



“Gheorghe Asachi” Technical University of Iasi, Romania



DESIGN AND PERFORMANCE EVALUATION OF A PLANT FOR GLYCEROL CONVERSION TO ACROLEIN

Ionut Banu*, Georgiana Guta, Costin Sorin Bildea, Grigore Bozga

University Politehnica of Bucharest, Department of Chemical and Biochemical Engineering,
313 Spl. Independentei, 060042 Bucharest, Romania

Abstract

The development of biodiesel industry in the recent past brought into discussion the valorization of glycerol as the byproduct of this technology. Dehydration of glycerol leads to acrolein, mainly used as a raw material in the production of acrylic acid and its esters. Several research efforts dealing with the synthesis of acrolein from glycerol are reported in the literature. However, they are limited to catalyst testing on laboratory scale, no attention being paid to the process feasibility at an industrial scale. The goal of this paper is to fill this gap by presenting an integrated design study of the glycerol dehydration process. A simplified kinetic model was developed based on published data, this one being able to predict with sufficient accuracy the rate of the main reaction and the formation of relevant by-products (carbonyl compounds, hydrocarbons, carbon monoxide and coke). A reaction system was designed, similar to the reactor-regenerator unit usually used in hydrocarbon catalytic cracking (FCC). Moreover, the operating conditions were determined in such a way to maximize the selectivity and ensure the autothermal operation. The reactor effluent is sent to a separation section consisting mainly in distillation units. Due to formation of a low-boiling azeotrope, extractive distillation is employed for separating the acrolein-water mixture, using a part of the fresh glycerol feed as solvent. For a set of typical operating conditions, the separation section was designed in Aspen Plus environment. An economic evaluation study was performed using Aspen Economic Evaluation module, following which an acrolein price of 1.13 EUR/kg was determined. By comparing this value with the market one of 3.3 EUR/kg, the feasibility of the proposed process from the economical point of view will be emphasized.

Key words: economic evaluation, glycerol valorization, kinetic model, plant design, reactor-regenerator system

Received: November, 2014; *Revised final:* March, 2015; *Accepted:* March, 2015

1. Introduction

The continuous increase in energy demand corroborated with the accentuate depletion of the fossil fuels resources, made the scientific world to give more attention to conversion of renewable and bio-degradable resources to bio-fuels and value-added chemicals.

The biodiesel industry knew a considerable development in the last decade, 1.6% of transport fuel used worldwide being represented by liquid biofuels (Nogueira, 2011). Considered as the most important biofuel, the biodiesel is produced from natural triglycerides (vegetable oils or animal fats)

and methanol through a catalytic transesterification process using either methanol or ethanol as a reagent (Corma et al., 2008; Olivieri et al., 2013). The byproduct of biodiesel industry is glycerol, produced with a ratio of 1 kg of glycerol to 10 kg of biodiesel (McNeil et al., 2012). The glycerol resulting from biodiesel industry, usually known as “raw glycerol” is an aqueous solution containing 80-85 wt.% glycerol. This raw glycerol can be subjected further to advanced separation processes to produce pure glycerol, but the purification processes can be rather difficult to implement, expensive and inefficient from the energetic point of view. Among the purification processes worth to be mentioned vacuum distillation

* Author to whom all correspondence should be addressed: e-mail: i_banu@chim.upb.ro; Phone: (+)4 021 402 3938

at pressures of 10^{-5} bar and 120°C , refining on ion exchange resins, membrane separation etc. (Bozga et al., 2011). As reported by Talebian-Kiakalaieh et al. (2014), over 1.54 million ton of glycerol is anticipated to be produced in 2015. Due to the high amount of glycerol released on the market, new utilizations of this chemical compound as “raw glycerol” have to be explored. The valorization of glycerol will produce also a decrease in biodiesel price from 0.63 to 0.35 USD/L as reported by Talebian-Kiakalaieh et al. (2014). Nowadays, glycerol has over two thousand different applications as pure compound in food and cosmetic industry, pharmaceuticals and personal care products industry, solvent or as a major ingredient in toothpastes as reported by Tan et al. (2013).

Several processes has been proposed for glycerol valorization, among them being worth to mention its conversion into acetals, steam reforming to obtain synthesis gas, conversion to acrolein and propane diols (Zaharia et al., 2013). Acrolein, an important chemical compound, is used as an intermediary in acrylic acid and its derivatives synthesis, methionine synthesis, as a monomer for acrylic resins or as a reagent in herbicides industry (Bozga et al., 2011). Glycerol can be converted to acrolein by dehydration in gas or liquid phase, using homogeneous or heterogeneous catalysts (Gu et al., 2012). The commercial technology for acrolein synthesis is based on gas-phase selective propylene oxidation in the presence of BiMoO_x catalyst, in a multi-step process involving utilization of chlorine (a corrosive reagent). The negative environmental impact as well as the economic drawback due to the continuous increase in propylene price, makes the acrolein synthesis from glycerol a commercially and environmentally attractive route (Bozga et al., 2011; Talebian-Kiakalaieh et al., 2014).

Several types of catalysts have been proposed in the literature for the conversion of glycerol to acrolein. Heteropolyacids catalyst supported on silica has been used by Chai et al. (2009). Total glycerol conversion along with selectivity in acrolein of about 87% was reported in the study of Chai et al, but with an increase catalyst deactivation due to coke deposition. Yadav et al. (2013) reported the activity of a dodecatungstophosphoric acid catalyst supported on mesoporous silica. Glycerol conversions of 94% with an acrolein selectivity of 80% were obtained, but severe catalyst deactivation due to coke deposition have been reported. The most promising type of catalysts for glycerol dehydration to acrolein is zeolites, materials possessing large surface area and sufficient acid sites. Gu et al. (2012) tested H-Beta, HY and HZSM-5 zeolites and among them, the latter shown a good catalytic activity in acrolein synthesis, due to the porous structure that ensure a significant specific surface area

In order to develop a kinetic model for the acrolein synthesis process from glycerol, detailed information about the distribution of by-products in typical operating conditions is required. From our

knowledge, there are only few studies in the literature reporting information about the by-products produced in glycerol dehydration to acrolein process. Sabater-Prieto (2007) used a WO_3/ZrO_2 catalyst, to perform the process in a fixed-bed reactor. Acetaldehyde, phenol, acrolein, propanal, acetone, hydroxyacetone have been identified in the reaction mixture, for reaction temperatures in the range $230 - 280^{\circ}\text{C}$ and atmospheric pressure, using aqueous glycerol solution of 20 wt %. Even if the catalyst deactivation plays an important role in the mentioned process, no relevant information can be extracted from the study of Sabater-Prieto (2007).

A comprehensive study regarding glycerol dehydration on a HZSM-5 catalyst was reported by Corma et al. (2008). A circulating bed reactor that allows catalyst regeneration in a continuous way was used and glycerol conversions over 86 % with selectivities in acrolein up to 62 %. A reaction scheme accounting for dehydration, cracking, and hydrogen transfer reactions catalyzed by the acid sites of the zeolite was reported. Acrolein was the major product, short olefins, aromatics, acetaldehyde, hydroxyacetone, acids, and acetone were identified and accounted through a complex reaction network. In order to develop a kinetic model, extensive information about reaction products distribution is required.

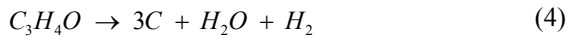
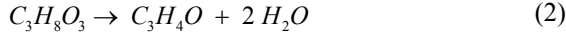
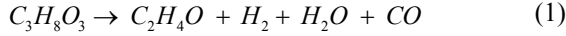
From our knowledge, no kinetic model that takes into account the distribution of by-products is reported in the literature. In order to efficiently design a chemical reactor, a representative kinetic model is required, and consequently, a first goal of our study is to develop a kinetic model for the glycerol dehydration to acrolein process. In spite of several research efforts, the acrolein synthesis process by glycerol dehydration is still limited to laboratory scale. The main goal of the present paper is to report and evaluate the conceptual design of a glycerol dehydration plant.

2. Development of a kinetic model

The experimental data, used in the present study to develop a kinetic model for the glycerol dehydration process to acrolein, has been published by Corma et al. (2008). The authors are reporting that the experimental work was performed on two types of reactors, a fixed-bed one and a circulating-bed reactor using a ZSM-5 type catalyst. The operating conditions are presented in Table 1. Several compounds have been identified as reaction byproducts in the mentioned study, among the most important being carbon monoxide, carbon dioxide, alkanes, olefins (ethylene, propylene, butene), acetaldehyde, acetone, 2-propenol, acetol, acids, BTX fractions and coke.

Due to the limited amount of experimental data, in the developed kinetic model the considered reaction products were restricted to acrolein (the main product), carbon monoxide, hydrocarbons (lumped as ethylene), carbonyl compounds (lumped

as acetaldehyde), and coke. The selectivities of glycerol transformation to products and by-products, as well as the glycerol conversion are given in Table 1. Based on the selected reaction products, the global reactions describing the stoichiometry of the glycerol dehydration process are represented by Eqs. (1-4):



The rates of these global reactions were written in terms of partial pressures following the classical power law approach. Each of the four kinetic constants was expressed in terms of two parameters by the Arrhenius relationship (Eq. 5).

$$k_i = A_i \exp\left(-\frac{E_i}{RT}\right) \quad (5)$$

The reactor model used in the estimation was written in the following hypotheses:

- one-dimensional plug flow model
- isothermal regime
- constant physical properties

The mass balance equation written in terms of degree of advancement of reactions is (Eq. 6).

$$\frac{d\xi_{mi}}{dx} = \frac{1}{WHSV} \cdot v_{Ri}^{(m)}; \quad x=0, \xi_{mi}=0, \quad i=1,4 \quad (6)$$

A nonlinear parameter estimation procedure based on the classical least-square method has been developed, and the model error function has the form given by Eq.(7), where y_i represents the experimental (exp subscript) and calculated (c subscript) values of glycerol conversion and the selectivities of its transformation into the byproducts taken into account (Puaux et al., 2007).

$$J = \sum_{i=1}^N e_i^T W e_i; \quad e_i = y_{\text{exp},i} - y_{c,i} \quad (7)$$

The parameter calculation was performed using the MATLAB® “lsqcurvefit” procedure coupled with the “ode15s” integration function. The calculated parameter numerical values are presented in Table 2.

The agreement between the calculated data and the experimental results are emphasized through the parity diagrams of the glycerol conversion (Fig. 1a) and selectivities of the products and byproducts (Fig. 1b). The results given in the parity diagram shows a good agreement between calculated and experimental conversion values as well as for the selectivities used in the estimation calculations. This finding is also supported by a very good correlation coefficient ($R^2=0.973$). The estimated parameter values are presented in Table 2.

Table 1. Experimental data used in kinetic model development (Corma et al., 2008)

Exp	Temperature, [K]	COR, [kg cat / kg feed]	WHSV, [h-1]	t_0 [s]	σ_{CO}	σ_{Hc}	$\sigma_{Acrolein}$	σ_{Coke}	$\sigma_{Carbonyl}$	X_G
1	773	11	431	0.7	0.104	0.094	0.39	0.062	0.35	1
2	773	48	55	1.4	0.16	0.179	0.232	0.177	0.252	1
3	923	45	121	0.7	0.268	0.296	0.11	0.057	0.269	1
4	563	12.6	282	1	0.034	0.019	0.588	0.206	0.153	0.98
5	623	5.6	1243	0.5	0.019	0.016	0.589	0.078	0.298	0.89
6	623	10.7	360	1	0.034	0.024	0.588	0.122	0.232	1
7	623	11.5	335	0.9	0.034	0.025	0.621	0.15	0.17	1
8	623	5.4	1315	0.5	0.021	0.019	0.591	0.101	0.268	0.86
9	623	9.9	388	0.9	0.029	0.028	0.586	0.162	0.195	0.97

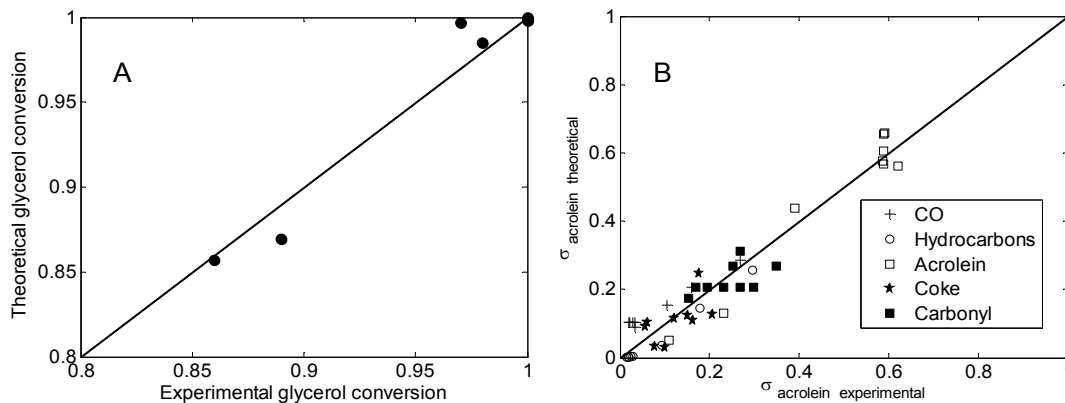


Fig. 1. Parity diagrams for conversion (A) and selectivities in byproducts (B)

Table 2. Estimated kinetic parameters

Chemical reaction	1	2	3	4
A_i , kmol kgcat ⁻¹ s ⁻¹ atm ⁻¹	3.75·10 ⁴	1.05·10 ⁴	6.31·10 ⁴	1.92·10 ²
E_i , kJ kmol ⁻¹	3.79·10 ⁴	2.7·10 ⁴	6.62·10 ⁴	1.05·10 ⁴

3. Design of the acrolein synthesis plant

The conceptual design of the glycerol dehydration plant was performed following the hierarchical procedures detailed in references (Dimian and Bildea, 2008; Dimian et al., 2014). In order to provide relevant details, the study will be divided in two parts, one regarding the analysis of the process in a reactor-regenerator system and the second dedicated to the design of the separation section to produce products with high purity. In this work, it was designed a glycerol dehydration plant with a production capacity of 100 000 t/y.

3.1. Analysis and design of the reactor-regenerator system

Due to the significant catalyst deactivation, Corma et al. (2008) proposed that the glycerol dehydration process to be carried out in a circulating bed reactor with continuous catalyst regeneration, a system similar with the one used in the fluid catalytic cracking of hydrocarbons. The schematic diagram of the reactor is given in Fig. 2. The aqueous solution of glycerol (80 wt %) is fed at the reactor inlet along with the regenerated catalyst and a dispersion steam flowrate that will enhance the catalyst transport over the reactor length and the vaporization of glycerol feed. The circulating bed reactor model was written in the following hypotheses: one-dimensional plug-flow of the gas phase and adiabatic regime, constant physical properties, gaseous phase and catalyst has the same temperature.

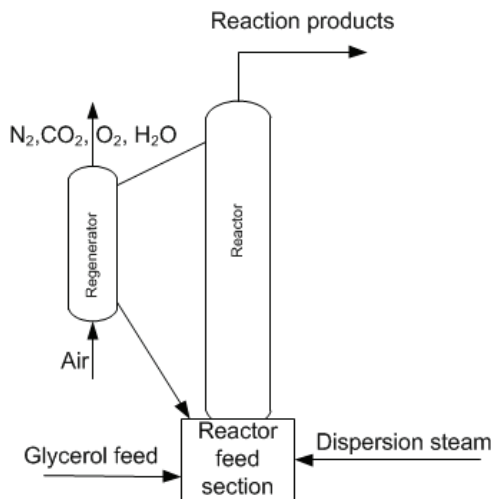


Fig. 2. Diagram of the reactor-regenerator system

The vaporization of the reaction mixture at the reactor inlet was considered instantaneous. The reactor model consisting in mass balance equations, thermal balance and pressure drop equations is expressed by differential Eqs. (8-10).

$$\frac{d\xi_{m,i}}{dx} = \frac{1}{WHSV} v_{R,i}^{(m)}; x = 0, \xi_{m,i} = 0, i=1,4 \quad (8)$$

$$\frac{dT}{dx} = \frac{(1-\varepsilon)\rho_{cat} A_t L \sum_i (-v_{R,i} \Delta H_{R,i})}{D_{m,sol} c_{s,g} + F_{cat} c_{s,cat}}; x = 0, T = T_r \quad (9)$$

$$\frac{dp}{dx} = -\rho_{cat} g(1-\varepsilon)L; x = 0, p = p_0 \quad (10)$$

The weight-hourly space velocity (WHSV) and the catalyst residence time have been expressed by Eqs. (11) and (12).

$$WHSV = \frac{D_{m,sol}}{t_{0,cat} D_{m,cat}} \quad (11)$$

$$t_{0,cat} = \frac{xL A_t (1-\varepsilon) \rho_{cat}}{D_{m,sol} COR} \quad (12)$$

The reaction rates were considered to be affected by the catalyst deactivation due to coke deposition by a function φ , depending on the temperature and catalyst residence time, with the decay coefficient expressed by an Arrhenius relation as for the FCC process (Ahari et al., 2008) (Eq. 13).

$$\varphi = \exp(-at_{0,cat}); a = a_0 \exp\left(\frac{-E_{cat}}{R_G T}\right) \quad (13)$$

In order to evaluate the possibility to operate the reactor in an autothermal regime, the thermal balance equations for reactor and regenerator were written. The necessary heat required for rising up the catalyst temperature comes from the coke combustion, according to the Eq. (14).

$$D_{m,cat} c_{s,cat} (T_{reg} - T_{i,reg}) + D_{m,aer} c_{s,aer} (T_{reg} - T_a) = D_{m,cat} c_{coke} X_{coke} (-\Delta H_{R,coke}) \quad (14)$$

The coke composition was taken as 92 % carbon and 8 % hydrogen (Corma et al., 2008). The amount of air necessary for the coke combustion was calculated from a stoichiometric relation, considering the combustion products to be only in CO₂ and H₂O, and taking into account a 20% (mol) excess of oxygen. The evaluation of thermal balance for the reactor took into account that the heat transported from the regenerator with the catalyst (at the regeneration temperature) is used for feed heating up, vaporization and raising further temperature to the required value for the reaction to be performed in adiabatic regime. The global heat balance equation for the regenerator is given by Eq. (14).

$$D_{m,cat}c_{s,cat}(T_{reg}-T_{e,r})=D_{m,G}c_{s,GL}(T_{vap}-T_{go})+D_{m,W}c_{s,WL}(T_{vap}-T_{go})+D_{m,G}\lambda_G+D_{m,W}\lambda_W \\ +D_{m,steam}c_{s,W}(T_r-T_s)+D_{m,G}c_{s,Gl}(T_r-T_{vap})+D_{m,W}c_{s,WV}(T_r-T_{vap})+Q_{react} \quad (14)$$

The reaction enthalpies calculated by using Kirchhoff law (Reid et al., 1987) were used to evaluate the reaction thermal effect by Eq. (15).

$$Q_{react}=\frac{D_{MC}}{3}\cdot\Delta H_{R,4}+D_{M,jc}\cdot\Delta H_{R,3}+(D_{M,A}+D_{M,jc})\cdot\Delta H_{R,2}+D_{M,carbonyl}\cdot\Delta H_{R,1} \quad (15)$$

In order to determine the reactor geometrical characteristics, a specific mass flowrate similar with the one in the FCC process was considered. The reactor diameter was evaluated by expressing the reactor cross-section by Eq. (17).

$$A_t=\frac{D_{m,tot}}{D_m} \quad (17)$$

The reactor length was determined from an iterative study having as main goal the evaluation of the regeneration temperature required for feed vaporization. The values of the geometrical characteristics of the circulating-bed reactor, as well as the physical properties and other data used in the simulation are presented in Table 3.

The value of the regeneration temperature determined by iterative calculations is 645 °C, value that ensure the efficient catalyst regeneration, being close to the ones implemented in the hydrocarbon catalytic cracking process.

The reactor simulation results in terms of glycerol conversion, temperature profile, selectivity in acrolein and coke concentration is presented in Fig. 3. Results evidence a total glycerol conversion at the reactor outlet (Fig. 3a) as well as a good selectivity in acrolein (around 44 %). Due to the reaction endothermicity, the reactor temperature is decreasing from the inlet to the outlet by 100 °C. The calculated coke concentration on the catalyst is relatively low (1.1 %), but even this small amount is sufficient to acquire the autothermal regime inside the reactor.

3.2. Design of the separation section

The design and performance evaluation of the separation section for the acrolein synthesis plant was performed in Aspen Plus environment. The proposed process flowsheet is presented in Fig. 4. To design the separation equipments, the components were ordered by their boiling points (Table 4), and the potential outlet streams were grouped into products (acrolein) and by-products (gases, carbonyl compounds).

Table 3. Reactor simulation data

Data	Symbol	Value	Unit	References and observations
Catalyst to oil ratio	<i>COR</i>	5.4	kg kg ⁻¹	Average value from Corma et al. (2008)
Glycerol feed flowrate	<i>D_{m,sol}</i>	18	kg s ⁻¹	Calculated
Dispersion steam flowrate	<i>D_{m,steam}</i>	1.8	kg s ⁻¹	Calculated
Catalyst density	<i>ρ_{cat}</i>	720	kg m ⁻³	ZSM-5 catalyst density
Reactor diameter	<i>D</i>	0.3	m	Calculated
Reactor height	<i>L</i>	10	m	Calculated
Void fraction	<i>ε</i>	0.75	-	Proposed value
Preexponential factor for deactivation constant	<i>a₀</i>	59100	s ⁻¹	Ahari et al. (2008)
Catalyst deactivation activation energy	<i>E_{cat}</i>	67210	kJ kmol ⁻¹	Ahari et al. (2008)
Catalyst specific heat	<i>c_{s,cat}</i>	1.2	kJ kg ⁻¹ K ⁻¹	Nakasaka et al. (2012)
Air specific heat	<i>c_{s,aer}</i>	1	kJ kg ⁻¹ K ⁻¹	Reid et al. (1987)
Air temperature at regenerator inlet	<i>T_a</i>	250	°C	Proposed value
Coke conversion in regenerator	<i>X_{coke}</i>	90	%	Proposed value
Carbon combustion enthalpy	<i>ΔH_{c,C}</i>	31500	kJ kg ⁻¹	Corma et al. (2008)
Hydrogen combustion enthalpy	<i>ΔH_{c,H}</i>	115000	kJ kg ⁻¹	Corma et al. (2008)
Glycerol vaporization enthalpy	<i>λ_{V,G}</i>	635	kJ kg ⁻¹	Aspen Hysys V 8.4 database
Water vaporization enthalpy	<i>λ_{V,W}</i>	900	kJ kg ⁻¹	Aspen Hysys V 8.4 database
Glycerol specific heat	<i>c_{s,GL}</i>	4.1	kJ kg ⁻¹ K ⁻¹	Aspen Hysys V 8.4 database
Water specific heat	<i>c_{s,W}</i>	6.9	kJ kg ⁻¹ K ⁻¹	Aspen Hysys V 8.4 database

Table 4. Reaction products destination and boiling points

Compound	Boiling point, °C	Destination
Hydrogen	-252.87	by-product
Carbon monoxide	-191.5	by-product
Hydrocarbons (C ₂ H ₄)	-103.7	by-product
Carbonyl compounds (C ₂ H ₄ O)	20.2	by-product
Acrolein	53	product
Water	100	recycle
Glycerol	290	recycle

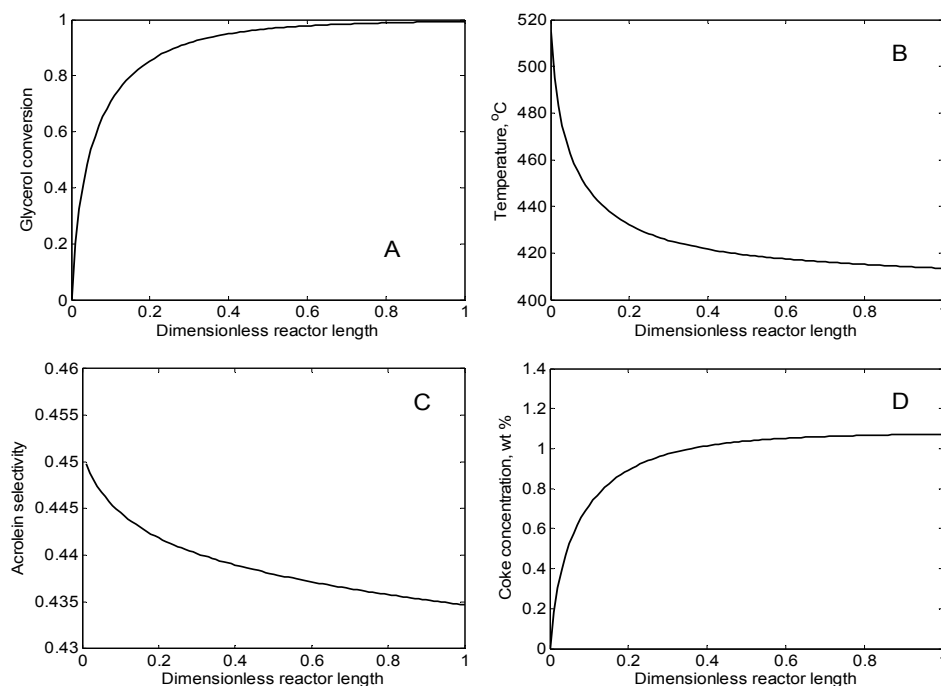


Fig. 3. Reactor simulation results

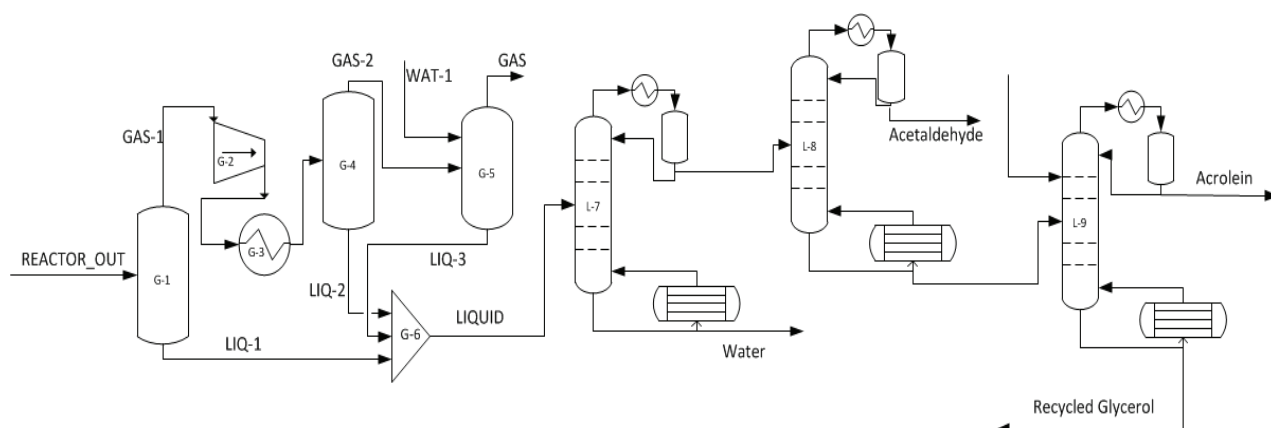


Fig. 4. Separation section flowsheet

In order to separate the gaseous components from the reactor effluent, a gas-liquid split section was proposed. Due to the low boiling point of the carbonyl compound present in the mixture, a compressor (G-3) is used to raise the operating pressure up to 10 bars, to ensure a separation of the acetaldehyde from the gaseous stream.

After a second high-pressure flash-separation, to acquire the complete removal of the gaseous components from the LIQUID stream, an adsorption column is used, with water as the adsorbent. The mass balance for the gas-separation section is presented in Table 5. The data emphasize the efficiency of the gas-separation, the LIQUID stream containing more than 95 % (acrolein, acetaldehyde) of the compounds of interest coming out from the reactor.

The separation of liquid phase was carried out in a series of distillation columns, where the components are separated by the “lights out first” rule. The column L-7 separates the heavy component

(water) from the LIQUID stream, the distillate stream consisting in mainly acrolein and acetaldehyde. The second distillation column (L-8) is removing the light component (acetaldehyde) in the distillate stream, with a purity of over 99 %.

The challenge in the proposed separation section remains the separation of the acrolein-water azeotrope that is to be broken in the distillation column L-9.

To achieve this separation, an extractive distillation is implemented, using pure glycerol as extracting phase, given the fact that the azeotrope glycerol-water is more stable than the previous one. The advantage of using this technique is the subsequent use of the glycerol-water solution resulting as the bottom stream in the distillation column L-9, as a feed for the dehydration reactor. The resulting top stream contains over 98 % acrolein as pure compound. In order to emphasize the efficiency of the liquid separation section, the mass balance for the main streams is presented in Table 6.

Table 5. Mass balance for gas-separation section

<i>Property</i>	<i>Reactor-out</i>	<i>Gas</i>	<i>Liquid</i>	<i>Wat-1</i>
Temperature, °C	410	34.4	23.7	20
Pressure, bar	1	10	10	10
Total mass flow, kg/hr	67768.40	6947.02	66225.9	5404.58
Components mass flow kg/hr				
Glycerol	326.33		326.33	
Carbonyl compounds	9461.56	288.54	9173.02	
Acrolein	13623.59	124.66	13498.9	
H ₂	628.54	620.04	8.495	
Water	37473.22	50.75	42827.0	5404.58
CO	6121.84	5736.51	385.32	
Hydrocarbons	133.31	126.50	6.807	

Table 6. Mass balance for the liquid separation section

<i>Property</i>	<i>Separation in</i>				<i>Separation out</i>			
	<i>REACTOR_OUT</i>	<i>WAT-1</i>	<i>ADS_GLY</i>	<i>Recycled glycerol</i>	<i>Acetaldehyde</i>	<i>Acrolein</i>	<i>Gases</i>	<i>Water</i>
Temperature, °C	410	20	80	115.5	23.8	51.9	33.3	148.5
Pressure, bar	1	10	1	1	2	1	2	5
Mole Flow, kmol/hr	3076.5	300	40	11362	203.7	241	551.1	2307.02
Total Mass Flow, kg/hr	67768.4	5404.8	3683.7	5009.1	8955.3	13335.3	7554.4	42002.5
Component mass flow, kg/hr								
Glycerol	326.3		3683.8	3683.7		trace	trace	326.3
Carbonyl compounds	9461.5			trace	8911.1	9.84	485.4	55.1
Acrolein	13623.5			trace	19.0	13243.5	146.4	214.6
H ₂	628.5				0.02		628.519	0.001
Water	37473.2	5404.5		1325.2	12.5	82.074	51.941	41406.1
CO	6121.8				11.6		6109.7	0.39
Hydrocarbons	133.3				1.02		132.2	0.003

A similar approach with the one presented in the literature (Zaharia et al., 2013) was implemented in our study. The design of the distillation columns was performed by using the DSTWU short-cut model from Aspen Plus (based on Underwood-Fenske and Gilliland approach). To achieve this, a minimum number of trays was specified along with the minimum reflux number. Then the rigorous distillation model “RADFRAC” was used, to adjust the values of the distillate flow rate in order to satisfy the products purities.

The column diameter has been evaluated by using the tray-sizing facility of Aspen Plus environment and the column height was calculated by considering 0.6 m tray spacing, and adding a 20 % distance to accommodate the top and bottom parts. In order to achieve the best separation efficiency with minimum investment, the tray number has been adjusted by closely inspecting the temperature profiles inside the distillation columns.

4. Economic evaluation of the acrolein synthesis plant

The total annual cost of the plant was considered to include the capital cost and energy cost, expressed by Eq. (18).

$$TAC = \frac{\text{capital cost}}{\text{payback period}} + \text{energy cost} \quad (18)$$

The payback period was considered 10 years. The capital cost includes the cost of reactor-regenerator system, mixers, gas-liquid separators, distillation columns (trays and heat exchangers) and other heat exchanging equipment. The economic evaluation was performed using literature data as well as Aspen Economic Evaluation 8.4 module.

In order to perform the evaluation of catalyst cost, an analogy with the “riser” reactor from the FCC process was taken into account, considering that the catalyst amount existent at a given time inside the reactor is about 100 t. It was also considered that the annual catalyst waste due to deactivation is 300 t.

The prices of raw materials taken from the literature are presented in Table 7. The prices of main equipment are given in Table 8.

Due to the complexity of the reactor-regenerator system, the direct cost of this equipment was evaluated by analogy with data presented in the literature (Nexant-Inc., 2006). The prices of utilities, in terms of steam, cooling water and electricity are given in Table 9. Taking into account the calculated data, the total project capital cost is $9.37 \cdot 10^8$ EUR and the utilities price is $1.9 \cdot 10^8$ EUR/yr.

Table 7. Raw materials prices

Raw Materials	Amount (t/yr)	Price/t (EUR)	Total price
Glycerol	450000	400	$1.80 \cdot 10^8$
Water	200800	0.21	42168
Catalyst	400	2200	$8.8 \cdot 10^6$

Table 8. Main equipment costs

Identifier	Operation	Total Direct Cost (EUR)	Equipment Cost (EUR)
G-1	Flash low pressure	183900	32000
G-2	Compressor	$2.85 \cdot 10^6$	$2.64 \cdot 10^6$
G-3	Heat exchanger	92000	18800
G-4	Flash high pressure	109700	19900
G-5	Adsorption column	200900	55400
L-2	Water separation column	3437500	2765100
L-3	Acetaldehyde separation column	6691100	5498200
L-4	Acrolein separation column	10531200	8357400
R-1/R-2	Reactor-regenerator system	2400000	1900000

Table 9. Utilities prices

Utility	Rate	Units	Rate Units	Cost per Hour (EUR h ⁻¹)
Electricity	2378.4	kW	kWh	184.3
Cooling water	9122.5	m ³	m ³ h ⁻¹	289.1
Steam	149.8	t	t h ⁻¹	2684.6

Using the calculated data, the production cost of acrolein was evaluated at 1.13 EUR/kg. Given that the market price is about 3.3 EUR/kg (<https://www.zauba.com/import-ACROLEIN-hs-code.html>, accessed on October 2014), this value show the ability of the proposed technological scheme to be feasible from the economic point of view as well as to produce chemicals with high purities.

5. Conclusions

The glycerol conversion to acrolein on zeolite catalysts is a process that can be performed in a reactor-regenerator system similar with the one used in the catalytic cracking of hydrocarbons.

The evaluation of thermal balance for this reaction system has shown that it can be operated in autothermal regime, lowering in this way the energy requirements.

Given that the main issue in the separation of reaction products is the breakdown of the acrolein-water azeotrope, its separation was achieved using glycerol in an extractive distillation unit.

The advantage of using glycerol is that the reaction products will not be unpurified with compounds non-existent already in the mixture. Taking into account the hypotheses used in the design of this process, the economic evaluation of the whole plant proved the feasibility of the proposed technology, the calculated production price of glycerol being much lower than the market one.

Acknowledgements

The work has been funded by the Sectoral Operational Programme Human Resources Development 2007-2013 of

the Ministry of European Funds through the Financial Agreement POSDRU/159/1.5/S/132395.

Nomenclature

A_t	- reactor cross section, m ²
C_{coke}	- coke concentration on catalyst, wt %
c_s	- specific heat, J kg ⁻¹ K ⁻¹
D_m	- mass flow rate, kg s ⁻¹
\dot{D}_m	- specific mass flow rate, kg s ⁻¹ m ⁻²
D_A	- diffusion coefficient of MMA in air, m ² s ⁻¹
ΔH_R	- reaction enthalpy (heat of reaction), J kg ⁻¹
$\Delta H_{R,coke}$	- coke combustion reaction enthalpy, J kg ⁻¹
k	- reaction rate constant, kmol ⁻¹ ·kg ⁻¹ ·s ⁻¹
p	- reactor pressure, bar
Q_{react}	- reaction thermal effect, kJ/kg
$ro2$	- correlation coefficient;
R_G	- the constant of ideal gas, J·mol ⁻¹ ·K ⁻¹
t_0	- residence time, s
T_a	- temperature of air at the regenerator inlet, K
$T_{e,r}$	- temperature of the catalyst at the reactor, outlet, K
T_{go}	- glycerol solution feed temperature, K
$T_{i,reg}$	- temperature of the catalyst at the regenerator inlet, K
T_r	- reactor temperature, K
T_{reg}	- catalyst regeneration temperature, K
T_s	- dispersion steam temperature, K
T_{vap}	- glycerol solution vaporization temperature, K
v_R	- reaction rate, kmol·kg ⁻¹ ·s ⁻¹
W	- weighting factors,
x	- dimensionless coordinate

Greek Letters

ε	- void fraction of the catalyst bed;
ξ_m	- reaction extent, kmol s ⁻¹ kg ⁻¹

Subscripts

A	- acrolein
$carbonyl$	- carbonyl compound

<i>cat</i>	- catalyst
<i>C</i>	- coke
<i>g</i>	- gas phase mixture inside the reactor
<i>G</i>	- glycerol
<i>GL</i>	- liquid phase glycerol
<i>GV</i>	- vapour phase glycerol
<i>hc</i>	- hydrocarbons
<i>sol</i>	- glycerol solution
<i>W</i>	- water
<i>WL</i>	- liquid phase water
<i>WV</i>	- vapour phase water

References

- Ahari J.S., Farshi A., Forsat K., (2008), A mathematical modeling of the riser reactor in industrial FCC unit, *Petroleum & Coal*, **50**, 15-24.
- Bozga E.R., Plesu V., Bozga G., Bildea C.S., Zaharia E., (2011), Conversion of Glycerol to Propanediol and Acrolein by Heterogeneous Catalysis, *Revista de Chimie*, **62**, 646-654.
- Chai S.-H., Wang H.-P., Liang Y., Xu B.-Q., (2009), Sustainable production of acrolein: Preparation and characterization of zirconia-supported 12-tungstophosphoric acid catalyst for gas-phase dehydration of glycerol, *Applied Catalysis A: General*, **353**, 213-222.
- Corma A., Huber G., Sauvanaud L., Oconnor P., (2008), Biomass to chemicals: Catalytic conversion of glycerol/water mixtures into acrolein, reaction network, *Journal of Catalysis*, **257**, 163-171.
- Dimian A.C., Bildea C.S., (2008), *Chemical Process Design*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
- Dimian A.C., Bildea C.S., Kiss A., (2014), *Integrated design and simulation of chemical processes*, Second edition., Elsevier B.V., Amsterdam, Netherlands.
- Gu Y., Cui N., Yu Q., Li C., Cui Q., (2012), Study on the influence of channel structure properties in the dehydration of glycerol to acrolein over H-zeolite catalysts, *Applied Catalysis A: General*, **429-430**, 9-16.
- McNeil J., Day P., Sirovski F., (2012), Glycerine from biodiesel: The perfect diesel fuel, *Process Safety and Environmental Protection*, **90**, 180-188.
- Nakasaka Y., Tago T., Konno H., Okabe A., Masuda T., (2012), Kinetic study for burning regeneration of coked MFI-type zeolite and numerical modeling for regeneration process in a fixed-bed reactor, *Chemical Engineering Journal*, **207-208**, 368-376.
- Nexant-Inc., (2006), *Equipment Design and Cost Estimation for Small Modular Biomass Systems, Synthesis Gas Cleanup, and Oxygen Separation Equipment; Task 1: Cost Estimates of Small Modular Systems*, San Francisco, California, On line at: <http://www.osti.gov/scitech/biblio/882499>, last accessed oct 2014.
- Nogueira L.A.H., (2011), Does biodiesel make sense?, *Energy*, **36**, 3659-3666.
- Olivieri G., Guida T., Salatino P., Marzocchella A., (2013), A techno-economic analysis of biodiesel production from microalgae, *Environmental Engineering and Management Journal*, **12**, 1563-1573.
- Puaux J.P., Banu I., Nagy I., Bozga G., (2007), A study of L-lactide ring-opening polymerization kinetics, *Macromolecular Symposia*, **259**, 318-326.
- Reid R.C., Prausnitz J.M., Poling B.E., (1987), *The Properties of Gases and Liquids*, 4th edition, McGraw-Hill Book Company, New York.
- Sabater-Prieto S., (2007), *Optimization of the dehydration of glycerol and a scale up in a pilot plant*, PhD Thesis, Rheinisch-Westfälischen Technischen Hochschule Aachen, Germany.
- Talebian-Kiakalaieh A., Amin N.A.S., Hezaveh H., (2014), Glycerol for renewable acrolein production by catalytic dehydration, *Renewable and Sustainable Energy Reviews*, **40**, 28-59.
- Tan H.W., Abdul-Aziz A.R., Aroua M.K., (2013), Glycerol production and its applications as a raw material: A review, *Renewable and Sustainable Energy Reviews*, **27**, 118-127.
- Yadav G.D., Sharma R.V., Katole S.O., (2013), Selective dehydration of glycerol to acrolein: development of efficient and robust solid acid catalyst MUICaT-5, *Industrial & Engineering Chemistry Research*, **52**, 10133-10144.
- Zaharia E., Bildea C.S., Bozga G., (2013), Conceptual design of glycerol hydrogenolysis plant, *Journal of Chemistry (Revista de Chimie)*, **64**, 430-434.