Energy 56 (2013) 193–206

Contents lists available at SciVerse ScienceDirect

Energy

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

Experimental study of the supercritical water reforming of glycerol without the addition of a catalyst

F.J. Gutiérrez Ortiz*, A. Serrera, S. Galera, P. Ollero

Departamento de Ingeniería Química y Ambiental, Universidad de Sevilla, Camino de los Descubrimientos, s/n, 41092 Sevilla, Spain

ARTICLE INFO

Article history:
Received 10 February 2013
Received in revised form
11 April 2013
Accepted 19 April 2013
Available online 31 May 2013

Keywords:
Reforming
Supercritical water
Glycerol
Hydrogen
Reaction pathway
Catalyst

ABSTRACT

Hydrogen production from the supercritical water reforming of glycerol was studied in a tubular reactor without adding a catalyst. Experiments were carried out at a pressure of 240 bar, temperatures of 750–850 °C, and glycerol feed concentrations of 5–30 wt.%. Likewise, the residence time was changed from 12 to 160 s, by handling the feed flow-rate. The dry gas is mainly consisted of H_2, CO_2, CO, CH_4. In addition, small concentrations of glycerol were measured in the liquid phase analysis, but barely traces of others like glycolaldehyde, glyceraldehyde, dihydroxyacetone and lactic acid were detected. Thus, two probable reaction pathways are discussed, which makes it possible to explain the experimental results by using a method applicable to other similar processes. The results showed that the glycerol conversion was almost complete, except at the highest glycerol feed concentration, in which the conversion was of 88%. Hydrogen yields from 2 to 4 mol H_2/mol glycerol were obtained at high and low glycerol feed concentrations, respectively, when operating at high temperature and residence time. Besides, it was verified the catalytic effect of the reactor material (Inconel 625) from the trend of the gas product yields with time and the structured carbon nanotubes encountered. The catalytic activity of the reactor material was decreasing to reach a steady state after a few tens of operating hours. This study illustrates that the reforming of glycerol using supercritical water without added catalyst is feasible to achieve a high-yield hydrogen production, and it encourages to continue the research line, to obtain a process economically interesting.

1. Introduction

A significant amount of glycerol is produced as a by-product during biodiesel production by transesterification of vegetable oils. By-product glycerol comprises a mixture of several other constituents, such as methanol, water, inorganic salts, free fatty acids, unreacted mono-, di-, and triglycerides, and methyl esters. The rising surplus of biodiesel-derived crude glycerol from the transesterification process requires a further processing, but conventional options for crude glycerol consist of refining it to a higher purity that is costly, especially for medium and small sized plants. Therefore, the development of novel processes for glycerol valorization is essential.

Among the possible routes, glycerol conversion into hydrogen as an energy carrier is one of the most attractive. Indeed, different reforming processes along this line have been studied and still go on, such as steam reforming [1–3], autothermal reforming [4–6] and aqueous phase reforming [7–9].

Reforming products include hydrogen and carbon monoxide in addition to carbon dioxide and methane. A catalyst is normally used to accelerate the reactions in the reforming process. Ni, Co, Ni/Cu, and noble metal (Pd, Pt, Rh) based catalysts all favor hydrogen production, with Ni being the most commonly used [10].

The use of supercritical water makes it possible to perform another type of reforming process. Supercritical water (SCW) has relevant thermophysical properties [11–14], such as a very low dielectric constant that reduces the number of hydrogen bonds and weakens their strength. Consequently, SCW has a high capability to solubilize gaseous organic molecules and allows a high diffusivity of the dissolved molecules. Furthermore, since SCW is extremely reactive, it may be possible to perform the process without adding a catalyst, although this must be experimentally verified. This is one of the main aims of this study.

Many of the above-mentioned studies are centered on the development and characterization of catalysts, because all of the mentioned reforming processes require to use a catalyst for a high and suitable glycerol conversion. However, SCW acts not only as a

* Corresponding author. Tel.: +34 95 448 72 68/60.
E-mail addresses: frajagutor@etsi.us.es, frajagutor@us.es (F.J. Gutiérrez Ortiz).

0360-5442/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.energy.2013.04.046

reactive but also as a catalyst in the reforming reaction, due to its high ion product, which allows SCW to act like an acid or base catalyst in the reactions. In fact, many organic chemicals that do not react in water without the presence of a strong acid or base catalyst may readily react under the hydrothermal condition of SCW. In recent years, extensive research has been carried out on a laboratory scale to assess various wet biomass gasification in SCW conditions, and now the technology is starting to show its economic competitiveness with other hydrogen production methods [15].

Some previous works have been focused on thermodynamic aspects of the process of glycerol reforming using supercritical water [16–18]. Likewise, some studies about biomass gasification by SCW without catalyst [19–23] and with catalyst [24–28] have been published. These studies state that catalyst-free supercritical water gasification usually results in a higher CO concentration due to an intrinsic low rate of the water–gas shift reaction. In general, almost all of them conclude that the use of catalysts significantly improves the conversion to gas and even that the process only works well in the presence of a catalyst.

Only some of the above-cited papers point out that a very high temperature is required to achieve acceptable conversions. A typical range of temperature for high temperature supercritical water gasification is between 550 and 700 °C, and even above. Indeed, due to the high reaction rates, complete gasification is achievable in the absence of catalysts, but all of the studies performed without catalyst were focused to very small biomass feed concentrations, generally lower than 10 wt.%.

Many efforts have been addressed to reduce the reaction temperature and, hence, the energy required to perform the process. The use of a catalyst makes it possible to get this aim because it lessens the activation energy of the reforming reaction. However, the activity of the catalysts gradually diminishes due to the coke deposition, which can be reduced by using low biomass feed concentrations. Thus, almost all of the previous studies deal with small feed concentrations, but values of 5–10 wt.% are too low to be of technical interest, as much as the energy sustainability and the economics of the process are concerned. Therefore, it is very important to test higher glycerol concentrations.

We have focused the operation toward high reforming temperatures and glycerol feed concentrations trying to make the process economically interesting. Previously, we have verified that a high yield of hydrogen can be obtained at temperatures higher than 800 °C and high glycerol concentrations [29]. However, the high temperatures involve severe heating requirements, which emphasize the importance of heat integration, i.e., the recovering of the heat flow from the hot streams to the incoming cold streams. We have also developed a heat-integrated process focused on using a high temperature and a glycerol feed concentration that assures the energy self-sufficiency, without adding a catalyst [30,31]. For this, a relatively high glycerol concentration is needed (22–27 wt.%, at 800 °C and 240 atm). Our previous papers were based on rigorous simulation, assuming equilibrium conversion. In this paper, a reforming process of glycerol using SCW was carried out in an empty tubular reactor, i.e., in the absence of a catalyst, by using glycerol feed concentrations of up to 30 wt.%. The observed effect of operating variables (temperature, residence time and glycerol feed concentration) on the process performance and approach to chemical equilibrium is discussed, using two probable reaction pathways.

2. Experimental section

2.1. Materials

The experiments were carried out with deionized water and pure glycerol (Panreac PRS-Codex 100% ± 1% purity). The deionized water was obtained by a high-performance water treatment process that combines an activated carbon and an ion-exchange resin (polymer). This unit makes it possible to reduce the water conductivity below 0.5 μS/cm.

2.2. Bench-scale plant

A glycerol–water mixture is first pumped to a desired pressure and then heated to the operating temperature inside an electrical furnace, in which the supercritical water reforming reactor is. The product gas with the excess of supercritical water leaving the reformer is cooled down to 40 °C and expanded in a back-pressure valve. The condensed water is separated from the gas stream by means of a gas–liquid separator. The gas and the liquid streams are then sampled and analyzed.

A basic diagram of the pilot plant is illustrated in Fig. 1, showing the main components and including the control and instrumentation. The design is flexible, and it is possible to perform, e.g., autothermal reforming using SCW, for future tests. Fig. 2 depicts a general picture of the pilot plant that includes its main components. On the front, the electrical furnace is depicted and in the backward, it can be seen the cooler, the first back-pressure control valve, pressure transmitters, liquid-gas knock-out drum, and gas mass flow meter. Table 1 shows the main characteristics of the plant units and devices.

The pump is a high-performance liquid chromatography (HPLC) of double piston (LabAlliance). The heating is performed by means of an electrical tubular furnace (Termolab), with six independent heating zones of 333 mm length each one, individually controlled and monitored (Eurotherm) by using six thermocouples (type K) and solid-state relays, to achieve isothermal conditions.

The reactor material is Inconel 625 (Autoclave Engineers), which is a nickel–chromium alloy that contains iron, molybdenum and niobium, as the other main components, and has high mechanical strength (high tensile, creep, and rupture strength) at high temperatures. The length of the reactor is 2.6 m, its outer diameter is 9/16″ (14.29 mm), and the inner diameter is 7.92 mm. Only 2.0 m are inside the furnace, so 0.3 m extend beyond each end of the furnace. The fittings and other tubing (nipples, adapters and couplings) were provided by Autoclave Engineers, including the connections between Inconel 625 and 316-SS parts of the plant, using coned-and-threaded connections.

The downstream cooler (Sentry) used is a compact double helical coil design with allows to minimize cooling water needs, and is made of 316 stainless steel. At the cooler outlet, an integrated porous element was located to separate particles larger than 1 μm.

The first pressure control-loop consists of a pressure transmitter (Bronkhorst), which is equipped with a diaphragm type piezoresistive pressure sensor, and a back-pressure valve (Badger). In a similar way, the second pressure control-loop was designed and assembled. In both loops, the pressure transmitter is furnished as integral part of the pressure controller.

The liquid level in the gas–liquid knock-out drum was controlled by two electronic vibrating level switches. The gas leaving the knock-out drum goes through a coalescing filter to capture the water aerosol that may be present in the gas and to drain it by gravity into the filter bowl. Downstream from the filter, the mass flow-rate of the gas is measured by a Coriolis flow meter (Bronkhorst), which gives optimum accuracy and response time.

The gas is then routed to a gas chromatograph (GC) and the liquid is sampled several times during the test and analyzed by an HPLC to detect the components present in the liquid phase and its concentration. Both the gas and liquid chromatographs will be described later.