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Hydrogen production by means pyrolysis and steam gasification of glycerol

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Abstract. The objectives of this work were to optimize the variables affecting pyrolysis and steam gasification of glycerol (by-product formed during biodiesel production); and to characterize the gaseous phase formed, in order to carry out its energetic use. The studied operation variables were reaction temperature (700-900 °C), water flow rate (0-0.173 $g \cdot min^{-1}$), glycerol flow rate (0.009-0.676 $g \cdot min^{-1}$) and carrier gas (nitrogen) flow rate (30-180 $cm^3 \cdot min^{-1}$). The most interesting phase (analyzed by gas chromatography) was the gas fraction. In this work, gas fraction was composed by H_2, CH_4, CO, C_2H_6, C_2H_4 and CO_2. The main gas generated was the hydrogen. Its generation was favoured by steam presence and its yield was increased in 224% in relation with pyrolysis process (default of water steam). The better conditions for studied process were 800 °C, 0.074 $g \cdot min^{-1}$ of water flow rate, 0.009 $g \cdot min^{-1}$ of glycerol flow rate and 60 $cm^3 \cdot min^{-1}$ of nitrogen flow rate. In these conditions, the volume of synthesis gas was 1.86 $L \cdot (g_{glycerol})^{-1}$ and its higher heating value (HHV) was 26.70 $MJ \cdot (kg_{glycerol})^{-1}$. This study indicated that the bio-glycerol is an excellent raw material in the obtaining of medium heating value gases. These gases could be used as fuel in industrial furnaces or domestic use.

Key words

Hydrogen production, glycerol, pyrolysis, steam gasification.

1. Introduction

Biodiesel is an alternative fuel to petrodiesel technically feasible, economically competitive, environmentally acceptable and easily available. For these reasons, biodiesel is attracting increasing attention world wide as a blending component or a direct replacement for diesel fuel in vehicle engines [1]. Globally, current energy policies reflect environmental issues including developing environmentally friendly technologies and increasing energy security and clean energy supplies. The implementation of the current directives about biodiesel triggers a huge demand for biodiesel [2].

The main way to make biodiesel is the transesterification of vegetable oils and animal fats. In this way the triglycerides from the feedstock react with a short-chain alcohol to form fatty acid methyl ester and glycerol. The reaction turn a mol of triglyceride into a mol of glycerol, in fact, 100 tons of glycerol per 1000 tons of biodiesel are obtained when transesterification occurs [1]. Glycerol is a highly versatile product and has a lot of uses. Almost two third of the industrial uses of glycerol are in food and beverage (23%), personal care (24%), oral care (16%) and tobacco (12%) [3]. In this way, the glycerol marketing would have a positive impact on the biodiesel manufacturing cost. However, the increasing available amount of glycerol due to the rapid growth of the biodiesel production has provoked a huge excess in glycerol market. In fact, the worldwide production of glycerol was more than 0.9 million tons in 2006, and in 2010 its production is estimated as high as 1.2 million tons [4]. This huge excess triggers glycerol market price depreciation because of this market is unable to absorb high amounts of the product. For these reasons and because of the glycerol contains impurities, the biodiesel industries are managing the glycerol excess as a waste. Therefore they suffer the impact of the increasing storage and management costs [5]. Taking into account these problems, it is important to explore other alternatives able to valorize high amount of glycerol. One of these glycerol valorization alternatives is its conversion into hydrogen.

Hydrogen is an environmentally friendly fuel as a feedstock for ammonia-based fertilizers or other chemicals as well as is gaining widespread applications with the advent of fuel cell technologies. At present, almost 95% of the world's hydrogen is produced from fossil fuels, hence, to develop an alternative source of hydrogen is very interesting [6]. Glycerol is a potential feedstock to produce hydrogen because 1 mol of glycerol can theoretically produce up to 4 mol of hydrogen. The main methods for the production of hydrogen from