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DESIGN, ECONOMIC EVALUATION AND PLANTWIDE CONTROL OF GLYCEROL KETALIZATION PLANT

Elena ZAHARIA[1], Costin Sorin BÎLDEA[2], Ovidiu MUNTEAN[3]

Preocupările privind valorificarea glicerinei brute în produse cu valoare The chemical transformation of glycerol into more economic valuable products receives increased interest during the recent years. The literature review reveals experimental studies concerning hydrogenolysis, acetalization, ketalization, estherification or etherification of glycerol, with emphasis on new catalysts and optimal reaction conditions. The design, economic evaluation and plantwide control the entire chemical plant is missing. This article fills this gap by presenting the design a glycerol ketalization plant, using acetone as co-reactant. The main product is solketal, an oxygenated (bio)diesel additive which reduces particulate emissions and improves the cold flow properties. Economic evaluation lead to a Total Annual Cost of $478 \cdot 10^3$ US$ / year, for a throughput of 3720 tonnes/year solketal. A plantwide control structure is suggested and evaluated by rigorous dynamic simulation. Aspen Plus and Aspen Plus Dynamics are used as efficient CAPE tools.

Keywords: glycerol, ketalization, conceptual design, dynamic simulation, economic evaluation

1. Introduction

The high growth of biodiesel production has resulted in serious surplus of glycerol in the market. Glycerol is an abundant carbon-neutral source for the synthesis of variety of chemical intermediates, detergents, fuel additives, food, drug and cosmetics industries etc. [1, 2]. Glycerol can be selectively transformed into many derivatives by various catalytic processes such as etherification with isobutene or *tert*-butanol [3], hydrogenolysis [4-6], acetylation with acetic acid or acetic anhydride and ketalization / acetalization with ketones / aldehydes [7, 8]. The products, glycerol *tert*-butyl ethers, acetyl-glycerol, solketal and glycerol acetals have been identified as valuable replacement of fuel additives which depends on depleting sources, price uncertainty and growing environmental concern of petroleum feedstock [9].

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[1] PhD. student, Dept. of Chemical and Biochemical Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: e_zaharia@chim.upb.ro

[2] Prof., Dept. of Chemical and Biochemical Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: s_bildea@upb.ro

[3] Prof., Dept. of Chemical and Biochemical Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: o_muntean@chim.upb.ro

Acetals and ketals of glycerol can be produced via homogeneous catalytic processes using as catalysts strong mineral acids such as H_2SO_4, HF, HCl or p-toluensuphonic acid [10-12], or via heterogeneous catalytic processes using zeolites [13], ion exchange resins such as Ambelyst 15 [14], Ambelyst 35 [7], Amberlyst 47 [15], zirconia and promoted zirconia catalysts, and Ni–Zr supported on mesoporous activated carbon catalyst [1]. Heterogeneous catalysts are environmental friendly and overcome most of the corrosion problems.

Solketal (2,2-dimethyl-1,3-dioxolane-4-methanol) can be used as a fuel additive to reduce the particulate emission and to improve the cold flow properties of liquid transportation fuels [14]. Solketal is obtained by catalytic condensation of glycerol with acetone, in the presence of an acid catalyst (Fig. 1).

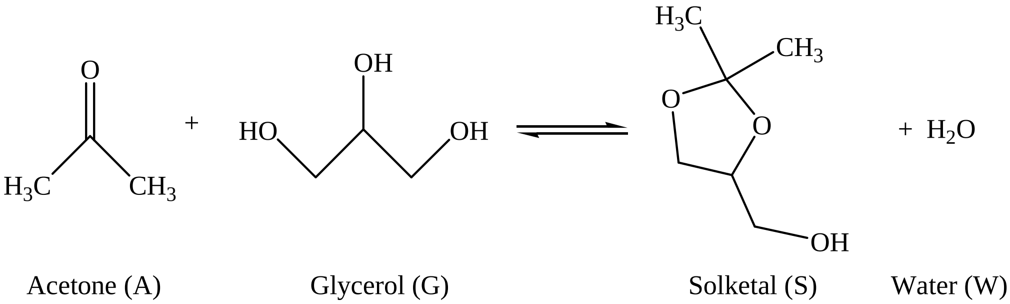

Fig. 1. Glycerol ketalization

In spite of several research efforts, the study of this potentially important reaction was limited to laboratory scale. In this contribution, we report the design of a solketal plant, achieved by using AspenPlus as a CAPE tool. This article is organized as follows. Next section presents the reaction equilibrium and kinetics, and the physical properties of the species involved in the process. Consideration of the Reactor – Separation – Recycle structure of the plant allows performing a preliminary mass balance. The next sections present details of the reactor and separation units, together with detailed stream report, equipment sizing and operating conditions. Then, a plantwide control structure is suggested and evaluated. Finally, the economic evaluation provides the Total Annual Cost.

2. Basis of design

In the following, we will present the design and evaluation of a solketal plant processing 296 kg/h of glycerol, assumed to be the by-product of a 37200 tones / year biodiesel plant. The initial data includes information about the equilibrium and kinetics of the chemical reaction and the physical properties of the species involved in the process.

The reaction follows a LHHW mechanism where two active centers are involved. When Amberlyst 35 is used as catalyst, the following relationships describe the reaction kinetics:

$$r = k\frac{c_G c_A\left(1-\frac{1}{K_c}\frac{c_S c_W}{c_G c_A}\right)}{\left(1+K_W c_W\right)^2} \tag{1}$$

where subscripts *G*, *A*, *S* and *W* refer to glycerol, acetone, solketal and water, respectively.

Experiments performed in a batch reactor, using 1% wt catalyst / glycerol, gave the following kinetic parameters [7]:

$$k = 3.98\times10^{-3}\exp\left(-\frac{55600\ kJ/kmol}{R}\left(\frac{1}{T}-\frac{1}{308}\right)\right)\ \mathrm{m^3/kmol/s} \tag{2}$$

$$\ln K_c = -11.308+\frac{3615.4}{T} \tag{3}$$

$$\ln K_w = -25.1925+\frac{7785.8}{T}\ \mathrm{m^3/kmol} \tag{4}$$

In order to improve the solubility of glycerol in acetone and the homogeneity of the solution, ethanol is added to the reaction mixture [7].

The boiling points of chemical species involved in the process and their azeotropes are presented in Table 1.

Table 1

Boiling points of chemical species and their azeotropes

Component	Boiling point
Binary azeotrope, homogeneous Acetone (0.9866); Water (0.0134)	56.13 °C (unstable node)
Acetone	56.14 °C (saddle)
Binary azeotrope, homogeneous Ethanol (0.9013); Water (0.0987)	78.18 °C (saddle)
Ethanol	78.31 (saddle)
Water	100 °C (saddle)
Solketal	189 °C (saddle)
Glycerol	287.7 °C (stable node)

3. Conceptual design

The Reactor – Separation – Recycle structure of the plant is presented in Fig. 2. Acetone (A) and ethanol (E) are the lightest components of the reactor-outlet mixture; therefore, they are recycled together. We note the formation of acetone-water and ethanol-water azeotropes, therefore this recycle stream will contain significant amounts of water (W). Solketal (S) and water are the intermediate boiling components which can be easily separated from glycerol (G). The large difference between the boiling points allows obtaining high-purity products and glycerol recycle.

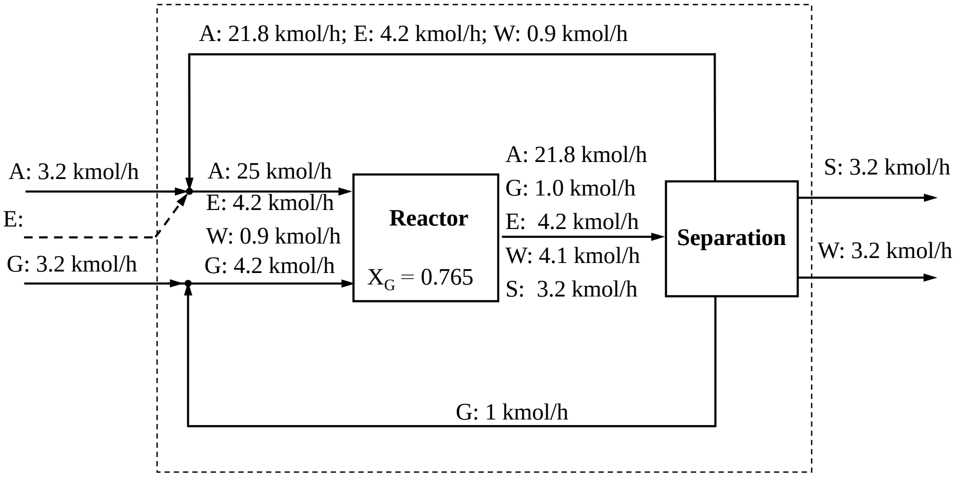

Fig. 2. Mass balance for the reactor – separation – recycle structure of glycerol acetalisation plant (A – acetone; G – glycerol; E – ethanol; W – water; S – solketal)

In order to obtain a preliminary mass balance of the plant, the conversion of the equilibrium-limited reaction must be specified. Fig. 3 presents the temperature dependence of the equilibrium conversion, calculated for different reactor-inlet acetone / glycerol (M_{AG}) and ethanol / glycerol (M_{EG}) molar ratios. The calculations took into account the amount of water in the reactor feed due to ethanol-water and acetone-water azeotropes.

Because the reaction is exothermal, the conversion decreases with temperature. Glycerol conversion is favored by large acetone excess. Adding ethanol as ethanol-water mixture has an opposite effect, because water is also a reaction product.

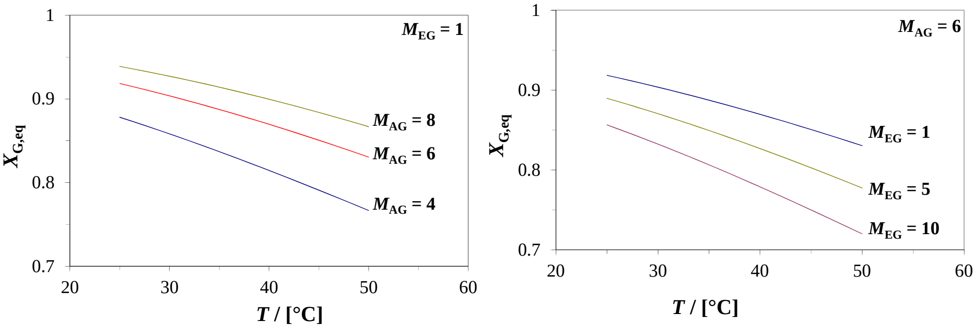

Fig. 3. Glycerol equilibrium conversion vs. reaction temperature, for different values of the Acetone / Glycerol ratio M_{AG} (left) and Ethanol / Glycerol ratio M_{EG} (right).

Based on results presented in Fig. 3, we choose the following reaction conditions: 35 °C; acetone / glycerol ratio – 6; ethanol / glycerol ratio – 1. The design aim for glycerol conversion X_G = 0.765, which is about 0.85% of the equilibrium value. This data allows performing the preliminary balance of the plant. Considering the separation section as a black-box which provides the product streams (solketal, water) and the recycles (glycerol and acetone-ethanol-water), the component flow rates in feed, recycle and product streams can be calculated. A summary of the results is presented in Fig. 2.

3.1. Design of the chemical reactor

Due to the small amount of catalyst that is necessary (1% wt. catalyst/glycerol), the reaction will be performed in a stirred tank reactor. This has the additional benefit of improved mass transfer of the reactants from the liquid bulk to catalyst surface. In order to account for external and internal resistance to mass transfer, we amended the kinetic constant (2) by an effectiveness factor η = 0.2. The catalyst can be retained inside the reactor by placing it in a basket, separation in a cyclone or an external decanting unit. The mathematical model consists of mass balance equations (5)-(6). The species concentrations c_k from the reaction rate (1) were calculated by assuming the following molar volumes (in m^3/kmol): 0.0732 (glycerol), 0.0740 (acetone), 0.0582 (ethanol), 0.0181 (water), 0.1243 (solketal). The reactor-inlet flow rates $F_{k,1}$ were taken from the preliminary mass balance (Fig. 2). A conversion X_G = 0.765 was specified. Solution of equations (5)-(8) leads to a reaction volume V = 3.4 m^3. In order to account for performance degradation due to additional amount of water being recycled, a volume of 4 m^3 will be used.

$$F_{k,2} - \left(F_{k,1} + \nu_k \cdot \xi\right) = 0, \text{ k = G, A, E, W, S} \qquad (5)$$

$$\xi - V \cdot \eta \cdot r\left(c_k\right) = 0 \qquad (6)$$

$$X_G - \frac{F_{G,1} - F_{G,2}}{F_{G,1}} = 0 \tag{7}$$

$$c_k = \frac{F_{k,2}}{\sum_k V_{\mu k} \cdot F_{k,2}} \text{ , } k = G, A, E, W, S \tag{8}$$

3.2. Design of the separation section

To design the separation section, the species found in the reactor effluent were ordered by boiling points points (Table 1) and the structure of the separation section was decided (Fig. 4). The separation-outlet streams are the product (solketal), by-product (water) and two recycles (acetone-ethanol-water and glycerol). Distillation was chosen as separation method, following the "lights out first" heuristic. Each column was designed using the rigorous RADFRAC model from AspenPlus. The first column (COL-1) separates the light components (acetone and ethanol) from the heavy ones (water, solketal and glycerol). Besides acetone (0.811 molar) and ethanol (0.156), the distillate contains some amounts of water, due to azeotropes formation. The bottom stream, containing water, solketal and glycerol is sent to the second column (COL-2), from which water is obtained as distillate (0.999 purity). The remaining mixture is further separated in column COL-3 to provide the solketal product as high-purity distillate and the glycerol recycle as bottoms.

The tray-sizing facility of AspenPlus was used to find the columns diameter. The height of the columns was calculated considering 0.6 m tray spacing and allowing 20% for the top and bottom parts. AspenPlus simulation also provided the reboiler and condenser duties. The condenser and reboiler areas were estimated considering a heat transfer coefficient of 500 W/m^2/K and a temperature difference of 20 degrees. The flow rate of cooling water was calculated considering a 10 degrees temperature increase.

The details of the separation section and the distillation columns sizing are presented in

Fig. 4 and Table 2. Detailed stream results are given in Table 3.

Table 2

Unit sizing and economic evaluation

Reactor		**REACTOR**	
Temperature / [°C]		35	
Pressure / [bar]		2	
Volume / [m^3]		4	
Flow / [kg/h]		2049	
Installed cost / [10^3 US$]		81.04	
Separation columns	**COL-1**	**COL-2**	**COL-3**
Number of trays	23	11	6

Reflux ratio	4	2	0.169
Distillate : Feed ratio	0.78	0.434	0.765
Diameter / [m]	0.9	0.3	0.45
Reboiler duty / [kW]	1227	137	38
Condenser duty / [kW]	- 1172	- 110	- 67
Installed cost / [10^3 US$]	553.05	116.27	75.01
Utilities / [10^3 US$ / year]	264.13	28.23	10.10
Heat exchanger		**HEATER**	
Temperature in / [°C]		54.1	
Temperature out / [°C]		35	
Pressure / [bar]		2	
Heat duty / [kW]		26	
Installed cost / [10^3 US$]		14.98	
Utilities / [10^3 US$ / year]		15.67	
Mixers	**MIX-A**		**MIX-G**
Temperature / [°C]	53.5		68.9
Pressure / [bar]	1		0.064
Volume Flow / [m^3/h]	2.197		0.313
Installed cost / [10^3 US$]	23.46		6.97

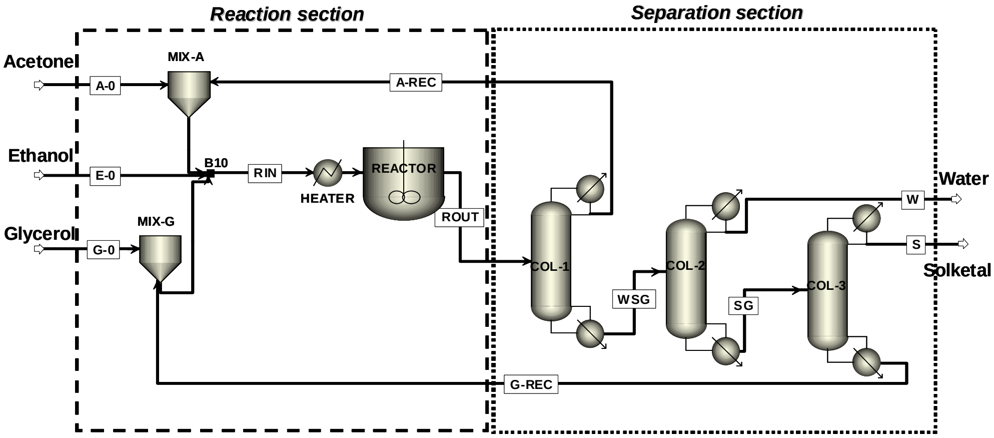

Fig. 4. Flowsheet of the glycerol ketalization plant

Table 3

Stream table

Stream name	G-0	A-0	A-REC	G-REC	RIN
Temperature / [ºC]	25	25	57	194	35
Pressure / [bar]	1	1	1	0.064	2
Mole flow / [kmol / hr]	3.22	3.22	26.87	0.99	34.29
Mass flow / [kg / hr]	296.2	186.8	1474.5	91.0	2048.7
Mole fraction					
GLYCEROL	1	0	0	1	012

ACETONE	0	1	0.81	0	0.73
WATER	0	0	0.03	0	0.03
SOLKETAL	0	0	0	0	0
ETHANOL	0	0	0.16	0	0.12

	ROUT	**WSG**	**SG**	**W**	**S**
Temperature / [ºC]	35	128	199.5	99	107
Pressure / [bar]	2	1.24	1.12	1	0.05
Mole flow / [kmol / hr]	34.29	7.42	4.20	3.22	3.22
Mass flow / [kg / hr]	2048.7	574.2	516.1	58.1	425.1
Mole fraction					
GLYCEROL	0.03	0.13	0.23	0	0
ACETONE	0.64	0	0	0	0
WATER	0.12	0.43	0	1	0
SOLKETAL	0.09	0.43	0.77	0	1
ETHANOL	0.12	0	0	0	0

4. Plantwide control

The plantwide control scheme is shown in Fig. 5. The glycerol feed rate is given by an upstream unit. The ratio between the reactor-inlet acetone and glycerol flow rates is set in a feedforward manner. The amount of fresh acetone is set by the level controller of the MIXER vessel. Reaction temperature and reactor levels are controlled by the duty and outlet flow, respectively. Control of the distillation columns is standard: condenser duty controls the pressure; levels in the reflux drum and column sump are controlled by the distillate and bottoms rate, respectively; a temperature in the stripping zone is controlled by the reboiler duty; the reflux is constant. Details of the control loops and controller tuning are given in Table 4.

Results of dynamic simulation are presented in Fig. 6. Starting from steady state, the production rate is increased (top diagrams) or decreased (bottom diagrams) by changing the plant-inlet flow rate of glycerol (G-0), from the initial value of 3.2 kmol/ to 4 kmol/h and 2.4 kmol/h, respectively.

Table 4

Solketal plantwide control – controller tuning

Controller	*PV, value & range*	*OP, value & range*	K_c, %/%	T_i, min
Glycerol mixer	Level = 0.625 m 0 … 1.25m	Outlet flow rate = 387.2 kg/h 0 … 774 kg/s	1	60
Acetone mixer	Level = 1.125 m 0.5 … 1.5m	Acetone feed = 3.21 kmol/h 0 … 6.4 kmol/h	1	60
	Outlet flow rate [kg/h] = 4.24 x glycerol mixer outlet flow rate			
Reactor				

	Level = 1.72 m 0 … 3.44 m	Outlet flow rate = 2048.7 kg/h 0 … 4100 kg/h	10	20
	Temperature = 35 °C 20… 50 °C	Duty = -0.0445×10^6 kcal/h -0.1×10^6 … 0 kcal/h	5	6
COL-1				
	Pressure = 1 bar 0.9 … 1.1 bar	Condenser duty = -1.0×10^6 kcal/h 0 … -2.0×10^6 kcal/h	2	12
	Reflux drum level = 1.875 m 0 … 3.75 m	Distillate product = 1474kg/h 0 … 3000 kg/h	1	60
	Sump level = 1.25 m 0 … 2.5 m	Bottoms product = 574.2 kg/h 0 … 1150 kg/h	1	60
	Stage 23 temperature = 99.6°C 90 … 110 °C	Reboiler duty = 1.05×10^6 kcal/h 0 … 2.1×10^6 kcal/h	1	20
COL-2				
	Pressure = 1 bar 0.9 … 1.1 bar	Condenser duty = -0.950×10^6 kcal/h 0 … -0.18×10^6 kcal/h	2	12
	Reflux drum level = 0.5 m 0 … 1 m	Distillate product = 58.12 kg/h 0 … 116 kg/h	1	60
	Sump level = 1.25 m 0 … 2.5 m	Bottoms product = 574.2 kg/h 0 … 1150 kg/h	1	60
	Stage 11 temperature =179.6°C 160 … 200 °C	Reboiler duty = 0.117×10^6 kcal/h 0 … 0.235×10^6 kcal/h	1	20
COL-3				
	Pressure = 0.05 bar 0 … 0.1 bar	Condenser duty= -0.058×10^6kcal/h 0 … -0.12×10^6 kcal/h	20	12
	Reflux drum level = 0.75 m 0 … 1.5 m	Distillate product = 425 kg/h 0 … 850 kg/h	1	60
	Sump level = 0.5 m 0 … 1 m	Bottoms product = 90.98 kg/h 0 … 180 kg/h	1	60
	Stage 7 temperature = 132.3 °C 120 … 150 °C	Reboiler duty = 0.032×10^6 kcal/h 0 … 0.065×10^6 kcal/h	1	20

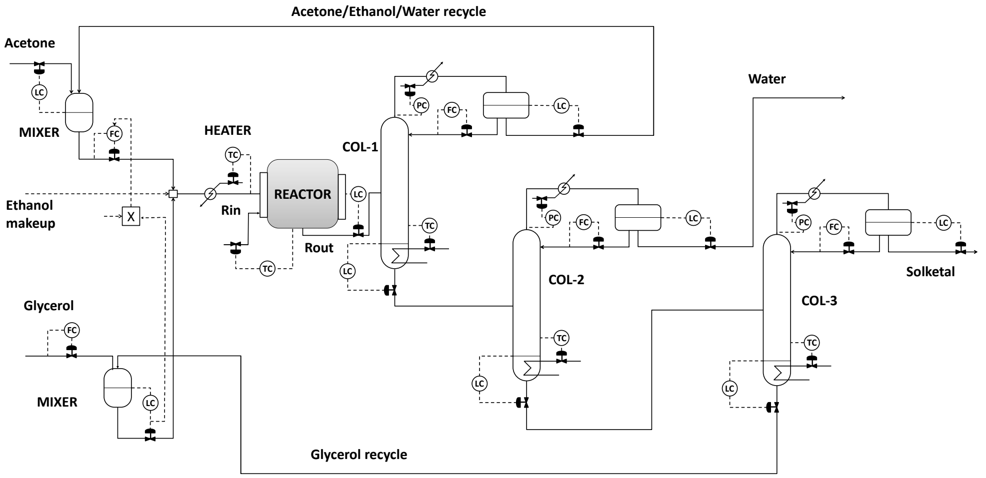

Fig. 5. Plantwide control scheme for ketalization of glycerol with acetone

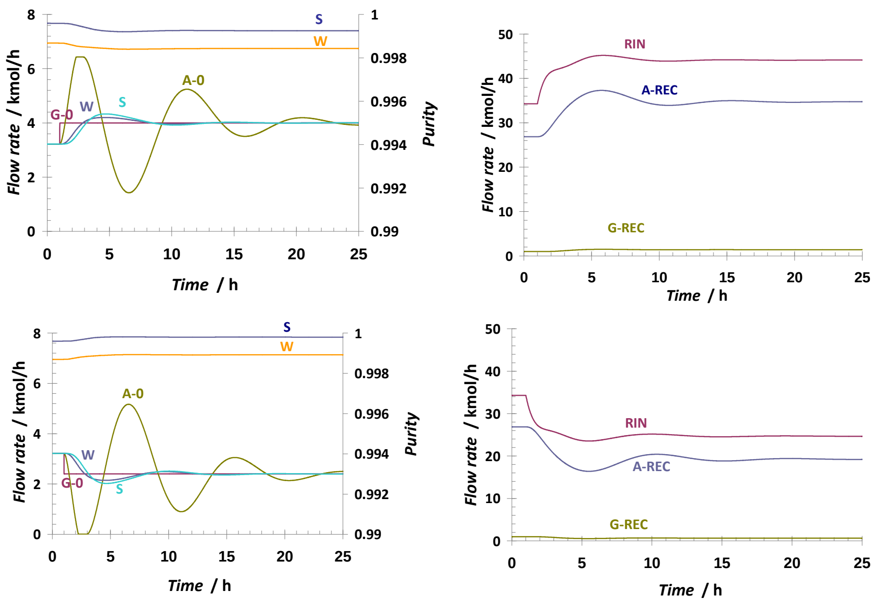

Fig. 6. Solketal plant – dynamic simulation results. Top - production rate increase by 25%; bottom - production rate decrease by 25%

The new production rate is reached in about 8 hours. As more glycerol is fed to the plant, the flow rate of fresh acetone (A-0) is adjusted to the stoichiometric value, although the duration of the transient regime is quite long. The purity of solketal and water products exceeds 0.998.

It should be remarked that other control strategies work equally well. For example, one can keep constant the reactor-inlet flow rate of acetone (instead of flow ratio). When the flow rate of fresh glycerol is available as manipulated variable, one can switch the flow and level control loops around the glycerol mixer.

5. Economic evaluation

The total annual cost of the plant (TAC) was calculated by equation (9):

$$TAC = \frac{\text{capital cost}}{\text{payback period}} + \text{energy cost} \tag{9}$$

A payback period of 5 years is used. The energy cost includes the costs of cooling water (0.08 US$/m^3) and steam ($5\cdot 10^{-6}$ US$/kJ). The capital cost includes the costs of reactor, glycerol mixer, heating and cooling and distillation columns (trays and heat exchangers).

The installed cost for the reactor, distillation columns and vessels was calculated by the following relationships [16]:

$$Installed\ Cost\ (US\$) = \left(M\ \&\ S\ index/280\right)\cdot\left(957.9\cdot D^{1.066}\cdot H^{0.82}\right)\cdot\left(2.18+F_c\right) \tag{10}$$

A M&S index of 1536.5 (year 2011) was used [17]. F_c is a factor that takes into account the material and the pressure.

$$F_c = F_m \cdot F_p \tag{11}$$

The pressure factor is given by (P in bar):

$$F_p = 1 + 0.0074\cdot\left(P-3.48\right) + 0.00023\cdot\left(P-3.48\right)^2 \tag{12}$$

The material factor F_m was taken as 1. The installed cost of the trays for the distillation columns is approximated by the equation:

$$Installed\ Cost\ (US\$) = \left(M\ \&\ S\ index/280\right)\cdot 97.2\cdot D^{1.55}\cdot F_c \tag{13}$$

F_c is a factor that takes into account the tray type (F_t) and the material (F_m). For the distillation columns, $F_t = 0$ (sieve trays) and $F_m = 1.0$ (carbon steel). The installed cost of heat exchangers is calculated by equation:

$$Installed\ Cost\ (US\$) = \left(M\ \&\ S\ index/280\right)\cdot\left(474.7\cdot A^{0.65}\right)\left(2.29+F_c\right) \tag{14}$$

F_c takes into account the material, design type and design pressure.

$$F_c = F_m \cdot \left(F_d + F_p\right) \tag{15}$$

The following values were used: $F_m = 1$ (carbon steel), $F_d = 1.35$ (for reboilers), $F_d = 0.8$ (for fixed-tube), $F_p = 0$ (less than 20 bar). The results of the economic evaluation are presented in Table 3.

6. Conclusions

Solketal can be manufactured by the ketalization of glycerol with acetone. The reaction can be carried on using Amberlyst 35 as catalyst, in a CSTR. The separation section includes three distillation columns. The plant has a good controllability, large production rate changes can be achieved. For a production rate of 3720 tonnes of solketal / year (3.22 kmol/h), the total annual cost of the plant is $478\cdot10^3$ US$/year, from which $304\cdot10^3$ US$/year utilities.

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