Use of Glycerol from biodiesel production: Conversion to added value products
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Use of Glycerol from biodiesel production: Conversion to added value products

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Abstract

A detailed study of main stages of a novel no-conventional process to obtain 1,3-propanediol (*PD*) from glycerol (*Gly*) has been made. Initially the volumetric productivity of *Gly* fermentation with *Klebsiella pneumoniae* bacterium was optimized for one and two continuous stages, where was necessary to study the multiplicity of stable steady states for the fermentation system selecting the conditions where higher concentrations of PD are found; and under optimal operation conditions the outlet PD concentration and the global yield are 0.4833 mol/l and 0.5481 molPD/molGly, respectively. For PD recovery from fermentation broth a no-conventional separation scheme was proposed, which consists first in a reactive-extraction with iso-butyraldehyde (iBAld) for produce 2-iso-propyl-1,3-dioxane (iPDOx) and water. The iPDOx is removed toward the organic phase by the aldehyde that acts simultaneously as reagent and solvent. The yield of reactive-extraction process is 85%. Finally *Static Analysis* (SA) for iPDOx hydrolysis system shows that is possible to obtain PD of high purity and recovery the aldehyde at the 88% in a reactive-distillation tower. SA also allowed obtaining the technological configuration of reactive-distillation tower and this technological synthesis was validated starting from simulations to both infinite/infinite and finite/finite (stages/reflux) conditions, using the ASPEN PLUS® software. For finite conditions the simulations showed that a conversion of 69% and 97.5% is reached for reflux ratios of 5.73 and 9.5 respectively.

Keywords: Glycerol fermentation; 1,3-Propanediol production; Reactive–extraction; Static analysis; Reactive–distillation.

1. Introduction

Glycerol is the lateral product of triglycerides transesterification with methanol for the biodiesel production, which this is obtained in a ratio of 1:10 weight glycerol/Biodiesel, and its a molecule that is easily available from bio-sustainable sources, it furthermore has a high functionality, that makes of glycerol a particularly attractive initiation point for the synthesis of a great number of intermediary and chemical products, like are those derived oxygenated that have a high potential in organic synthesis. Due the increment in the use of materials metylester (i.e. biodiesel) as combustible preservatives, can expected an increment in their production and an inevitable invasion of glycerol in the market, carrying thus an oversupply and consequently a fall of glycerol price, where this would become a feedstock cheaper in the chemical synthesis. For this reason the plants of biodiesel production should work on the transformation of glycerol toward a product with more added values and of high demands. Glycerol oversupply has made fall its price, form that the price of refined glycerol for 1996 was US $1/lb, and in 2003 were US $0.50/lb [*Tyson et-al (2004)*], nowadays the average price is US $0.34/lb [*ICIS pricing (2007)*]. Additionally, 1,3-propanediol is a compound that is produced in large quantities and that also has a remarkable growth in the market as was showed by *Dasari et-al (2005)*, furthermore they indicated that the production is upper to one million annual pounds in United States with an annual growth in the market of 4%..

An analysis about the different possibilities of glycerol transformation available in the bibliography was carried out previously [*Posada and Cardona (2006*)]. This works was made with the purpose of proposing a technological scheme for glycerol exploitation obtained as lateral product in the biodiesel production. The alternatives of glycerol transformation found are: oxidation on metallic catalysts as *Pt*, *Pd* and *Au* with electronic promoters as *Bi* and *Pb*, where from their derived oxygenated the glyceric acid have the highest yield which are between 50 and 70% [*Solomon et-al (1995), Garcia et-al (1995), Gallezot (1997), Barrault et-al (2002), Porta and Prati (2004), Demirel-Gulen et-al (2005), Dimitratos et-al (2005), Hutchings (2005)*]. Hydrogenolysis to glycols on catalysts as *Ru*, *Cu* and *Pt* are other possibilities, but the high rate of degradation of products makes that the yield toward propylene-glycol be lower to 50% [Tessie *(1987), Casale ang Gomez (1993, 1994), Ludwig and Manfred (1997), Lahr and Shanks (2003, 2005), Dasari et-al (2005)*]. For etherification to polyglycerols on zeolites and mesoporous material it was found that it has low conversion and selectivity, where yield toward monoglycerol is near 30%, and furthermore, the products that are obtained have little demand [*Gerald et-al (1993), Lutz et-al (1998), Clacens et-al (2002)*]. Pyrolysis and gasification are two alternatives from which it is possible to obtain products of degradation (as acetaldehyde, formaldehyde, methanol) and synthesis gas (CO and H_2) respectively. Pyrolysis presents the lowest selectivity and conversion with yields lower than 10% for each one of the products [*van Swaaij (2000), Buhler et-al (2002), Matsumura et-al (2005)*]. On the other hand, for the gasification the yield toward synthesis gases this between 40 and 90%. These processes are characterized because they require extreme operation conditions such as temperatures between 700 and 1100K and/or pressures up to 350 bar [*Xu et-al (1996), Antal et-al (2000), Mozaffarian et-al (2004),*

Valliyappan (2004)]. The last possibility found is the bioconversion of the glycerol toward 1,3-propanediol for a great amount of species such as *Klebsiella pneumoniae* [*Solomon et-al (1995), Deckwer (1995), Menzel et-al (1997), Barbirato et-al (1998), Xiu et-al (2002, 2004), Chen et-al (2003)*], *Enterobacter agglomerans* [*Barbirato et-al (1997, 1998)*], *Citrobacter freundii* [*Barbirato et-al (1998)*] and *Clostridium butyricum* [*Barbirato et-al (1998), Himmi et-al (1999), Papanikolaou et-al (2000), González-Pajuelo et-al (2004)*], among others [*Bouvet et-al (1995), tested 1123 microorganisms that represent 126 types of bacterial species and was reduced their study at 8 of these species*]. Furthermore some that can be obtained by genetic modifications as for example *Clostridium acetobutylicum* [*Abbad-Andaloussi et-al (1995), González-Pajuelo et-al (2005)*]. From all these bacteria, *Klebsiella pneumoniae* in its wild form is the most interesting because of their yield, productivity and resistance to both reagents and products. Also operative and economic aspects of all the alternatives were analyzed, such as operation conditions, separation equipment, yields of reactions, and demand of products, finding that the most appropriate of all possibilities is the glycerol bioconversion toward 1,3-propanediol, because additionally this compound has a great demand due to its use as a monomer in the synthesis of several polyesters such polytrimethylene terephthalate (PTT) and polyethylene terephthalate (PET), which improves the chemical and mechanical properties in comparison with other similar monomers. The 1,3-propanediol can also be used commercially as extending of chains for polyurethanes, as lubricant, solvent, and as functional fluids (*i.e. antifreezes, unfreezing and transfer of heat*); besides as additive in foods, cosmetics, liquid detergents, wetter of tobacco, flavoring and fragrances, paintings and animal food, and as precursor in chemical and pharmaceutical industry. Finally the biodegradability of natural plastics containing 1,3-propanediol is higher compared with a totally synthetic polymers [*Barbirato et-al (1998), Deckwer (1995)*].

Another reason for which is important the 1,3-propanediol production is because this is produced conventionally from petrochemistry industry for a variety of routes. For example *(i)* hydroreformilation of ethylene oxide in a acid means with phosphine, water, carbon monoxide and hydrogen, *(ii)* For hydration of acrolein followed for a reduction to 1,3-propanediol [*Kirk-Othmer (1994, 1996)*].and also for chemical routes of low selectivity as *(iii)* the hydrogenolysis over Ru to produces glycols and the etherification over zeolites and mesoporous materials [*Gerald et-al (1993), Lutz et-al (1998), Clacens et-al (2002)*]. Then, based on the previous work of selection of the most appropriate alternative that has been outlined above, for the glycerol transformation obtained as lateral product in the biodiesel production is established the biotransformation using the bacteria *Klebsiella pneumoniae DSM-2026* like the process to evaluate next.

1,3-propanediol purification from fermentation broth is a study case much more complex that the same glycerol fermentation, then a higher effort is required in this sense and on the contrary this problem not has been sufficiently boarded. Historically the 1,3-propanediol recovery has presented many inconveniences due to both its high hydrophilic character and its high boiling point ; for these reasons nowadays the process not has been scale-up at industrial level.

Some patented conventional processes for 1,3-propanediol recovery from the broth of fermentation after a series of separation stages of solids as are microfiltration, ultrafiltration and nanofiltration [*Adkesson et al (2005)*] use a train of distillation towers of high vacuum, but before should be eliminated near 80% of the initial liquid that is basically water [*Ames (2002), Powell et-al (2004)*], and in some cases until 90% of humidity is retired [*Adkesson et al (2005)*], the process continues with two distillation towers, in the first one are retired the compounds that have a boiling point higher than 1,3-propanediol and it operates to an absolute pressure of 55 mmHg, in the second one are retired the components of smaller boiling point that 1,3-propanediol, and it operates to 20 mmHg absolute. Then for the resulting liquid a hydrogenation reaction is carried out [*Seapan et-al (2005)*] to obtain more volatile components and subsequently they pass through other two distillation towers, and again in the first one are retired those with boiling points higher at the 1,3-propanediol, this tower operates to 35 mmHg and in the last one are retired those with smaller boiling point, this last one operates 45 mmHg of absolute pressure, as was the case of the previous towers. An alternative process for 1,3-propanediol recovery is starting from selective adsorbents as zeolites and coal [*Corbin and Norton (2001)*], but these materials are not wholly selective and for this reason a second purification stage is required; these materials also present a low yield of adsorption, only 0.12 g 1,3-propanediol/g zeolite for a total recovery of 1,3-propanediol of 94.7%, with a H-ZSM-5 of average pore size 5.5 Å.

Another bibliographically available focus is a process of reactive-extraction that has as principle to change the hydrophilic character of 1,3-propanediol, starting from the reaction with a carboxylic acid or an aldehyde, this reaction is well-known as *Cyclic Acetalization*, producing *2-alkyl-1,3-dioxanes* that are hydrophobic compounds easily extractable by an organic phase, allowing an effective separation of low energy cost. This way was initially proposed by *Malinowski (2000)* who worked with acetaldehyde as reagent and evaluated a series of solvents as o-xylene, ethylbenzene and toluene. *Liu et-al* (2005, 2006) tested propionaldehyde, butyraldehyde and iso-butyraldehyde, which can act simultaneously as reagent and solvent, and the main advantage that presents this proposal is the requirement of only one compound to carry out both the reaction and the extraction, also the evaluated aldehydes are also less volatile and less soluble in water than those initially proposed.

Now considering that the *Cyclic Acetalization* is an equilibrium reaction, and that the product of interest is 1,3-propanediol the authors *Malinowski (2000)* and *Liu et-al (2005, 2006)* have recommended that this it can be recovered by hydrolysis reaction of *2-alkyl-1,3-dioxane* in a reactive distillation tower, mainly to avoid the problems generated by the chemical equilibrium of reactive system, recovering so much aldehyde as 1,3-propanediol both with high purity. In this way aldehyde would make part of a circuit closed in the system of recovery of 1,3-propanediol from the fermentation broth. This last alternative from a distance presents a great quantity of advantages so much operative as economics with regard to the other ones two alternatives available in the literature, which are: the train of distillation towers of high vacuum and big energetic requirements and the zeolites of low selectivity and

little yield. Additionally this proposed novel for processing scheme of 1,3-propanediol production from glycerol as lateral product presents a great potential for the biodiesel industry, which should be studied completely and with this aim a first operative analysis of global process is made next.

To conclude this section the studies carried out by *Liu et-al (2005, 2006)* shown that the best alternative among the evaluated aldehydes is iso-butyraldehyde, because it is not very soluble in water (11g/100gAgua), has middle boiling temperature (64.3 ºC), and the acetalization product is the less soluble one in water [*Samant (1998)*], in other words it presents the best distribution coefficients among phases; also the reported constant equilibrium is not extremely big, this is advantageous thinking in the later hydrolysis process by reactive-distillation for 1,3-propanediol recovery. Then next the study of glycerol transformation toward 1,3-propanediol is shown, starting from a fermentation with *K. pneumoniae* bacteria continued by a reactive-extraction process with iso-butyraldehyde and the later hydrolysis of *2-iso-propyl-1,3-dioxane* toward the product of interest, 1,3-propanediol and iso-butyraldehyde recovered that it can be recycled.

2. Glycerol Fermentation to 1,3-Propanediol By *Klepsiella Pneumoniae:*

As it was shown above among all the possible bacterial species to carry out the glycerol fermentation toward 1,3-propanediol the most appropriate is *Klebsiella pneumoniae DSM-2026*, given their yield, productivity and resistance to substrate, products and sludge. For this bacteria is known that presents a metabolic overflow of products and consequently inhibition in cellular growth, it carries to a no-lineal phenomenon, like is multiplicity of stable states, hysteresis and oscillations in stability of system [*Xiu et-al (2004)*].

The following kinetic model has been sufficiently explained [*Menzel et-al (1997), Xiu et-al (2002, 2004)*]. The equations (1) to (5) describe material balances for biomass, substrate and products, which are suitable for dynamic state in fermentation of multiple stages and for a feed stream that can contain each one of species that are in the fermentation system:

$$\frac{dX_i^{Out}}{dt} = D_i\left(X_i^{In} - X_i^{Out}\right) + \mu_i X_i^{Out} \tag{1}$$

$$\frac{dC_{G,i}^{Out}}{dt} = D_i\left(C_{G,i}^{In} - C_{G,i}^{Out}\right) - q_{G,i} X_i^{Out} \tag{2}$$

$$\frac{dC_{PD,i}^{Out}}{dt} = D_i\left(C_{PD,i}^{In} - C_{PD,i}^{Out}\right) + q_{PD,i} X_i^{Out} \tag{3}$$

$$\frac{dC_{HAc,i}^{Out}}{dt} = D_i\left(C_{HAc,i}^{In} - C_{HAc,i}^{Out}\right) + q_{HAc,i} X_i^{Out} \tag{4}$$

$$\frac{dC_{EtOH,i}^{Out}}{dt} = D_i\left(C_{EtOH,i}^{In} - C_{EtOH,i}^{Out}\right) + q_{EtOH,i} X_i^{Out} \tag{5}$$

Specific rates of cell growth, consumption substrate and products formation are given by the equations (6) to (11). Where the equation (6) that describes the specific rate of cellular growth represent a kinetic model with inhibition by all substrate and products, as show the kinetic parameters $C_G^*, C_{PD}^*, C_{HAc}^*, C_{EtOH}^*$ that are the critical concentrations, which do reference to the concentration of each component where the biological activity stops.

$$\mu_i = \mu_{\max} \frac{C_{G,i}}{C_{G,i} + K_S} \left(1 - \frac{C_{G,i}}{C_G^*}\right) \left(1 - \frac{C_{PD,i}}{C_{PD}^*}\right) \left(1 - \frac{C_{HAc,i}}{C_{HAc}^*}\right) \left(1 - \frac{C_{EtOH,i}}{C_{EtOH}^*}\right) \tag{6}$$

$$q_{G,i} = m_G + \frac{\mu_i}{Y_G^m} + \Delta q_G^m \frac{C_{G,i}}{C_{G,i} + K_S^*} \tag{7}$$

$$q_{PD,i} = m_{PD} + \mu_i * Y_{PD}^m + \Delta q_{PD}^m \frac{C_{G,i}}{C_{G,i} + K_{PD}^*} \tag{8}$$

$$q_{HAc,i} = m_{HAc} + \mu_i * Y_{HAc}^m + \Delta q_{HAc}^m \frac{C_{G,i}}{C_{G,i} + K_{HAc}^*} \tag{9}$$

$$q_{EtOH,i} = q_{G,i} Y_{(EtOH/G),i}^m \tag{10}$$

$$Y_{(EtOH/G),i}^m = \frac{b_1}{(c_1 + D_i C_{G,i})} + \frac{b_2}{(c_2 + D_i C_{G,i})} \tag{11}$$

For critical concentrations in equation (6) is takes the second series of parameters that was fit by *Menzel et al.(1997)*, which have a deviation global average of 8.6% for 29 evaluated stable states, contrary to the first series of parameters that have a deviation global average of 12.6%, and besides has been fit from data of fermentation with *K. pneumonae* and *C. butyricum*, which were used by *Menzel et-al (1997), Xiu et-al (2002, 2004)*.

The analysis of multiplicity of stable states is carried out as function of two independent variables of operation, which are dilution rate *D* in first fermentation stage and feed glycerol concentration C_{G0}. Where the concentration feed of other one species becomes equal to zero. Figure 1 show different conditions of steady stable state in fermentation system with one single stage only for biomass and 1,3-propanediol, but similar figures can be obtained for residual glycerol, acetic acid and ethanol, where for this case the unstable steady state not has been calculated. Vertical lines in the curves indicate the limit of the region where multiplicity of stable states exists. Dotted line (red) shows the conditions of "*wash out*" of fermentation in a single stage for each dilution rate; this lines gives the extreme conditions of operation i.e. where the dilution rate equals to the rate cellular growth ($\mu_i = D_i$).

To carry out an operative optimization of the process the stable steady states that generate higher concentrations of 1,3-Propanediol in the first tank of fermentation (superior curves in figure 1.b.) are selected, aiming to optimize a process in two stages in continuous, and then this will be the criterion of selection in the mathematical model of fermentation, when calculations are carried out in the region of multiplicity of stable states.

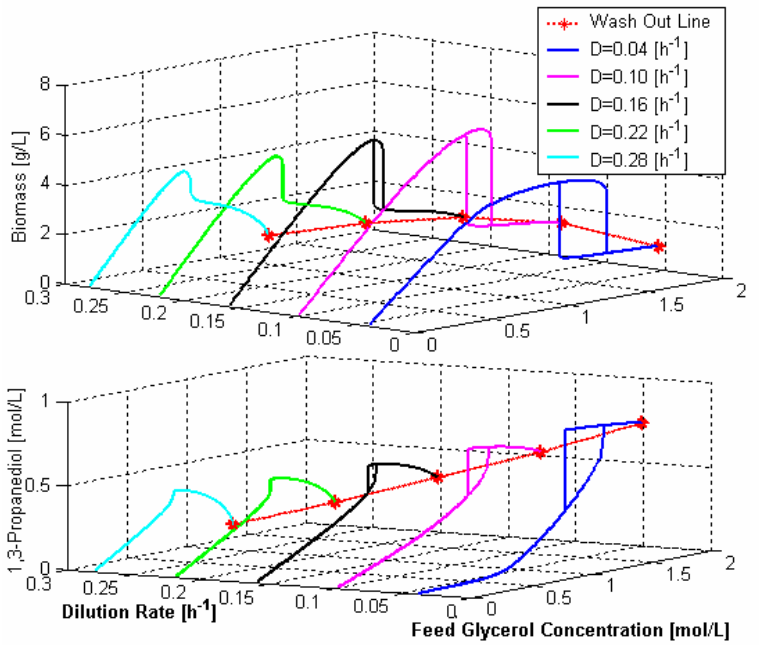


Figure 1: Multiple steady stables states for Glycerol fermentation with K. Pneumoniae, as function of feed Glycerol concentration and dilution rate a) Biomass conc. [g/l]. b) 1,3-Propanediol conc.[mol/l]

The optimization of the volumetric productivity for glycerol fermentation in a process carried out in two continuous stages in series is made in two parts, in the first one the productivity in the first stage fermentation is optimized considering that the only one feed is glycerol in watery solution, therefore this is the first independent variable, the feed glycerol concentration and is take as second independent variable the dilution rate in the first tank. The second part consists on optimizing the productivity in the second tank of fermentation taking only the optimum dilution rate of the first tank that is result of previous calculation and then is taken as independent variables the feed glycerol concentration and the dilution rate in the second tank of fermentation. This way the first function to optimize this given by the equation (12) that is the volumetric productivity referred to conditions of the first fermentation tank:

$$Pr_1 = C_{PD1} D_1 \tag{12}$$

The numeric method used in the optimization to find the operative conditions under which the higher productivity of 1,3-propanediol is reached was *Levenberg-Marquardt* [*Edgar et-al (2001)*] applied to maximum. The figure 2 show with level curves the productivity reached in the first fermentation tank as function of both dilution rate and feed glycerol concentration. The points A, B and the union line indicates a discontinuity in the level surface that is the result of working under the conditions of maximum yield of 1,3-propanediol in the operation zone where multiplicity of stable states occurs; this discontinuity can be seen from the figure 1 as the first vertical line in growing sense of feed glycerol concentration for each one dilution rate. Optimum productivity calculated is 0.1076 mol/(l*h), to a dilution rate of 0.2821 h^{-1} and with feed glycerol concentration of 0.6882 mol/l, under these conditions the respective 1,3-propanediol concentration is 0.3811 mol/l.

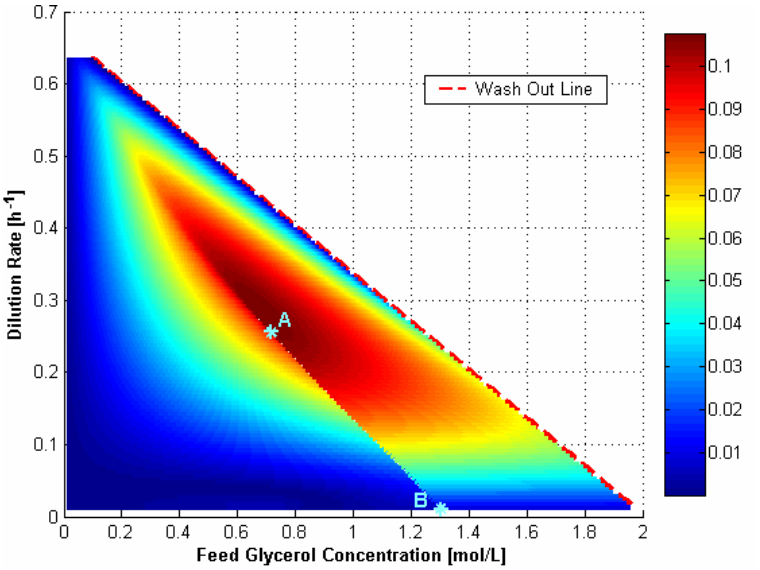


Figure 2: Level curves of 1,3-Propanediol productivity in Glycerol fermentation as function of dilution rate and feed Glycerol concentration, under condition of higher yield toward 1,3-Propanediol.

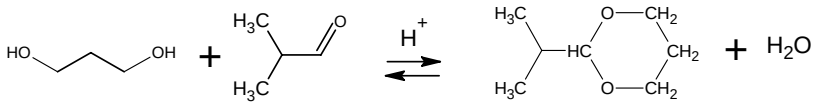
Now to optimize the second stage of fermentation the productivity it is calculated as the change of concentration of 1,3-propanediol by unit of volume like is shown by the equation (13), referred to conditions of the second fermentation stage.

$$\mathrm{Pr}_2 = D_2\left(C_{PD2} - C_{PD1}\right) \tag{13}$$

Mathematical model to optimize the second stage of fermentation requires that the equations (1) to (11) are solved in stable state for each one of the tanks of fermentation. Again the numeric method *Levenberg-Marquardt* [*Edgar et-al (2001)*] is applied, but this time the dilution rate for the first tank is fixed at 0.2821 h^{-1} like it had been indicated previously, where the independent variables are feed glycerol concentration and dilution rate in the second fermentation tank. The result of the optimization of productivity in the second fermentation tank is 0.1128 mol/(l*h), for a dilution rate of 0.79 h^{-1} with a feed glycerol concentration of 0.8817 mol/l and where the outlet concentration of 1,3-propanediol for the first one and second stage of fermentation is 0.3405 and 0.4833 mol/l respectively. This way a global molar yield of the process of 0.5481 1,3-propanediol/glycerol is reached.

3. Recovery of 1,3-Propanediol from the broth of fermentation:

3.1. Reactive-Extraction of 1,3-Propanediol with iso-butyraldehyde: Reactive-extraction is a simultaneous reaction-separation process that has as objective the separation of a component from a liquid mixture, starting from a reversible reaction that changes the physiochemical properties of an objective compound and a second liquid phase that allows the migration of the new one compound to this phase. These systems are governed by two driving forces, the solubility of both components in each phase, and the given by the chemical reaction.



(14)

1,3-Propanediol cyclic acetalization with iso-butyraldehyde toward 2-iso-propyl-1,3-dioxane shown in the equation (14) is a reversible reaction that is carried out with acids catalysts, as show *Liu et-al (2005)* with tests of reactive-extraction carried out to different pH condition with H_2SO_4 like catalyst, or acids resins of cationic-exchange like Amberlyst or Dowex can also be used.

Predictive model to calculate the phase equilibrium is compared with experimental data reported by *Liu et-al (2005)* which are concentrations of 2-iso-propyl-1,3-dioxane in each one of the phases, but these experimental data present some theoretical problems to adjust them with a model thermodynamic of activity as NRTL, used in this work and where the binary interaction parameters were obtained in ASPEN PLUS based on contribution groups methods. These inconsistencies are referred for example to a higher solubility of 2-iso-propyl-1,3-dioxane in aqueous phase to 15 ºC that to 30 ºC, and the experimental data to 50 ºC present the highest solubility between the reported data, as it shows it the figure 3.a. contrary case is presented with the calculated values where a variation so high of solubility with the temperature not happen and the solubility increases also with the temperature like it could be expected.

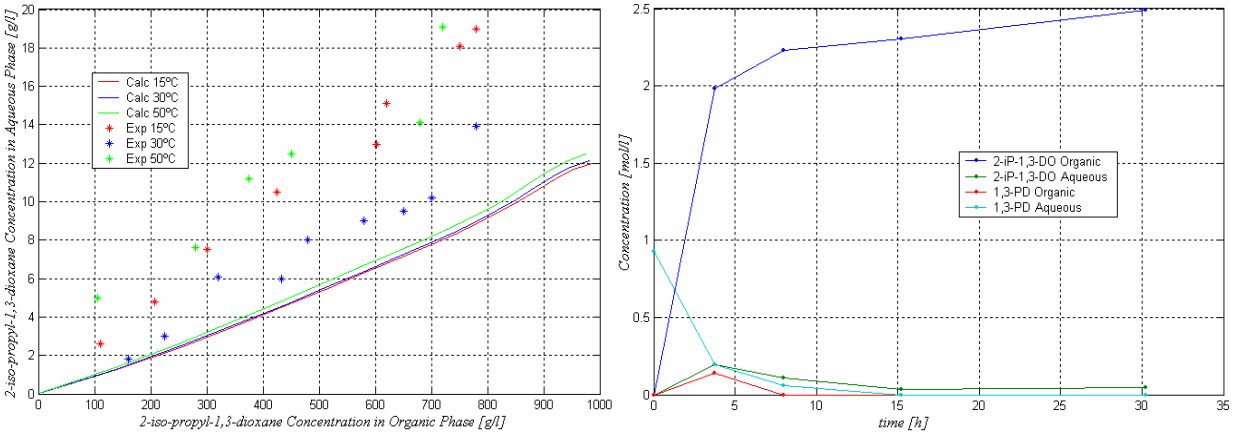


Figure 3, Liquid Phases Distribution in the Reactive System of Cyclic Acetalization
a. L-L Phase Equilibrium, experimental and calculated b. Kinetic of Cyclic Acetalization, pH=1.22

In kinetics study of cyclic acetalization three different tests carried out 20 ºC with a 1,3-propanediol initial concentration of 0.9235 mol/l with pH of 1.22, 1.53 and 1.90, show that 1,3-propanediol react more quickly to higher acid conditions. For example for a pH of 1.22 the 1,3-propanediol are consumed completely after single 15 minutes of initiate the reaction (See figure 3.b.) and for pH of 1.53 and 1.90 are required 120 and almost 300 minutes to achieve the same effect in the reaction system respectively [*Liu et-al (2005)*], like can be concluded starting from the great increase in the reaction time as a function of pH on the reaction medium.

Both the high concentrations of 2-iso-propyl-1,3-dioxane reached in organic phase and the low concentration of this same component in aqueous phase, added the quick consumption of 1,3-propanediol makes of the reactive-extraction a highly efficient process for the cyclic acetalization of 1,3-propanediol with iso-butyraldehyde to very high acid conditions, being reached a recovery of 87% in form of 2-iso-propyl-1,3-dioxane [*Liu et-al (2005)*]. Under these same operative conditions and using equilibrium models the reactive -extraction process has been simulated by means of ASPEN PLUS, where the main results are shown in the table 1, as are flows and fractions molar for the stream process, feed and both phases organic one and aqueous one. As a result of this simulation can see that the yield molar of reaction is 95,5% and the purity of the organic stream is 81.7% where the rest is basically water that can be used in the later stage of 2-iso-propyl-1,3-dioxane hydrolysis by reactive-distillation, , this would avoid an intermediate stage to purify the organic stream.

Table 1, *Simulation Results of 1,3-propanediol acetalization for reactive-extraction*

Component	**Molar Flow [mol/h]**			**Molar fraction**		
	Feed	**Aq. Phase**	**Org. Phase**	**Feed**	**Aq. Phase**	**Org. phase**
1,3-PD	50	1,29601	0,889668	0,5	0,031165	0,01523
i-BuAld	50	0,011304	2,174374	0,5	0,000272	0,037223
W	0	40,1904	7,623917	0	0,966457	0,130514
2-iP-1,3-DO	0	0,08759	47,72673	0	0,002106	0,817033

3.2. Hydrolysis of 2-iso-propyl-1,3-dioxane by Reactive-Distillation:

1,3-propanediol recovery is carried out by 2-iso-propyl-1,3-dioxane hydrolysis that is the inverse reaction of the cyclic acetalization shown in the equation (14) and this also is catalyzed by a medium acid. This reaction presents a great restriction due to the chemical equilibrium, since for a relationship stoichiometric of feeding the conversion varies almost lineally from 8 up to 26% for a temperature interval of between 300 and 500 K. For this reason reactive distillation process it is presented like an attractive alternative because the reaction and the separation are carried out simultaneously, increasing the driving force for the reaction when are again concentrated the reagents. To determine both the operational viability and the best configuration in the reactive-distillation tower (*reaction zone localization*) Static Analysis is applied (SA) this is the main tool in the qualitative study of the reactive distillation processes, this requires a minimum initial information and is based on the thermodynamic topological analysis of reactive system and in the selection of states stable limits of highest conversion.

Static Analysis (SA): SA was developed by *Serafimov et-al (1971)* and has been sufficiently illustrated for *Pisarenko et-al (2001)* and validated in multiple reactive systems [*Serafimov et-al (1999), Giessler et-al (1999, 2001)*]. The considerations that should be made to carry out the *Static Analysis* are that the reaction this under equilibrium conditions and that the reactive distillation column operate to reflux and total efficiency, in other words to conditions (∞/∞).Operation parameters are a

relationship among the flows of products (P/W), volume and localization of the reaction zone, which can be altered inside some limits of advance of each chemical reaction changing the volume in the reaction zone and their arrangement inside the column.

Initially to carry out the thermodynamic topological analysis of the reactive system the singular points of this system are characterized as show the table 2. Of where can be conclude that only exists one distillation region, then it is possible to visualize it as a bouquet of residue curves that leave from the azeotrope of minimum boiling point and that arrive at 1,3-propanediol pure. For direct separation (formulated distilled) three distillation subregions are obtained. And for indirect separation (bottoms formulated) two distillation subregiones are founded in the concentrational simplex.

Table 2, *Singular Points of Reactive System for 1,3-Propanediol Acetilation with iso-butyraldehyde to 1 atm.*

Component	Clasification	Type	Temperature	X1	X2
Az. H2O-iBuAld	Unstable Node	Heter.	61,35 ºC	0,2079	0,7921
iBuAld	Saddle	Homog.	64,10 ºC	1	---
Az. H2O-2iP13DO	Saddle	Heter.	92,87 ºC	0,7449	0,2551
H2O	Saddle	Homog.	100.00 ºC	1	---
2iP13DO	Saddle	Homog.	138,12 ºC	1	---
13PD	Stable Node	Homog.	214,40 ºC	1	---

Starting from this topological characterization of the reactive system five different conditions are obtained to evaluate in the feeding mixture [*see Pisarenko et-al (2001)*] so much for direct separation (distilled formulated) as for indirect separation (bottom formulated). All these conditions are governed for characteristic special, as in direct separation with two conditions particularly important, the feeding that for a total conversion of reagent limit generates for the line of material balance the 1,3-propanediol pure and the equimolar feeding, and is also evaluated three feeding relationships that are before, among and after of these two conditions. In a same way it was made for the indirect separation, and for this case is evaluated the feeding relationship that to total conversion of reagent limit generates for the line of material balance the binary azeotrope of minimum boiling point, besides of the other conditions already specified.

The reactive distillation tower configuration more appropriate obtained as a result of the Static Analysis is for a feeding molar ratio of 0.377645/0.622355 2-iso-propyl-1,3-dioxane/water where the relationship of products flows (P/W) is 1.6445. Heterogeneous binary azeotrope with minimum boiling point composed by water-iso-butyraldehyde is the obtained as distilled and for bottoms 1,3-propanediol pure is obtained. Also, starting from the trajectories of residual curves was determined that the reactive zone should be located over the inferior part, and then the superior part would be the rectification section. Additionally to help to the reaction has been recommended in the literature that the most volatile reagent is added to the final of the reactive zone and the less volatile one in the superior part.

Simulation: Reactive distillation tower for 2-iso-propyl-1,3-dioxane hydrolysis toward 1,3-propanediol and iso-butyraldehyde has been carried out in ASPEN PLUS and it can be divided in two parts, in the first one the simulation is made to conditions ∞/∞ (stages/ reflux), and then was possible to verify that the system is adjusted to the suggested trajectory and lower this condition the system is not affected by factors as the equilibrium constant, reaction kinetics or phenomena as the self-extractive, proven for the reached conversion of 99.824% for the reactive distillation process. In second instance the simulation is carried out under conditions that here they are named as operative or finite, this allowed to analyze the strong effect that has the self-extractive phenomenon in the yield of the tower due to the 2-iso-propyl-1,3-dioxane, and this it can be understood as a non-lineal variation in the relative volatility of the system with the change of concentrations for a mixture multicomponent. Starting from the study of the curves of relative isovolatility was possible to determine like with a redistribution of the feeding flows a higher conversion of reagent limit is achieved leaving intact the other operative conditions for the reactive tower. The results of the two final simulations carried out to finite conditions and considering the redistribution of the feeding flows is shown in the table 3, where the characteristics common for the reactive distillation tower they are: 45 stages, with the reactivate zone among the stages 8 and 44. The relationship of distilled to feed is 0.567. 2-iso-propyl-1,3-dioxane are fed in the stage 9 and a total of 100 Kmol/h of water is fed to the tower in 5 different streams. The reflux relationships for each one of the evaluated towers are 7.18387 and 9.51497.

Table 3, *Simulation Results for 2-iso-propyl-1,3dioxane Hydrolysis for reactive distillation*

Variable	**Tower 1 (*R: 7,18387*)**		**Tower 2 (*R:*9,51497*)***	
Iterations	92		27	
Total Conversion	0,85079964		0,97354874	
Stream	**Distilled**	**Bottom**	**Distilled**	**Bottom**
Temperature [K]	335,699883	430,696983	334,801007	476,705974
Molar Fraction				
Water	0,33126242	0,00745032	0,22647652	0,00299881
IBuAld	0,64202284	0,00074819	0,77098598	0,00020373
2-iP-1,3-DO	0,02671473	0,14105458	0,00253749	0,02324778
1,3-PD	3,15E-10	0,8507469	2,41E-11	0,97354967
Total Flow [Kmol/h]	1,0209522	0,7711478	1,00000076	0,79209924

This way finally is shown that to achieve high conversions for this process it is necessary to work under conditions of high reflux, what can be due to the low constant of equilibrium, for this reason is open the possibility to select reflux conditions that generate a high or almost total conversion of the dioxane respectively, where the selection of one alternative finally will depend of requirements of purity, energy consumption and economic aspects of the process. The study made along this document shows the technological feasibility to carry out the glycerol transformation toward 1,3-propanediol of high purity starting from non-conventional technologies, what represents a potential use of this compound in the industries of biodiesel production.

Conclusions:

The sense of this work is born with the purpose of to give him value added to the glycerol that is obtained as lateral product in the biodiesel production and to generate a commercially important product and of high demands. Then among the multiple possibilities of glycerol transformation available, in this work was decided approach the biotransformation toward 1,3-propanediol, a compound used monomer in the synthesis of polymers as PTT and PET.

A new scheme of glycerol processing based on non-conventional technologies was proposed and simulated in its main structures, as is the fermentation in two continuous stages that was optimized in spite of the presence of multiplicity of stable states in the first tank of fermentation. Subsequently for reactive-extraction process the importance of the medium acid it was shown as well as the potential of this process with theoretical yields of until 95%, from simulations carried out in ASPEN PLUS. Finally for reactive distillation process the Static Analysis allowed to determine the operational viability, the best configuration of the reactive distillation tower and the operation conditions, this add to the analysis of the self-extractive phenomenon, it allowed to establish a new configuration of the water feeding streams improving the yield of process, but due to the small equilibrium constant for hydrolysis reaction a high reflux relationships are required to reach an important yield as it was shown in the final part of this work.

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