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Syngas methanation from the supercritical water reforming of glycerol

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An overall heat-integrated process of SCW (supercritical water) reforming of glycerol for methanation of the syngas obtained and power generation is proposed and analyzed. Methanation is the methane synthesis from the hydrogenation of CO and CO_2. The SCW reforming is performed at 240 bars. Reforming temperatures from 700 °C to 900 °C and glycerol feed concentrations between 25 wt.% and 50 wt.%, needed to reach an energy self-sufficient process, are studied. For methanation, three adiabatic, fixed-bed reactors are connected in series with intermediate gas cooling, operating at 30 bars. The exit temperatures of these reactors range from 600 °C to 300 °C, respectively. The feed for the methanation section is previously conditioned by a Pressure Swing Adsorption unit to achieve a stoichiometric number of 3. The recommended operating conditions are a reforming temperature of 800 °C and a glycerol concentration of 33 wt.% to obtain 0.166 kg CH_4/kg glycerol, 0.433 kWe/kg glycerol and an overall energy efficiency of 61.6%, which may increase up to 76.1% if the hot water leaving the process at 90 °C is considered (cogeneration water). The results of this process were compared to those of the methanol synthesis, previously published, resulting in a better performance, because the carbon proportion converted into methane is higher than into methanol from SCW reforming of glycerol, and the higher specific overall value for the methane production, which considers the price of the product and the electricity jointly.

1. Introduction

Biodiesel is a product obtained by a transesterification process (methyl ester formation) from animal fats and vegetable oils, which react with an alcohol (normally, methanol) that acts as an acyl acceptor. In order to improve the reaction, a catalyst is used, mainly based on alkali such as sodium methylate, or sodium/potassium hydroxide. Glycerol is a by-product of the transesterification reaction.

The recovery of glycerol is an aspect directly related to the production cost, since the amount of glycerol generated represents about 10 wt.% of the biodiesel produced. Glycerol is eliminated from the process by decantation and when the biodiesel is washed with water. Normally, glycerol and esters are separated into two layers and the lower layer of glycerol is removed and after purified. Thus, the heavy stream leaving the transesterification reactor (raw glycerol with a purity of 50%) can be converted into crude glycerol (with a purity of 80%) or can be further refined to a pure glycerol (pharmaceutical glycerol with a purity of 99.7%). The substances present in the crude glycerol stream are mainly methanol, water, inorganic salts, free fatty acids, unreacted mono-, di-, and triglycerides, and methyl esters.

Until the 2008 economic downturn, biodiesel production was growing at a faster rate than bioethanol production, the other main biofuel to substitute petroleum fuels. Beginning in 2011, biodiesel production started to recover from the economic recession, surpassing its maximum peak level reached in 2008 [1]. In the U.S.A, e.g., biodiesel production increased from 28 million gallons in 2004 to 1076 million gallons in 2013 (computed only from January to October) [2]. Therefore, the rising excess of crude glycerol requires a further processing to get a competitive price. However, conventional options for crude glycerol consist of refining it to a higher purity that is high costly, especially for medium and small sized plants. For that reason, new uses and ways of glycerol valorization are necessary.

One of the most attractive routes is the glycerol conversion into synthesis gas (syngas) for obtaining high-value chemicals. There are different catalytic reforming processes, such as steam reforming, autothermal reforming and aqueous phase reforming, which generate hydrogen and carbon monoxide in addition to carbon dioxide and methane. Nevertheless, the use of SCW (supercritical water) makes it possible to perform another type of reforming

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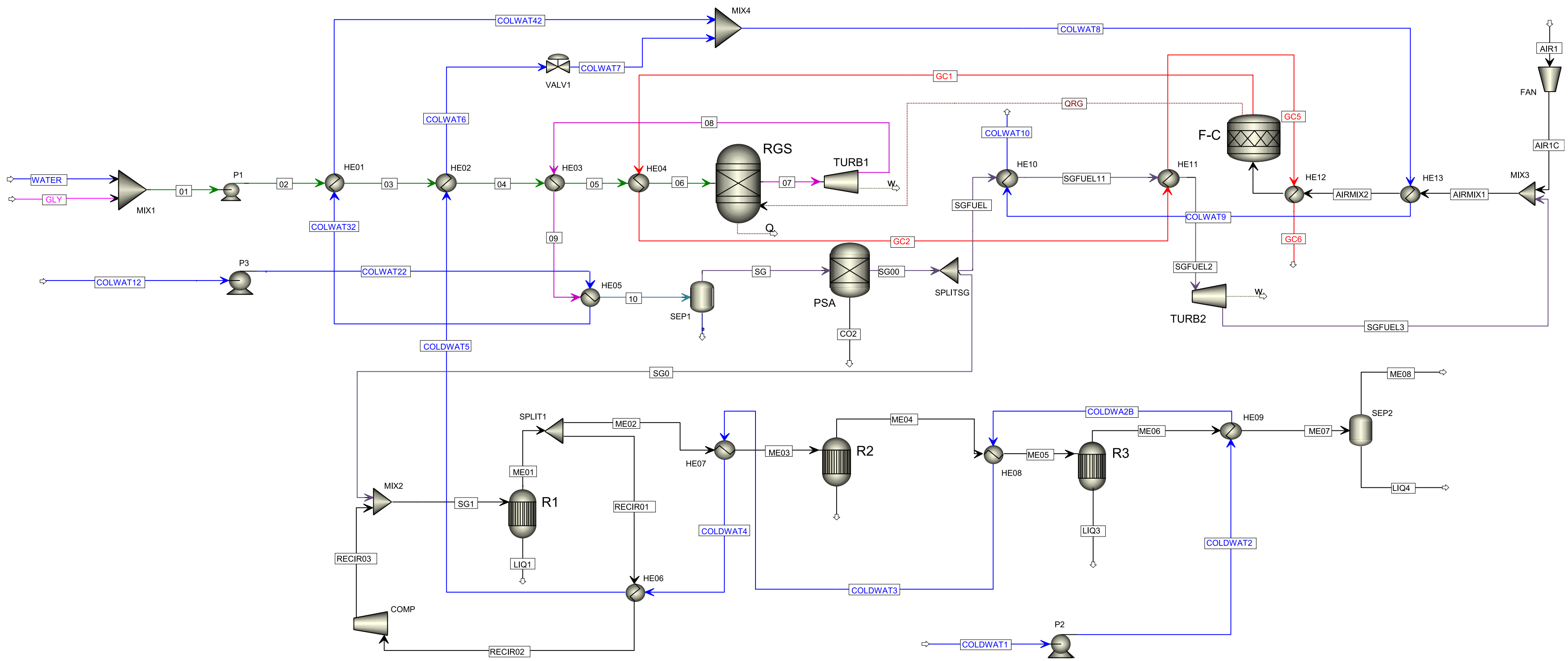

Fig. 1. Heat-integrated flow sheet for methanation and power generation via supercritical water reforming of glycerol.