



Modelling the composition of the gas obtained by steam reforming of glycerine



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ARTICLE INFO

Article history:

Received 5 January 2017
Received in revised form 7 March 2017
Accepted 23 March 2017
Available online 19 May 2017

Keywords:

Steam reforming
Glycerine
Hydrogen
Surface response methods

ABSTRACT

In this work, we studied the influence of the variables temperature (T), water/glycerine ratio (R), and flow rate of the feeding water/glycerine solution (\dot{V}_{W+G}) on the non-catalysed steam reforming of glycerine. The experiments were carried out on a bench-scale equipment and the margins of the processing variables R, T, and \dot{V}_{W+G} were 0.7–3.3 wt wt⁻¹, 682–1018 °C, and 8.5–35.5 mL min⁻¹, respectively. The implementation of a Design of Experiment–Response Surface Methodology approach (DoE/RSM) allowed us to analyse the importance of each variable, as well as their interactions, in both the composition and the energetic features of the dry gas stream obtained. The temperature and the water/glycerine ratio played the principal role in determining the concentration of the main components (H₂, CO, CH₄, and CO₂) and the low heating value of the resulting dry gas stream. The effect of both variables was likely related with their influence on the thermodynamic equilibrium of the different reactions taking place (reforming, water-gas shift, and methanation reactions). Two variables were defined in order to evaluate the efficiency of the glycerine gasification: the steam-reforming efficiency (SRE) and the carbon gasification efficiency (CGE). On the other hand, the rate at which the energy can be supplied by the installation (LHV) was strongly affected by all the three processing variables and was mainly related with the volumetric flow rate of the dry gas stream, while the LHV played a secondary role. The predicted ranges of H₂, LHV, and LHV were 25.8–60.7%, 9.03–14.40 MJ N m⁻³, and 0.47–5.26 kW, respectively. In all cases, high interactions between the processing variables were detected, putting in evidence the usefulness of the DoE/RSM approach.

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1. Introduction

Fossil fuels are the main resources used to meet the current energy demand. However, in recent years, increasing awareness of global warming and the unsuitability of current energy schemes have prompted studies on the efficient use of renewable resources. In this context, techniques adding value to biomass and improvement of the processes involved in its exploitation have been investigated in order to increase the value of various wastes, and the search for novel, economical, environmentally benign methodological approaches.

During the last few years, scientists have focused their attention on hydrogen production technologies, because of its importance in fuel cells and high energy content gases (syngas) and its promising use as a carbon free energy carrier.

Thus, hydrogen is an attractive resource of energy since it is one of the cleanest, lightest, and most efficient fuels [1]. The use of

hydrogen as fuel for transport and for electricity production with fuel cells systems has become an attractive option of sustainable energy systems. However, it is an energetic vector, which means that it is not naturally found and, like electricity, must be produced from primary energy sources. Nowadays, most of the H₂ yield is being produced from steam reforming of fossil fuels [2,3], which are still the most abundant and economically feasible raw materials. An important drawback of this procedure is the concomitant production of CO₂, a greenhouse gas that is the main contributor to global warming. As a result, the interest in finding a clean method for hydrogen production has increased in the last few years. In this sense, the steam reforming of biomass may play an important role because of the neutral carbon balance of this material.

In recent years, the demand and production of biodiesel has increased tremendously. During the transesterification reactions of vegetable oils and fats for biodiesel production, around 10 wt % of the raw material is transformed into glycerine [4]. This process involves the alcohol (glycerol) displacement of the triglyceride structure, by means of the incorporation of another short alcohol

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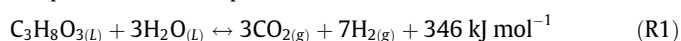
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chain (methanol or ethanol). This causes the separation of the three fatty acid molecules forming the original triglyceride, which remain as methyl or ethyl esters [5]. Glycerine is a highly versatile product and it is used in a broad spectrum of applications like food industry and pharmaceutical formulations. The amounts of raw glycerine produced every year are increasing constantly [6,7], as the demand for biofuels is on the rise. However, only a fraction of the produced glycerine could be used in the food and pharmaceutical market. On the other hand, these industries require high purity glycerine. These purification stages are costly and need additional equipment, which are not affordable for all the producers of biodiesel. For these reasons, it is necessary to find out new, economically feasible applications of this by-product.

On this subject, glycerine can be regarded as a potential feedstock to produce hydrogen because, according to its chemical formula ($C_3H_8O_3$), it is possible to obtain 4 mol of hydrogen from 1 mol of raw glycerine [8]. Generally, the resulting gaseous mixture has hydrogen (H_2), carbon monoxide (CO), methane (CH_4), and carbon dioxide (CO_2) as main components. This gaseous mixture can be further used as an industrial feedstock to generate heat and power [9,10], H_2 production [11–14] and synthesis of liquid fuels [15–17].

Recently, authors are involved in the study of the oxidation, partial oxidation and non-oxidation glycerine steam reforming, including the use of catalyst in order to improve the process yields. As revealed in the work done by Lin [18] or by Veiga and Bussi [19], the most common catalyst used are Ni, Co, Rh, Pt, Ru and Ir, using alumina, zirconia, silica and magnesia as support. Most studies are showing the effect of the use of these materials, and the different process variables [20–22].

According to literature and industrial production, several techniques can be employed to produce hydrogen from glycerine: via steam reforming (SR) [23], (partial oxidation) gasification [24], autothermal reforming [25], aqueous-phase reforming (APR) [26,27], and supercritical water reforming [28]. In this work, non-catalysed steam reforming reaction has been carried out. In this process, the glycerine reacts with steam to produce hydrogen and carbon dioxide. The steam reforming is the most commonly used method for producing hydrogen in the chemical industry. The steam reforming process is highly endothermic. In general, the process can be depicted as follows:



The resulting gas, rich in hydrogen, can be used as a fuel in internal combustion engines, fuel cells, and to produce chemicals such as ammonia and methanol.

Among the studies found in this field, the conversion of glycerol can be highlighted [2], studying how the concentration of hydrogen was achieved via aqueous-phase reforming (APR) with Pt/ Al_2O_3 catalyst and identified that optimum temperature for hydrogen production with APR was determined as 230 °C. It was found that hydrogen concentration in the gas product increased with decreasing glycerol concentration in the feed.

Also, an alternative way to produce H_2 is the biomass gasification; Luo et al. [29] studied the influence of the temperature in the hydrogen production; the amount of steam during the gasification reactions showed a relevant influence in the hydrogen production, resulting in improved gas quality and carbon yield. The steam/biomass ratio used was in the interval between 0 and 2.8 wt%, showing a maximum hydrogen content at 2.10 ratio, with a concentration equal to 52.7%.

Other researchers such as Gao [30] found different data on the calorific values in the range of 8.10 and 13.40 MJ $N m^{-3}$, getting a hydrogen/biomass ratio in the range of 45.05 and 135.40 $g_{H_2} kg_{biomass}^{-1}$. Li [31] noticed an increase of the hydrogen yield at higher temperatures values of either catalysis.

Though many studies have focused on the hydrogen production from reforming biomass or glycerine, not many systematic studies in the literature have been reported to reveal the effects of temperature, flow rate and concentration of the feed stream, not only on the composition but also on the energetic features of the syngas stream. Moreover, most studies have been carried out following the classical “step-by-step” method, by which a processing variable is changed at a time, thus not allowing us to determine the interactions between variables.

Given this context, the objective of the present work was to provide added value to glycerine, a sub-product of the biodiesel industry producing a high quality syngas, by its steam reforming. In particular, a bench-scale steam reforming process was tested, studying the influence of three processing variables: temperature (T), water/glycerine ratio (R), and flow rate of the feeding water/glycerine solution (\dot{V}_{W+G}). To gain deeper insight into the steam reforming of glycerine and a more realistic interpretation of the results, a DoE/RSM (Design of Experiments/Response Surface Methodology) approach was used. This is a particularly useful strategy for investigating interactions between variables, which would have been hard to verify if a classical ‘one variable at a time’ approach had been used.

2. Experiments

2.1. Materials

The crude glycerine, raw material, was obtained from a local biodiesel production plant Bioenergética Extremeña S.L (Valdetores, Badajoz, Spain) that utilises waste vegetable oil as the raw material for biodiesel production via the alkali mediated transesterification process. Table 1 shows the main characteristics of the crude glycerine. The raw glycerine was heated at 110 °C during 2 h, which results in the elimination of water and the precipitation of the salts, decreasing the ash content. After filtering, the purified glycerine was stored until further utilization for the preparation of the water-glycerine mixtures.

Table 1
Properties of the crude glycerol.

<i>Composition</i>	
Glycerol (wt.%)	77.6
Ashes (wt.%)	4.2
H_2O (wt.%)	11
Matter organic non-glycerol (wt.%)	6.84
<i>Ultimate analysis</i>	
C (wt.%)	30.3
H (wt.%)	8.68
O (wt.%) ^a	60.952
N (wt.%)	0.016
S (wt.%)	0.052
<i>Proximate analysis</i>	
Wet (wt.%)	16.37
Volatile matter (wt.%)	75.18
Fixed carbon (wt.%)	0
Ashes (wt.%)	8.99
<i>Physical properties</i>	
Density (g/cm^3)	1.261
Molar mass	92.094
Melting point (°C)	291
Boiling point (°C)	563
Viscosity (Pa s)	1.5
Flash point (°C)	433
Autoignition temperature (°C)	623
Heating value (MJ/kg)	19

^a Determined by difference.

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