A hydrogen future? An economic assessment of glycerol utilization derived from the biodiesel process for hydrogen production.

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The fuels that are currently used in the transport sector are almost entirely based on fossil sources (approximately 98 %). The efforts to provide a viable solution have focused on the development of biofules, i.e., fuels that are ultimately derived from biomass sources and can thus be considered carbon neutral [1]. As a result biodiesel has moved from being a niche energy source in the European transport sector to being a significant source of road transport fuel, with the EU 27 experiencing an increase in the use of biodisel of over 70% between 2007 and 2012. The principal byproduct of the biodiesel industry is glycerol, as every 100 g of oil undergoing the transesterification process produces 10 g of glycerol as byproduct [2], and production of glycerol had exceeded 2.2 million metric tones worldwide in 2012 (Fig. 1) [3]. The growing amounts of glycerol that began to be dumped onto a relatively stable market have caused a near total collapse in glycerol prices; whilst in 2006 crude glycerin (80% glycerol) cost about 125 €/ton, in 2011 the price had dropped to approximately 20 €/ton.

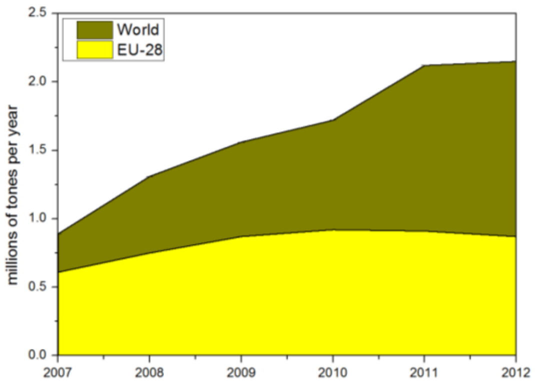

Figure 1. World and EU-28 glycerol production in millions of tones per year from 2007-2012 (calculations based on an average biodiesel density of 0.86 g/cm^3)

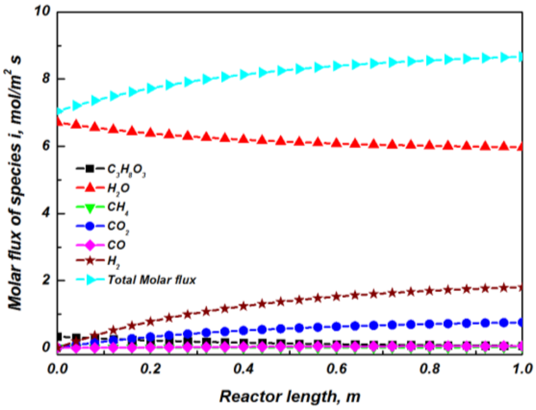

Figure 2. Molar flux of species

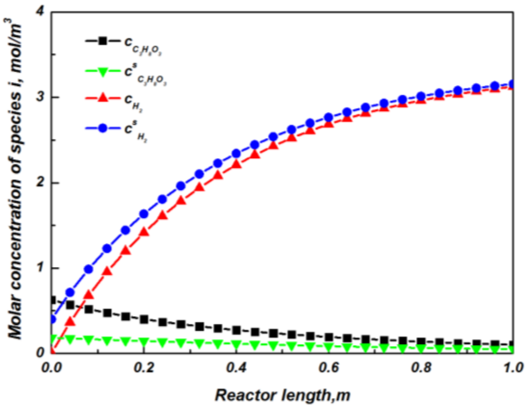

Figure 3. Molar concentration of species

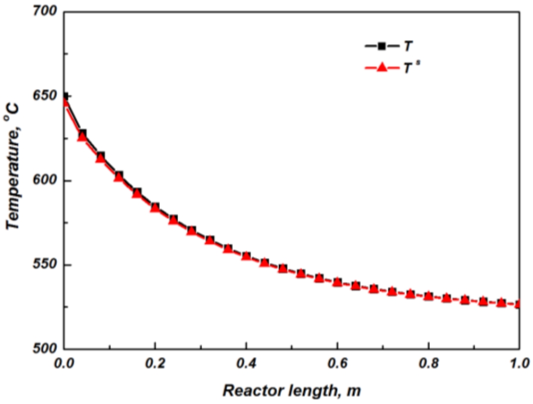

Figure 4. Bulk and particle surface temperature

However, glycerol could potentially be used for the production of hydrogen, a clean energy source with numerous uses, whose demand is expected to greatly increase in the future, mainly due to technological advancements in the fuel cell industry. Hydrogen can be produced from glycerol by different catalytic reactions, with the steam reforming reaction attracting most of the researcher's attention, partially due to the fact that the process is widely used in industry, and would require only minor alterations in existing systems if the feedstock was changed from natural gas or naphtha to glycerol [4]. The other reason that makes the steam reforming of glycerol attractive can be deduced from Eq. (2), which states that every mole of glycerol fed to the reactor can theoretically produce seven moles of hydrogen.

$$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2 \tag{1}$$

The study presented herein aimed at calculating the investment cost of a reactor for the glycerol steam reforming reaction on a small industrial scale (production of hydrogen equivalent to 1 MW of electrical power). For that purpose, a 1-D heterogeneous reactor model was developed to describe the steady-state behaviour of the steam reforming tubular fixed bed reactor and the nonlinear boundary value problem was solved using the ATHENA Visual Studio software [5]. The solution of the problem permits the evaluation of glycerol conversion and hydrogen yield. Figure 2 depicts the distribution of the molar fluxes of the reactant species along the reactor length. It is obvious that steam is in abundance (steam to glycerol feed molar ratio = 20/1), whereas glycerol conversion exceeds 80% and hydrogen yield tends to its thermodynamic value. Figure 3 depicts bulk and particle surface concentrations for the main reactant, namely glycerol and the main product, i.e., hydrogen. It is obvious that in a reactor of the scale designed herein only minor mass transport limitations occur; however, they appear to be more prominent for glycerol due to its heavier molecule and lower effective diffusivity. Figure 4 depicts bulk and particle surface temperature along the reactor length. Heat transport limitations appear to be negligible for the reactor designed herein. However, intraparticle mass and heat transport limitations were not taken into consideration and were replaced by effectiveness factors.

The investment cost consists mainly of the total cost of the equipment, the vessel and the tubes that will house the catalytic system for the reaction. Other apparatuses included in the process simulation have not been taken into account in this cost analysis. The results of the economic evaluation of a fixed – bed reactor for hydrogen production of 360,000 mol/day are summarized in Table 1.

Table 1. Economic evaluation of a fixed – bed reactor of 360,000 mol/day hydrogen production from glycerol steam reforming for an 8% Ni/Al catalyst

Parameter	Definition	Industrial scale
D	Reactor diameter, in	60.14
L	Reactor length, in	49.21
F_m	Factor for SS 316	2.1
C_a	Factor, $	99.74
t_h	Thickness of the vessel, in	0.50
p_m	Density for SS 316, lbm/in^3	0.29
W	Weight of the vessel, lb	1348.72
C_b	Factor, $	12,024
C	Cost of the vessel, $	124,990
D_t	Tube diameter, ft	0.033
L	Catalyst bed length, ft	3.281
C_{tube}	Cost of a tube, $	13.50
N	Number of tubes	29,181
C_{tubes}	Total cost of tubes, $	393,925
C_{total}	Total cost, $	518,914
$C_{total,\ 2015}$	Cost in the year 2015, $	639,863

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