Journal of the Taiwan Institute of Chemical Engineers 000 (2017) 1–9

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Hydrogen production from olive-pomace by catalytic hydrothermal gasification

Murat Sert*, Dilek Selvi Gökkaya, Nihal Cengiz, Levent Ballice, Mithat Yüksel, Mehmet Sağlam

Department of Chemical Engineering, Ege University, 35100 Bornova, Izmir, Turkey

ARTICLE INFO

Article history:
Received 29 August 2017
Revised 16 November 2017
Accepted 19 November 2017
Available online xxx

Keywords:
Biomass
Olive pomace
Hydrothermal gasification
Hydrogen

ABSTRACT

Hydrogen as a clean energy source has great potential to reducing the dependence on fossil fuels and environmental pollution. For this reason, the production of hydrogen from renewable source will decrease this dependence and pollution. In this study, production of hydrogen from olive pomace was investigated. The experiments were performed at batch autoclave between 300 °C and 600 °C temperatures and a pressure of 200 atm–425 atm range. In addition to these parameters, the effect of catalyst (Trona, K_2CO_3 and KOH) was also investigated. H_2, CO_2, CH_4, CO and small amount of C_2–C_4 hydrocarbons were identified in gaseous products. H_2 formation increased with increasing temperature and decreased with pressure increase. Hydrogen formation has the highest value as 16.80 mol/kg biomass at 600 °C in the presence of KOH catalyst. Besides the effect of KOH, the presence of K_2CO_3 and Trona catalysts also increased the formation of hydrogen. The pressure affected the gasification yield and hydrogen composition in gaseous product.

© 2017 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

1. Introduction

Today, world energy demand is supplied by fossil fuels and almost all motor vehicles are powered by gasoline, diesel and natural gas [1]. Due to environmental concerns, especially greenhouse gases, economical reasons and also depletion of the fossil fuels or non-renewable energy resources, researches have focused on production of valuable chemicals and energy from clean and renewable sources like biomass [2]. So, replacing the intermediates or the products derived from petroleum with renewable sources is indispensable. The most promising alternative for valuable chemicals and for oil today is biomass. As an inexhaustible energy resource, biomass is abundant and can be grown almost each part of the world. The most important feature of biomass is to be converted to valuable chemicals such as hydrogen, methane, carbon dioxide and energy. The most outstanding title alternative to petroleum derived products is hydrogen which is clean energy source. For more than three decades, hydrogen energy is one of the most researched topics [3–6]. It can be used for transportation as well as power stations [7]. Hydrogen is mainly produced by thermochemical methods; such as steam reforming from fossil fuels due to economic reasons when compared to biomass energy [4,8,9]. But this way of hydrogen production give rise to increase in carbon dioxide emission in the atmosphere. In contrast to conventional methods like pyrolysis, reforming or thermal gasification, hydrogen production from biomass by sub or supercritical water is one of the remarkable research fields. Especially, high water content biomass can be converted to combustible gases like hydrogen, methane or carbon monoxide by supercritical water gasification (SCWG) without drying procedure. Conversely, water as a reaction medium, behaves as reactant during SCWG process [5,10,11]. The main purpose of SCWG which is accepted as environmental friendly process is to obtain hydrogen from wet biomass at lower temperatures when compared to classical gasification techniques. Supercritical water has unique characteristics and ability to suppress char formation during the decomposition of organic compounds. At temperatures of near-critical and supercritical point (347.8 °C and 22.1 MPa), water dissociated to form both the H_3O^+ and the OH^- ions. Because of acidic and alkaline character of supercritical water, it behaves as a catalytic precursor for acidic or basic reactions [10,12].

The olive oil industry is mainly located in Mediterranean countries such as Spain, Turkey, Italy or Tunisia. The olive oil extraction produces large amount of waste which pollutes soil and water. So, olive mill wastes represent an important environmental problem in Mediterranean areas where they are generated in huge quantities in short periods of time. Turkey is one of the Mediterranean countries and produces approximately 700 kt of olive and 120 kt of olive pomace in a year [13,14]. Olive pomace has high phenol

* Corresponding author.
E-mail address: murat.sert@ege.edu.tr (M. Sert).

https://doi.org/10.1016/j.jtice.2017.11.026
1876-1070/© 2017 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

Please cite this article as: M. Sert et al., Hydrogen production from olive-pomace by catalytic hydrothermal gasification, Journal of the Taiwan Institute of Chemical Engineers (2017), https://doi.org/10.1016/j.jtice.2017.11.026

content, lipid and organic acid concentrations turn them into phytotoxic materials, but these wastes also contain valuable resources such as a large proportion of organic matter and a wide range of nutrients that could be recycled. The estimated quantities of wastes derived from the olive oil industry in the EU accounts for 6.8 million tons/year with a promising energy content of around 18 MJ/kg [15].

Olive pomace conversion can be performed by thermochemical or biochemical transformations. Thermochemical processes consist of combustion, gasification, pyrolysis and also hydrothermal processes [16]. Olive pomace is the by-product of olive oil centrifugation process and it consists of about 65% of water due to addition of water during extraction process [17]. So, gasification, pyrolysis and combustion processes require the drying process, high moisture content reduces the calorific value and increases the storages cost. Due to requirement of drying and also high energy consumption, ash production, hydrothermal conversion has attracted considerable attention.

Some studies deal with the hydrothermal gasification of biomass samples having high moisture content (70–95%) [18–20]. So, hydrothermal gasification technique using supercritical water is a promising way for utilization of biomass having high moisture and production of hydrogen as main product.

There are many studies concerning the effect of catalyst type on gasification yield for hydrothermal gasification. Yanik et al. [6] concluded that K_2CO_3, torna, red mud and Raney-Ni are effective catalyst of supercritical water extraction of cotton stalk and corncob. Homogeneous offer some superiority in hydrothermal gasification such as elimination of mass transfer limitation and the improvement of water–gas shift reaction. Jarana et al. [21] studied the catalytic effect of KOH on SCWG of organic waste and they found the acceleration water–gas shift reaction by adding KOH. Besides high catalytic activity and ease of usage catalyst eliminate the deactivation problem due to the adsorption of intermediate products on the catalyst surface.

The behavior of olive pomace gasification and the composition of products still need more research and the parameters affecting the composition of gaseous product should be highlighted. According to literature, there is not any study concerning the hydrothermal gasification of olive pomace which is abundant and important type of biomass in Mediterranean countries.

In this study, hydrothermal gasification of olive pomace using supercritical water was studied to produce gaseous products. For this purpose, olive pomace that was remaining solid after olive oil production was subjected to batch hydrothermal gasification in the absence/presence of catalyst. The reactions were performed at 300, 400, 500 and 600 °C and Trona, K_2CO_3 and KOH were used as catalyst in SCWG study. The effects of temperature, pressure and catalyst on the gasification yield and the composition of gaseous product have been investigated.

2. Experimental study

2.1. Samples

In this study, olive pomace samples were dried then sieved to obtain a $<$ 0.1 mm fraction for the experiments. The proximate, ultimate, and component analysis results are given in Table 1. The solutions of K_2CO_3, Trona and KOH (99.0% purity, Sigma–Aldrich) were prepared in a concentration of 10 wt% and as used as the catalyst.

C, H, N, S contents were measured by elemental analyzer. To determine the content of inorganic elements, olive pomace sample was converted to ash at 550 °C, then the dissolution process was applied with HCl. After these steps, elements such as Ca, Mg, Al, Fe and others were determined with ICP-OES analyzer. Cellulose, lignin and hemicellulose contents were measured based on VAN SOEST method in our laboratory.

Table 1
Proximate and ultimate analysis of olive pomace.

Proximate analysis (%)	
Moisture	10.00
Ash	3.90
Protein	10.50
Composition (dry ash free, %)	
Extractives	18.40
Cellulose	32.70
Hemicellulose	16.20
Lignin	30.60
Ultimate analysis (dried, %)	
C	51.28
H	5.86
N	0.95
S	0.11
K	1.28
Ca	0.47
Mg	0.07
Al	0.05
Fe	0.05
Cr	0.01
Cu	0.01
Mn	0.04
Zn	0.02

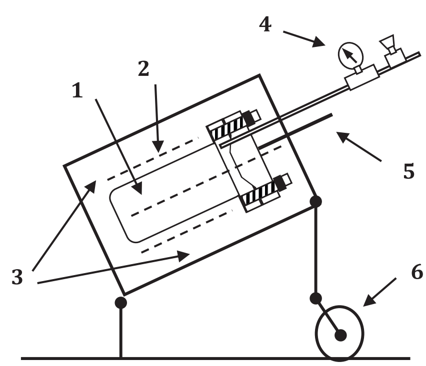

Fig. 1. Schematic presentation of batch autoclave.

2.2. Experimental procedure

The hydrothermal gasification experiments were carried out in a SS 316, batch autoclave, having an internal volume of 100 cm^3. The assembly included a rotating shaker with an eccentric and a temperature controller with a PID controller. The diagram of the reactor was given in Fig. 1.

The hydrothermal gasification system contains gas discharging pipes, furnace, temperature and pressure control units, autoclave agitation system, gas collection and measurement units with high pressure valves. The cover of reactor was closed after adding the feedstock solution into the steel reactor. 15 ml of feed solution was also injected to the reactor for the experiments that were carried out at temperatures of 300 °C, 400 °C, 500 °C, 600 °C. The amount of feed was decreased for 600 °C to overcome potential high-pressure risks. The valves were closed after purging air by inert gas N_2. The system was heated up to reaction temperature rapidly and operation was continued during reaction time of 1 h at the desired reaction temperature. The operating parameters are: 400 °C, 500 °C and 600 °C for temperature, 205, 275, 345 and 425 atm for pressure, 10 wt% K_2CO_3, KOH and Trona solutions as catalyst.

Download English Version:

https://daneshyari.com/en/article/7104882

Download Persian Version:

https://daneshyari.com/article/7104882

Daneshyari.com