Distillery wastewater (DWW) feedstock used in this work was obtained from a local beet-based ethanol manufacturer and used as received. The wastewater was diluted as needed with deionized water in order to prepare 20, 30 and 40 wt% solutions for experiments.

Elemental analysis (dry base) and thermogravimetric analysis (TGA) were carried out in an external laboratory. The empirical chemical formula of the DWW was found to be $C_{0.2511} H_{0.4265} O_{0.2925} N_{0.0298}$. Detailed characteristics of the received wastewater are listed in Table 2.

2.2. Experimental apparatus and procedure

Subcritical water gasification of DWW experiments were carried out in a stainless steel 316 L batch autoclave, with a volume of 160 mL (including its tubing). The reactor assembly included a

Table 1
Summary of operating conditions in previous studies on hydrothermal gasification of industrial wastes and wastewaters.

Feed type	System	Temperature (°C)	Pressure (Mpa)	Reaction time	Catalyst	Ref.
Polyvinyl alcohol-contaminated wastewater	Continuous	450–600	20–36	20–60 (s)	KOH	Bo et al. [15]
Polyethylene glycol-contaminated wastewater	Continuous	390	24	60–300 (s)	Ni/ZrO₂, Co/ZrO₂, W/ZrO₂	Yan et al. [16]
Real aqueous organic waste	Continuous	600–700	24	Not mentioned	RuNi/-Al₂O₃, RuNi/AC	Zhang et al. [35]
Olive mill wastewater	Continuous	400–600	10–30	30–150 (s)	Non-catalytic	Kipcak et al. [9]
Olive mill wastewater	Continuous	400–600	25	30 (s)	Non-catalytic, with H_2O_2	Kipcak and Akgun [19]
Oily wastewater	Continuous	500–650	25–41	180–220 (s)	KOH	Zhiyong and Xiuyi [20]
Organic waste of coal dewatering	Batch	200–350	20	Not mentioned	Ni/Carbon	Nakagawa et al. [36]
Tannery waste	Batch	500	28–40	60 (min)	Red mud, Trona and Raney Ni	Yanik et al. [37]
Domestic wastewater	Batch	500	25	5–60 (min)	Non-catalytic	Sawai et al. [8]
Ethanol production waste	Batch	400	Not mentioned	15–240 (min)	Ru/G	Shirai et al. [18]
Beet-based distillery wastewater	Batch	300–375	8.9–21	15–45 (min)	Non-catalytic	This work