BABEȘ-BOLYAI UNIVERSITY

FACULTY OF CHEMISTRY AND CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

ABSTRACT

PhD Thesis

COMPLETE INTEGRATION OF GLYCEROL INTO THE BIODIESEL PRODUCTION PROCESS.

PURIFICATION AND CONVERSION TO A VALUE ADDED PRODUCT

Eng. Ancuta Roxana TRIFOI

Scientific supervisor

Prof. Dr. Eng. Paul Şerban AGACHI

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Politehnica of Bucharest

Prof. dr. eng. Valentin Pleșu- Faculty of Applied Chemistry and Materials Science, University
Politehnica of Bucharest

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Key words : Biodiesel, glycerol, molecular distillation,acetals, glycerol formal

1. Introduction

The thesis's approach is of international interest, because it focuses on an industrial co-product valorisation, in particular glycerol from biodiesel industry. The thesis presents a method for glycerol purification (molecular/short path distillation) and its valorisation to a product used as biofuel additive – glycerol formal.

The first objective of the thesis is the purification of crude glycerol, in order to gain some added value as a feed stock in a wide variety of industrial applications. Molecular distillation process for glycerol concentration was developed and tested at laboratory and pilot scale.

The second objective of the thesis is the conversion of purified glycerol to a value added product, used as an additive to improve fuel proprieties. The condensation of glycerol with formaldehyde to form glycerol formal compound, was studied in acid catalysis.

2. Theoretical background

2.1. Glycerol from biodiesel industry

Crude glycerol is yielded at about 10% (wt/wt) of biodiesel, as co product in the biodiesel production process. Until 2005 supply of raw glycerol in the market remained relatively stable, when the world production of biodiesel started to increase as it is used on large scales in the transport sector, especially for road vehicles, in aviation, to generate electricity, for cooking and in maritime transport (14).

The demand for biodiesel is not driven by the demand for glycerine and the availability of crude glycerol has been increased, and led to low sale prices, from 25 cents/lb in 2004, to less than a half in 2011, approximately 8 cents/lb. The crude glycerol price trend is presented in Figure 3.

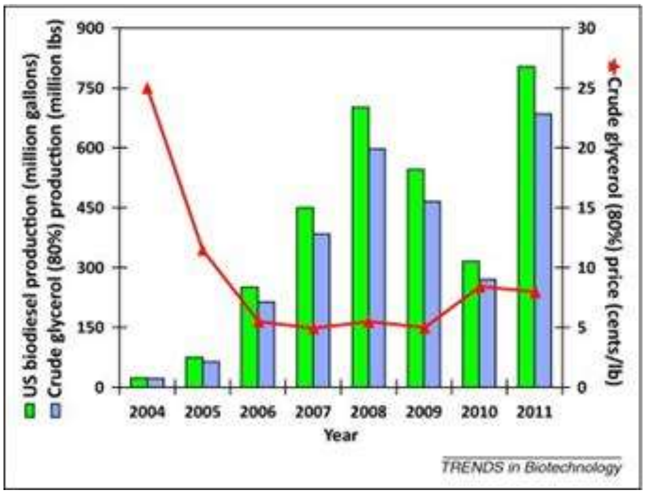


Figure 3. Crude glycerol price trend **(15)**

Because the glycerol market is currently undergoing radical changes, driven by very large supplies of glycerol arising from biodiesel production, researchers and industry have been looking at new uses for glycerine to replace petrochemicals as a source of chemical raw materials, and in a relatively few years there have been an impressive series of achievements (16). The crude glycerol from biodiesel process possesses very low value because of its impurities and it can be used as it is for other compounds synthesis, it requires refining. It contains, apart from traces of methanol, also water, salts and MONG (Matter Organic Not Glycerol) (39; 40).

2.2. Glycerol purification methods

Different methods have been used to purify crude glycerol: distillation, filtration, chemical treatment, adsorption, ion exchange (using resin), extraction, decantation and crystallization and for a high effectiveness two or more methods are combined (42).

Distillation is the most commonly used method for glycerol purification, it produces high purity glycerol but at low yields. This technology is an energy intensive process because of its high heat capacity, requiring a high supply of energy for vaporization (44). Chemical treatment of crude glycerol is another commonly used method. It has lower costs than other technologies, but the purity of the product is also lower.

Ion exchange method is advantageous because is low cost and it can be easily scale up, but it is unfeasible for high salt content glycerol, the regeneration costs for resins are high and results large quantities of waste water (52). The technology using membranes is environment compatible, it has low energetic requirements and it's operation is very simple, but for the industrial scale the membrane separation technology is not fully optimized (57). With a novel process called *Ambersep BD50*, the glycerol has a purity of 99.5 wt % and has lower energy requirements compared to the traditional distillation process (58).

2.3. Glycerol acetals as diesel additives

The valorisation of glycerol to glycerol acetals and ketals is of current interest for the researchers because they constitute excellent compounds for diesel and biodiesel blends, to improve the octane number and the cold flow properties, reduce particulate emission and gum formation (9; 12; 10).

To prepare glycerol acetal/ketal, the components are glycerol and an aldehyde or a ketone. Acetal formation is a reversible reaction via a two step mechanism. Glycerol reacting to aldehydes/ ketones results cyclic acetals (Figure 5).

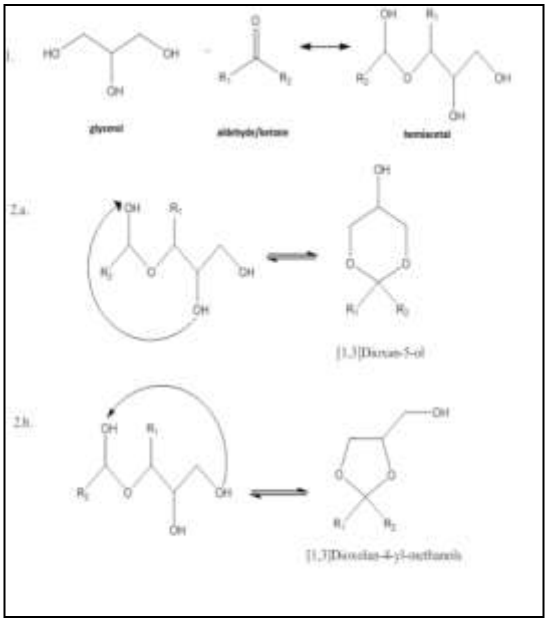


Figure 5. Reaction mechanism of glycerol with aldehydes/ketones (63)

For glycerol acetalisation with aldehydes or ketones various types of catalysts has been tested and reported in the literature: natural catalysts (silicates and aluminosilicates), supported catalysts (impregnated catalysts: salts, oxides, acids, metals), catalysts obtained by precipitation (salts, oxides), organic catalysts (ion exchange resins) etc.

Chapter 3. Glycerol purification by molecullar distillation

3.1. Molecular distillation process description

Molecular distillation, also known as short path distillation or evaporative distillation is used for purification and separation of heat sensitive products, under high vacuum, up to 0.001 torr. The degree of separation effected by molecular distillation is comparable to that produced by a simple batch distillation and it is greatest when components differ in boiling point by 50°C or more (95).

Block diagram of a molecular distillation plant contains the degasification part, the molecular distillation column, the vacuum and the measurement and control system (Figure 7).

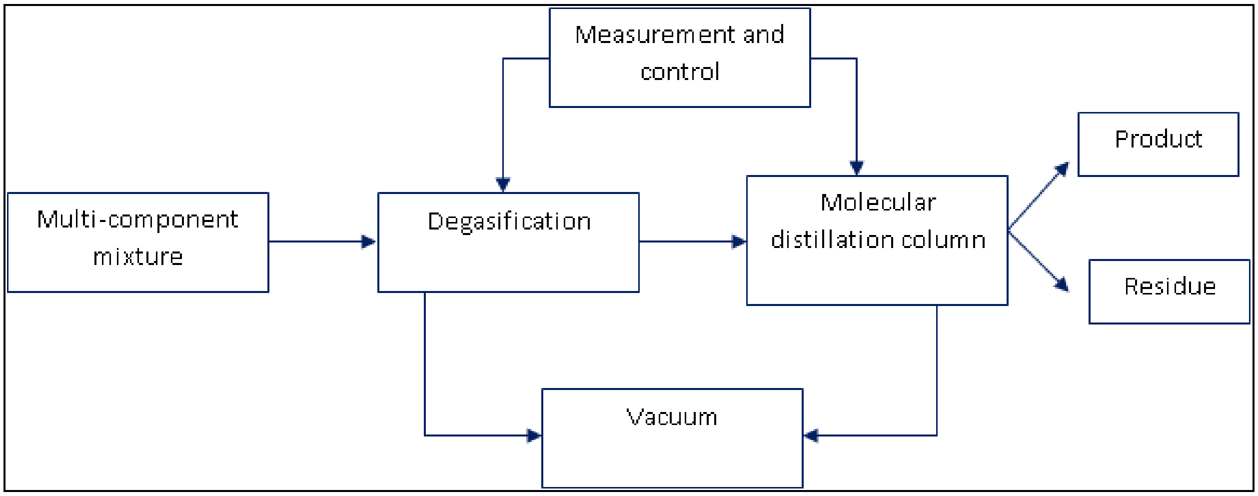


Figure 7. Block diagram of a molecular distillation process (98)

The parameters that describe the molecular distillation process and evaluated for the glycerol evaporation are: the mean free path of the molecules, the Knudsen number, theevaporation rate and the thickness of the falling film.

3.2. Experimental equipment

The laboratory and the pilot level experiments were carried out on falling film type column, at Research Institute of Organic Auxiliary Products SA, Medias Romania.

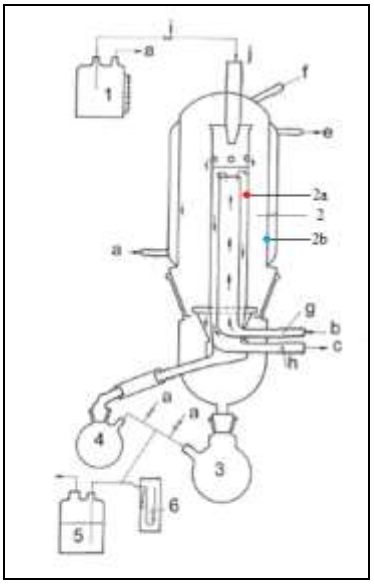


Figure 8. The laboratory falling film distillation column

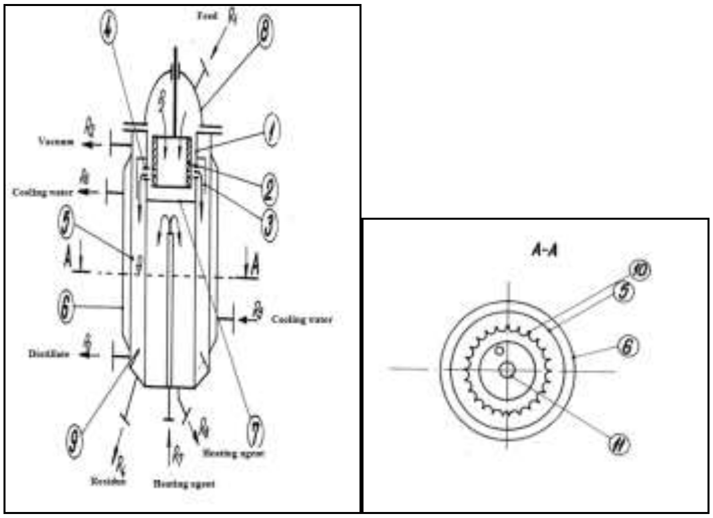


Figure 11. Pilot falling film distillation column scheme. Vertical and horizontal view

3.3. Theoretical analysis of the molecular distillation process parameters. Case study- Glycerol evaporation

3.3.1. The mean free path

Figure 12 shows the mean free path for glycerol (λ), calculated at different pressures in 373-493 K temperature range. The glycerol molecules can reach the cooling surface if their mean free path is higher than 0.8 cm, for the laboratory column and 1.75 cm for the pilot column and this condition is accomplished for pressures below 0.3 mmHg. The mean free path of the impurities (such as methyl ester, free fatty acid, mono- , di- and tryglycerides) is smaller and the distance between the evaporator and condenser and can be separated effectively due to the difference between mean free paths and molar masses.

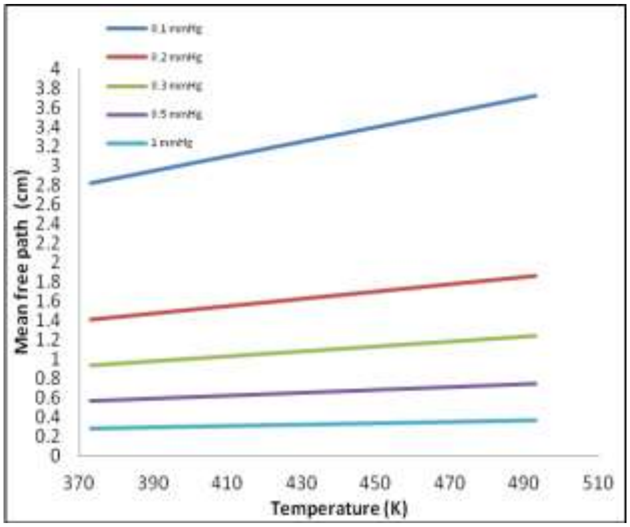


Figure 12. Effect of temperature on glycerol mean free path

3.3.2. The Knudsen Number

The distillation rate was evaluated through the Knudsen number (Figure 13). At a pressure of 0.1mmHg, the Knudsen number is in the intermediate range 0.05<Kn<10, showing a proper distillation rate and these conditions are the best to run the process.

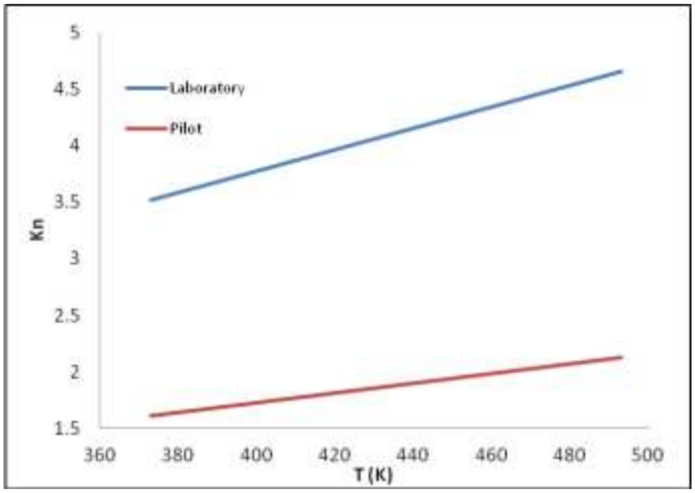


Figure13. Effect of temperature on Knudsen number

3.3.3. The evaporation rate

The evaporation rates (relative and effective) were calculated through Langmuir Knudsen equation, for a temperature range between 373K-423K and their dependence of temperature is shown in Figure 14. The values of the efficiency factor *f* are about 0.98 for the laboratory column and 0.9 for the pilot plant column. The difference between efficiency factors is due to the columns design, but both are closer to the the values of relative evaporation rate.

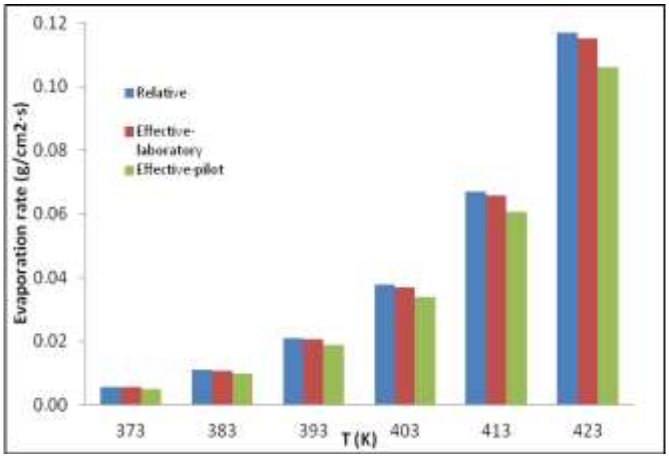


Figure14. Evaporation rate at different temperatures

An increased heat supply to the evaporated liquid causes its temperature to rise and thus induces the rise of saturated vapour pressure and distillation rate increase. An increase of the temperature with 50°C, lead to an increase of the distillation rate by twenty times. The relative evaporation rate at 373 K is about 0.0056 g/cm^2s and at 423 K is 0.1169 g/cm^2s.

3.4. Experimental part

To compare the results of the molecular distillation, a batch distillation has been also undertaken at laboratory level.

3.5. Results and discussions

The maximum yield obtained in vacuum batch distillation was 58.85%, at 6mmHg and 160°C. The reduction in the amount of distilled glycerine obtained could be a result of three possibilities: (1) the formation of acroleine due to lose of water from glycerine at low pH. (2) The formation of poly-glycerol as a result of polymerization of glycerol at high pH in presence of high temperature and excess sodium hydroxide. This becomes part of bottom product. (3) The oxidation of glycerol to form glycerose a mixture of dihydroxyacetone and glyceraldehyde (112)

3.5.2. Molecular distillation of crude glycerol -laboratory experiments

At the laboratory level the water was removed by batch distillation at about 333 K and 40 mmHg, because the plant was not adapted to remove the water in the same system. The composition of the glycerol after water removal was: 92.28% glycerol.

The influence of the feed flow rate and temperature on product yield and glycerol purity was studied.

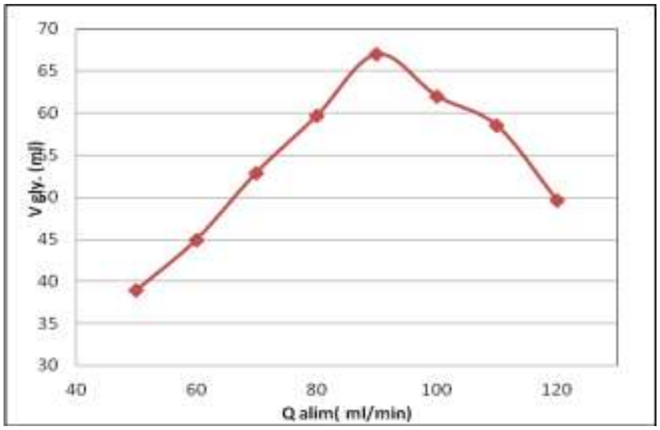


Figure 15. Influence of feed flow rate on distillate volume of glycerol

The volume of the distilled fraction should increase with the feed flow rate, but experimentally approached a maximum value at 90 ml/min, after that the collected volume of glycerol started to decrease (Figure 15), due to the thickness of the evaporating falling film. At higher feed flow rates, the thickness of the film is larger, the velocity of the film is bigger and the contact with the heated surface is not enough for evaporation.

The thickness of the falling film was further analysed for feed flow rates from 80 ml/min to 110 ml/min, at 373 K, as shown in Figure 16. As expected, the thickness of the film increase when the feed flow increase.

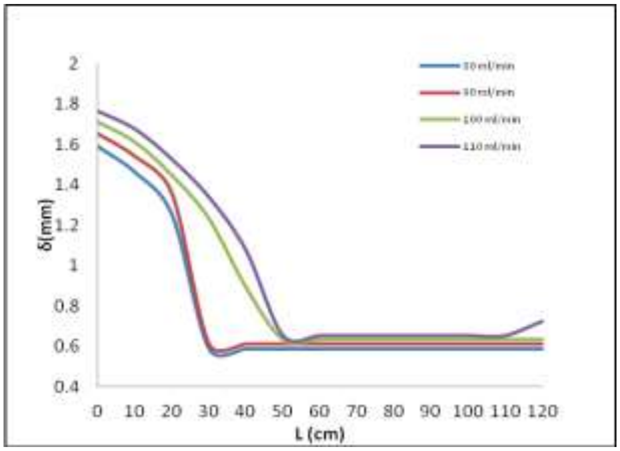


Figure 16. Evaporating film thickness estimation at different feed flow rates. T=373 K

Temperature is also an important parameter because an increase in temperature can increase the mobility of the impurities too. At a feed flow rate of 90 ml/min, the purity of the distillated glycerol has been 99.2% at 393 K and at higher temperature is decreases (Figure 17).

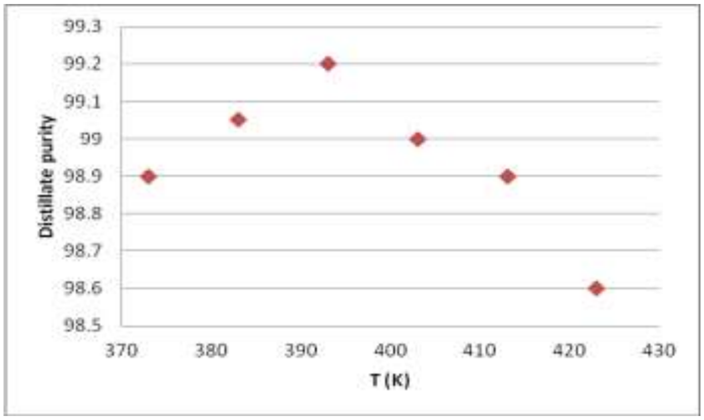


Figure17. Influence of temperature on distillate purity at 0.3 mmHg; Q=90ml/min

At the working pressure of 0.3 mmHg and for a distance between the evaporator and condenser of 0.8 cm, the purity obtained for glycerol, in the distillate stream was about 99% (98.6-99.24%) in the temperature range of 373K-423K.

3.5.3. Pilot plant tests

The light fraction (water and other volatiles) has been removed from the mixture in the same system, by heating the mixture in the dosing tank, under vacuum (323 K and 15 mmHg).

The mass balance obtained for the pilot experiments is listed in Table 6. The experiments were carried out at 0.1 mmHg, from 373 K-423 K, at the optimum feed flow rate estimated from the laboratory experiments. The feed flow rate, was now calculated from the film thickness. At a film thickness of 1.65 mm at the beginning of evaporation, resulted a feed flow rate of about 16.7 kg/h. The yield in glycerol is about 83.24%.

Table 6. Mass balance for molecular distillation process on pilot plant

Experiment	Feed Mass (kg)	Distillate (kg)	Residue (kg)	Loss (%)	Yield (%)
1 T=393 K	11.4	10.3	2.14	1.49	83.24
2 T=403K	11	9.4	1.4	1.87	76.06
3 T=413 K	13.4	11.5	1.63	2	75.95
4 T=423 K	12.8	10.8	1.75	1.9	74.6

The characteristics of the product, obtained at 393 K and 0.1 mmHg, operating at a feed flow rate of 16.7 kg/h mixture, are: glycerol content 98.9%; water: 0.85%; ash content: 0.01% and the MONG determined by difference are 0.24%.

Comparing these results with the results obtained by vacuum distillation but for the batch process, it can be concluded that molecular distillation can improve the yield of the glycerol. The maximum yield in achieved in batch distillation was 58.85% and by molecular distillation was 83.24%.

3.6. Analytical procedures

3.6.1. Determination of glycerol content

The glycerol concentration was determined by HPLC method, on a Jasco Chromatograph (Japan) . The separation was achieved on a Carbosep Coregel 87H3 column (300 x 7.8 mm) at temperature of 70 ºC. The mobile phase was a sulphuric acid 0.01 M solution. The flow rate was 1 mL min^{-1} .

The retention time for glycerol is RT = 8.2 min (Figure 19) and the calibration curve shows a very good correlation factor, r=0.9992 (Figure 20) for the concentration range analysed (1-20 mg/ml).

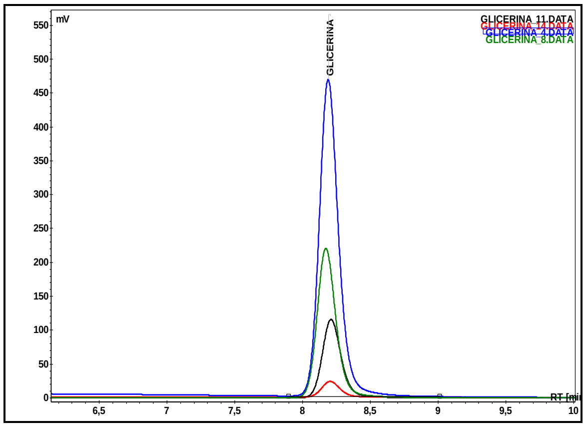


Figure 19. Glycerol peak at RT=8.2 min

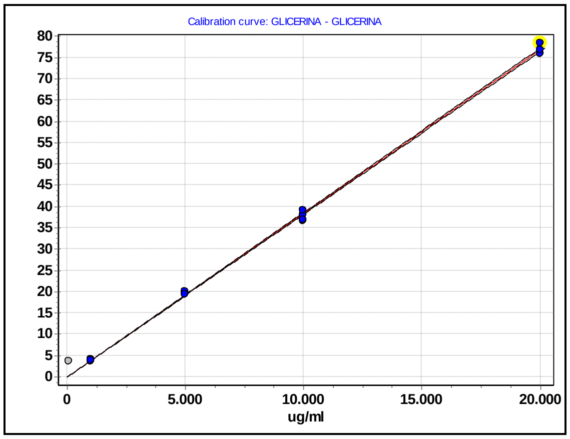


Figure 20. HPLC Calibration curve for glycerol

3.6.2. Determination of water content

The water was determined following the standard method ISO 2097:1972 *" Glycerol for industrial use- Determination of water content- Karl Fisher method"* (115), using Metrohm 701 KF Titrino apparatus.

3.6.3. Determination of ash content

Ash content was analysed according to the Standard method ISO 2098:1972 *“ Glycerol for industrial use- Determination of ash-Gravimetric method”* (116), by burning a quantity of glycerol in a furnace.

3.6.4. Determination of MONG

The MONG, matter organic non-glycerol was calculated by the difference from a hundred of the glycerol, water and ash content according to the Standard method ISO 2464:2000 “Crude glycerine for industrial use – Calculation of Matter (Organic) Non-Glycerol (MONG)” (117).

3.6.5. Changes in the functional groups investigation

The FTIR analysis were done to investigate the changes in the functional groups found in the purified glycerol compared to crude glycerol. FTIR analyses were carried out using ATR – FTIR technique on a Bruker Tensor 27 Spectrometer controlled with the OPUS software. The samples were analysed on a ZnSe crystal. The resulted spectrum for glycerol, are shown in Figure 21. The main functional groups of ultra pure glycerol includes the O-H stretching at 3300 cm^{-1}, C-H stretching at 2880 cm^{-1} and 2930 cm^{-1}, C-O-H bending at 1330 cm^{-1} to 1420 cm^{-1}, C-O stretching from 1100 cm^{-1} as primary alcohol to 1450 cm^{-1}, representing secondary alcohol, O-H bending at 920 cm^{-1} and also the H2O bending at 1650 cm^{-1}. The spectra of crude glycerol additionally showed strong FTIR peak at 1730 cm^{-1} indicating the presence of impurities. The sharp peak at 1730 cm^{-1} indicate the presence of C=O compounds of an ester or carboxylic acid of fatty acid. For the purified glycerol the sharp peak at 1730.

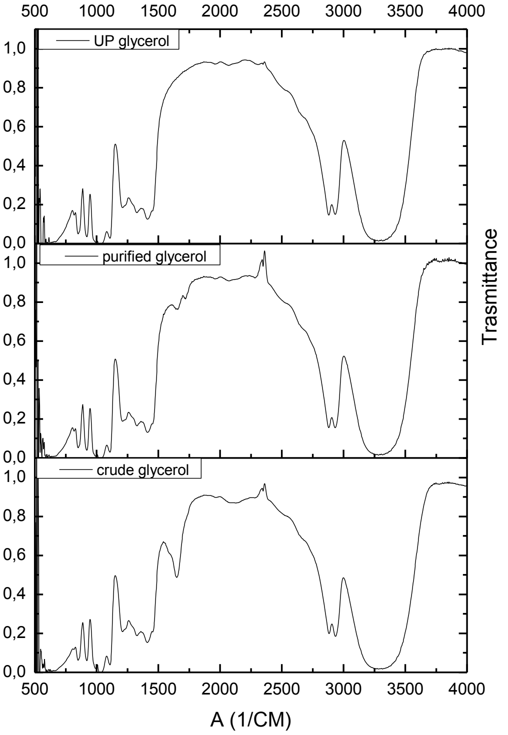


Figure 21. ATR-FTIR spectra for glycerol: Ultra pure glycerol; purified glycerol and raw glycerol

3.7. Conclusions

A theoretical analysis of the molecular distillation process has been developed for glycerol evaporation case. The condition for the molecular distillation process is that the mean free path of the molecules to be higher than the distance between the evaporator and condenser of the column. It resulted that the mean free path of the molecules is higher than the distance for pressure below 0.3 mmHg (for laboratory column) and below 0.2 mmHg for pilot plant column, for temperatures up to 493 K.

The influence of feed flow rate and evaporator temperature on yield and purity of glycerol was determined. The experiments were carried out at laboratory and pilot level.

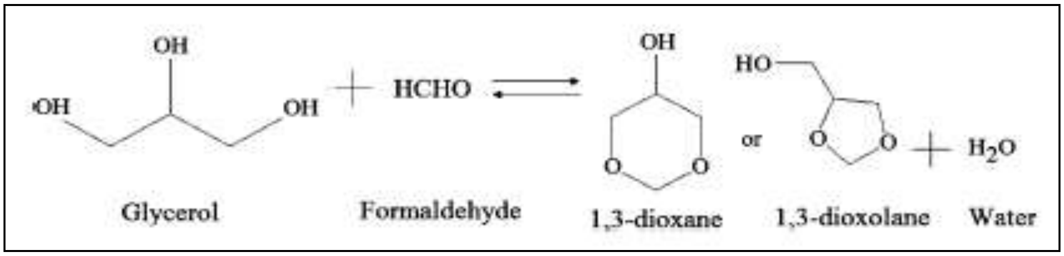
The influence of feeding flow rate and of evaporator temperature were investigated and resulted that the quantity of the distillate glycerol increase with the feed flow rate up to one point and after that decrease. This is explained due to the thickness of the evaporating film which increase with the feed flow rate and has been estimated from the equation expressing the flow of a liquid on a tube.

From the results it can be concluded that molecular distillation is an effective tool for glycerol purification because the purity in glycerol was improved from 84% up to 99%, with a good yield of about 80-83%.

Chapter 4. Glycerol formal synthesis

4.1. Process description

Glycerol formal is a mixture of 5-hydroxy-1,3-dioxane and 4-hydroxymethyl-1,3-dioxolane.
The reaction scheme for acetalization of glycerol with formaldehyde is given by the following equation (72; 7):



The objective of this study is to use the glycerol, purified as described in previous chapter for the synthesis of glycerol formal, in acid catalyses, without to remove the water from the system, in a solvent free process.

The block scheme for the glycerol formal synthesis, studied in this thesis is presented in Figure 23.

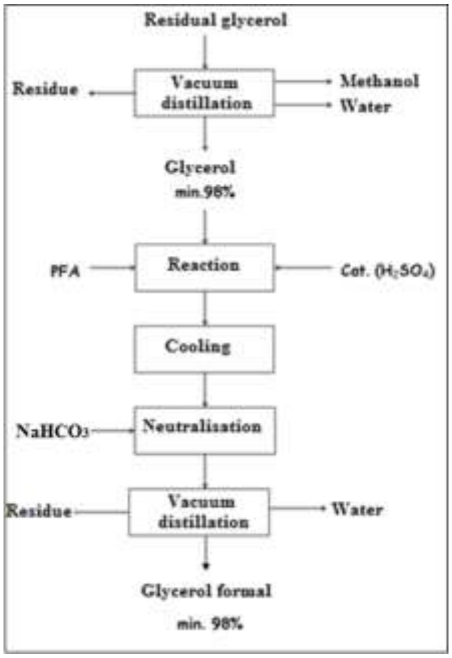


Figure 23. Block Scheme for glycerol formal synthesis

4.2. Experimental set-up

The experiments were carried out in a 1 L glass reactor provided with a mechanical stirrer, a total reflux condenser to condense all the vapors and a thermometer for temperature monitoring. The reaction temperature was controlled by an external thermostat.

The materials used for the synthesis are: **the purified glycerol,** obtained by molecular distillation as described in the previous chapter, p**-formaldehyde (95%)**, catalyst- **H_2SO_4 (98%)**, neutralizer- **$NaHCO_3$** and solvent **-toluene** (for preliminary experiments).

The polymer p-formaldehyde is insoluble in glycerol and therefore the reaction between glycerol and araformaldehyde in the presence of heterogeneous catalyst is negligible.

4.3. Results and discussions

To evaluate the process the influence of feed composition, of temperature and of stirring speed were evaluated.

4.3.1. Influence of feed composition

a) The effect of the solvent

The effect of the solvent (toluene) on the reaction system was investigated in order to check if it influences the equilibrium to be shifted to the right, because of the water removal.

It resulted that for glycerol acetalisation with p-formaldehyde , it is not necessary to use a solvent to shift the equilibrium to the right. Furthermore, the solvent does not improve the reaction time or GF yield and it is toxic, expensive and occupy a large volume of reactor, so the solvent free synthesis is preferred.

b) The effect of feed mole ratios

Different feed molar ratios (glycerol to p-formaldehyde = 1:1 to 1.4:1) were tested in order to check if the excess of a reactant influences the equilibrium of the reaction. All the experiments were performed at 373K and 800rpm, with 0,44 wt % of sulphuric acid catalyst.

It resulted that the higher glycerol formal yield was obtained after 3 h of reaction at a molar ratio of glycerol : p-formaldehyde of 1.2:1 (figure 26). At a stoichiometric ratio the yield in glycerol formal was 94.4% after 4 hours of reaction and at 1.2:1 molar ratio the yield was 98.05% after 3 h of reaction.

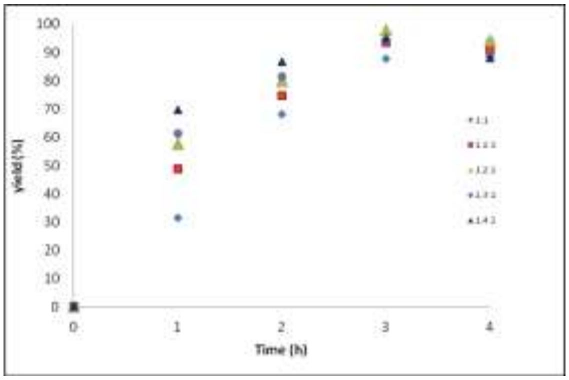
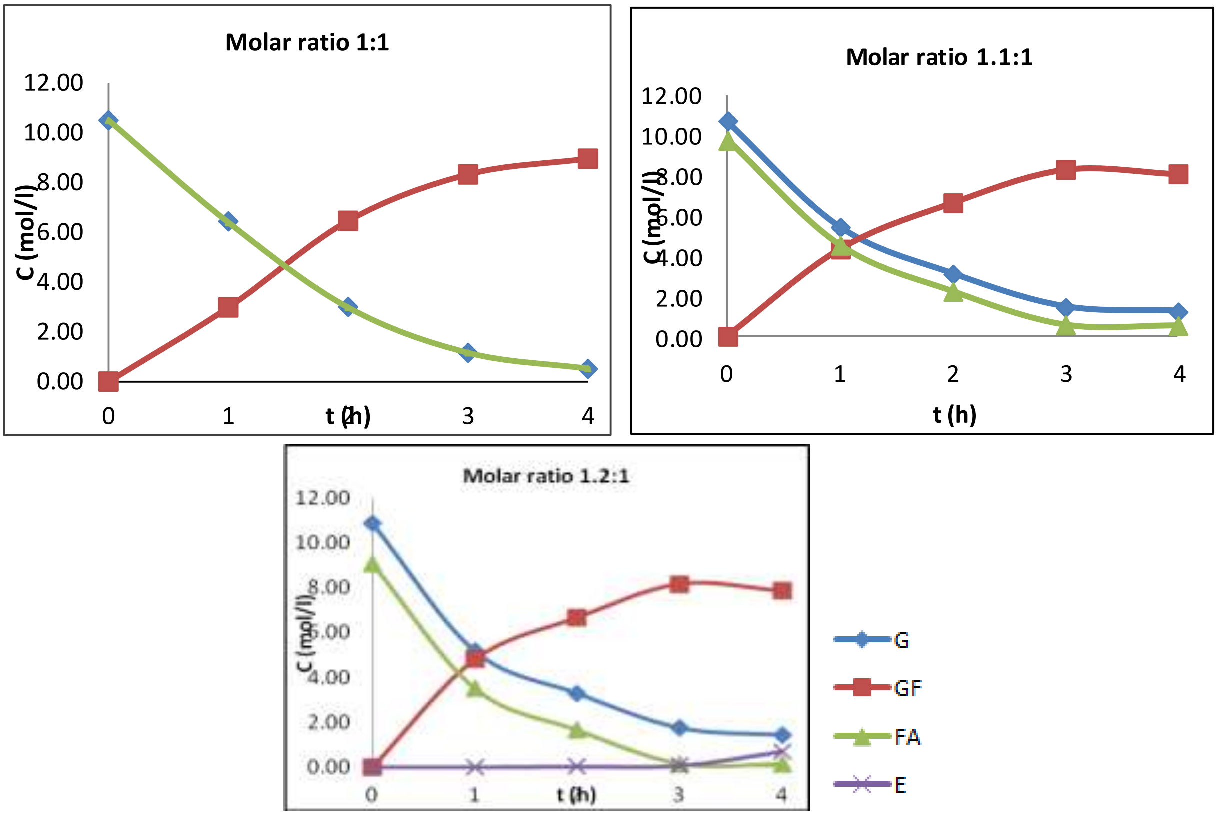


Figure 26. Glycerol formal yield at different molar ratio of glycerol: p-formaldehyde.

T= 373 K; cat. 0,44wt%

In all the cases, when an excess of glycerol was used, the maximum yield was achieved after 3 h of reaction, after that it started to decrease. This is due to the appearance of a co-product of condensation of glycerol formal with glycerol. This can been also concluded from the concentration of glycerol in time, because after three hours, the glycerol concentration continue to decrease, meanwhile the yield in glycerol formal decrease after three hours. For a glycerol: formaldehyde molar ratio of 2:1 or more the presence of the co-product (E) is more obviously (Figure 27). The higher yield in glycerol formal is for a glycerol:formaldehyde molar ratio of 1.2:1, after three hours of reaction, but it also appears the co-product resulted from the etherification of glycerol with glycerol formal, which make the product separation more difficult and the further experiments were carried out in a stoichiometric molar ratio.


Molar ratio 1:1

Molar ratio 1.1:1

Molar ratio 1.2:1

Figure 27. Concentration of the reactants and products in time at different glycerol:formaldehyde molar ratio. T=373 K

4.3.2. Influence of temperature

Different temperatures were tested and as in all the previous experiments the tests were performed with 0,44 wt% of catalyst and at 1000 rpm. In this case 1:1 glycerol to formaldehyde molar ratio was used.

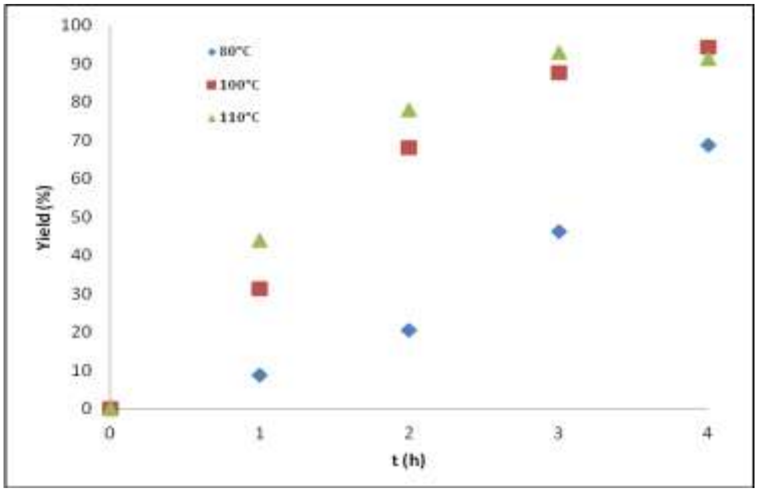


Figure 28. Effect of the temperature on product yield. 1:1 glycerol to formaldehyde molar ratio, 0,44wt% catalyst and at 1000 rpm.

For the acetalization reaction of glycerol and formaldehyde, an increase of temperature does not imply any significant change of the equilibrium conversion above 373 K (Figure 28 and Figure 30) only the reaction rate increases when the temperature increases, but also the byproduct formation is favored.

4.3.3. Influence of stirring speed

In order to avoid mass transfer resistance the effect of stirring speeds was also studied. The experiments were carried out at 400 rpm; 650 rpm and 1000 rpm and no important effect of the agitation on the conversion rate was observed, in the first part of the synthesis. (Figure 29).

The experiments were performed with a stoichiometric feed ratio (1:1 of glycerol to formaldehyde molar ratio) at 373 K with 0.44 wt% catalyst.

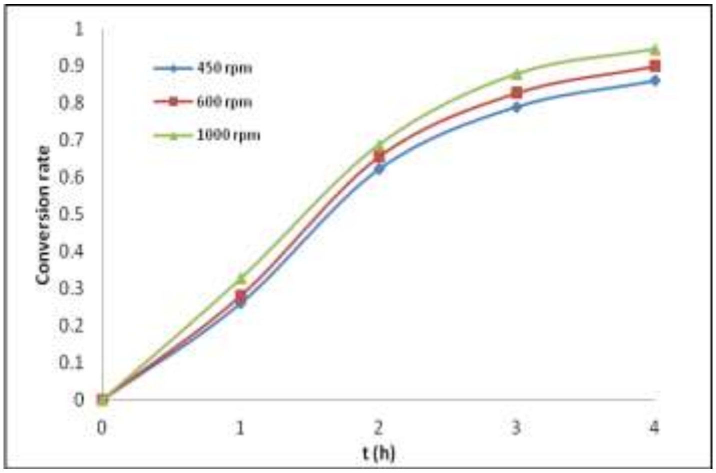


Figure 29. Effect of stirring speed on formaldehyde conversion rate. G:FA =1:1 molar ratio; T =373 K, 0.44%wt catalyst.

The effect of the temperature is much higher over the reaction rate than the mass transfer is, but the stirring speed influences the process, more after the product is formed, because in the first part of the reaction there is almost no difference between the conversion rates at different stirring speeds, but as the product is formed with the reaction evolution, a slight difference between conversion rates at different stirring speed is observed.

4.3.4. Process analysis

The process analysis was done in order determine the activation parameters for the reaction between glycerol and p-formaldehyde, necessary to develop the mathematical model of the process.

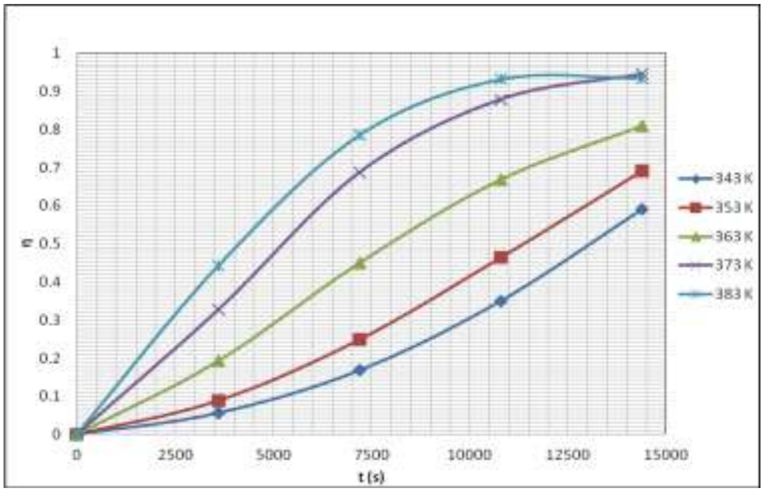


Figure 30. Formaldehyde conversion rate at different temperatures

The activation parameters, the preexponential factor A and the activation energy were determined from the linearization of Arrhenius equation, ln (k)=ln A-Ea/RT (Figure 31), which present a good correlation (r>0.9) for all the conversion grades.

The activation energies for the glycerol formal synthesis decrease when the conversion increase (see table 10), showing that the reaction is not only kinetically controlled but also by the mass transfer. This is also confirmed by the results obtained at different stirring speeds.

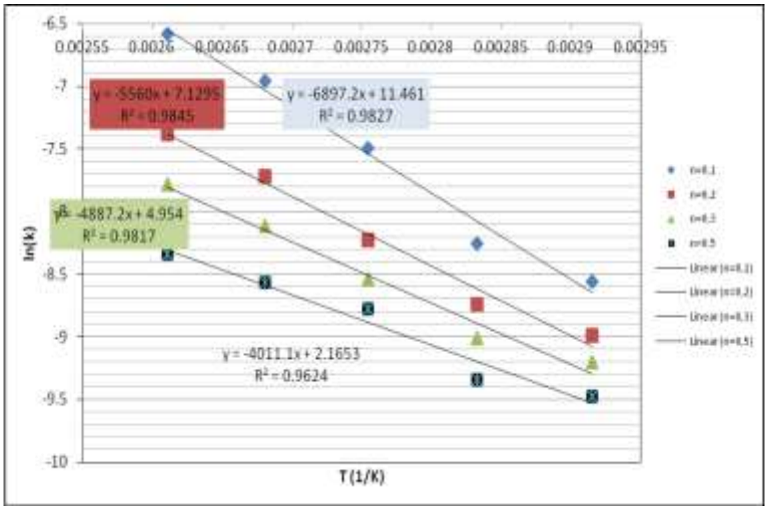


Figure 31. ln(k)=f(1/T)

Table10 Activation parameters for the reaction between glycerol and p-formaldehyde at different conversion grades

n	Ea(kcal/mol)	A
0.1	13.71124	11.46
0.2	11.05328	7.12
0.3	9.715356	4.95
0.5	7.973868	2. 16

The synthesis of glycerol formal from glycerol and formaldehyde is a mixt process, controlled not only kinetically but as by the mass transfer, consideration that has to be taken into account when a detailed model of the process is developed.

4.4. Analytical procedures

4.4.1. Formaldehyde determination

Formaldehyde concentration was determined by titrimetric method with ammonium chloride (122), which is based on the reaction:

$$6CH_2O+4NH_3 \longrightarrow (CH_2)_6N_4 + 6H_2O$$

4.4.2. Determination of Glycerol and Glycerol formal

The sample were analyzed by gas chromatography coupled with mass spectroscopy (GC-MS), using using a flame ionization detector (FID). The column was an Agilent capillary column DB-1: 60 m X 0.53 mm X 5 µm, used with Helium as the carrier gas.

A representative spectra is presented in Figure 32. The retention time (RT) for glycerol formal is 9.37 min, where both of the isomers can be observed. The glycerol RT is 14.19 min. and other heavy compounds (polyether) present in the sample have the RT 26.9 min.

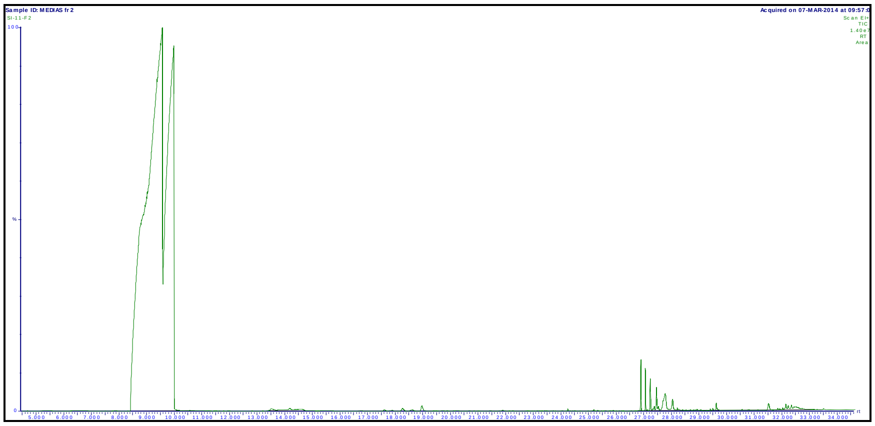


Figure 32. GC spectra of glycerol formal

4.4.3. Determination of water content

The water content was determined by Karl Fisher method, using Metrohm 701 KF Titrino apparatus.

4.4.4 Changes in the functional groups investigation

The changes were investigated using ATR-FTIR technique, and the analysis were carried out on a Bruker Tensor 27 Spectrometer (on a ZnSe crystal) controlled with the OPUS software. The resulted spectrum for the reactants, glycerol and an aqueous solution of formaldehyde and for the product, glycerol formal are presented in Figure 33.

The IR spectra of acetals and ketals, presents 4-5 bands between 1040-1200, for the C-O-C bending (123), that can be seen in the Figure 33. The wide band for O-H stretching at 3300 cm^{-1}, is smaller for glycerol formal and it is moved to 3420 cm^{-1} indicating that the O-H group was consumed in the reaction.

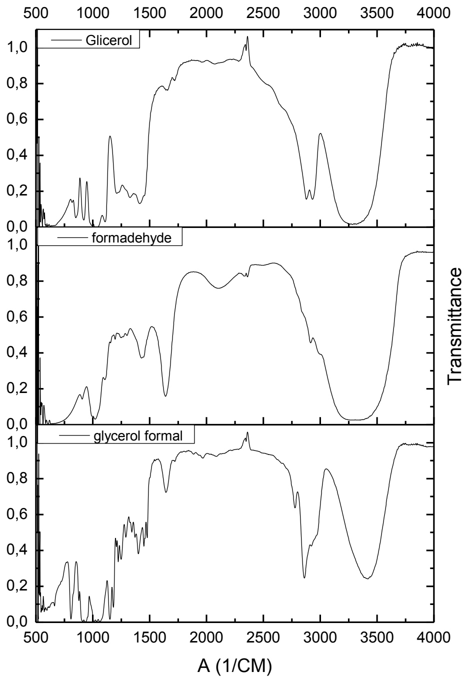


Figure 33. IR spectra for glycerol formal synthesis.

The characteristics of the obtained product are:

Table 11. Glycerol formal characteristics

Crt.	Characteristics	Values
1	Glycerol formal content (%)	98
2	Glycerol (%)	0.29
3	Polyols (%)	1.7
4	Appearance	colorless

4.5. Conclusions

In this work, we present results of glycerol formal synthesis using p-formaldehyde and purified glycerol. Effects of various reaction conditions, including reaction temperature, molar ratio of reactants, and stirring speed have been examined in order to assess the viability of converting glycerol to this acetal product.

Formaldehyde acetals are stable to hydrolysis and it is not necessary to use a solvent to shift the equilibrium to the right, by water removal. Furthermore, the solvent does not improve the reaction time or GF yield and it is toxic, expensive and occupy a large volume of reactor, so the solvent free synthesis is preferred. The higher yield in glycerol formal was achieved for a glycerol:formaldehyde molar ratio of 1.2:1, after three hours of reaction (98.05%), but it also appears the co-product resulted from the etherification of glycerol with glycerol formal, which make the product separation more difficult.

An increase of temperature does not imply any significant change of the equilibrium conversion above 373 K (Figure 28 and Figure 30) only the reaction rate increases when the temperature increases, but also the byproduct formation is favored. The stirring speed also influences the process, but after the product is formed, because in the first part of the reaction there is almost no difference between the conversion rates at different stirring speeds, but as the product is formed with the reaction evolution, a slight difference between conversion rates at different stirring speed is observed.

The activation energies for the glycerol formal synthesis decrease when the conversion increase (see table 10) and from their values (> 10 kcal/mol), results that the reaction is not only kinetically controlled but also by the mass transfer. This is also confirmed by the results obtained at different stirring speeds.

The aim of this study was the process analysis of glycerol formal synthesis and the results presented in this work provide information to understand similar acetalisation processes between glycerol and other aldehyde/ketones, with different catalysts and establish a theoretic basis for development of large-scale glycerol acetal production process, that can offer new insights for glycerol conversion to added-value products such as diesel additives.

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