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Evaluation of energy efficient low carbon hydrogen production concepts based on glycerol residues from biodiesel production

*Zsolt Tasnadi-Asztalos, Paul-Serban Agachi, Calin-Cristian Cormos**

Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, 11 Arany Janos Street, RO-400028 Cluj-Napoca, Romania

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ABSTRACT

The need to develop energy efficient low carbon conversion processes is of critical importance today. Hydrogen production concepts using glycerol resulted as byproduct from biodiesel production, at industrial scale (100,000 Nm^3/h hydrogen equivalent to 300 MW_{th}), with and without carbon capture was evaluated in the present paper. Three hydrogen production routes based on glycerol processing with carbon capture were investigated: the first two concepts are based on glycerol steam and autothermal catalytic reforming coupled with gas–liquid absorption for carbon capture. The third concept is based on innovative energy-efficient chemical looping cycle using ilmenite as oxygen carrier. Similar designs without carbon capture have been developed for glycerol autothermal and steam reforming to quantify the energy penalty for carbon capture. The assessments show that chemical looping is by far the most promising option in terms of overall energy efficiency (higher than 72%) and carbon capture rate (higher than 97%). Reforming-based glycerol processing concepts with CO_2 capture based on gas–liquid absorption have significantly lower energy efficiency (55–65%) and carbon capture rate (57–70%). Among evaluated reforming technologies, steam conversion performs better than autothermal option.

Introduction

In the last decades it has become clear that the fossil fuel resources are limited and their usage generate a significant environmental impact (e.g. global warming by greenhouse gas emissions). The continuous growth of world energy demand leads to a faster depletion of fossil fuel resources. To combat the climate change by limiting the greenhouse gas emissions, new energy efficient low CO_2 emission conversion technologies are needed [1]. Among them, the deployment of biofuels (e.g. biodiesel, bioethanol) and renewable energy sources (e.g. solar, wind) take a special place [2]. Political and economic instruments are put in place to stimulate the renewable energy sector, for instance at European Union (EU) level 20% of the energy demand is predicted to be covered by renewables by 2020 [3].

Biodiesel is one renewable biofuel with very good perspective to reduce the oil-based fuels for transport sector.

* *Corresponding author*. Tel.: +40 264 593833; fax: +40 264 590818.
E-mail address: cormos@chem.ubbcluj.ro (C.-C. Cormos).
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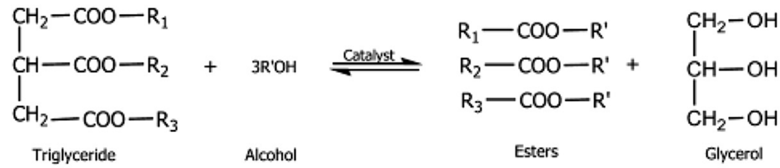
Biodiesel is obtain by catalytic trans-esterification of triglycerides using methanol (see reaction 1).



(1)

Glycerol is the main byproduct from biodiesel production (one ton of glycerol is produced to ten tons of biodiesel) [4]. No particular large scale usage for glycerol residues resulted from biodiesel production is available today. The chemical utilization of glycerol residues from biodiesel production is complicated by its low purity (mixture with unreacted methanol, triglycerides, salts and catalysts) and high energy intensity required for distilation.

Another energy carrier with good future prospective in energy, chemical and transport sectors is hydrogen. Currently hydrogen is mainly produced from fossil fuels (e.g. coal gasification and natural gas catalytic reforming) [5–7]. Hydrogen is seen as an important energy carrier for the future low carbon economy in combination with renewable sources and decarbonised fossil fuels. Apart of boosting renewable energy sources, Carbon Capture and Storage (CCS) technologies and improving overall energy efficiency of the conversion routes are seen as important methods to develop the future low carbon economy. 30% cut of CO_2 emissions compared to 1990 levels as well as 20% save of predicted energy consumption levels by improving the energy efficiency are targeted to be realized at EU level by 2020 [3].

Hydrogen-fuelled applications for various industrial sectors (e.g. heat and power generation, PEM fuel cells for transport sector, petro-chemical conversion etc.) are under way. In term of environmental impact, hydrogen is one of the cleanest energy carriers. Accordingly, renewable-based hydrogen production concepts are of particular importance. If these hydrogen production technologies are equipped with carbon capture feature additional environmental benefits are generated (near zero or even negative fossil CO_2 emissions).

This paper evaluates various innovative hydrogen production options using glycerol residues, as feedstock, simultaneous with carbon capture. There are several glycerol reforming possibilities for hydrogen production (e.g. conventional steam reforming, autothermal reforming), as well as carbon capture options (e.g. gas–solid and gas–liquid systems) to be integrated in the overall plant design [8,9]. Glycerol steam reforming for hydrogen production implies the following global reaction [10]:

$$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2 \quad \Delta H = +128\ kJ/mol \tag{2}$$

Global reaction conditions (pressure, temperature, ratios, catalysts etc.) for reforming are determined so as to minimize the byproduct formation (see reactions 3–9) [11,12].

$$C_3H_8O_3 \leftrightarrow 4H_2 + 3CO \tag{3}$$

$$CO_2 + CH_4 \leftrightarrow 2H_2 + 2CO \tag{4}$$

$$CO + H_2O \leftrightarrow H_2 + CO_2 \tag{5}$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \tag{6}$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \tag{7}$$

$$C_3H_8O_3 \rightarrow C_3H_6O_2 + H_2O \tag{8}$$

$$C_3H_8O_3 \rightarrow C_3H_6O_3 + H_2 \tag{9}$$

The syngas produced from glycerol reforming is then shift converted with steam. The water gas shift (WGS) reaction has a double purpose in overall glycerol reforming process: one to concentrate the syngas energy in form of hydrogen-rich gas and two to transform the carbon species into carbon dioxide which can be then captured by gas–liquid absorption process [13–15]. After carbon capture (pre-combustion capture configuration), the hydrogen-rich gas is purified by Pressure Swing Adsorption (PSA) to the desired specification. This work considers hydrogen purity higher than 99.95% (vol.) to be compatible with chemical applications as well as PEM fuel cells. The PSA tail gas and additional hydrogen-rich gas are used, in an external burner, to cover the heat duty of the reforming reaction.

Autothermal reforming can also be used for glycerol conversion to hydrogen. Apart of conventional steam reforming, an oxygen stream is used to totally oxidize (exothermic reaction) part of the glycerol to cover the reforming endothermic reaction. In this plant configuration, no external burner is needed for the reforming reactor, the tail gas is used to generate power to cover the ancillary plant consumption. In both steam reforming and autothermal reforming configuration, the available hot streams are used to generate steam which then is expanded in a steam turbine to produce power. Co-generation of hydrogen and power (both total decarbonised energy vectors) is one additional attractive feature of these conversion routes which is evaluated in this work.

Another emerging promising carbon capture option to be integrated in energy conversion systems is based on chemical