

CE-405: EVALUATION OF QUATERNARY AMMONIUM CATALYSTS FOR TRANSESTERIFICATION OF TRIGLYCERIDES

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Biodiesel is produced by transesterification of vegetable oils or animal fats with alcohols usually lower alcohols such as methanol and ethanol, in the presence of a catalyst. Most commercial biodiesel processes use homogenous base catalysts, as they result in a rapid reaction and over 95% conversion. However, homogenous base catalysts cannot be economically recovered, and necessitate a glycerol neutralisation step and place a greater load on a number of downstream separation steps. Replacing liquid homogeneous catalysts with solid heterogeneous catalysts is expected to yield a cleaner product and result in lower production costs, as the catalyst will not have to be continually replaced. Separation of heterogeneous catalysts can be easily achieved using filtration. In this work, the catalytic performances of seven strong base type 1 anionic polymeric resins (PA306s, PA308, HPA25, DIX2, DIX4 and DIX8) with the functional group of $-N(CH_3)_3^+$, are compared against tetramethylammonium hydroxide (TMAOH) in the transesterification of triacetin. The transesterifications were performed in well-mixed isothermal batch reactors at 60°C, 450rpm, with 6:1 methanol to triacetin molar ratio. Almost complete conversion was obtained when using TMAOH with concentration of 5.5 mmol/L, in less than 3 minutes. On reducing the concentration of TMAOH to 0.6875 mmol/L, the time taken to achieve nearly complete conversion was increased to 30 minutes. In comparison, about 90% conversion was achieved by the PA306s after 3 hours with the concentration of 5.5 mmol/L. Two of these resins, PA306s and PA308, gave above 95% conversion at 5.5 mmol/L after 6 hours reaction. No deactivation was observed on PA306s and A26 over five cycles. In addition, the residual activity studies showed that they did not leach. Although anionic polymeric resins are less active than the TMAOH, they have the potential to be developed and improved as heterogeneous catalysts for transesterification, as they are stable to leaching and maintain their conversion.

Keywords: *Anion Exchange Resins, Quaternary Ammonium, Triacetin.*

• INTRODUCTION

Transesterification is the general term used to describe an important class of organic reactions in which an ester is transformed into another ester through an interchange of the alkoxy moiety. The reaction is also known as alcoholysis since it takes place by exchanging the alcohol groups and where the original ester reacts with an alcohol. In transesterification reactions, one mole of triglycerides in the vegetable oil or animal fat reacts with three moles of alcohol in the presence of a base or acid catalyst, producing three moles of the respective fatty acid alkyl esters and one mole of glycerol as a by-product [1]. Since transesterification is an equilibrium reaction, the alcohol to be exchanged is generally added in excess in order to achieve a high yield of the desired ester.

Nearly all the processes use homogeneous base catalysts since they give conversion rates to biodiesel of over 95%. Even though reproduction of biodiesel using homogeneous base-catalysts involves a rapid process resulting in high conversion rates with minimal side reactions, it is still not very commercially competitive compared to petroleum diesel due the factors; i) the catalyst cannot be recovered; ii) the use of homogeneous catalyst necessitates the neutralization of glycerol at the end of the reaction; iii) there is limited

use of continuous processing methodologies; and iv) the processes involved are very sensitive to presence of water and free fatty acid [2]. Replacing liquid homogeneous catalysts with solid heterogeneous catalysts is expected to yield a product that does not require neutralization, leading to lower processing costs, because the catalyst will not have to be continually replaced.

Several types of heterogeneous base catalysts have been developed for the transesterification of vegetable oils into biodiesel over the past few years. Among these, ion exchange resin with a quaternary ammonium functional group (QN^+OH^-) have been identified as an alternative to homogeneous base catalysts that suitable for transesterification in biodiesel production, due to their physical strength, as they are not easily degraded by oxidation or hydrolysis and the better conversion rates achieved [3,4]. In this present paper, a systematic study on the performance of seven commercial ion exchange resins was reported for the transesterification of triacetin with methanol. Their transesterification activity was compared at identical catalyst concentrations according to their active base sites. Their reusability and residual activity were screened to evaluate their activity and stability, respectively. Finally, their transesterification performance was measured against that of the homogeneous quaternary ammonium catalyst, tetramethyl ammonium hydroxide (TMAOH). In addition, triacetin is used as model triglyceride in this study, due to its structural simplicity, which makes the identification and quantification of reaction products easier.

• **MATERIALS AND METHODS**

Determination of Ester Content in Triacetin

The method used was modified from [1]. The instrument used was a Hewlett-Packard 5890 Series II gas chromatograph equipped with a flame ionisation detector (FID) and autosampler. The column was a Varian CP-Wax 52 CB capillary column (Varian, USA) 30 m in length, with an internal diameter of 0.32 mm, and film thickness of 0.25 μm . The carrier gas was helium. Data were acquired and processed using the Clarity chromatography station (Data Apex) for Windows software. The split flow was measured at 18.5 mL/min with a bubble flow meter.

The reaction samples were diluted with 2-propanol at the ratio of 1:2.2 (v/v) reaction mixture to 2-propanol. The toluene used as an internal standard, had been diluted in 2-propanol at the ratio of 1:16 (v/v). 1 μL of this mixture was injected into the column using the autosampler. The oven temperature was held at 50°C for 4 minutes, and then increased at the rate of 30°C/min to 180°C, and kept there for 2 minutes before again being increased at the rate of 30°C/min to 210°C and held there for 15 minutes. The total running time was nearly 30 minutes per injection. The injector and detector were maintained at 255°C and 280°C, respectively.

Transesterification of Triacetin

Several catalysts were sourced from different manufacturers. These included the homogeneous catalyst, tetramethyl ammonium hydroxide or TMAOH (Sigma-Aldrich, UK) and seven heterogeneous catalysts: Amberlite™ A26 (Rohm and Haas, USA); Diaion™ PA306s, Diaion™ PA308 and HPA25 from the Mitsubishi Chemical Corporation (Japan); and Dowex™ 1X2, 1X4 and 1X8 from the Dow Chemical Company (USA).

In order to have same amount of quaternary ammonium between the homogeneous and heterogeneous catalysts, the catalyst used was based on the catalyst active sites instead of catalyst weight. All of the heterogeneous catalysts were subjected to CHN analysis to determine their site density before use. The 500 mL batch reactor (Ken Kimble Ltd., UK) used in this study was designed to avoid any mass transfer limitation. The reactor was heated by a water jacket connected to a heater-circulator. The reactor was fitted with a condenser and a sampling port to allow small aliquots to be withdrawn for analysis.

90 mL of reagent grade methanol (Fisher Scientific, UK) was added to the batch reactor and mixed with 70 mL of triacetin, 99 wt. % (Sigma-Aldrich, UK). The molar ratio of methanol to triacetin was

maintained at 6:1 (mol/mol). The reaction mixture was then heated to 60°C in a water bath. Once at the desired temperature, transesterification was initiated by charging the catalyst, and the reaction mixture was mixed with an overhead stirrer.

1 mL samples were taken initially and then at specified time intervals, filtered and stored for analysis. Quenching of the heterogeneous catalyst was achieved by filtration. The homogeneous catalyst TMAOH was quenched using acetic acid. Transesterification was carried out for two and six hours with the homogeneous and heterogeneous catalyst, respectively. The reaction products were then analysed by gas chromatography. The transesterification experiments were repeated in order to determine standard deviations, which were on average $\pm 3\%$, based on triacetin conversion.

Reusability and Residual Activity Studies

1 mL samples were taken initially and stored. Then, the reaction mixture was heated to 60°C in a water bath. Once at 60°C, transesterification was initiated by charging with 5.5 mmol active sites of a catalyst. The catalysts were mixed with an overhead stirrer at 450 rpm, and transesterification was carried out for an hour. The reaction mixture was then filtered to separate the reaction mixture in liquid form from the solid catalyst. In the residual activity measurement, 1 mL of the liquid reaction mixture was taken and stored. Then, the rest of the liquid reaction mixture was added to the three-necked round-bottomed flask and transesterification was performed for another four hours without the catalyst.

In the reusability measurement, the solid catalyst filtrate from the previous experiment was added to a new reaction mixture containing 45 mL of reagent-grade methanol and 35 mL of triacetin. The experiment was then run for an hour before the catalyst was filtered and a new reaction mixture introduced. The experiment was repeated for four cycles.

Catalyst Characterization

1. Elemental (CHN) Analysis. Elemental analysis (CHN) was performed in order to identify the nitrogen content in the quaternary ammonium (QN⁺OH⁻) catalyst beads. This represented the functional group of this catalyst, as it was the only nitrogen-containing component. Active site density was then calculated based on nitrogen content. This was measured using a Carlo Erba 1108 elemental analyser, controlled with CE Eager 200 software.

2. NMR Analysis. The stability of the heterogeneous catalyst is a crucial parameter in this study. In order to identify whether or not any leached occurred, the catalyst resin was tested with ¹H Nuclear Magnetic Resonance (NMR). The NMR samples were prepared using 0.137g of solid, suspended in 1.4 mL of deuterated methanol (CD₃OD) and then heated at 60°C overnight under a nitrogen atmosphere. The solvent was then filtered from the solid. Then, the filtrate was subjected to a ¹H NMR, which was run on a JEOL Lambda 500 spectrometer operating at 500.16 MHz. 32 scans were acquired with a relaxation delay of 2s. ¹H chemical shifts quoted relative to tetramethylsilane.

• RESULTS AND DISCUSSION

Evaluation of Heterogeneous Quaternary Ammonium IERs

The physicochemical properties of the seven selected heterogeneous quaternary ammonium ion exchange resins (IERs) are summarized in Table 1 below. From the table, it can be observed that D1X8 has the highest site density of 3.87 mmol active sites. This active base site density was estimated by measuring

nitrogen content in the CHN analysis. It was assumed that every nitrogen in a quaternary ammonium functional group represents an active base site.

The triacetin conversion versus time for the transesterification of triacetin using various IERs is shown in Figure 1 below. Among the catalysts tested, the order of reactivity was: D1X2 > PA306s > PA308 > D1X4 > D1X8 > A26 > HPA25. It can be observed that the catalytic activity of the IERs decreased with increase in the crosslinking density. HPA25 has the highest crosslinking at 25% and produced the lowest triacetin conversion. In contrast, D1X2 with the lowest crosslinking at 2%, resulted in the highest triacetin conversion. In addition, more than 95% triacetin conversion was obtained using D1X2 after 30 minutes, and the reaction was nearly complete after 2h. It can also be observed that D1X2 demonstrated a higher initial reaction rate compared to the other IERs. Overall, more than 90% of triacetin conversion was obtained for all the IERs after 6h transesterification, except for HPA25.

Table 1: Physicochemical properties of the fresh IER catalysts

Ion Exchange Resins	A26	PA306s	PA308	D1X2	D1X4	D1X8	HPA25
Crosslinking Density (%) ^a	11	4	4	2	4	8	25
Particle Size (mesh) ^a	25-35	60-100	30-40	50-100	50-100	50-100	60
Site Density (mmol active sites/g) ^b	3.31	3.56	3.37	3.76	3.68	3.87	2.38
Ion Exchange Capacity (meq/g) ^c	1.889	1.915	1.900	1.982	1.940	2.024	1.780
Apparent Density (g/cm ³) ^d	0.439	0.538	0.582	0.513	0.579	0.585	0.577

^a Information obtained from the manufacturer

^b Based on the elementary analysis of the fresh catalyst after washing and drying

^c Evaluated according to ASTM D2187 [9]

^d Evaluated using the graduated cylinder method according to ASTM D1895 [10]

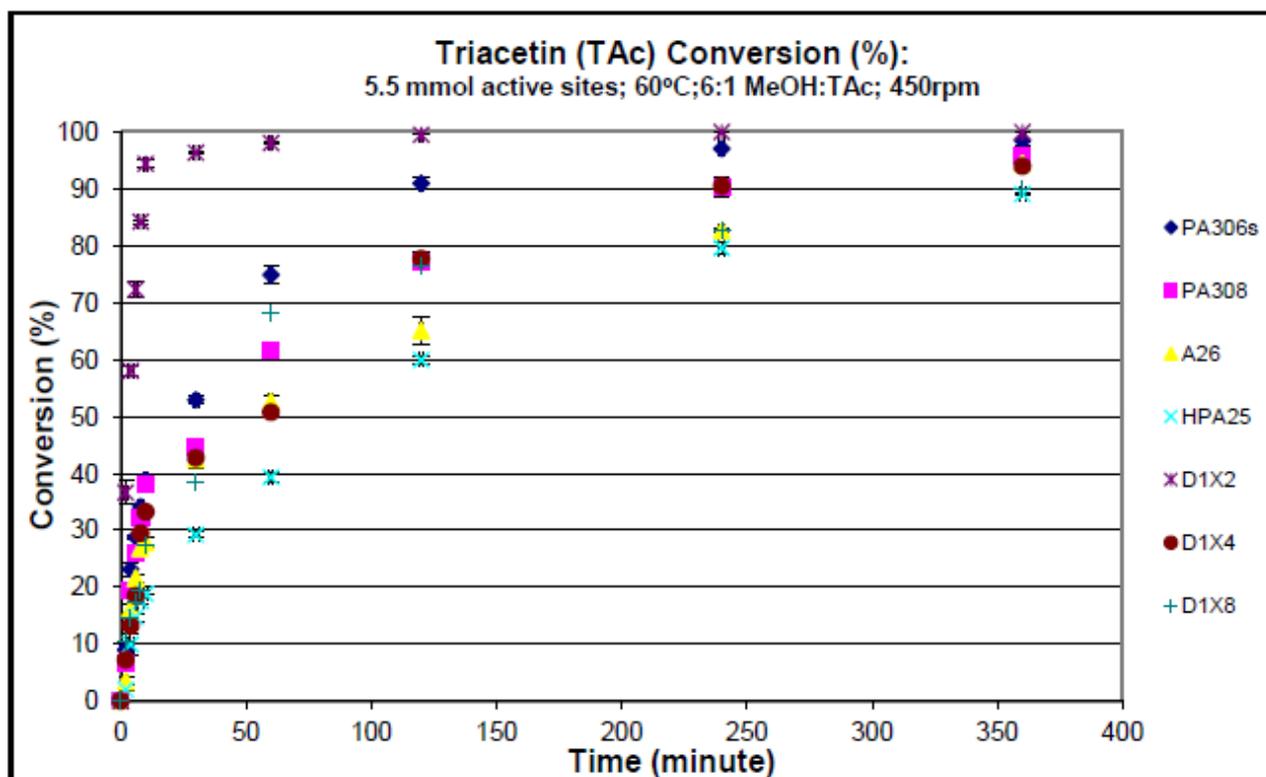


Figure 1 Triacetin Conversion of Different IERs.

These results were consistent with those results obtained by [4] who compared four anion exchange resins, PA306, PA306s, PA308, and HPA25, in the transesterification of triolein. From their experimental

work, PA306, PA306s, and PA308, which have the lowest crosslinking densities, produced higher triolein conversion compared to HPA25. They concluded that crosslinking density has significant effect on transesterification.

Table 2: Turn Over Frequency of the IERs

Ion Exchange Resins	TOF s ⁻¹
PA306s	0.021
PA308	0.016
A26	0.009
HPA25	0.006
D1X2	0.081
D1X4	0.017
D1X8	0.012

The turnover frequency (TOF) was calculated to evaluate the IER catalysts based on their reaction rate per active site. Turnover frequency is a more quantitative method of comparing catalysts and is based here on the estimated number of base active sites [1]. TOF is defined as the number of catalytic cycles per unit time, which depends on many parameters including the form of the catalyst, temperature, pressure, and concentration [5]. In the present work, TOF was calculated using initial reaction rate data for rates of conversion of triacetin below 10%, and their values are reported in Table 3.2. It can be observed from that HPA25 had the lowest TOF, followed by A26. The TOF value for A26 at 0.009 s⁻¹ was slightly lower than that obtained by [3], which was 0.011 s⁻¹. In contrast, D1X2 had the highest TOF at 0.081 s⁻¹. It was suggested by [3] that higher DVB crosslinking has restricted the accessibility to the location of active sites since some reactive groups are buried inside the microspheres, remaining unapproachable for large reactant molecules.

Reusability and Residual Activity of Ion Exchange Resins

From the results of the reusability study shown in Figure 2 below, it is clear that only PA306s and A26 maintained their activity. Moreover, the triacetin conversion remained at 70% for PA306s, while for A26, it stayed at approximately 55% over 5 cycles. A significant drop in activity was identified for D1X2, where triacetin conversion decreased from 96% to 72% after the first cycle. The D1X2 catalyst then retained their levels of activity over the next two cycles, before further decreasing to 62% in the fourth cycle.

In contrast, there were steady declines in activity per cycle for PA308 and D1X4. D1X8 also exhibited a substantial decrease in activity, especially over the first three cycles. It was proposed by [4] that the reduction in transesterification activity is due to the neutralization of the active sites by fatty acid molecules.

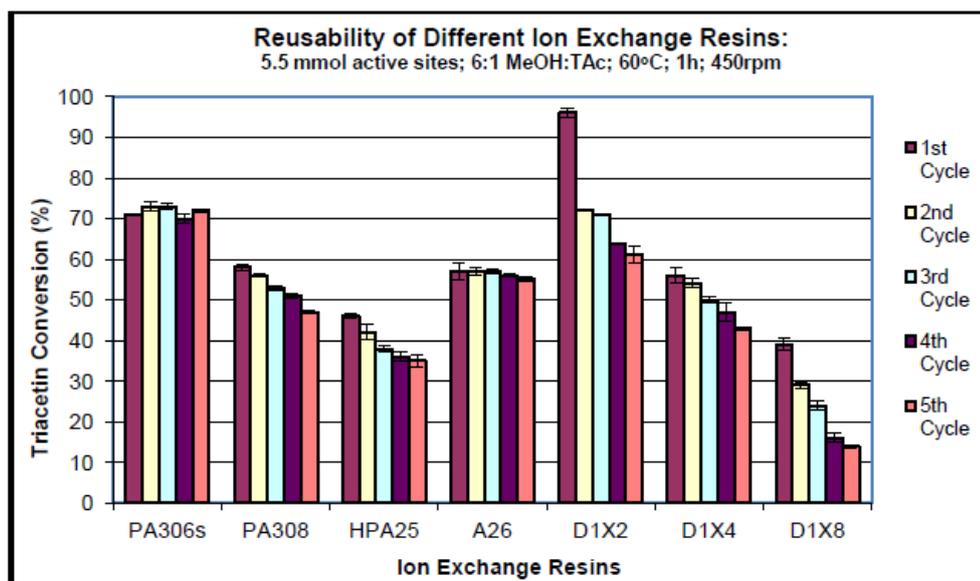


Figure 2 Reusability of Different IERs in the Transesterification of Triacetin

Table 3: Progress of Transesterification After Removal of IERs

Ion Exchange Resins	Triacetin Conversion After 4h (%)	Methyl Acetate Yield After 4h (%)
PA306s	No Changes	No Changes
PA308	No Changes	No Changes
A26	No Changes	No Changes
HPA25	No Changes	No Changes
D1X2	0.75 ± 0.10	0.40 ± 0.10
D1X4	0.60 ± 0.10	No Changes
D1X8	1.35 ± 0.13	0.75 ± 0.10

In order to identify whether the reduction in activity was due to the leaching of the active species, all of the IERs were subjected to the residual activity study. The results are tabulated in Table 3 above. It can be observed that, surprisingly, triacetin conversion was found in the residual reaction mixtures of each of the Dowex™ IERs, signalling leaching of the active sites. The highest triacetin conversion was 1.35 ± 0.13 %, for D1X8. In contrast, triacetin conversion of 0.6 ± 0.10 % was detected after 4h transesterification using D1X4. No changes in triacetin conversion were found for A26, PA306s, PA308, and HPA25, implying that these four IERs are very stable. Overall, it can be observed in Table 3.3 that there were only small variations in the triacetin conversion and methyl acetate yield, where these values were less than 1.5%.

In general, it is proposed that the reduction in the transesterification activity could be due to three factors: firstly, neutralization of active sites as described by [4]; secondly, the deactivation of the catalyst by glycerol sticking to the resin polymers; and thirdly, the leaching of the base active sites, particularly in D1X2, D1X4 and D1X8, which can be seen in Table 3. However, it can be clearly observed that the significant drop in activity of D1X2 in the first cycle as shown in Figure 2, did not match the level of triacetin conversion found in the residual activity test in Table 3.

Consequently, to test if the active species leached into the reaction mixture, all of the fresh catalysts were suspended in 1.4 ml of deuterated methanol (CD₃OD) and heated at 60°C overnight under a nitrogen atmosphere. The solvent was filtered from the solid catalyst, and tested with ¹H Nuclear Magnetic Resonance (NMR). The resulting spectra for D1X2 and A26 are displayed in Figure 3, showing that no proton peak are presents in the range 2.1 to 2.3 ppm, which corresponds to trimethylamine [6].

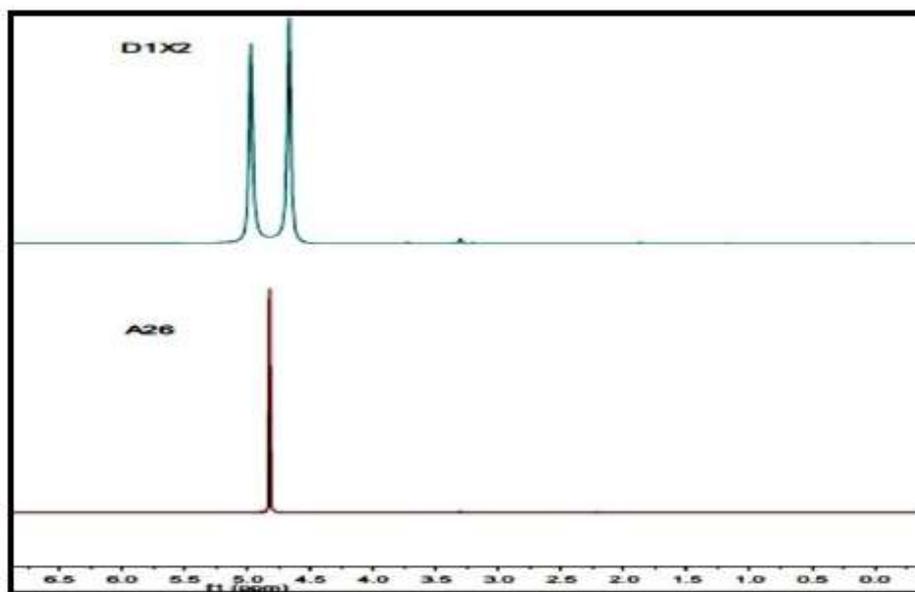


Figure 3 ^1H NMR Spectrums for D1X2 (above) and A26 (bottom)
Evaluation of Tetramethylammonium Hydroxide (TMAOH)

The performance of homogeneous tetramethylammonium hydroxide (TMAOH) at different concentrations is shown in Figure 4 below. It can be observed that the reaction rate increases with concentration of TMAOH. It can also be observed that using the 5.5 mmol/L of TMAOH, an almost complete conversion of triacetin was obtained in less than 3 minutes. Figure 4 also clearly shows that the reaction rate with TMAOH dropped significantly at lower concentrations, and triacetin conversion exceeded 90% only after 60 minutes when using 0.344 mmol/L of TMAOH. In addition, it can be seen that dissimilar trend was obtained on the plot of 0.344 mmol/L, which assumed as a result of mass transfer resistance. The results shown in Figure 4 agree well with those of [3], who achieved 52% and 90% triacetin conversions using 0.03 mmol/L of NaOH after just 2 and 15 minutes, respectively. Overall, the reaction rate using TMAOH was very high when compared to those of the heterogeneous IERs shown in Figure 1.

The only record in the literature of transesterification performed with TMAOH was a study by [7], who used rapeseed oil at a molar ratio of methanol to oil of 8:1 (mol:mol) at 65°C. Here, transesterification was almost complete by 15 minutes when a high concentration of TMAOH of approximately 33.0 mmol/L was used. It should be noted that transesterification using homogeneous catalysts proceeds by the formation of the methoxide ion as the active species. Base-catalyzed transesterification is an addition-elimination reaction involving nucleophilic attack by the methoxide anion on a carbon atom of the carbonyl groups ofacylglycerols, resulting in the elimination of the oxygen atom attached to the 'glycerol backbone' of the triglyceride molecule and the formation of a methyl ester [8]. Since the methoxide anion is formed by the reaction of methanol with hydroxide ions (OH^-), then the concentration of methoxide increases with that of OH^- from TMAOH when it is added to the reaction mixture. This results in an increase in triacetin conversion, as illustrated in Figure 4.

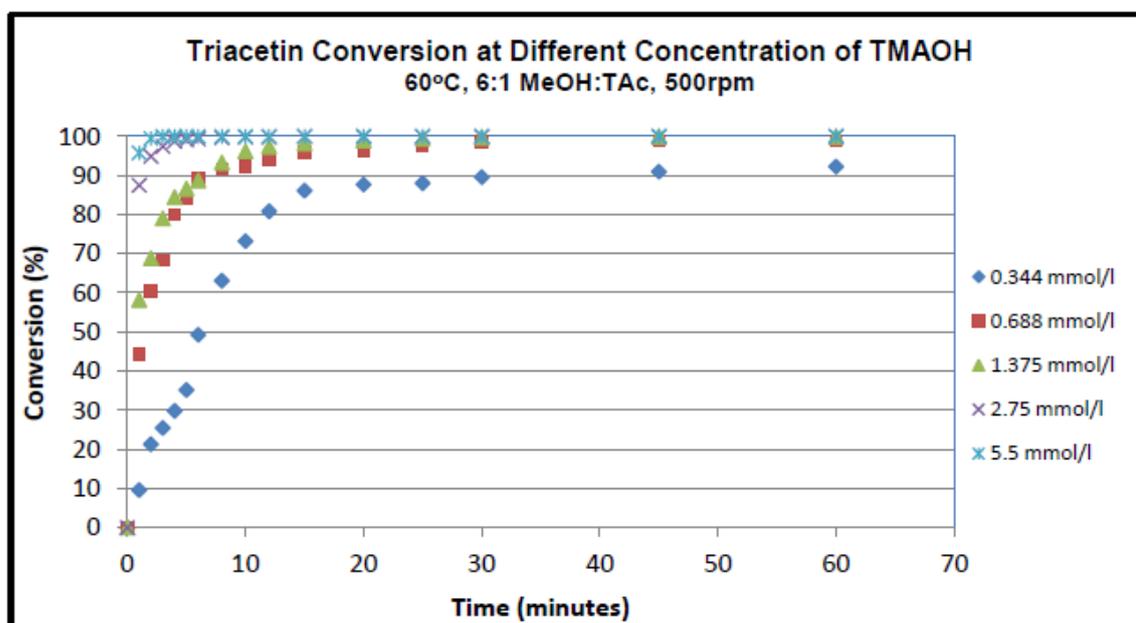


Figure 4 Transesterification of Triacetin at Different Concentration of TMAOH

• CONCLUSION

The evaluation of the performance of the heterogeneous quaternary ammonium catalyst in the transesterification of triacetin was conducted using seven types of ion exchange resin (IER). The comparison between IERs was made in terms of the concentration of active base sites. This value was measured via CHN analysis, by assessing the nitrogen content, assuming that every nitrogen atom represented an active base site in a quaternary ammonium functional group. It was found that the order of reactivity of the IERs was: D1X2 > PA306s > PA308 > D1X4 > D1X8 > A26 > HPA25. It was also found that triacetin conversion decreased with increasing crosslinking density with the highest crosslinking at 25%, HPA25 obtained a lower triacetin conversion when compared to D1X2 with the lowest crosslinking at 2%.

In assessing reusability and stability, it was found that only PA306s and A26 were able to maintain their activity after the fifth cycle. A significant drop in activity was identified for D1X2, with triacetin conversion reduced from 96% to 72% after just one cycle. Triacetin conversion was found in the residual reaction mixtures after transesterification for each of the Dowex™ IERs. The highest triacetin conversion was 1.35 ± 0.13 %, with D1X8. However, the NMR spectra showed that no proton peak corresponds to trimethylamine presents in the range 2.1 to 2.3 ppm. No changes in triacetin conversions of the residual activity were found for A26, PA306s, PA308, and HPA25, implying that these four IERs were very stable.

It is suggested that the reduction in transesterification activity could be due to three factors: neutralization of active sites; catalyst deactivation by glycerol sticking to the resin polymers; and leaching of the base active sites, particularly for D1X2, D1X4 and D1X8, although this could not be detected by NMR analysis.

Experiments testing the performance of homogeneous tetramethylammonium hydroxide (TMAOH) indicated its reaction rate was much faster when compared to those of the heterogeneous IERs at the same concentration, but slower than NaOH. An almost complete triacetin conversion was obtained using 5.5 mmol/L of TMAOH after less than 3 minutes.

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