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# Techno-economic and environmental performances of glycerol reforming for hydrogen and power production with low carbon dioxide emissions

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## ABSTRACT

This paper is evaluating from the conceptual design, thermal integration, techno-economic and environmental performances points of view the hydrogen and power generation using glycerol (as a biodiesel by-product) reforming processes at industrial scale with and without carbon capture. The evaluated hydrogen plant concepts produced 100,000 Nm<sup>3</sup>/h hydrogen (equivalent to 300 MW<sub>th</sub>) with negligible net power output for export. The power plant concepts generated about 500 MW net power output. Hydrogen and power co-generation was also assessed. The CO<sub>2</sub> capture concepts used alkanolamine-based gas–liquid absorption. The CO<sub>2</sub> capture rate of the carbon capture unit is at least 90%, the carbon capture rate of the overall reforming process being at least 70%. Similar designs without carbon capture have been developed to quantify the energy and cost penalties for carbon capture. The various glycerol reforming cases were modelled and simulated to produce the mass & energy balances for quantification of key plant performance indicators (e.g. fuel consumption, energy efficiency, ancillary energy consumption, specific CO<sub>2</sub> emissions, capital and operational costs, production costs, cash flow analysis etc.). The evaluations show that glycerol reforming is promising concept for high energy efficiency processes with low CO<sub>2</sub> emissions.

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## Introduction

The continuous increase of world energy demand and the fossil fuels depletion make compulsory the development of renewable energy sources at industrial scale. In addition, the greenhouse gas emissions (especially CO<sub>2</sub>) associated with the fossil fuel usage put a high pressure on the fight against climate change [1]. Accordingly, the high energy efficient and

low carbon applications need to be developed for the future low carbon economy. Quantifiable targets were defined and enforced by political instruments to stimulate the reduction of greenhouse gas emissions and to boost the renewable energy sector. For instance at European Union level, 40% cut of CO<sub>2</sub> emissions compared to 1990 levels and 27% of the energy demand covered by renewables are set to be accomplished by 2030 [2].

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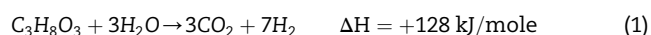
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Beside industrial sectors (e.g. heat and power, metallurgy, cement, chemicals etc.), the transport sector is one with high fossil CO<sub>2</sub> emissions [3]. A promising solution to curb the CO<sub>2</sub> emissions from transport sector represents the usage of renewable fuels e.g. bioethanol, biodiesel etc. Biodiesel is a renewable fuel being a promising alternative of the fossil diesel with positive environmental impact, non-toxic, biodegradable and near zero CO<sub>2</sub> emission. Biodiesel is typically made by chemically reacting lipids (e.g. vegetable oil, soybean oil, animal fat etc.) with alcohol (usually methanol) producing fatty acid esters. The main by-product of biodiesel production process is glycerol [4].

Referring to the energy carriers to be widely used in future low carbon economy; hydrogen and power are considered suitable options not involving greenhouse gas emissions at the point of use (only when renewables or fossil fuels with carbon capture are used). Hydrogen can be produced from a variety of fossil fuels (e.g. natural gas, oil, coal etc.) or renewable sources (e.g. wind, solar, biomass etc.). Glycerol is seen as an attractive fuel for hydrogen and power generation considering the production output derived from the biodiesel production (at much higher rates that required by chemical industry). Considering that the residual glycerol from biodiesel production is derived from renewable sources, this makes glycerol a potentially economically viable and environmentally friendly option. To chemically transform glycerol into usable compounds for energy and chemical sectors, the reforming process has received considerable attention [5].

Glycerol catalytic reforming for hydrogen and other energy carriers/chemicals takes place through glycerol dehydrogenation onto the catalyst surface followed by water gas shift or methanation reactions. The reforming process takes place under the action of a metal catalyst capable of breaking C–C bonds into smaller molecules (e.g. CH<sub>4</sub>, CO<sub>2</sub>, CO, H<sub>2</sub>O, C<sub>2</sub>H<sub>4</sub>O). Most studies for hydrogen production from glycerol were mainly focused on noble metal-based catalysts and commercially available catalysts with low cost. For the glycerol steam reforming for hydrogen production (which can then be used for various applications), more sustainable, a low-cost catalyst is recommended: Ni – Mg – Al, Ni – Cu – Al, Ni – Cu – Mg, Ni – Mg, Ni – Al catalysts [6,7].

The major drawback of glycerol steam reforming is the carbon formation due to cracking processes of organic compounds [8]. To both minimize carbon formation and favour the hydrogen production, the experimental and numerical studies [9,10] concluded that the glycerol steam reforming is to be performed at high temperatures (700–900 °C) with high water to glycerol ratio. The reaction pathway involves complex reactions such as: steam reforming (1), glycerol decomposition (2), water gas shift (3) and methanation (4):



The first three reactions increase the hydrogen yield of the process, the fourth one (methanation) decreases the hydrogen yield but it improves the thermal balance of the process (the PSA tail gas is used to provide the heat for reforming reactions). The final hydrogen yield of the processes (before PSA) is in the range of 76–83%.

The thermo-chemical conversion of glycerol to hydrogen and power based on catalytic reforming process (both conventional steam reforming and oxygen autothermal reforming) is presented in this paper. For hydrogen production concepts, an output of 100,000 Nm<sup>3</sup>/h hydrogen (equivalent to 300 MW<sub>th</sub>) was considered to be comparable with existing industrial size applications [11]. For power production concepts, a net power output of about 500 MW was considered based on a hydrogen-fuelled Combined Cycle Gas Turbine (CCGT). This power output was selected to be comparable with similar studies and existing industrial applications [3]. Hydrogen and power co-generation was also assessed. The key novelty aspects concern the techno-economic and environmental assessment of an industrial size glycerol reforming plant for hydrogen and power generation with/without CO<sub>2</sub> capture.

Another important challenge that lay in front of the whole industrial sector is the pressing need to reduce the greenhouse gas emissions. Low carbon industrial size applications need to be developed to curb the CO<sub>2</sub> emissions especially in heat and power systems. This paper evaluates a pre-combustion carbon capture method (based on chemical gas–liquid absorption) used in conjunction with glycerol reforming for hydrogen and power generation. Although glycerol can be seen as a renewable energy source with low to negligible fossil CO<sub>2</sub> emissions, capturing CO<sub>2</sub> will contribute to the development of innovative energy conversion systems with negative fossil CO<sub>2</sub> emissions. The overall system can be seen as capturing CO<sub>2</sub> from atmosphere (via photosynthesis), chemical conversion (biodiesel production from lipids followed by glycerol reforming) and underground storage in geological reservoirs (e.g. saline aquifers, depleted oil and gas reservoirs) or use for Enhanced Oil Recovery (EOR) purposes.

### Conceptual design of hydrogen and power generation based on glycerol reforming processes, main design assumptions and energy integration aspects

Two glycerol reforming technologies were assessed: conventional steam reforming (with heat provided by an external burner fed with hydrogen purification tail gas) and oxygen autothermal reforming. The carbon capture concepts used alkanolamine-based gas–liquid absorption process in a pre-combustion capture configuration. As solvent used, Methyl-DiEthanol-Amine (MDEA) was considered as illustrative example due to its improved performances (lower corrosion, higher CO<sub>2</sub> loading etc.) [12]. Similar glycerol reforming designs without carbon capture have been evaluated to quantify the energy and cost penalties.

The evaluated glycerol reforming plant concepts were divided in two categories as follow: the hydrogen production plants (Cases 1):

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