



Original Research Paper

Glycerol transesterification with ethyl acetate to synthesize acetins using ethyl acetate as reactant and entrainer

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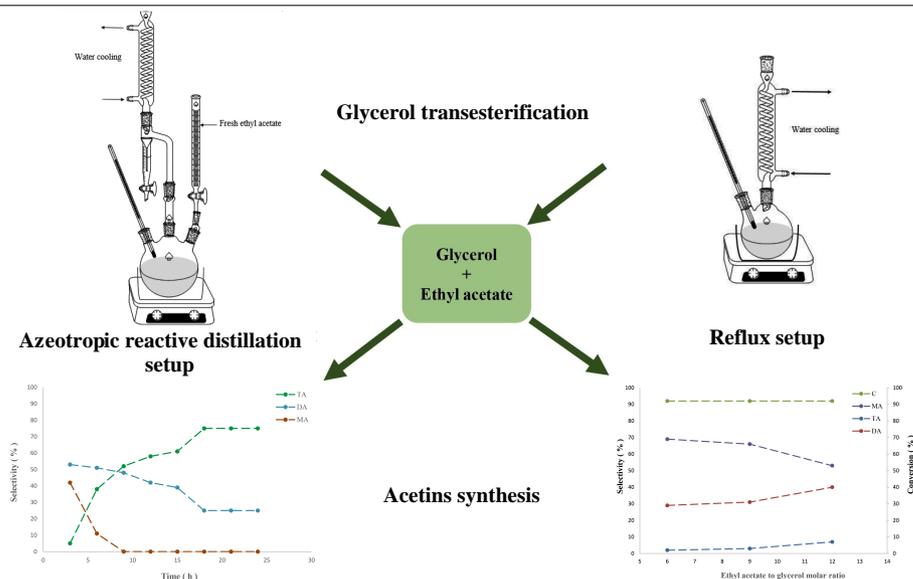
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HIGHLIGHTS

- Novel strategy for biodiesel glycerol valorization was introduced.
- Transesterification of glycerol with ethyl acetate was investigated using ethyl acetate as reactant and entrainer.
- Removal of ethanol from the reaction medium increased triacetin selectivity by about 39%.
- Sulfuric acid showed the highest selectivity to the most desirable products, i.e., diacetin and triacetin.

GRAPHICAL ABSTRACT



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ABSTRACT

Transesterification of glycerol with ethyl acetate was performed over acidic catalysts in the batch and semi-batch systems. Ethyl acetate was used as reactant and entrainer to remove the produced ethanol during the reaction, through azeotrope formation. Since the azeotrope of ethyl acetate and ethanol forms at 70 °C, all the experiments were performed at this temperature. Para-toluene sulfonic acid, sulfuric acid, and Amberlyst 36 were used as catalyst. The effect of process parameters including ethyl acetate to glycerol molar ratio (6-12), reaction time (3-9 h), and the catalyst to glycerol weight (2.5-9.0%), on the conversion and products selectivities were investigated. Under reflux conditions, 100% glycerol conversion was obtained with 45%, 44%, and 11% selectivity to monoacetin, diacetin, and triacetin, respectively. Azeotropic reactive distillation led to 100% conversion of glycerol with selectivities of 3%, 48% and 49% for monoacetin, diacetin, and triacetin. During the azeotropic reactive distillation, it was possible to remove ethanol to shift the equilibrium towards diacetin and triacetin. Therefore, the total selectivity to diacetin and triacetin was increased from 55% to 97% through azeotropic distillation.

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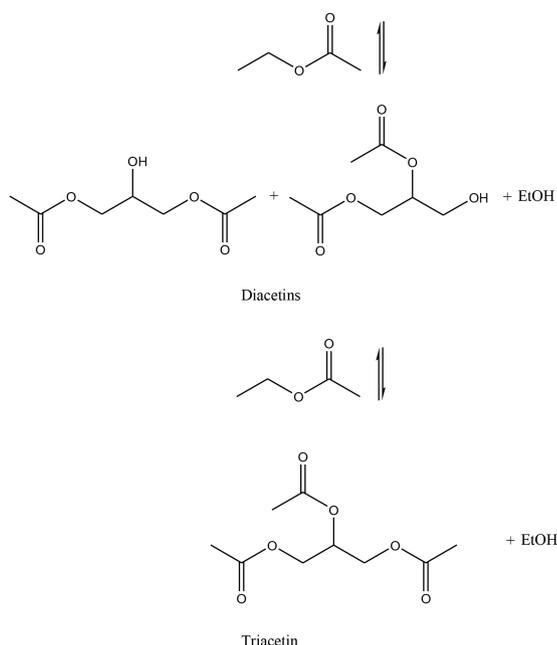
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1. Introduction

Biodiesel is one of the renewable fuels whose global production is estimated to reach 37 million metric tons in 2020 (Kale et al., 2015). The major by-product of the conventional biodiesel process is glycerol which is produced at an approximate rate of 10wt.% (Kale et al., 2015). Such dramatic rise in the availability of biodiesel glycerol has led to significant price declines in the market and therefore, has marked glycerol as attractive feedstock for the synthesis of various valuable chemicals (Corma et al., 2007; Behr et al., 2008). One important category of glycerol derivatives is glycerol acetates, also known as acetins. Acetins are mono-, di-, and triacetate esters of glycerol, which are named monoacetin (MA), diacetin (DA), and triacetin (TA), respectively. These chemicals have extensive applications especially as fuel additive (Melero et al., 2007; Zhou et al., 2008; Rastegari et al., 2015).

Acetins can be synthesized via direct esterification of glycerol with acetic acid/acetic anhydride or transesterification of glycerol with methyl/ethyl acetates (Bremus et al., 1981; Goncalves et al., 2008; Rezayat and Ghaziaskar, 2009; Ferreira et al., 2011; Morales et al., 2011; Goncalves et al., 2012; Rastegari and Ghaziaskar, 2015). Among all, the most common way is direct esterification of glycerol with acetic acid. This process has some drawbacks, especially relatively low selectivity to TA (Otera, 1993). Utilization of acetic anhydride could improve the reaction to yield TA with a selectivity close to 100%. However, this procedure is not convenient, due to much higher price of acetic anhydride in comparison with acetic acid as well as its associated health hazards (Otera, 1993).

Another possible method for acetins synthesis is transesterification of glycerol with methyl acetate (Morales et al., 2011). This process suffers from relatively low selectivity towards the most desirable products, i.e., DA and TA, despite using a high ethyl acetate to glycerol molar ratio of 50. As shown in Scheme 1, transesterification reaction consists of three consecutive steps. Each step is reversible and chemical equilibrium limits the extent of the reaction. According to Le Chatelier's principle, one way to push a reversible reaction forward is using excess molar ratios of reactants. However, this approach could result in relatively low selectivity towards DA and TA (Morales et al., 2011). Another method is to remove one or more products from reaction medium. This could be done through using an entrainer to form azeotrope with the unavoidable reaction by-product, and to remove it from reaction medium continuously. In the transesterification of glycerol with methyl/ethyl acetates, acetate could be used as reactant and entrainer, because acetate has the ability to form an azeotrope with the by-product, i.e., methanol/ethanol.



Scheme 1. Transesterification of glycerol with ethyl acetate.

Methyl acetate can form azeotrope with the reaction by-product, methanol, at temperature of 53.8 °C. While the azeotrope of ethyl acetate with the reaction by-product, ethanol, forms at temperature of 70 °C. According to the published literature, the reaction temperature is an effective parameter on products selectivities (Morales et al., 2011), which should be determined when selecting reactants. Since the transesterification of glycerol with ethyl acetate occurs at higher temperature (70 °C) compared with methyl acetate (53.8 °C) and given the fact that higher temperature would improve diacetin and triacetin selectivity, ethyl acetate was selected as the reactant in this work. The aim of this study was to investigate transesterification of glycerol with ethyl acetate under reflux conditions and azeotropic reactive distillation to evaluate if the removal of the reaction by-product could improve the selectivities of DA and TA. Different acid catalysts, either homogeneous or heterogeneous, were used to optimize the process parameters.

2. Materials and Methods

2.1. Materials

Glycerol (purity of 99.9%), ethyl acetate (purity > 99%), acetic acid (purity of 99.85%), 2-ethylhexanol (purity of 99%), absolute ethanol (purity of 99.9%), DA (purity of 50%), and TA (purity > 99%) were supplied from Emery Oleochemicals (Malaysia), Petroimem Sepahan Co. (Iran), Fanavaran Petrochemical Co. (Iran), Tat Chemicals Co. (Iran), Bidestan Co. (Iran), Fluka (Germany), and Fluka (Germany), respectively. Amberlyst 36, para-toluene sulfonic acid (PTSA) (purity > 95%), and sulfuric acid (purity > 95%) were supplied by Sigma-Aldrich (Germany), Farzin Chemicals Co. (Iran), and Merck (Germany), respectively. MA (purity > 95%) was synthesized by the method described in our previous study (Rastegari and Ghaziaskar, 2015) and its concentration was verified by gas chromatography equipped with a flame ionization detector (GC-FID).

2.2. Methods

2.2.1. Batch system

Transesterification of glycerol with ethyl acetate was conducted in a three-necked 250 mL round bottom glass flask. All the experiments were performed at atmospheric pressure. For azeotropic reactive distillation, a Dean-Stark apparatus and a Graham condenser were installed on the top of the flask (Fig. 1), while under the reflux conditions, only the Graham condenser was used (Fig. 2).

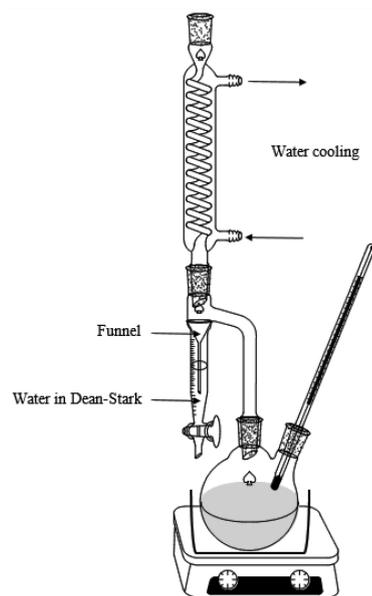


Fig. 1. Schematic presentation of the azeotropic reactive distillation setup used for separation of ethanol from reaction medium in the transesterification of glycerol with ethyl acetate.

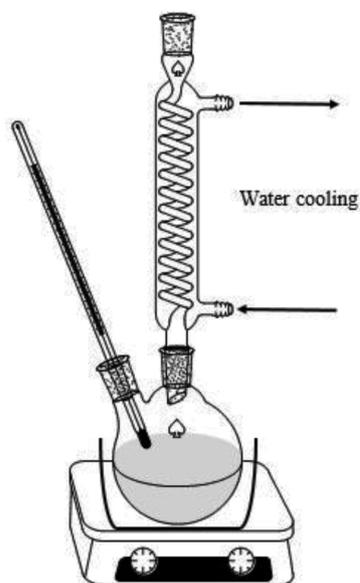


Fig.2. Schematic presentation of the reflux setup used for the transesterification of glycerol with ethyl acetate.

The reaction medium was kept under strong magnetic stirring. The flask was heated using an oil bath and a thermometer was used to measure the vapor temperature. Experiments were initiated by the introduction of prepared reaction mixture into the flask, followed by heating until the reaction mixture reached the desired temperature, then the catalyst was added. During the reaction in the azeotropic reactive distillation experiments, the residual ethyl acetate and produced ethanol would rise to the top of the flask, entering the Dean-Stark and flowing through the Graham condenser where the stream would be condensed. Then the condensate would enter the funnel placed inside the Dean-Stark side arm (Fig. 1). Since ethyl acetate and ethanol are miscible, while ethyl acetate is not soluble in water, half of this side arm was filled with water. The condensed ethanol and ethyl acetate are lighter than water, so they flowed through water by exiting the funnel's bottom. Ethanol is soluble in water while ethyl acetate solubility is limited. So, ethanol was separated from ethyl acetate by dissolving in water and ethyl acetate containing low amounts of ethanol flowed back to the flask. In this way, some ethanol was removed from the reaction medium. Comparison of the obtained results in these two systems could help to investigate the effect of removing ethanol from reaction medium. It must be mentioned that all the experiments were performed at temperature of 70 °C, because ethyl acetate and ethanol azeotrope mixture boils at this temperature (Kale et al., 2015).

2.2.2. Semi-batch system

In this section, transesterification of glycerol with ethyl acetate was performed in a designed semi-batch system which is shown in Figure 3. The aim of this experiment was to investigate the effect of simultaneous introduction of fresh ethyl acetate into reaction medium and ethanol removal on the glycerol conversion and products selectivities. To achieve that, glycerol was placed in a three neck flask and temperature was elevated with the aid of an oil bath. After temperature stabilization at 70 °C, ethyl acetate was introduced into the flask through one neck, while the produced ethanol left the flask through the other neck. Introduction of fresh ethyl acetate to the reaction medium and removal of the by-product, i.e., ethanol, could help the reaction to proceed.

2.3. Analytical method

Before sample analysis, the homogeneous catalysts were removed by addition of sufficient amounts of solid sodium hydrogen carbonate to each sample. After that, samples were dried by addition of solid sodium sulfate. A gas chromatograph (3420, BEIFEN, China) equipped with a flame ionization

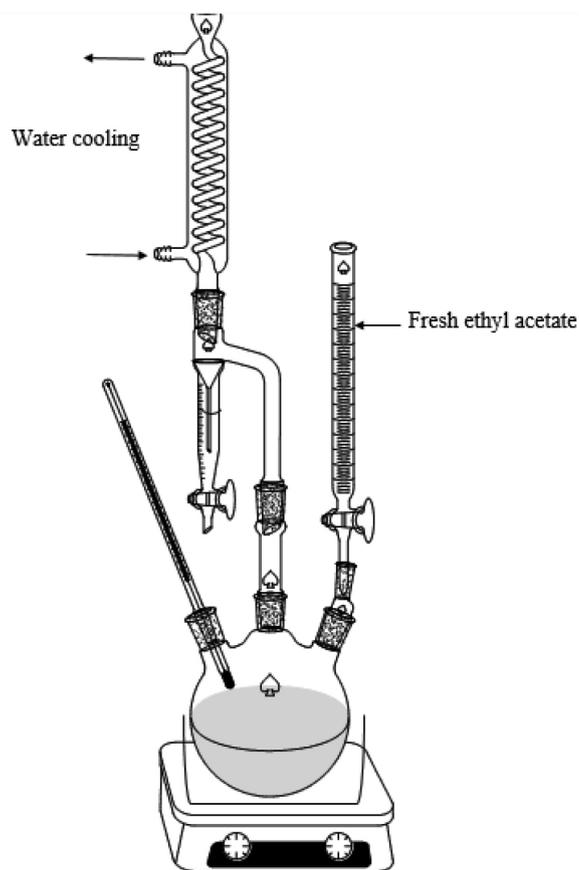


Fig.3. Schematic presentation of the azeotropic reactive distillation semi-batch setup used for the transesterification of glycerol with ethyl acetate.

detector (FID) was used for analysis. The separation was carried out in an HP-5 capillary column (i.d. = 0.25 mm, length = 30 m, film thickness = 0.25 μm) using nitrogen as carrier gas. All injections were made in the split mode (split ratio of 1:30) and the following temperature program was used: 80 °C ramped to 90 °C at 3 °C.min⁻¹, then programmed to 280 °C, where it was held for 5 min. The injector and the detector temperature were set at 280 °C and 300 °C, respectively. Quantification was performed by injecting some standard solutions containing 2-ethylhexanol as an internal standard and integrating the peak areas to draw the calibration curves. The glycerol conversion, each product selectivity, and yield were calculated as reported by Morales et al. (2011).

3. Results and Discussion

3.1. Effect of ethanol removal from the reaction medium

As shown in Scheme 1, transesterification of glycerol with ethyl acetate is a consecutive reaction by stepwise formation of MA, DA, and TA. Each step is equilibrium limited and ethanol is produced as an unavoidable by-product. According to Le Chatelier's principle, the equilibrium could be shifted towards the products either by using one reactant in excess or by removing one of the products during the reaction. Therefore, azeotropic reactive distillation was used to investigate the effect of continuous removal of ethanol to shift the equilibrium towards the products. The results of azeotropic reactive distillation and reflux system are compared in Figure 4. Transesterification in the reflux setup led to higher selectivities to DA and TA, at the first and the second steps. At the first step, the selectivity values of 57%, 28%, and 3% were obtained for MA, DA, and TA, respectively. While these values were changed to 41%, 47%, and 12%, at the second step, respectively. At both steps, the glycerol conversion was

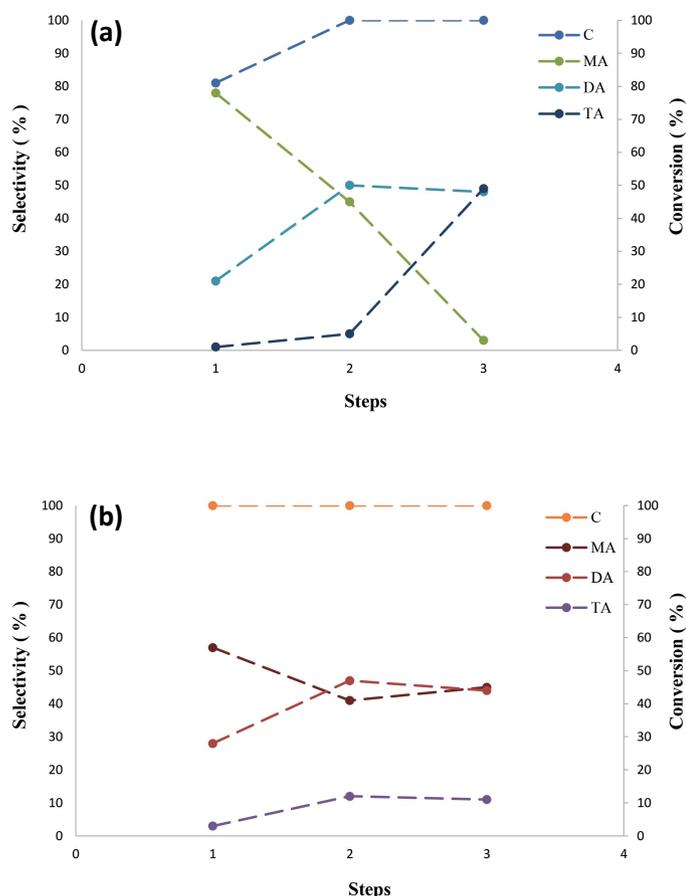
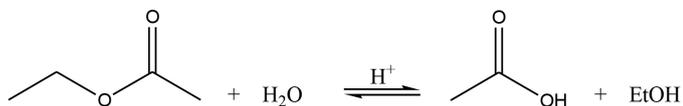


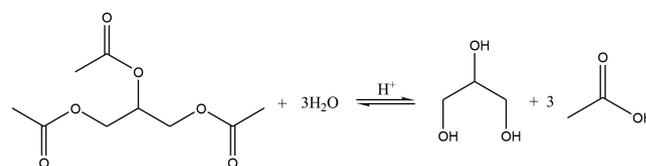
Fig.4. Glycerol conversion and products selectivities for consecutive steps of glycerol transesterification with ethyl acetate at temperature of 70 °C, ethyl acetate to glycerol molar ratio of 12, after 7h of reaction and using Amberlyst 36 as catalyst; results for (a) the azeotropic reactive distillation setup and (b) the reflux setup.

100%. Under azeotropic reactive distillation, only 81% of glycerol was converted into acetins at the first step, but all of the glycerol was consumed at the second step. The total selectivity obtained to DA and TA at the first and the second steps of azeotropic reactive distillation were 22% and 55%, respectively. However, the third step of the azeotropic reactive distillation, led to better results for DA and TA selectivities. In the azeotropic reactive distillation system, MA, DA, and TA selectivity were 3%, 48%, and 49% while these values stood at 45%, 44%, and 11% under reflux conditions, respectively.

These observations could be attributed to the extent of the reaction progress. At the beginning of the reaction, the glycerol concentration was high, while acetins were not present in large amounts. As shown in Scheme 1, the reaction of 1 mole of glycerol would produce 3 moles of ethanol. Hence, the transesterification produced a large amount of ethanol at initial steps, which entered the Dean-stark and then flowed back to the flask. Due to the water solubility in ethanol, some water would enter the reaction medium too. As illustrated in Schemes 2, and 3 water could hydrolyze ethyl acetate and acetins. At initial steps, acetins concentrations were low and, therefore, ethyl acetate might be hydrolyzed producing ethanol and acetic acid.



Scheme 2. Ethyl acetate hydrolysis in presence of water in acidic medium.



Scheme 3. TA hydrolysis in the presence of water in acidic medium.

According to Le Chatelier's principle, ethanol shifts the equilibrium limited transesterification reaction to produce reactants. Therefore, the glycerol conversion, DA and TA selectivities were lower than the amounts obtained under reflux conditions at the first and second steps.

As illustrated in Figure 4, at the third step, under azeotropic reactive distillation, DA and TA selectivities were higher than the obtained values for the reflux system. These observations could be related to the presence of acetic acid in the reaction medium. Under azeotropic reactive distillation conditions, removal of ethanol could accelerate ethyl acetate hydrolysis compared with the reflux system. Ethyl acetate hydrolysis produced acetic acid and, therefore, the amount of the produced acetic acid was higher than the amounts in the reflux system. Presence of acetic acid prevented the hydrolysis of acetylated derivatives. In addition, acetic acid could catalyze the reaction (Kale et al., 2015). Therefore, at the third step, under azeotropic reactive distillation, the transesterification of glycerol with ethyl acetate resulted in higher selectivities to DA and TA.

Although the third step of the azeotropic reactive distillation led to more favorable results, the reflux setup was used for the subsequent studies. More specifically, the duration of each step was 7h and the first step of the transesterification in the reflux system resulted in more favorable outcomes and accordingly, using the reflux system was less time consuming and also required relatively less quantity of chemicals. Hence, the reflux system was used in the process development studies to quickly evaluate the feasibility of the glycerol transesterification with ethyl acetate.

3.2. Effect of catalyst type

It is well documented that esterification/transesterification reactions require acid catalysts and that the strength of the acid used is an important factor affecting the kinetics of the reaction (Rastegari and Ghaziaskar, 2015). To investigate the effect of catalyst on the reaction progress, first a control reaction was conducted in the absence of any catalysts with an ethyl acetate to glycerol molar ratio of 12. It was observed that the conversion of glycerol was above 10%. Moreover, MA was the major product with a selectivity of 81% and only small amounts of DA and TA with selectivities of 15%, and 4%, respectively, were detected. This behavior is probably due to the presence of acetic acid indicating a homogeneously-driven acid catalysis (Saka et al., 2010).

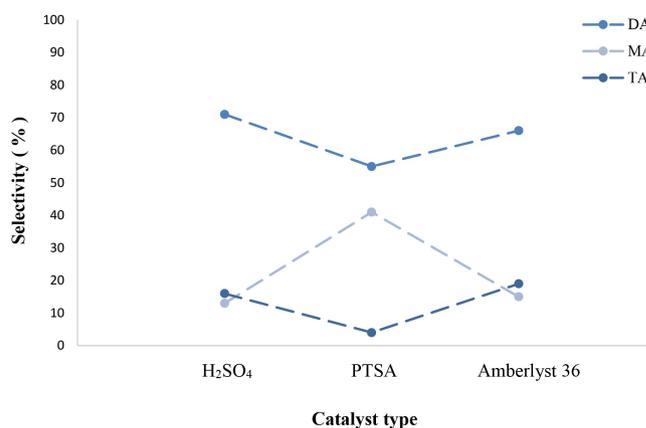


Fig.5. Effect of catalyst type on the products selectivities in the transesterification of glycerol with ethyl acetate at temperature of 70 °C, ethyl acetate to glycerol molar ratio of 12, in the reflux setup after 7h of reaction.

Then, in order to investigate the effect of catalyst type, sulfuric acid, PTSA, and Amberlyst 36 were used. According to the data presented in Figure 5, sulfuric acid was the most effective catalyst and yielded a better selectivity of about 87% to DA and TA. While PTSA was found to possess a selectivity of 41% to MA. As mentioned earlier, the acid strength of a given catalyst has a significant influence on its catalytic activity and selectivity (Kale et al., 2015). Overall, sulfuric acid led to the most favorable results and was chosen as the catalyst for the subsequent experiments.

3.3. Effect of catalyst quantity

Effects of catalyst quantity on the products selectivity as well as glycerol conversion were studied using 2.2wt.%, 4.5wt.%, 6.8wt.%, and 9.0wt.% sulfuric acid to glycerol. The reaction conditions were temperature of 70 °C and ethyl acetate to glycerol molar ratio of 12. The results obtained are shown comparatively in Figure 6.

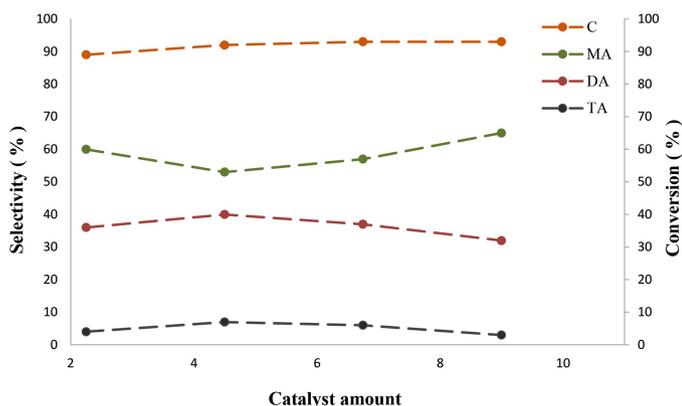


Fig.6. Effect of sulfuric acid quantity on the glycerol conversion and products selectivities in the transesterification of glycerol with ethyl acetate at temperature of 70 °C, ethyl acetate to glycerol molar ratio of 12, in the reflux setup after 7h of reaction.

By increasing the catalyst quantity from 2.2wt.% to 4.5wt.%, the selectivity to DA and TA was increased while further increases of sulfuric acid quantity, decreased the selectivity. According to Scheme 2, the acid catalyst can hydrolyze ethyl acetate, producing ethanol, which is the by-product of the transesterification reaction. Therefore, the transesterification reaction would shift towards the reactants. Accordingly, the catalyst quantities higher than 4.5wt.% was not found effective in proceeding the reaction forward. Overall, it was revealed that 4.5wt.% of sulfuric acid was suitable to obtain the most favorable results. On this basis, further investigations were performed with this amount of sulfuric acid. It is worth mentioning that the formation of by-products was not observed in these experiments due to the low temperature used, i.e., 70 °C.

3.4. Effect of reaction time

In a batch setup, the reaction time could exert important effects on the selectivity of the products. In order to investigate the effect of this parameter, reaction durations of 3h, 5h, 7h, and 9h were taken into account. These experiments were conducted at temperature of 70 °C, ethyl acetate to glycerol molar ratio of 12, and in the presence of 4.5wt.% of sulfuric acid. The results obtained are presented in Figure 7. As expected in a consecutive reaction, an increase in DA and TA selectivities were observed together with a decrease in MA selectivity by extending the reaction time from 3h to 7h. Further increases of the reaction time had no significant impacts on the reaction (ANOVA). These observations are ascribed to the accumulation of ethanol molecules in the medium as the reaction progressed. Therefore, reaction duration of 7h was selected as the optimum reaction time.

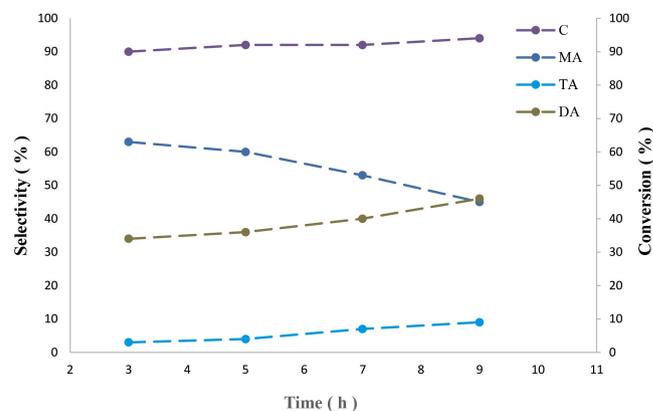


Fig.7. Effect of the reaction time on glycerol conversion and products selectivities in the transesterification of glycerol with ethyl acetate at temperature of 70 °C, ethyl acetate to glycerol molar ratio of 12, in the reflux setup, by using 4.5wt.% sulfuric acid as catalyst.

3.5. Effect of ethyl acetate to glycerol molar ratio

The molar ratio of ethyl acetate to glycerol is one of the important variables affecting the products selectivities. According to Le Chatelier's principle, using excess ethyl acetate is beneficial but from the economic point of view, using large amounts of reactants would negatively impact the economic viability of the process. Therefore, the effect of different ethyl acetate to glycerol molar ratio (i.e., 6, 9, and 12) was investigated. As illustrated in Figure 8, the maximum selectivity to DA and TA was obtained for molar ratio of 12. Nevertheless, the changes in the selectivity to the most desirable product, i.e., TA, was not high enough (lower than 10%) in the range investigated. It has been previously shown that a high methyl acetate to glycerol mole ratio of 50 would be needed to achieve a total selectivity of about 74% for DA and TA which is not practical (Morales et al., 2011). Hence, higher molar ratios were not investigated in the reflux setup. However, the effect of simultaneously introducing excess fresh ethyl acetate to the reaction medium and ethanol removal was investigated in the azeotropic reactive distillation setup, which is described in the following section.

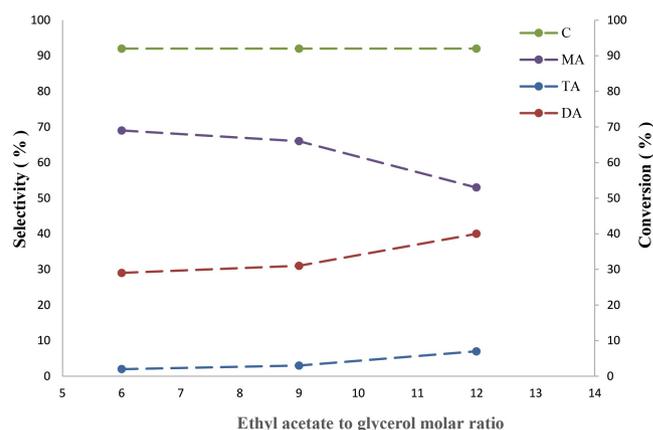


Fig.8. Effect of ethyl acetate to glycerol molar ratio on glycerol conversion and products selectivities in the transesterification of glycerol with ethyl acetate at temperature of 70 °C, in the reflux setup, by using 4.5wt.% sulfuric acid as catalyst after 7h of reaction.

3.6. Semi-batch transesterification

The effect of simultaneously introducing excess fresh ethyl acetate to the reaction medium and ethanol removal was investigated in the azeotropic

reactive distillation setup. The reaction was performed at temperature of 70 °C by using 4.5wt.% of sulfuric acid. The reaction was monitored for 24h to study the changes in the product distribution with time under continuous ethyl acetate introduction and ethanol removal. As shown in Figure 9, after 3h of the reaction, a glycerol conversion of 100% was obtained without formation of any by-products. After 9h of reaction, there was no MA in the reaction medium and it was fully converted into DA and TA. After 18h, selectivities of 25% and 75% were obtained for DA and TA, respectively, and the reaction reached an equilibrium. Overall, 100% selectivity for TA was not obtained due to the lack of sufficient time for reaction. Moreover, at initial stages, there were many hydroxyl functional groups in glycerol and its esterified derivatives, and so effective collisions could happen in a short time. However, by passing time and reaction of more hydroxyl functional groups, there were not enough opportunities for effective collisions and hence, the probability of the ethyl acetate molecules colliding the reactive sites must have been reduced, and the reaction progress stopped.

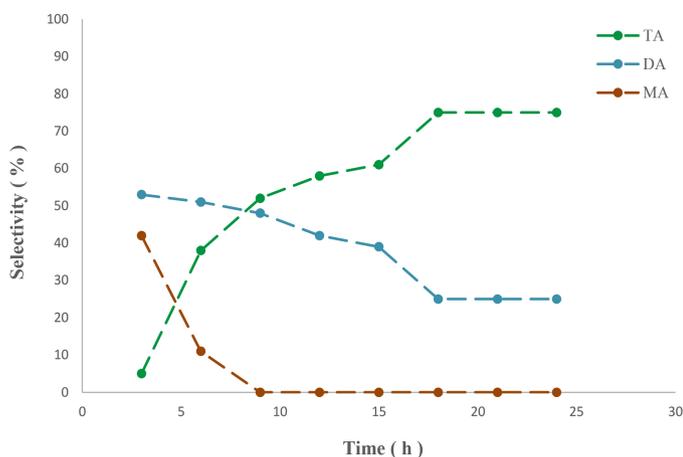


Fig.9. Effect of glycerol transesterification with ethyl acetate in the semi-batch system, at temperature of 70 °C and by using 4.5wt.% sulfuric acid as catalyst.

4. Conclusions

Transesterification of glycerol with ethyl acetate was studied using ethyl acetate as reactant and entrainer. Using azeotropic reactive distillation setup for ethanol removal from the reaction medium was not effective after 7h of reaction. This was ascribed to the introduction of water into the reaction medium through dissolving in ethanol and subsequently hydrolyzing ethyl acetate. Sulfuric acid showed the most favorable performance among the different catalysts investigated. All the experiments were performed at temperature of 70 °C in which the formation of the by-products was not observed. Simultaneous addition of fresh ethyl acetate to the reaction medium in a semi-batch system, and ethanol removal, led to 100% glycerol conversion with selectivities of 25% and 75% for DA and TA, respectively, after 18h of reaction. These selectivities to DA and TA were obtained herein because fresh ethyl acetate acted as excess reactant and as entrainer for ethanol removal from reaction medium.

Acknowledgements

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References

[1] Behr, A., Eilting, J., Irawadi, K., Leschinski, J., Lindner, F., 2008. Improved utilization of renewable resources: new important derivatives of glycerol. *Green Chem.* 10, 13-30.

[2] Bremus, N., Dieckelmann, G., Jeromin, L., Rupilius, W., Schutt, H., 1983. Process for the continuous production of triacetin. U.S. Patent 4,381,407.

[3] Corma, A., Iborra, S., Velty, A., 2007. Chemical routes for the transformation of biomass into chemicals. *Chem. Rev.* 107(6), 2411-2502.

[4] Ferreira, P., Fonseca, I.M., Ramos, A.M., Vital, J., Castanheiro, J.E., 2011. Acetylation of glycerol over heteropolyacids supported on activated carbon. *Catal. Commun.* 12(7), 573-576.

[5] Goncalves, V.L., Pinto, B.P., Silva, J.C., Mota, C.J., 2008. Acetylation of glycerol catalyzed by different solid acids. *Catal. Today.* 133-135, 673-677.

[6] Goncalves, C.E., Laier, L.O., Cardoso, A.L., Silva, M.J., 2012. Bio additive synthesis from H3PW12O40 catalyzed glycerol esterification with HOAc under mild reaction conditions. *Fuel Process. Technol.* 102, 46-52.

[7] Kale, S., Umbarkar, S.B., Dongare, M.K., Eckelt, R., Armbruster, U., Martin, A., 2015. Selective formation of triacetin by glycerol acetylation using acidic ion exchange resins as catalyst and toluene as entrainer. *Appl. Catal., A.* 490, 10-16.

[8] Melero, J.A., Van Grieken, R., Morales, G., Paniagua, M., 2007. Acidic mesoporous silica for the acetylation of glycerol: synthesis of bio additives to petrol fuel. *Energy Fuels.* 21(3), 1782-1791.

[9] Morales, G., Paniagua, M., Melero, J.A., Vicente, G., Ochoa, C., 2011. Sulfonic acid-functionalized catalysts for the valorization of glycerol via transesterification with methyl acetate. *Ind. Eng. Chem. Res.* 50(10), 5898-5906.

[10] Otera, J., 1993. Transesterification. *Chem. Rev.* 93(4), 1449-1470.

[11] Rastegari, H., Ghaziaskar, H.S., 2015. From glycerol as the by-product of biodiesel production to value added monoacetin by continuous and selective esterification in acetic acid. *J. Ind. Eng. Chem.* 21, 856-861.

[12] Rastegari, H., Ghaziaskar, H.S., Yalpani, M., 2015. Valorization of biodiesel derived glycerol to acetins by continuous esterification in acetic acid: focusing on high selectivity to diacetin and triacetin with no byproducts. *Ind. Eng. Chem. Res.* 54(13), 3279-3284.

[13] Rezayat, M., Ghaziaskar, H.S., 2009. Continuous synthesis of glycerol acetates in supercritical carbon dioxide using Amberlyst 15. *Green Chem.* 11(5), 710-715.

[14] Saka, S., Isayama, Y., Ilham, Z., Jiayu, X., 2010. New process for catalyst free biodiesel production using subcritical acetic acid and supercritical methanol. *Fuel.* 89(7), 1442-1446.

[15] Zhou, C.H.C., Beltramini, J.N., Fan, Y.X., Lu, G.M., 2008. Chemoselective catalytic conversion of glycerol as a biorenewable source to valuable commodity chemicals. *Chem. Soc. Rev.* 37(3), 527-549.