

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

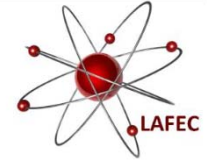
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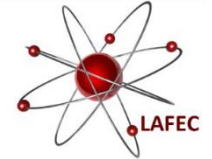
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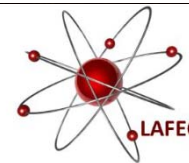
Introduction



Introduction

- The fuels that are currently used in the transport sector are almost entirely based on non-renewable sources. Efforts to provide a viable solution have focused on the **development of biofuels**, i.e., fuels that are ultimately derived from biomass sources and can thus be considered carbon neutral
- **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 biodiesel of over 70% between 2007 and 2012
- **The EU has a target to deliver 10% of energy in transport from renewable sources** by 2020, and separately, to reduce the GHG lifecycle emissions of transport fuels by 6% by 2020 – so biodiesel production will increase further
- One of the barriers for the further development and commercialization of biodiesel is its **high production cost**, which is caused by the price of raw materials. Thus, the industry needs to find new and innovative ways of maximizing its profits either by bringing down the cost of raw materials and/or by **making use of its existing waste streams**
- **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





Glycerol's properties and use (1/3)

- Glycerol (1,2,3-propanetriol) is the **oldest organic molecule isolated by humans** (around 2800 BC), with the heating of fats in the presence of ash, which led to the production of soap. However, credit for its discovery is attributed to the Swiss pharmacist K.W. Scheele, who isolated this compound in 1779, by heating of a mixture of olive oil and litharge (PbO)
- Glycerol is a **colorless, odorless, viscous** liquid that has a syrupy-sweet taste. Its hygroscopic properties are caused by the three hydrophilic hydroxyl groups that it contains
- Glycerol's use in plastic and resin manufacturing, and food, cosmetics and pharmaceutical industries is due to its C₃ framework and polyfunctional hydroxyls; in fact **glycerol is known to have over 2000 industrial uses**
- Glycerin is **completely miscible in many substances**. Among them are: alcohol (methyl, ethyl, isopropyl, n-butyl, isobutyl, secondary butyl, and tertiary amyl); ethylene glycol, propylene glycol, trimethylene glycol monomethyl ether and phenol. Solubility of glycerin in acetone is 5% by weight; in ethyl acetate it's 9%. It's slightly soluble in dioxane and ethyl, and partially insoluble in superior alcohol, fatty acids and hydrocarbonate, as well as in chlorinated solvents such as hexane, benzene, and chloroform





Glycerol's properties and use (2/3)

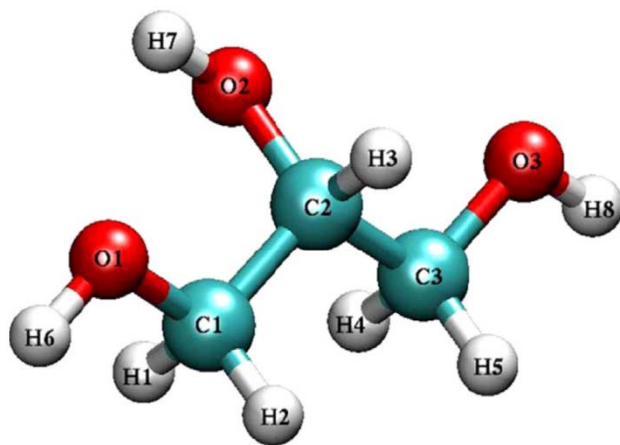


Figure 1. Molecular structure of glycerol

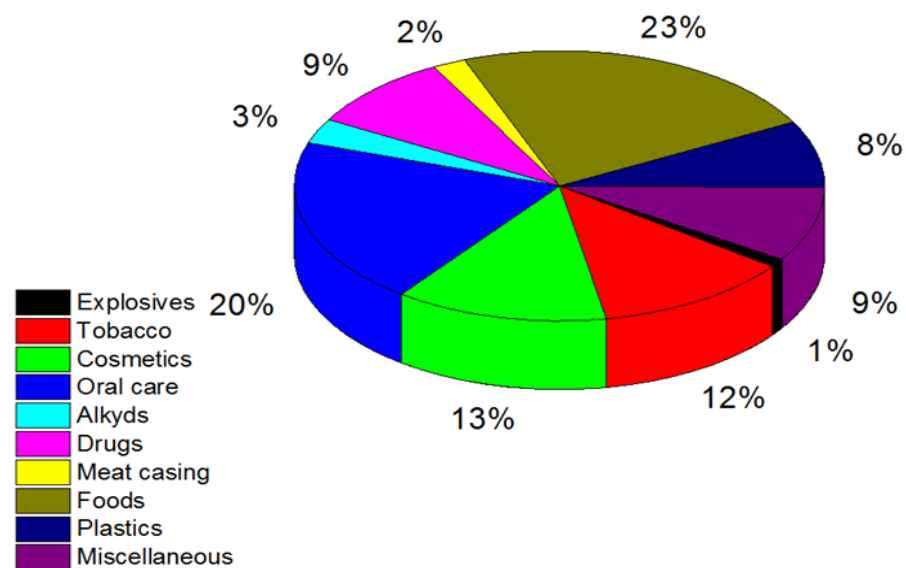
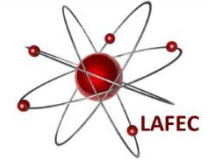


Figure 2. Global market of glycerol



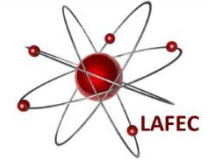
Glycerol's properties and use (3/3)

- **Glycerin is very viscous:** at normal temperatures it remains a viscous liquid even at 100% concentration without crystallizing. At low temperatures, concentrated glycerin solutions tend to super cool as high viscosity fluid. Viscosity rises at first until it quickly becomes vitreous around $-89\text{ }^{\circ}\text{C}$. Aqueous glycerin solutions (at different concentrations) tend to have lower viscosity
- **At low temperatures glycerin tends to super cool instead of crystallize.** Aqueous glycerin solutions resist freezing and are used as antifreeze in cooling systems
- **Glycerin does not oxidize in the atmosphere** in normal conditions, but can be easily oxidized by other oxidants
- Glycerol has **low volatility and low vapor pressure**, which is strictly linked with its hygroscopic property



Crude glycerol

- **The glycerol obtained from the biodiesel process is crude**, as it contains non-reacted and partially reacted fats, free fatty acids, methanol, esters and salts, and thus, **it cannot be easily used as raw material in the industries mentioned above**
- The conventional biodiesel production process uses a 6:1 molar ratio of methanol to oil which helps the reaction to be completed. However, this process often results in an excess of alcohol that ends up in the glycerol layer. Usually the methanol is recovered via relatively inexpensive flashing or distillation; however, the purification of glycerol (with its high boiling point) via distillation is **much more expensive** and thus more often than not, it is being avoided
- At present, a large portion of the overall production of glycerol (over 15 %) goes into animal feed stock, another 15% is used as additive for manufacturing cement of enhanced performance (enhanced concrete strength, and grinding and handling aid for cement) replacing petrochemical amines and glycols, the rest is being **incinerated**



Valorization of crude glycerol

- Glycerol can be valorised through the oxidation, dehydration, acetylation, etherification, esterification, acetalization and ammoxidation processes for the production of chemicals (such as, citric acid, lactic acid, 1,3-dihydroxyacetone, 1,3-propanediol, dichloro-2-propanol, acrolein, **hydrogen**, and ethanol)
- As glycerol is a polyol with 3 hydroxyl groups, it presents different reactivities and thus multiple chemistries, ranging from redox (oxidations and hydrogenolysis) to acid-catalyzed processes (etherifications, esterification). Thus, dehydrations and oligomerisations have to be designed and optimized
- The development of chemical platforms, the design of more stable and active catalysts, as well as the different processing techniques for glycerol's valorization, are still **significant challenges that are yet to be fully addressed**

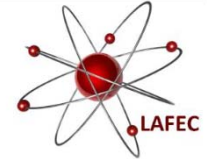




Glycerol consumption market

- The Asia-Pacific region has become the largest consumer of refined glycerin, Western Europe is the second largest and North America the third largest consumer. These three regions accounted for 87% of world consumption in 2012
- Europe imports refined and crude glycerin from Asian countries and is considered a typical importer of this resource
- The United States is also a glycerin importer, receiving product from Indonesia, Malaysia, Argentina, and Europe
- Asia exports on a large scale to global and regional markets, and glycerin is a local end product. In recent years China has surged in the market as a large importer, in addition to having local production. What's more, due to the growing petroleum and chemical industries in Asia, much of the glycerin production had before been exported to the United States, but with growing freight costs, most of this production ended up going to China
- The worldwide **glycerin market is known for its unpredictable and complex nature**, since it is a byproduct. Production of the chemical is directly affected by the demand by various end-use segments

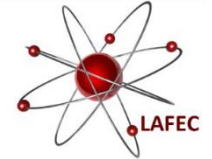




Glycerol prices

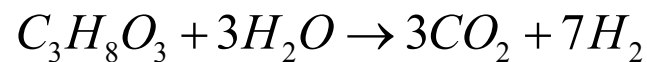
- From the 1970s until the year 2004, crude glycerol had a stable price between 1200 and 1800 US\$/ton. **Market and production conditions were stable**
- This relatively stable market has been drastically altered by the arrival of biodiesel. With stable prices, there was no need to obtain historical glycerol prices for the savings of the biofuel industry because in the traditional petrochemical market, the value of glycerol was essential to maintain the business model. Though the petrochemical industry did know that biodiesel would succeed and the volumes would be large, they were incapable of understanding how effective it would be
- The subsidy policies and regulations proposed in the United States and the European Union for transportation fuel rose the production of biodiesel and growing amounts of glycerol began to be dumped onto a relatively stable market; in 2005 the **stable prices went into free fall**
- Most chemical companies involved in glycerol production had problems purifying it or eliminating it because of its high cost, which lead various businesses to close - the price of glycerol fell to around 330 US\$/ton

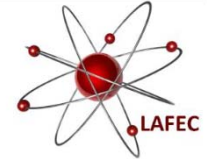




Hydrogen production (1/2)

- Hydrogen can be produced from glycerol by catalytic reactions such as, **steam reforming** (GSR), oxidative steam reforming (OSR), auto-thermal reforming (ATR), aqueous phase reforming (APR), and supercritical water (SCW) reforming
- The reaction that has attracted most attention is that of the steam reforming, 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
- The other reason that makes the steam reforming of glycerol attractive can be deduced from the main reaction, which states that **every mole of glycerol fed to the reactor can theoretically produce seven moles of hydrogen**





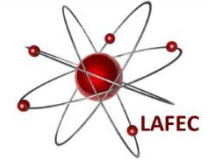
Hydrogen production (2/2)

- The target for the glycerol steam reforming reaction is to develop an active catalyst that inhibits coke formation and CO production
- Noble metals are less sensitive in carbon deposition but the catalysts that are most widely used are based on nickel
- Ni has good intrinsic activity, especially if the Ni is highly dispersed over the support and also because of its lower prices compared with noble metals
- Alumina is attractive as support because of its high specific surface area (which facilitates metal dispersion) and its mechanical and chemical resistance under reaction conditions. However, it is also known that carbon deposition and catalyst sintering, both factors that result in the de-activation of the catalyst, are also promoted when alumina is used as support





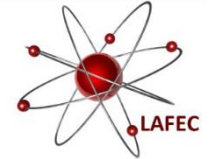
Economic sustainability



Case study

- The study presented 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)
- The study is based on the use of 8% Ni/Al₂O₃ catalyst, produced by the wet impregnation method
- This particular method for catalyst preparation was chosen because it is a relatively simple technique well fitted to the industry requirements
- Experimental results performed in our lab, showed that the Ni/Al catalyst could achieve significant glycerol conversions that reached up to 80% at 650 °C
- This experimental data were also used here to obtain the appropriate kinetics expressions and parameters, by parameter estimation method





Reactor design (1/5)

- At the range of 400-750 °C, a first order reaction kinetics with respect to glycerol concentration fitted well to the experimental data. The reaction kinetics can be expressed as:

$$r_{SRG} = k_{SRG} P_{C_3H_8O_3}$$

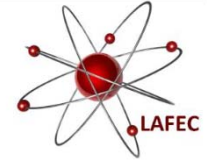
It stands when steam is in abundance
(Glycerol to steam molar ratio 20/1)

- where $P_{C_3H_8O_3}$ is the partial pressure of glycerol (bar) and k_{SRG} is rate constant of the reaction given by:

$$k_{SRG} = k_{SRG,0} e^{\left(\frac{-E_a}{RT}\right)}$$

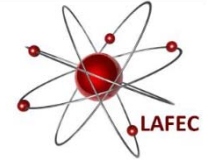
- where $k_{SRG,0}$ is the Arrhenius pre-exponential factor ($\text{mole/Kg}_{\text{catalyst}} \cdot \text{s} \cdot \text{bar}$), E_a is the activation energy (Joule/mole), R is the universal gas constant (Joule/mole·K), T the absolute temperature (K). Kinetic parameter values are given in the following table.

$k_{SRG,0}$	$1.5 \cdot 10^3 \text{ mole/Kg}_{\text{catalyst}} \cdot \text{s} \cdot \text{bar}$
E_a	33,286.76 Joule/mole



Reactor design (2/5)

- The catalytic steam reforming reaction of glycerol for hydrogen production took place in a fixed – bed reactor at atmospheric pressure.
- A tubular reactor at industrial scale was designed with the purpose of producing 1 MW of electricity using hydrogen as combustion fuel. The heating value of hydrogen was assumed to be at its lower limit, i.e., 120 MJ/Kg.
- A heterogeneous fixed bed reactor model that takes explicitly into account external mass and heat transport phenomena was developed, whereas resistance to internal mass and thermal transport were replaced by effectiveness factors, corresponding to each reaction
- Physicochemical properties of the gaseous reaction mixture were continuously calculated along the reactor length

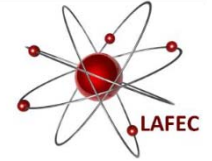


Reactor design (3/5)

- In order to design an industrial multi – tubular reactor it is essential to create a scale up system for the operating conditions and parameters.
- The following assumptions were applied in the model:
 - Steady state conditions
 - Constant bed porosity and uniform particle size
 - Plug flow with negligible radial but substantial axial mass and thermal dispersion
 - Five reactive (CH_4 , CO_2 , H_2O , CO , H_2) and one inert (He) species
 - Isothermal, adiabatic or thermo stating conditions can be set

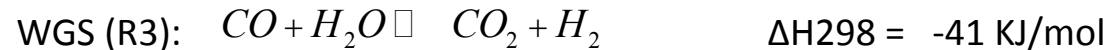
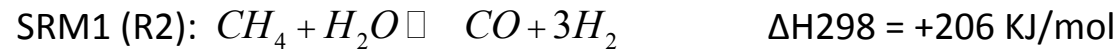
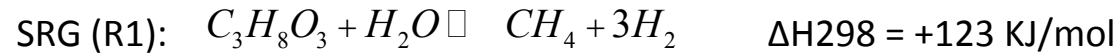
Parameter	Definition	Bioglycerol (lab.Scale)
T_{in}	Inlet temperature, °C	650
P	Inlet pressure, bar	1
D_t	Internal diameter of the tube, m	0.01
L	Catalyst bed length, m	1
D_p	Catalyst particle diameter, m	$4 \cdot 10^{-3}$
ρ_B	Catalyst bulk density, Kg/m^3	570

Table. The operating conditions and parameters of the reactor design

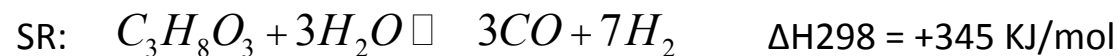


Reactor design (4/5)

- Three major reactions were included in the model, namely steam reforming of glycerol (SRG), steam reforming of methane (SRM1) and water gas shift (WGS):



- Thus, the overall reaction of hydrogen production from steam reform of glycerol can be written as:





Reactor design (5/5)

- Besides the kinetic expression for the SRG (R1) reaction the following **kinetic expressions** were used taken from the literature:

$$r_{SRM1} = \frac{k_{SRM1}}{P_{H_2}^{2.5}} \left(P_{CH_4} P_{H_2O} - \frac{P_{H_2}^3 P_{CO}}{K_{SRM1}} \right) \frac{1}{\Omega^2}$$

$$r_{WGS} = \frac{k_{WGS}}{P_{H_2}} \left(P_{CO} P_{H_2O} - \frac{P_{H_2} P_{CO_2}}{K_{WGS}} \right) \frac{1}{\Omega^2}$$

where,

$$\Omega = 1 + K_{CO} P_{CO} + K_{H_2} P_{H_2} + K_{CH_4} P_{CH_4} + K_{H_2O} \frac{P_{H_2O}}{P_{H_2}}$$

Table. Van't Hoff parameters for species adsorption

Species	K_{oi} (bar^{-1})	ΔH_i (J/mol)
CH_4	6.65×10^{-4}	-38,280
H_2O	$1.77 \times 10^5 \text{ bar}$	88,680
CO	8.23×10^{-5}	-70,650
H_2	6.12×10^{-9}	-82,900

Table. Arrhenius kinetic parameters

Reaction	k_{oj} ($mol/kg_{cat}.s$)	E_i (J/mol)
SRM1	$1.17 \times 10^{15} \text{ bar}^{0.5}$	240,100
WGS	$5.43 \times 10^5 \text{ bar}^{-1}$	67,130

- Reaction equilibrium constants** are given by:

$$K_{SRM1} = e^{\left(\frac{26,830}{T_s} + 30.114 \right)} \text{bar}^2$$

$$K_{WGS} = e^{\left(\frac{4,400}{T_s} - 4.036 \right)}$$

- The **temperature dependence** of Arrhenius kinetic parameters and Van't Hoff species adsorption parameters is expressed as:

$$k_j = k_{oj} e^{\left(\frac{E_j}{RT} \right)}$$

$$K_i = K_{oi} e^{\left(\frac{\Delta H_i}{RT} \right)}$$

Reaction rates

- By summing up the reaction rates, r_j , of all reactions j to which a species i is participating, the rate of production or consumption of that species is determined. For the present reaction scheme, taking also into account the corresponding stoichiometric coefficients, the reaction rates are expressed respectively by:

$$r_{C_3H_8O_3} = -\eta_1 r_1$$

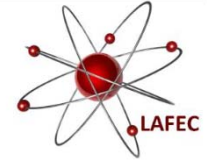
$$r_{H_2O} = -\eta_1 r_1 - \eta_2 r_2 - \eta_3 r_3$$

$$r_{CH_4} = \eta_1 r_1 - \eta_2 r_2$$

$$r_{CO_2} = 2\eta_1 r_1 + \eta_3 r_3$$

$$r_{CO} = \eta_2 r_2 - \eta_3 r_3$$

$$r_{H_2} = 3\eta_1 r_1 + 3\eta_2 r_2 + \eta_3 r_3$$



Model equations

- Species molar fluxes

$$\frac{1}{L} \frac{\partial N_i}{\partial z} = -k_{im} a_p (c_i - c_i^s)$$

- Species bulk concentrations

$$N_i = v c_i - \frac{\varepsilon}{L} c D_z \frac{\partial x_i}{\partial z}$$

- Species surface concentrations

$$k_{im} a_p (c_i - c_i^s) = -(1 - \varepsilon) \rho_B \sum_{j=1}^{N_{Rx}} \eta_j \nu_{ij} r_j$$

- Bulk temperature

$$\frac{1}{L} \frac{\partial E}{\partial z} = \frac{k_z}{L^2} \frac{\partial^2 T}{\partial z^2}$$

- Solid temperature

$$h_g a_p (T - T^s) = -\rho_s \sum_{ij=1}^{N_{Rx}} \eta_j (-\Delta H_{Rj}) r_j$$

- Total molar flux

$$N = \sum_{i=1}^{N_c} N_i$$

- Total bulk concentration

$$c = \frac{\rho}{M}$$

- Superficial velocity

$$N = v c$$

- Total surface concentration

$$c^s = \sum_{i=1}^{N_c} c_i^s$$

- Pressure

$$\frac{1}{L} \frac{\partial P}{\partial z} = \frac{v^2}{L} \frac{\partial \rho}{\partial z} - \frac{\rho v^2}{d_p} \frac{1 - \varepsilon}{\varepsilon} \left[150 \frac{1 - \varepsilon}{\text{Re}} + 1.75 \right]$$

- Density

$$\rho = \rho(x_i, T, P)$$

- Mean molecular weight

$$M = M(x_i, T, P)$$

- Energy flux

$$E = \rho v H(x_i, T, P)$$

- Enthalpy

$$H = \sum_{i=1}^{N_c} x_i \left(H_{f,i}^0 + \int_{T_{ref}}^T c_{p,i} dT \right) + H^R$$

Mass and heat transport properties were obtained from empirical correlations suitable for industrial scale reactors, as functions of local values of dimensionless Reynolds, Prandtl and Schmidt numbers according to:

$$D_z, k_z, k_{im}, h_g = f(\text{Re}, \text{Pr}, \text{Sc}_i)$$



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Results & Discussion

Molar flux of species

- For the numerical solution of the above nonlinear boundary value problem the PDAPLUS solver of ATHENA Visual Studio software was used. The solution of the problem permits the evaluation of glycerol conversion and hydrogen yield.
- The figure below 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.

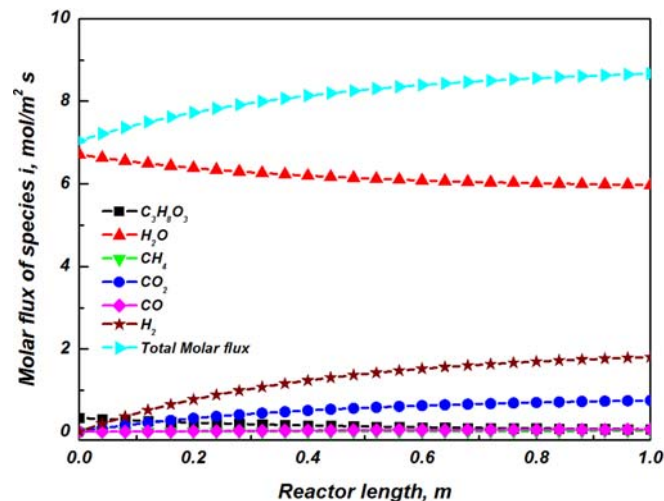


Figure. Molar flux of species



Bulk and particle surface concentrations

- 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.

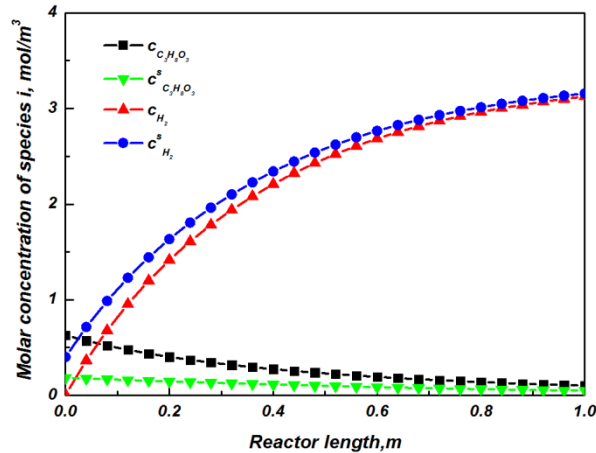


Figure. Molar concentration of glycerol and hydrogen

Bulk and particle surface temperature

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. Parameter estimation procedure described earlier gave the following values for the effectiveness factors of each reaction:

$\eta_1 = 9.78 \cdot 10^{-3}$
 $\eta_2 = 1.00$
 $\eta_3 = 0.00$ (WGS is of minor importance here).

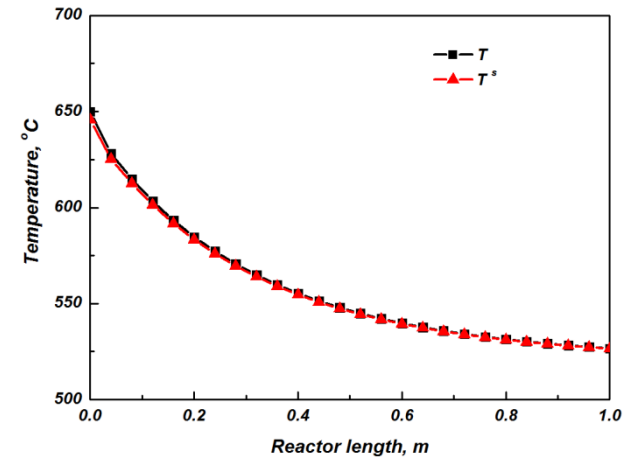


Figure. Bulk and particle surface temperature

Initial operating conditions and parameters

- From the hydrogen yield of a single tube and the total hydrogen production needed for the plant design the number of tubes necessary to achieve the goal can be computed. The results of the reactor design at inlet reaction temperature of 650 °C and for hydrogen production of 720 Kg/day are summarized at the following Table:

Parameter	Definition	Industrial scale
T_{in}	Inlet temperature, °C	650
P_{in}	Inlet pressure, bar	1
ϵ	Bed porosity	0.3946
ϵ_A	Volume change	1.23
$X_{C_3H_8O_3}$	Degree of glycerol conversion, %	83.52
F_{H_2}	Hydrogen production, mol/day	360,000
$F_{GLYC,0}$	Feed glycerol flow, mol/day	66,446.39
Q_{tube}	Flow in each tube, m ³ /s	$4.19 \cdot 10^{-5}$
V	Total reactor volume, m ³	2.29
D_t	Tube diameter, m	0.01
D	Reactor diameter, m	1.53
D_p	Catalyst particle diameter, m	$4 \cdot 10^{-3}$
L_t	Catalyst bed length, m	1
L	Length of the reactor, m	1.25
N	Number of tubes	29,181

Table. Operating conditions and parameters for a fixed – bed reactor for hydrogen production of 720 Kg/day (1 MW of electrical power) at reaction temperature 650 °C



Investment cost

- 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 [7]. **Other apparatuses included in the process simulation have not been taken into account in this cost analysis.**
- The cost analysis is based on the production of hydrogen of 360,000 mol/day (1 MW), resulting in the parameters that are shown in the previous Table. The purchase cost of the cylindrical vessel is calculated by the following equation:

$$C = f_m C_b + C_a$$

- where f_m is a factor for the used material, which plays an important role for the resistance in corrosiveness. In this study, the material is stainless steel 316 and $f_m = 2.1$.

$$C_a = 246D^{0.7936}L^{0.7068}$$

Factor C_a , where D is the diameter of the vessel, in and L is the total length of the reactor, in.

$$W = (t_h^2 + t_h D)\pi L \rho_m$$

The weight of the vessel, lb_m , where t_h is the thickness of the vessel, in and ρ_m is the density of the construction material, lbm/in^3

$$C_b = \exp\left[9.1 - 0.2889 \ln(W) + 0.04576(\ln W)^2\right]$$

Factor C_b

$$C_{tube} = 121.2D_t^{0.99}L_t$$

Cost of a tube, where D_t is the tube diameter, ft and L_t is the bed length, ft.

$$C_{tubes} = NC_{tube}$$

The total cost of the tubes, using the total number of the tubes in the reactor, N

Initial and Optimized Economic evaluation

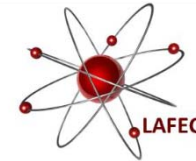
- Economic evaluation of a fixed – bed reactor for hydrogen production from glycerol steam reforming for an 8% Ni/Al catalyst (optimized reactor, $T_{in}=800\text{ }^{\circ}\text{C}$, $W/G=6.0$, $Q_{i,in}=4.0\text{ ml/min}$, $t_{oper}=20\text{ yr}$)

Parameter	Definition	Industrial scale (initial)	Industrial scale (optimized)
D	Reactor diameter, m	1.53	1.22
L	Reactor length, m	1.25	0.67
F_m	Factor for SS 316	2.1	2.1
C_a	Factor, \$	99,740	49,089
t_h	Thickness of the vessel, m	0.013	0.013
ρ_m	Density for SS 316, kg/m^3	8027	8027
W	Weight of the vessel, kg	612	261
C_b	Factor,\$	12,024	8,329
C	Cost of the vessel, \$	124,990	66,579
D_t	Tube diameter, m	0.01	0.01
L	Catalyst bed length, m	1	0.53
C_{tube}	Cost of a tube, \$	1.35	0.66
N	Number of tubes	29,181	14,875
C_{tubes}	Total cost of tubes, \$	39,374	9,820
$C_{total,2000}$	Total cost, \$	164,364	76,399
$C_{total,2015}$	Cost in the year 2015, \$	190,484	88,540
F_{H_2}	Hydrogen production, mol/day	360,000	720,000
C_{ne}	Net annual earnings, \$	-99,331	406,928



Conclusions

- Glycerol production from the biodiesel industry is fast becoming a critical waste management issue – **its valorization is a key factor for the economic sustainability of biodiesel/ bio-refinery plants.**
- Rigorous mathematical optimization techniques are required for optimal reactor design for the utilization of glycerol via the steam reforming reaction.
- A mathematical model for the GSR was developed along with detailed techno-economical optimization techniques that led to optimal reactor design, which proved crucial for optimizing (maximizing) key financial factors, such as net annual earnings or total investment return.



Thank you

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