



Thermodynamic modelling and energy balance of direct methanation of glycerol for Bio-SNG production



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ABSTRACT

Glycerol can be considered a waste product when the cost of processing is higher than the processed glycerol value. In these situations, conversion of glycerol to an energy vector may be more beneficial. The aim of this work was to design and assess the feasibility of a process for low temperature steam reforming of glycerol (GLT-SR). GLT-SR is a novel form of direct methanation that produces a CH₄ rich, renewable fuel gas (Bio-SNG) that could substitute the current natural gas consumption associated with biodiesel production.

In this work, thermodynamic modelling to determine the conditions that suited CH₄ production and minimised carbon below 600 K as well as the impact of molar steam to carbon ratio (S/C) and pressure on the biomass to fuel efficiency of a GLT-SR plant were carried out using Aspen Plus® (V8.8) chemical processing software. Operating at 8 atm provided the benefits of high conversion to CH₄ whilst minimising the outlet reformer temperature and achieving the required inlet temperature for catalyst operation.

The Bio-SNG produced had an LHV of 16.7 MJ kg⁻¹ and had properties like landfill gas and biogas. An energy balance of the process determined that the electricity demand was negligible due to the low energy use of pumps and fans without the need for compressors. Operating at 8 atm, the production of Bio-SNG in the GLT-SR plant has the potential to offset 30% of the natural gas embodied energy requirement or 8.9% of the total embodied energy requirement for soybean biodiesel production from farm to use.

1. Introduction

Global production of biodiesel and the co-product glycerol have increased in the last two decades [1]. As nations strive to decarbonise transport fuels, global production of biodiesel is forecasted to double from 20 billion litres in 2009 to 41 million litres in 2025 with biodiesel transesterification producing as much as 10 wt% glycerol as a by-product [2].

Typically, glycerol represented an important area of profitability for biodiesel refineries. As production of biodiesel, and therefore glycerol has increased, supply of glycerol has become entirely independent of demand resulting in consistently low glycerol prices [3]. Current low economic value of glycerol in crude and purified forms, as well as the environmental toxicity, increases the pressure on biodiesel refineries as the costs for storage, transport, post treatment and disposal have remained the same. In the UK, as of 2008, where it is not possible to send the crude glycerol for purification or an alternative beneficial use, it must be consigned as waste [4].

Several methods are available to convert glycerol into higher value

chemicals or green fuels. He et al., 2017 provides details on these methods when using crude glycerol as a feedstock and includes; fermentation, digestion, gasification, pyrolysis, liquefaction, combustion and steam reforming. The main focus for studies in the area of producing green fuels by thermochemical processes is to produce hydrogen or syngas as the main product by gasification or reforming [5]. Several of these studies combine crude or pure glycerol with another biomass feedstock to enhance the process or act under supercritical or hydrothermal conditions and are not reviewed in this work.

Techniques for glycerol reforming include steam, partial oxidation, autothermal, aqueous, supercritical water reforming and have been reviewed by Schwengber et al. [6]. In addition sorption enhanced reforming [7–9] and dry reforming [10] have been reviewed.

Steam reforming (SR) of pure glycerol to produce hydrogen has received significant research emphasis over the last decade. SR of glycerol requires the addition of steam to glycerol in a suitable steam to carbon ratio over a catalyst at elevated temperatures. The popularity of the steam reforming process using glycerol feedstock is owed to how well SR has been established at industry level with more abundant and

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cheap organic feedstocks such as natural gas. Steam methane reforming is still used today to generate a significant proportion of the world's commercial hydrogen.

Moreover, if glycerol steam reforming processes become viable, minimal modifications will be required for steam methane reforming plants to switch to glycerol feed when compared to the other, less well established techniques such as aqueous phase reforming or supercritical water gasification, which are yet to reach this stage [11].

The main disadvantages of steam reforming when compared to the other reforming methods are the high temperatures, and therefore high energy input, required to vaporise the glycerol and water and provide adequate conditions for syngas and hydrogen production [12].

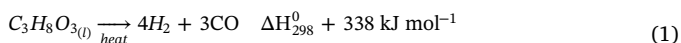
Steam reforming is mentioned in several different reviews in addition to He et al. [5] and Schwengber et al. [6]. Bagnato et al. [13] presents work on glycerol steam reforming and the main areas of catalyst development with a focus on membrane reactors. Rodrigues et al. [11] describes and compares glycerol steam reforming with carbonation and acylation with an emphasis on catalysis and experimental analysis with a thermodynamics-based discussion of glycerol steam reforming. The overarching theme is that glycerol can become a sustainable source of hydrogen, closing the loop for biodiesel refineries and increasing their profit.

Utilising pure glycerol rather than crude avoids the contaminants from biodiesel transesterification and allows simpler modelling. The majority of glycerol steam reforming studies are based on pure glycerol. Of significant interest for this work are the thermodynamic studies that have been carried out for steam reforming of pure glycerol above 550 K (277 °C) [14–19]. Silva et al. [20] published a review including the thermodynamics of glycerol steam reforming and progress with different catalysts. The focus of the thermodynamic studies is to determine operating conditions that favour H₂ and inhibit CH₄ and carbon (coking) production.

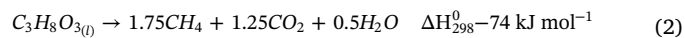
Fewer studies have been carried out using crude glycerol and He et al. 2017 reviews works converting crude glycerol to hydrogen and syngas [5]. In addition to these works production of syngas by non-catalysed steam reforming of crude glycerol by experiment [21] and production of hydrogen by; steam reforming of crude glycerol using nickel supported on activated carbon [22], rhodium over MgAl₂O₄ [23] and Ni-La-Ti mixed oxide catalysts [24], and dry autothermal reforming (ATR) of crude glycerol with *in situ* hydrogen separation by thermodynamic modelling [25] have been reported.

A direction that has not yet been fully explored is direct synthesis of methane from waste glycerol at low temperatures and pressures to produce a renewable fuel gas (Bio-SNG). Operating at low temperatures and pressures avoids the high energy costs associated with steam reforming and safety issues with supercritical conditions. Hydrogen is produced during the initial decomposition of glycerol (Eq. (1)) which is readily available for the steam reforming reaction. Carrying out steam reforming of glycerol by direct methanation without additional hydrogen creates an upper theoretical limit on methane production. The theoretical maximum CH₄ that can be produced from one mole of glycerol is shown in Eq. (2) by combining the glycerol decomposition (Eq. (1)), water gas shift (Eq. (3)) and carbon monoxide methanation (Eq. (4)) and was mentioned by Schubert et al. [26]. Whilst the CO₂ methanation pathway in Eq. (5) is possible, it consumes more hydrogen for the same yield of methane and is dependent on the water gas shift reaction for CO₂ production. Carbon formation can inhibit methane production in steam reforming reactions and occurs by disproportionation of CO in Eq. (6) (Boudouard reaction) as well as CO and CO₂ hydrogenation in Eq. (7) and Eq. (8).

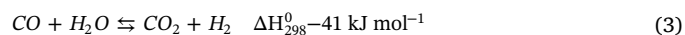
Glycerol Decomposition to Syngas



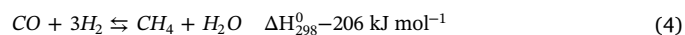
Glycerol Autothermal Reforming (direct methanation of glycerol)



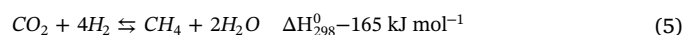
Water Gas Shift



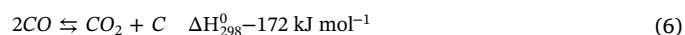
CO Methanation



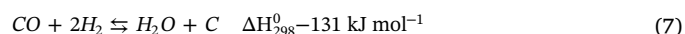
CO₂ Methanation



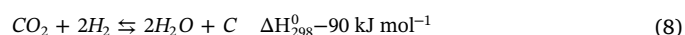
CO Disproportionation (Boudouard)



CO Hydrogenation

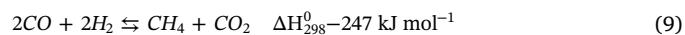


CO₂ Hydrogenation



The concept of direct methanation was first recorded by Meyer. H et al. (1976). Meyer described the improvements over the conventional syngas methanation process by reacting equimolar concentrations of CO and H₂ in Eq. (9). Whilst the stoichiometry is the same as combining the CO methanation and water gas shift, the difference was that CO₂ was produced directly rather than by water gas shift [27].

Combined CO methanation and CO Shift



To date, there has been one experimental study on a direct synthesis of methane from glycerol was carried out by Imai Hiroyuki [28]. Silica modified nickel catalysts were used to directly methanate a solution of pure glycerol and water at a steam to carbon ratio of 1.71 (50 wt% glycerol), 1.14 (60 wt% glycerol) and 0.73 (70 wt% glycerol) at temperatures between 593 K and 723 K and pressures of 1–30 atm.

Converting glycerol to methane represents an opportunity to produce a renewable energy carrier that is like biogas or landfill gas and can therefore operate within current gas infrastructures. To minimise economic expenditure the following methods could be applied: effective heat integration to maximise efficiency, install the process on site at biodiesel refineries to minimise transport and logistics costs, minimise power requirements by utilising the Bio-SNG without upgrading and minimise external thermal energy demand by combusting some of the Bio-SNG on site to produce steam and closing the loop.

Producing the Bio-SNG on site at the biodiesel refinery would provide a source of renewable fuel that could substitute natural gas used for heat and power, thereby reducing the refineries dependence on fossil fuel whilst simultaneously preventing waste and improving the energy efficiency of the biodiesel plant. An example of how the Bio-SNG could replace natural gas in a soybean biodiesel refinery is shown in Fig. 1.

Based on the thermodynamic literature, it is widely agreed that favouring CH₄ rather than H₂ production requires low steam to carbon ratios and temperatures with elevated pressures [14,16,29]. More specifically temperatures below 900 K, pressures greater than 1 atm and an S/C above the minimum for negligible solid carbon product but lower than three. Above 950 K CH₄ is almost inhibited due to steam methane reforming at 1 bar [29]. Increasing pressure reduces solid carbon up to 850 K but increases solid carbon formation above 850 K [16]. Reactions that favour solid carbon are: thermal decomposition, cracking, and CO disproportionation (Eq. (6)). Minimising carbon product is integral to prolonging catalyst life and activity in reactors as well as maximising the conversion of glycerol carbon to CH₄.

The minimum temperature for methanation is limited by the activity of catalysts. The minimum temperature advised for the commercial PK-7R low temperature CO methanation catalyst created by

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