



SYNTHESIS OF ACETINS FROM ETHYL ACETATE VIA TRANSESTERIFICATION WITH GLYCEROL USING A SULPHONIC ACID TYPE ION-EXCHANGE RESIN

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Demand for biodiesel has increased over the years as a substitute to petrol and diesel due to its environmental-friendly nature and lower cost. Glycerol being major by-product of the process constitutes 10 wt.% of the products hence conversion of glycerol to value added products such as acetins in the plant reduces the production cost of biodiesel. The present work focuses on the transesterification reaction between glycerol and ethyl acetate over heterogeneous catalyst, Amberlyst-15(wet). The batch studies were carried out and the effect of reaction parameters such as reaction time (1-7 h), glycerol to ethyl acetate molar ratio (1:3-1:12), temperature (50-70 °C), catalyst loading (2-5 w/w%) have been studied. The maximum conversion of glycerol obtained at (G : EA) molar ratio 1:6, reaction temperature of 70 °C and 4 w/w% catalyst loading for 7 h was 97.71 % and the selectivity of mono-, di- and triacetins were 36.7, 60.7 and 2.51 %, respectively. This provides an eco-friendly and sustainable path for valorisation of biodiesel derived glycerol.

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INTRODUCTION

In present years due to considerable utilization of fossil fuels there is lot of ecological disturbance globally.¹ Worldwide the transportation sector is depended on fossil fuel to a major extent. The attention is consequently focused on cleaner fuels that can effortlessly replace fossil fuels i.e., biofuels. This would assist to tackle the depletion of worldwide energy reserves and environmental pollution.² Bio-diesel, a renewable fuel, possessing the characteristics comparable to petroleum, has gained huge interest in the current years.³ Biodiesel which serves as a green substitute to diesel is synthesized by transesterification of vegetable oils (Soya bean oil, palm oil etc.) or animal fats with an alcohol such as methanol and ethanol.⁴⁻⁶ Though biodiesel is a greener fuel and penetrated the market internationally, it has not realized its potential due to the formation of a substantial amount of by-product i.e., glycerol.⁷ Various researchers have explored different routes to give value addition to glycerol, which in turn enhances the economic value of biodiesel. Conversion of glycerol to acetins by esterification or transesterification reactions is an effective way to make use of glycerol.⁸ The products obtained from the esterification or transesterification are mono-, di- and triacetins. These products have wide applications especially as food additives, safety plasticizers, solvents, biodegradable polyesters etc.^{9, 10}

Literature review on synthesis of acetins via esterification of glycerol using acetylating agent such as acetic anhydride and acetic acid reveals that studies were made with heteropoly acids^{11,12} ion exchange resin, zeolites, and mixed oxides.¹³⁻¹⁵ Limited attempts were made for conversion of

glycerol of acetins through transesterification route using homogeneous and heterogeneous acid catalysts.¹⁶

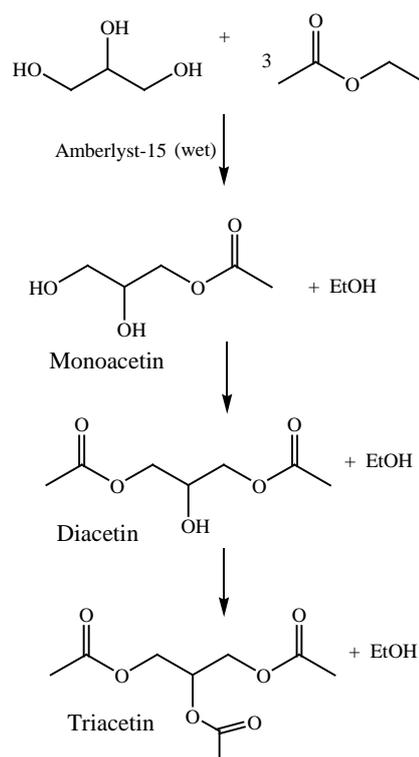


Figure 1. Transesterification of glycerol with ethyl acetate.

Homogeneous catalysts have various boundaries such as difficulty in removal from reaction mixture, non-reusability and corrosion of equipment. As per the literature in our purview this is the first work being reported for the conversion of glycerol with ethyl acetate to acetins by transesterification over Amberlyst-15 (wet). The main objective of this work is to propose a viable eco-friendly and

sustainable route to convert glycerol resulting from biodiesel production to value added products acetins using Amberlyst-15 (wet) catalyst. This article focuses on obtaining optimum operating parameters, so studies were conducted by varying parameters such as reaction time, mole ratio of reactant (glycerol: ethyl acetate), reaction temperature and catalyst loading (weight of catalyst to the weight of reaction mixture). The reusability studies were done and reported. The present work provides a path for the continuous conversion of biodiesel derived glycerol to value added products. The esterification reaction of glycerol with ethyl acetate over Amberlyst-15 (wet) is presented in Fig. 1.

EXPERIMENTAL

Materials

Glycerol (purity of 99.9 %) was supplied by Hi-Media Laboratories Pvt. Ltd., Ethyl acetate (purity of 99 %) and Amberlyst-15 (wet) was supplied by Sigma Aldrich. It is a macro-porous based ion exchange resin containing a strongly sulfonic acid group. It acts as an excellent strong acid catalyst. It has good reusability property. The significant properties of Amberlyst-15 (wet) are listed in Table 1.

Table 1. Properties of Amberlyst-15 (wet).

Appearance	Hard spherical particles
Matrix	styrene-divinylbenzene (macro reticular)
Particle size	<300 μm
Hydrogen ion capacity	4.7 meq g^{-1} by dry weight
Moisture	$\leq 1.6\%$

Procedure

The experimental setup consists of a three-necked round bottomed flask equipped with an oil bath, magnetic stirrer, water-cooling condenser, thermometer and a temperature controller. When the desired temperature is reached, calculated amount of glycerol and ethyl acetate were added to the flask and the catalyst was also charged into the mixture. The amounts of glycerol and ethyl acetate to be added were calculated based on the molar ratio to be maintained for the reaction. After the addition of desired amount of catalyst into the reaction mixture the reaction time commences. Samples were collected at regular intervals. After the reaction is completed, the catalyst was removed by filtration and the reaction mixture was analysed using GC. Experiments were conducted thrice to minimize the error.

Analysis of sample

The periodically collected samples were analysed using GC (Mayura Analytical LLP Model 1100). 0.1 μL of the sample was withdrawn with a syringe and injected to the GC column equipped with capillary column (silphenylene polysiloxane, (30 m, 250 μm , 0.25 μm) with nitrogen as the carrier gas at 40 mLmin^{-1} and programmed temperature of 120-150 $^{\circ}\text{C}$. The products monoacetin (MA), diacetin (DA)

and triacetin (TA) were identified based on their retention times by utilizing predetermined calibration data of known pure compounds. Glycerol conversion, yield and selectivity of acetins were calculated as follows (Eqns. 1, 2 and 3), where X = MA, DA or TA.

$$\phi_G (\%) = \frac{[G]_{\text{reacted}}}{[G]_{\text{initial}}} \times 100 \quad (1)$$

$$Y_X (\%) = \frac{[X]_{\text{formed}}}{[G]_{\text{starting}}} \times 100 \quad (2)$$

$$S_X (\%) = \frac{[X]_{\text{formed}}}{[G]_{\text{reacted}}} \times 100 \quad (3)$$

where ϕ_G is the glycerol conversion, Y_X is the yield of X^{th} product, S_X is the selectivity for the X^{th} product, $[G]$ is the glycerol concentration.

RESULTS AND DISCUSSION

Influence of reaction time

In batch studies, the time of reaction is an important parameter as it affects the yield and selectivity of the products. In order to understand the influence of time, the studies were conducted with 1:6 mole ratio of glycerol : ethyl acetate (G : EA) at 70 $^{\circ}\text{C}$ and 4 w/w% Amberlyst-15(wet) catalyst loading for 8 h at 600 rpm. Fig. 2a depicts the variation of glycerol conversion with time. From Fig. 2a results it was evident that with increase in reaction time from 1 to 7 hours there has been significant rise in glycerol conversion from 37.36 to 97.71 %. As predicted in a series reaction, the glycerol conversion and yield of monoacetin and diacetin improved with increase in time from 1 to 7 h (Fig. 2b). The reason for longer reaction time could be due to the Amberlyst-15(wet) diffusion resistance to glycerol and further hindrance to the glycerol molecule to enter into the interior resin surface of the catalyst. With progress of reaction the movement of the reaction blend enhances with the formation of products, acetins and ethanol. These are the reasons for Amberlyst-15(wet) showing longer time in glycerol conversion of 7 hours as compared to with Amberlyst-15 (dry).¹⁶ It can also be observed the conversion of glycerol decreased at 8 h might be due to the formation of ethanol, the reversible reaction takes place leading to the reactants. Whereas the formation of diacetin is favoured after 7 h. As this formation is not significant hence a reaction time of 7 h was chosen as optimum for further studies.

The molar ratio of reactants (G : EA) is an important parameter affecting the conversion rate. According to Le Chatelier's principle, using excess molar ratio of reactants, the conversion of equilibrium limited reaction can be enhanced. The transesterification of glycerol is equilibrium limited reaction the study of this parameter is significant.

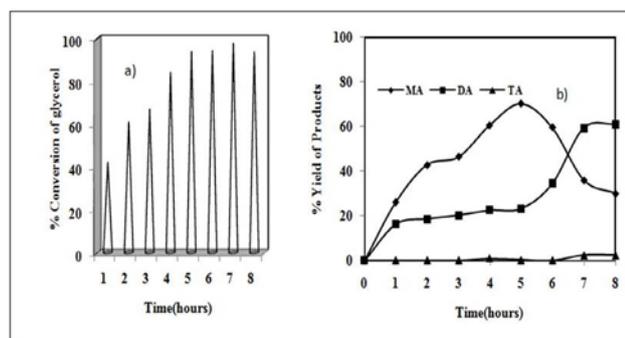


Figure 2. Influence of reaction time on a) glycerol conversion b) yield of products under optimized conditions.

Influence of molar ratio

The effect of different reactant molar ratio of (G : EA) 1:3, 1:6, 1:9, and 1:12 were studied at a reaction temperature of 70 °C, catalyst loading of 4 w/w% for 7 h at 600 rpm. Fig. 3 depicts results of the variation of glycerol conversion with molar ratio of reactants.

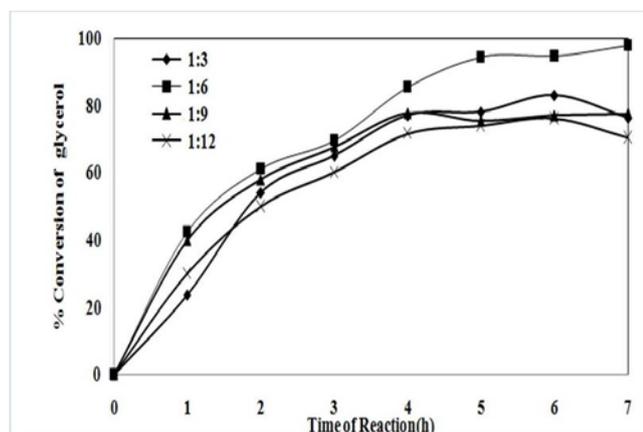


Figure 3. Influence of (G:EA) molar ratios on glycerol conversion, under optimized conditions.

The conversion of glycerol with (G : EA) molar ratio of 1:3, 1:6, 1:9, and 1:12 were 78.79, 97.7, 77.57 and 70.42 %, respectively. Fig.4 depicts the variation of acetins selectivity with molar ratio.

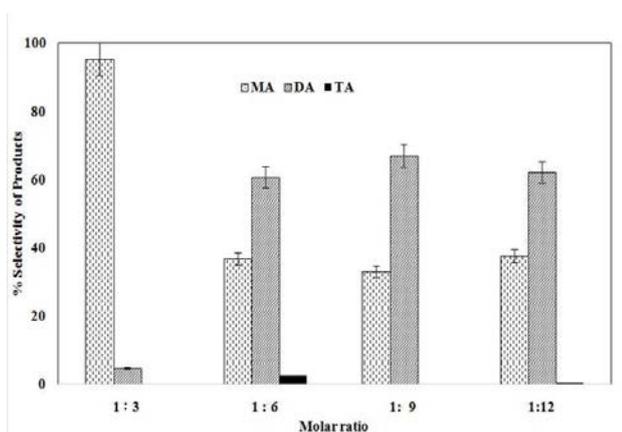


Figure 4. Influence of (G : EA) molar ratios on product selectivity under optimized conditions.

The selectivity's of products at 1:3 molar ratio were 95.3 % MA, 4.68 % DA at 1:6 were 36.7 % MA, 60.7 % DA and 2.51 % TA; at 1:9 were 32.9 % MA and 67.1 % DA; at 1:12 were 37.6 % MA, 62.2 % DA and 0.25% TA. The maximum conversion of glycerol to acetins was obtained at molar ratio of 1:6. The decrease in conversion on glycerol for the molar ratio 1:9 could be due to the reason that, excess ethyl acetate concentration may hinder the transesterification reaction by diluting the active reacting species i.e. glycerol leading to decrease in mass transfer of glycerol and subsequently reaction rate. Hence for further studies, molar ratio of 1:6 has been chosen as the optimum value.

Influence of reaction temperature

The experimental studies carried out at a particular temperature are useful for obtaining a rate constant. Further the studies at different temperature are useful in determining the activation energy for the reaction.¹⁷ The reaction was carried out at (G : EA) molar ratio of 1:6, catalyst loading of 4 w/w % and at different temperatures, 50, 60 and 70 °C. The reaction temperatures were chosen based on the boiling point of the reactants so that the loss of reactant was avoided.

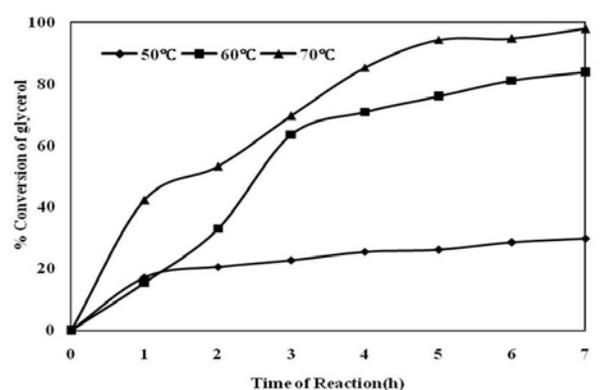


Figure 5. Influence of temperature on conversion of glycerol, under optimized conditions.

The conversion of glycerol obtained at 50, 60 and 70 °C were 29.81, 83.75 and 97.7 % as shown in Fig.5. The selectivity's obtained at 50 °C were 36.55 % MA and 63.45 % DA, at 60 °C were 51.11 % MA and 48.88 % DA, at 70 °C were 36.7 % MA, 60.7 % DA and 2.51 %, Fig. 6. Indeed, at lower temperature of 50 °C it was difficult for the reactants to contact the active sites of the inner and outer sites of the Amberlyst-15 (wet) resin due to the viscosity of the reaction mixture. This resistance was the main reason for low glycerol conversion at 50 °C. As the temperature increased, the viscosity of the glycerol is reduced and this in turn results in lower viscosity of the reaction mixture, which results in more accessibility to active sites of the resin results in higher conversion at 70 °C. Similar observations were reported by Shafiei et.al in their work.¹⁸

Influence of catalyst loading

The rate of the chemical reaction can be increased by using proper amount of the catalyst due to availability of a new low energy pathway for the conversion of reactants to products. The effect of catalyst loading on transesterification

of glycerol with ethyl acetate was studied with catalyst loading of 2, 3, 4 and 5 w/w% with (G : EA) molar ratio of 1:6 and reaction temperature of 70 °C at 600 rpm.

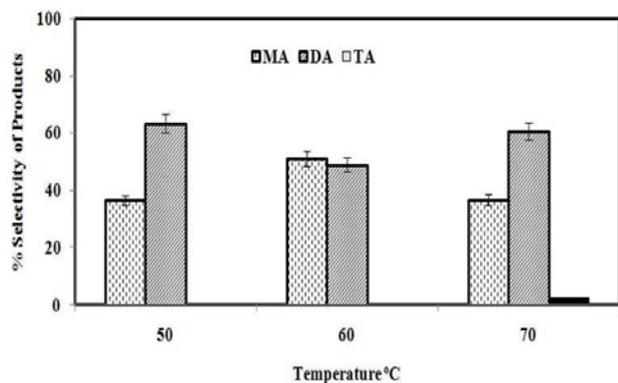


Figure 6. Effect of temperature on product selectivity under optimized conditions.

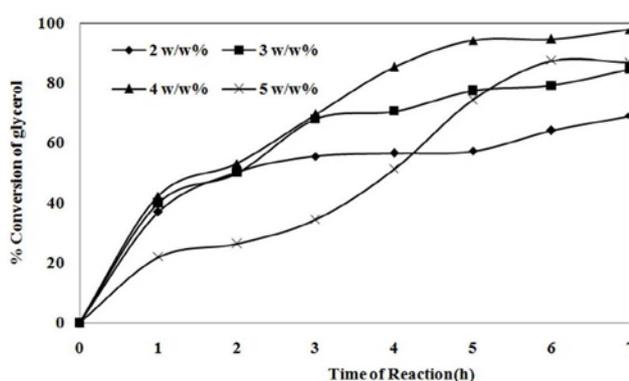


Figure 7. Influence of catalyst loading on conversion of glycerol, under optimized conditions.

The conversion of glycerol obtained with 2, 3, 4 and 5 w/w% catalyst loading were 69.08, 84.75, 97.71 and 86.91 % respectively as shown in Fig. 8. The selectivity's obtained at 2 w/w% were 51.77 % MA and 48.22 % DA, at 3 w/w% were 47.54 % MA and 52.54 % DA, at 4 w/w% were 36.7 % MA, 60.7 % DA and 2.51 % TA, at 5 w/w% were 45.46% MA, 53.63 % DA and 0.89 % TA (Fig. 8). With increase in catalyst loading from 2 to 4 w/w% the glycerol conversions was increased from 69.08 to 97.71 % and even the selectivity from monoacetin to diacetin enhanced due to the increase in active sites whereas for 5 w/w% loading the glycerol conversion dropped to 86.91 % and the selectivity declined. The reason for decline in glycerol conversion with increase in catalyst loading may be due to overloading of active sites which hinders the mass transfer phenomena, with increasing the viscosity of the reaction medium. Hence the catalyst loading greater than 4w/w% was found not effective for transesterification of glycerol with ethyl acetate to proceed forward.

Overall, it can be concluded 4 w/w% catalyst loading was appropriate to obtain the encouraging results. The selectivity towards triacetin is very low as the number of active sites on Amberlyst-15 (wet) is not enough to catalyse the triacetin and only the formation of diacetin was favourable.¹⁹

Comparison with literature

From literature review it was evident that very few reports are available on transesterification of glycerol with ethyl acetate to acetins. Meireles and Pereira¹⁶ have reported various homogeneous and heterogeneous catalysts for synthesis of acetins through transesterification of glycerol with ethyl acetate. Among the studied catalysts, the homogeneous catalysts were found to be active catalyst with more selectivity towards triacetin compared to heterogeneous catalyst. It was reported complete glycerol conversion was obtained at 90 °C, reaction time of 10 h for 1:30 molar ratio of G : EA.¹⁶ Shafiei et al.¹⁸ have reported synthesis of acetins through transesterification of glycerol with ethyl acetate using batch, semi batch and reactive distillation system using homogenous catalyst. They concluded that semi batch system gave 100 % glycerol conversion after 18 h of reaction time with selectivity of

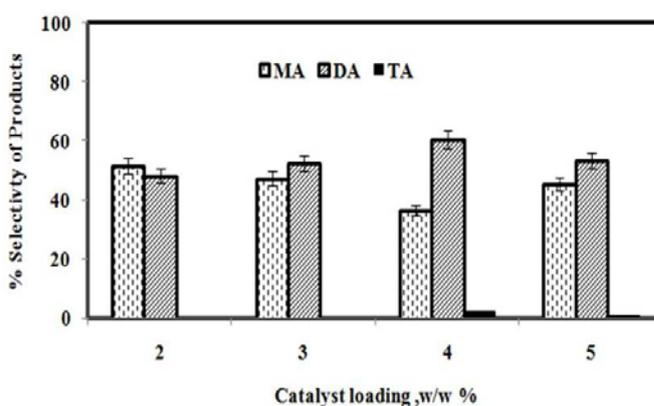


Figure 8. Influence of catalyst loading on product selectivity under optimized conditions.

Reusability of Catalyst

For industrial process to be an environmentally friendly and economical recycling of the catalyst is a significant feature. To regenerate Amberlyst-15 (wet) after a reaction of 7 h the catalyst was separated from reaction mixture by filtration, washed with methanol and n-hexane, and dried at 80 °C for 3 h.²⁰

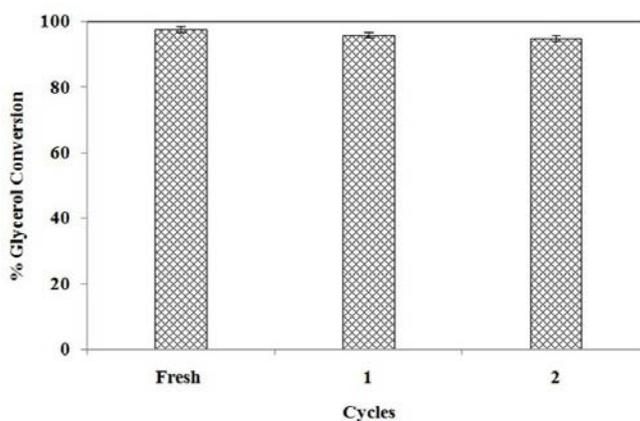


Figure 9. Reusability studies.

The reusability studies were conducted for three runs and the glycerol conversion obtained were 97.71, 95.95 and 94.89 % respectively. Fig. 9 shows that the catalyst exhibits good reusability without much significant loss in activity.

CONCLUSIONS

The environmentally economical benign route has been investigated for the conversion of biodiesel derived glycerol into fine chemicals. The maximum glycerol conversion of 97.71 % was obtained for (G : EA) molar ratio 1:6, reaction temperature of 70 °C and 4 w/w% catalyst loading for 7h and the selectivities of mono-, di-, tri-acetins were 36.7, 60.7 and 2.57 % respectively. Although the production of acetins via transesterification process demands longer reaction times with the use of heterogeneous catalysts Amberlyst-15(wet). It employs ethyl acetate, a reagent of lower cost and toxicity and generates by product ethanol, a low toxicity substance which acts as a raw material for other processes. Further studies can be carried out using reactive distillation as the transesterification reaction is equilibrium limited the application of reactive distillation can help in enhancing the glycerol conversion as well as yield of triacetin by removal of ethanol.

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