Comparison of Novozyme 435 and Purolite D5081 as heterogeneous catalysts for the pretreatment of used cooking oil for biodiesel production

This item was submitted to Loughborough University's Institutional Repository by the/an author.

Citation: HAIGH, K.F. ... et al., 2013. Comparison of Novozyme 435 and Purolite D5081 as heterogeneous catalysts for the pretreatment of used cooking oil for biodiesel production. Fuel, 111, pp.186-193.

Additional Information:

- This article was published in the journal, Fuel [© Elsevier Ltd.] and the definitive version is available at: http://dx.doi.org/10.1016/j.fuel.2013.04.056

Metadata Record: https://dspace.lboro.ac.uk/2134/12418

Version: Accepted for publication

Publisher: © Elsevier Ltd.

Please cite the published version.
This item was submitted to Loughborough’s Institutional Repository (https://dspace.lboro.ac.uk/) by the author and is made available under the following Creative Commons Licence conditions.

For the full text of this licence, please go to: http://creativecommons.org/licenses/by-nc-nd/2.5/
Comparison of Novozyme 435 and Purolite D5081 as Heterogeneous catalysts for the Pretreatment of Used Cooking Oil for Biodiesel Production

Kathleen F. Haigh\textsuperscript{a}, Sumaiya Z. Abidin\textsuperscript{a,b}, Goran T. Vladisljevi\textsuperscript{c}, Basudeb Saha\textsuperscript{a,c}

\textsuperscript{a}Department of Chemical Engineering, Loughborough University, Loughborough, Leicestershire, LE11 3TU, United Kingdom
\textsuperscript{b}On study leave from Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang Darul Makmur, Malaysia
\textsuperscript{c}Department of Applied Sciences, Faculty of Engineering, Science and the Built Environment, London South Bank University, London, SE1 0AA, United Kingdom

ABSTRACT:

The catalytic action of two types of catalysts, an ion-exchange resin, Purolite D5081 and an immobilized enzyme, Novozyme 435, was compared for the esterification pretreatment of UCO for the preparation of biodiesel. The reactions were carried out using a jacketed batch reactor with a reflux condenser. The effect of mass transfer limitations was investigated and it was shown that internal and external mass transfer limitations were negligible. An immobilized enzyme, Novozyme 435, was investigated because it has been shown to give a high conversion of FFAs. This catalyst has been compared to an ion-exchange resin, Purolite D5081, which was developed for the esterification of UCO for the production of biodiesel. It was found that a conversion of 94\% was achieved using Purolite D5081 compared to 90\% conversion with Novozyme 435, however, the optimum methanol to FFA

* Corresponding author. Tel: +44(0) 2078157190. Fax: +44(0) 2078157699. Email address: b.saha@lsbu.ac.uk
ratio for Purolite D5081 was 98:1 compared to 6.2:1 for Novozyme 435. In addition, it has been found that with Novozyme 435 there are side reactions which result in the formation of additional fatty acid methyl esters (FAME) and FFAs at longer reaction times.

**KEYWORDS:**

Biodiesel, Fatty Acid Methyl Esters (FAME), Esterification, Novozyme 435, Purolite D5081 ion exchange resin

1. **Introduction**

Extensive research has been carried out to identify renewable materials to replace fossil fuels and a similar calorific value means that vegetable oils are being considered as a potential replacement for petro-diesel. The first diesel engines were designed to run on vegetable oil [1] although this was subsequently changed to lower viscosity petro-diesel. High viscosity fuels such as vegetable oil are not suitable for use in modern direct injection diesel engines because they cause engine deposits which lead to a deterioration in performance and engine damage [1–3].

The viscosity of vegetable oil can be reduced by means of a transesterification reaction, which converts the triglycerides, in vegetable oil, to biodiesel. A schematic representation of this reaction is shown in Fig. 1. Biodiesel is defined as mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats [4]. The transesterification process is relatively simple and well understood [1,3,5], with the most process using methanol as the reagent and an alkaline catalysts such as sodium or potassium hydroxide to form fatty acid methyl esters (FAME).

**Fig. 1.** Schematic representation of the transesterification reaction
Vegetable oil is an expensive raw material [6,7] and there are ethical concerns regarding the use of a potential food source as fuel [5]. As a result alternative raw materials have been investigated and these include non-edible oils such as *Jatropha Curcas* [8], by-products from oil refining such as palm fatty acid distillate [9], animal fats, algal oil [10] and used cooking oil (UCO) [5,11]. UCO is a waste material and this means that it is possible to reduce the amount of waste going to landfill and use a relatively cheap material. UCO contains free fatty acids (FFAs), which form due to hydrolysis of triglycerides during cooking [12] and this results in a saponification side reaction during transesterification, when a base catalyst is used [13]. The saponification reaction consumes the catalyst and can form an emulsion which makes separating the products difficult and reduces biodiesel yield [5]. In addition, most biodiesel specifications impose an upper limit on the FFAs content [2] as they can cause engine damage due to deposit formation.

FFAs can be removed by using an esterification reaction which converts the FFAs to biodiesel with a short chain alcohol such as methanol and an acid catalyst and a schematic of is shown in Fig. 2. Currently most esterification processes use homogeneous catalysts such as sulfuric or sulfonic acid [5,14], however, homogenous catalysts are difficult to separate from the products, generate large amounts of waste water, and require expensive materials to prevent associated corrosion [15]. As a result solid acid catalysts such as ion-exchange resins have been investigated as heterogeneous esterification catalysts with high FFA conversions reported [12,16,17]. Acid catalysts can also be used for transesterification, however, the reaction rate is much slower [10].

![Fig. 2. Schematic representation of the esterification reaction](image-url)

Advances in enzyme technology are providing a greater choice of lipases to be investigated for use in biodiesel production with research to date focusing on
transesterification however hydrolysis and esterification [9,11] reactions can also be used to form biodiesel. Novozyme 435, Candida antarctica Lipase B immobilized on acrylic resin, has been investigated for the transesterification of the triglycerides in various vegetable oils and UCO [18–20] and it was found that high conversion rates were possible with stepwise addition of methanol and long reaction times. Hydrolysis of triglycerides to fatty acids followed by the esterification of fatty acids to biodiesel has been investigated to make use of raw materials which contain a mixture of fatty acids and triglycerides such as crude palm oil, acid oil by-product and UCO [21–23]. It has been shown that Novozyme 435 can be used to catalyse transesterification and hydrolysis reactions for the production of biodiesel however the fastest reaction rates are achieved when Novozyme 435 is used to esterify free fatty acids [24]. The work to date has focused on the esterification of material with a high concentration of free fatty acids such as palm fatty acid distillate which contains more than 93 wt% FFAs [9] and soybean oil deodorizer distillate containing 80 wt% FFAs [25]. To date the use of Novozyme 435 to convert the FFAs in UCO to biodiesel prior to transesterification has not been reported.

Although acid and enzyme catalysts catalyse both esterification and transesterification, the reaction rates for transesterification are often much slower compared to using a basic catalyst [26] and as result this work has focused on the esterification reaction as a pre-treatment process. The aim of this work is to determine if Novozyme 435 can be used to pretreat UCO and how the catalyst compares with an effective ion-exchange resin. The ion-exchange resin, Purolite D5081 has been developed for the pretreatment of UCO and has been reported to give a high conversion of FFAs in UCO [16].

2. Methods

2.1 Materials

Methyl ester standards were purchased from Sigma. Purolite D5081 was donated by Purolite International and Novozyme 435 was donated by Novozymes UK Ltd. Purolite D5081 was received in a wet form, washed with methanol and dried in a vacuum oven at
100 °C prior to use. Novozyme 435 used as supplied. The UCO was supplied by GreenFuel Oil Co Ltd., UK and has an average molecular weight of 278 g/mol and an FFAs content of approximately 6.4 wt%. The methanol, tert-butanol, toluene and 2-propanol were purchased from Fisher Scientific UK Ltd. All solvents were analytical grade and used as supplied.

2.2 **Catalyst Characterization**

Surface area, pore volume and average pore diameter were determined from adsorption isotherms using a Micromeritics ASAP 2020 surface analyser as follows: The samples were degassed by means of a two-stage temperature ramping, followed by sample analysis at -195.15 °C using liquid nitrogen. The Brunauer–Emmett–Teller (BET) method was used to calculate the surface area, average pore diameter and total pore volume.

True Density was measured using a Micromeritics Multivolume Pycnometer 1305 with helium as the gas.

In order to investigate internal mass transfer limitations a portion of catalyst was separated into size fractions using a series of sieves on a Fritsch analysette shaker. The amplitude was set to 10 and the catalyst sieved for 120 min. Particles retained by the 710 μm sieve were defined as the large fraction while those passed through the 500 μm sieve were defined as the small fraction. Particle size distribution (PSD) analysis was carried out using a Coulter LS 130 Particle Analyzer with particle size measurement over the range 0.1 μm to 900 μm. The Fraunhofer optical model was used for the measurement of the distribution pattern. The samples were introduced into the dispersion module with isopropyl alcohol as the solvent.

A scanning electron microscope (Carl Zeiss, Leo 1530 VP) was used to study the morphology of the ion exchange resins. Prior to analysis samples of each catalyst were crushed using a mortar and pestle. Fresh catalyst beads and ground powder were then mounted on aluminium stubs using double sided adhesive carbon dots and then gold coated.
2.3 Esterification of UCO

The esterification reactions were carried out using a jacketed batch reactor with a reflux condenser as illustrated by Fig. 3. The stirrer motor was a Eurostar Digital IKA-Werke. The temperature was monitored by means of a Digitron, 2751-K thermocouple and this information was used to set the temperature on the Techne, TE-10D Tempette water bath. The UCO and methanol were added to the reactor and heated to the required temperature, after sampling, the catalyst was added to initiate the esterification reaction. The sample tube was fitted with metal gauze to prevent withdrawal of catalyst when taking samples and the samples withdrawn by means of a syringe. All samples were analyzed for the FFAs content and selected samples analyzed for FAME concentration.

![Diagram of experimental set-up](image)

Fig. 3. Schematic of the experimental set-up

2.4 Recycling of Novozyme 435 and Purolite D5081.

Upon completion, catalysts were filtered from the reaction medium and Purolite D5081 was washed with methanol then dried. Novozyme 435 was washed with tert-butanol and freeze-dried. The reaction time for the reusability cycles was kept at 8 h for all experiments.

2.5 Analysis

FAME concentration was determined using gas chromatography mass spectrometry (GC-MS) (Hewlett Packard HP-6890), equipped with a DB-WAX (J & W Scientific) capillary
column, (30 m x 0.25 mm) packed with polyethylene glycol (0.25 µm film thickness); Helium at a flow rate of 1.1 mL/min was used as the carrier gas. The amount of sample injected was 2 µL. The temperature of the injector and detector was 250 °C. The initial oven temperature was 70 °C held for 2 minutes, then increased at 40 °C/min up to 210 °C, then increased at 7 °C/min up to 230 °C and the final temperature held for 11 minutes. Methyl heptadecanoate was used as the internal standard. Sample preparation for FAME analysis depended on the type of sample. In order to determine the fatty acid composition of the UCO, a sample of oil was first derivatized. A 100 mg was dissolved in 10 mL hexane and then derivitized using 100 µL of a 2 M potassium hydroxide in methanol solution. Components were mixed using a vortex mixer and then centrifuged. The supernatant was then analysed by GC-MS. The experimental samples were dissolved in hexane, internal standard was added and the FAME concentration analyzed using GC-MS.

The %FFAs of all samples was determined by titration using the ASTM D974 method. 2 g of sample was dissolved in 100 mL of a solution of toluene:2-propanol:water (volume ratio of 100:99:1) and titrated using p-naphtholbenzein indicator.

3. Results and Discussion

3.1 Catalyst Characterisation Data.

A summary of catalyst properties is given in Table 1 and from this data it can be seen that in terms of the particle size distribution Novozyme 435 has a larger spread of particle sizes with the average particle size smaller than Purolite D5081. While Purolite D5081 has a larger surface area than Novozyme 435 and could have a greater number of accessible catalytic sites, Novozyme 435 is more porous and has a bigger pore diameter which may aid the conversion of larger molecules.
Table 1: Summary of the Catalyst Properties

<table>
<thead>
<tr>
<th></th>
<th>Immobilized Enzyme Novozyme 435</th>
<th>Ion-exchange resin Purolite D5081</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nature of Catalyst</strong></td>
<td><em>Candida Antarctica</em> lipase B (CALB) immobilised on acrylic resin</td>
<td>Sulphonated polystyrene cross-linked with divynlbenzene</td>
</tr>
<tr>
<td><strong>Physical appearance</strong></td>
<td>White spherical beads</td>
<td>Black spherical beads</td>
</tr>
<tr>
<td><strong>Particle size distribution</strong>&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$d_{10}$ ($\mu$m)</td>
<td>252</td>
<td>396</td>
</tr>
<tr>
<td>$d_{50}$ ($\mu$m)</td>
<td>472</td>
<td>497</td>
</tr>
<tr>
<td>$d_{90}$ ($\mu$m)</td>
<td>687</td>
<td>639</td>
</tr>
<tr>
<td><strong>BET surface area (m$^2$/g)</strong></td>
<td>81.6</td>
<td>387</td>
</tr>
<tr>
<td><strong>Total Pore Volume (cm$^3$/g)</strong></td>
<td>0.45</td>
<td>0.39</td>
</tr>
<tr>
<td><strong>Average pore diameter (nm)</strong></td>
<td>17.7</td>
<td>4.1</td>
</tr>
<tr>
<td><strong>True Density (g/cm$^3$)</strong></td>
<td>1.19</td>
<td>1.31</td>
</tr>
<tr>
<td><strong>Porosity (-)</strong></td>
<td>0.349</td>
<td>0.338</td>
</tr>
</tbody>
</table>

<sup>a</sup>$d_{x0}$ is the diameter corresponding to $x0$ volume % on a relative cumulative particle diameter distribution curve.

Fig. 4. SEM micrographs with Fig. 4(a) showing the external surface of a Novozyme 435 bead and Fig. 4(b) showing cross-section of the internal structure of Novozyme 435. Fig. 4(c) shows the external surface of Purolite D5081 and Fig. 4(d) shows a cross-section of the internal structure of Purolite D5081.
The surface morphology of the catalyst beads are shown in Figs 4(a) and (c) and from this it can be seen that Purolite D5081 has a very smooth surface with very few surface features. In comparison Novozyme 435 has a lot of surface features. A sample of each catalyst is crushed and an example of the internal surface morphology is shown in Fig. 4(b) and Fig. 4(d). From these figures it can be seen that both catalysts have very similar structures, however microspheres in Purolite D5081 are slightly bigger compared to Novozyme 435.

3.2 Composition of UCO

A sample of UCO was derivitised to fatty acid methyl esters using methanol and a sodium hydroxide catalyst. The fatty acid methyl ester concentrations were determined using GCMS [16] and the resulting fatty acid composition is shown in Table 2. This composition is similar to the typical fatty acid distribution for soybean oil [11].

<table>
<thead>
<tr>
<th>Component</th>
<th>% (wt/wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linoleic Acid (C18:2)</td>
<td>43.3</td>
</tr>
<tr>
<td>Oleaic Acid (C18:1)</td>
<td>36.0</td>
</tr>
<tr>
<td>Palmitic Acid (C16:0)</td>
<td>13.4</td>
</tr>
<tr>
<td>Stearic Acid (C18:0)</td>
<td>3.8</td>
</tr>
<tr>
<td>Linolenic Acid (C18:3)</td>
<td>3.6</td>
</tr>
</tbody>
</table>

3.3 Effect of Methanol on Conversion

Fig. 5 shows the effect of the mole ratio of methanol to FFAs on conversion. From this data it can be seen that the effect of the mole ratio varies significantly for the two catalysts. In the case of Purolite D5081 conversion increases with an increase in mole ratio tending towards a maximum above which further increase in mole ratio will not increase conversion and is a typical trend for chemical catalysts. A methanol to FFA mole ratio of 98:1 was
selected as the optimum because further increase in mole ratio resulted in very small increase in conversion.

In comparison, Novozyme 435 catalysis is more sensitive to changes in the mole ratio and a high conversion is possible with much lower mole ratios. In this case it can be seen there is an optimum methanol to FFA mole ratio in the range of 5.9-6.2:1 with mole ratios below this value suggest there is insufficient methanol for the reaction and increasing the methanol above this range results in a decrease in conversion due to poisoning of the catalyst. Methanol is known to poison enzymes including Novozyme 435 [9,27] and in the case of transesterification where much larger quantities of methanol are required the issue has been mitigated by stepwise addition of methanol. A large reduction in the methanol requirement results in a higher throughput and increased process safety.

Fig. 5. Effect of the mole ratio of methanol to FFA on conversion of FFAs, where Fig. 5(a) is the overall conversion trend for various mole ratios using Novozyme 435 and Fig. 5(b) is the conversion
at 2h using Novozyme 435. Fig. 5(c) is the overall conversion trend for Purolite D5081 and Fig. 5(d) is the conversion at 2h for Purolite D5081.

3.4 Investigation of External Mass Transfer Limitations on Conversion

Vegetable oil and methanol are poorly miscible and the use of a heterogeneous catalyst leads to the formation of a three phase system with limited mass transfer between the three phases [7], reducing the reaction rate. An organic solvent can be used to improve contacting, however this will need to be removed from the final product [9] thus eliminating the process step saving of using a heterogeneous catalyst. External mass transfer resistance refers to the resistance across the solid-liquid interface in heterogeneous catalyst systems due to the formation of a boundary layer around catalyst particles. Increasing the stirring speed of the impeller in a batch reactor reduces the thickness of the boundary layer and improves solid suspension. The effect of increasing the stirring speed for Novozyme 435 is shown in Fig. 6. Fig. 6 shows that the increase in conversion is small with increasing stirrer speed, however, in order to be certain that mass transfer limitations have been eliminated, for this work a stirrer speed of 650 rpm was selected for subsequent work. It has been reported that for Purolite D5081, an impeller speed of 350 rpm was sufficient to eliminate external mass transfer resistance [16].

The differences in stirrer speeds required for good mixing can be explained in part by the differences in the composition of the reaction mixtures as this will affect the formation of the boundary layer around the catalyst. The solubility of methanol in UCO was found to correspond to a mole ratio of 16:1. For Novozyme 435 a mole ratio of 6.2:1 was used and the methanol was fully dissolved in the UCO while for Purolite D5081, the mole ratio was 98:1 and an emulsion was formed. The other factor to consider is that the catalyst should be fully suspended in the reaction medium and this is affected by the size and density of the catalyst particles.
3.5 Investigation of Internal Mass Transfer Limitations on Conversion.

Internal mass transfer resistance is due to the resistance of flow inside the particles and reducing the particle size reduces the diffusion path length and thus internal mass transfer resistance. The catalysts were sieved into various size fractions and Fig. 7 shows the particle size distributions investigated using Novozyme 435, where the overall fraction ($d_{50} = 472 \, \mu m$) represents the size distribution received from the manufacturer.

Fig. 6. Effect of rotational stirring speed on conversion when Novozyme 435 is used as the catalyst. The reaction conditions are: temperature = 40 °C, catalyst loading = 1 wt%, mole ratio = 7.8:1 methanol to FFAs.

Fig. 7. A plot of the particle size distributions of the Novozyme 435 size fractions used to investigate internal mass transfer limitations.

Fig. 8 shows that there are intra-particle diffusional limitations when using Novozyme 435 in the size range supplied by the manufacturer, with the slowest initial reaction rate
corresponding to the largest particle size fraction ($d_{50} = 829 \mu m$). For the smaller size fractions it can be seen that the difference in reaction rates is much smaller compared to the large size fraction, however, the difference in average particle size is also smaller.

![Graph showing the effect of particle size distribution of Novozyme 435 on conversion.](image)

**Fig. 8.** Effect of particle size distribution of Novozyme 435 on conversion. The reaction conditions are: temperature = 50 °C, catalyst loading = 1 wt%, mole ratio = 6.2:1 methanol to FFA.

Purolite D5081 was reported to have no internal mass transfer limitations for the typical particle size supplied by the manufacturer [16]. In this case a sieved fraction with an average particle size ($d_{50}$) of 463 µm was compared to the original particle size distribution ($d_{50} = 497 \mu m$). Overall the particle sizes investigated using Novozyme 435 were smaller than Purolite D5081 implying that lower conversion rates are likely due to the microstructure of the catalyst.

### 3.6 Effect of Temperature on Conversion.

The maximum recommended reaction temperature for Purolite D5081 is 120 °C, and for the enzyme catalyst it is 70 °C, whilst the boiling point of methanol is 65 °C. It has been previously reported that for Purolite D5081 increasing temperature increased conversion, however as the temperature approached the boiling point of methanol there were concerns with methanol loss and as a result 60 °C was selected as the optimum temperature[16]. Fig. 7 shows the effect of temperature on conversion when Novozyme 435 is used as the catalyst. From this data it can be seen that it is possible to get a relatively high initial reaction rate with temperatures as low as 30 °C and hence this reaction could be carried out
in warmer countries without any supply of additional heating. From Fig. 9 it can be seen that for temperatures of 50 °C and above, the conversion reaches a maximum and then decreases significantly. After 24 h of reaction, the effect of temperature on FFAs and FAME concentration is shown in Fig. 10. From this data, it can be seen that the amount of FAME formed is higher than expected based on the amount of FFAs with the amount of FAME formed increases with an increase in temperature. This suggests that side reactions are occurring with the other components of the oil. Lipases such as Novozyme 435 break down lipids and this means that they can catalyse other reactions with the order of preference being esterification > transesterification > hydrolysis reactions [24]. The formation of additional biodiesel is beneficial, however, the main purpose of this work is to reduce the FFAs concentration in order to avoid downstream processing problems and ensure the final biodiesel specification is met. As a result, 50 °C has been selected as the optimum temperature because it gives the highest FFAs conversion and a high initial reaction rate.

![Fig. 9. Effect of temperature on conversion of FFAs using Novozyme 435 as the catalyst. Reaction conditions are: catalyst loading = 1 wt%, mole ratio = 6.2:1 methanol to FFA](image-url)
Fig. 10. The effect of temperature on the concentration of FFAs and FAME using Novozyme 435. Reaction conditions are: catalyst loading = 1 wt%, mole ratio = 6.2:1 methanol to FFA

3.7 Effect of Catalyst Loading on Conversion

Fig. 11(a) shows the catalyst loading for Purolite D5081 and Fig. 11(b) refers to Novozyme 435. From this data it can be seen that similar catalyst loadings are required for both catalysts with the optimum loading for Purolite D5081 of 1.25 wt% and for Novozyme 435 it is 1.00 wt%. This suggests that these catalysts have similar activities.
Fig. 11. Effect of catalyst loading on conversion where Fig. 11(a) is for Novozyme 435 and Fig. 11(b) is for Purolite D5081.

3.8 Comparison of Catalysts

A summary of the optimum reaction conditions for both catalysts is given in Table 3. Given that there is a large difference in the effect of mole ratio on conversion depending on the choice of catalyst it would not be meaningful to compare these catalysts at the same reaction conditions. A comparison of conversion for the two catalysts at their optimum conditions is shown in Fig. 12. From this data it can be seen that with Novozyme 435 the initial reaction rate is faster, however, the conversion after 600 min of reaction time is slightly lower with Novozyme 435 reaching 90% compared to 94% with Purolite D5081. In addition, a higher impeller stirring speed is required with Novozyme 435 in order to mitigate external
mass transfer limitations. Novozyme 435 offers numerous benefits over Purolite D5081 because a high conversion is achieved at a much lower mole ratio, lower temperature and catalyst loading. In particular, the significant reduction in methanol requirements suggests that for the same equipment size a much higher capacity is possible and the process will be safer. A disadvantage is that the cost of enzymes tends to be much greater than that for ion-exchange resins.

Table 3. Comparison of the Optimum Reaction Conditions for Novozyme 435 and Purolite D5081

<table>
<thead>
<tr>
<th></th>
<th>Novozyme 435</th>
<th>Purolite D5081</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol to FFA mole Ratio</td>
<td>6.2:1</td>
<td>98:1</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>50</td>
<td>60</td>
</tr>
<tr>
<td>Catalyst Loading (wt%)</td>
<td>1.00</td>
<td>1.25</td>
</tr>
<tr>
<td>Stirrer Speed (rpm)</td>
<td>650</td>
<td>350</td>
</tr>
</tbody>
</table>

Fig. 12. Comparison of conversion for Novozyme 435 and Purolite D5081 at the optimum conditions for each catalyst as specified in Table 3.

3.9 Catalyst Reusability

Fig. 13 shows the effect of reusing Novozyme 435 on conversion. From this data it can be seen that for cycles 2 and 3 there is a reduction in the FFAs conversion although the
reduction is slightly less from cycle 2 to cycle 3 compared to the reduction from cycle 1 to cycle 2 indicating that the reduction in conversion is stabilizing. This data is not following the expected equilibrium trend as conversion increases to a maximum and then decreases. This is similar to the trend observed in Fig. 9 indicating that for experimental conditions that are considered stressful for Novozyme 435 there is a change in the conformation of the enzyme which changes the type of reaction catalyzed.

Fig. 13. Investigation into the reusability of Novozyme 435

From the data in Fig. 13 it can be seen that the maximum conversion occurs between 180-240 min and in this range the decrease in conversion between cycles is approximately 5%. In the case of Purolite D5081 it was found at 500 min there was a decrease in conversion of approximately 10% per cycle[16]. It was found that with Purolite D5081 there was leaching of the active species during cycle 1 resulting in a homogenous contribution to the catalysis and this increased the initial reaction rate for cycle 1. The subsequent decrease in conversion was attributed to pore blockage by the vegetable oil.

4. Conclusions

The catalytic action of two types of catalysts, an ion-exchange resin, Purolite D5081 and an immobilized enzyme, Novozyme 435 was compared for the esterification pretreatment of UCO for the preparation of biodiesel. Both catalysts gave a good conversion of FFAs to biodiesel in UCO with the optimum reaction conditions summarised in Table 3. A slightly
higher conversion of 94% is possible with Purolite D5081 compared to 90% conversion of FFAs using Novozyme 435. It was found that using Novozyme 435 as the catalyst resulted in a large reduction in the amount of methanol required with the optimum mole ratio going from 98:1 methanol to FFA with Purolite D5081 to a mole ratio of 6.2:1. However, this decrease in the mole ratio changed the composition in the reaction medium and as a result a much higher stirring speed was required in order to eliminate mass transfer limitations. Relatively high reaction rates were possible with Novozyme 435 at a temperature of 30 °C indicating that this reaction could be carried out without heating in some parts of the world. Side reactions with Novozyme 435 at vigorous reaction conditions such as high temperatures and during the reusability study were found indicating a change in conformation of the enzyme under these conditions. One of the advantages of a heterogeneous catalyst is that they can be reused and in the case of Novozyme 435 it was found that there is a lot of potential to reuse this catalyst providing the reaction time is short.

Acknowledgements

We would like to thank EPSRC for the PhD scholarship to KH and Universiti Malaysia Pahang and Malaysian Government for the PhD scholarship to SZA. We would also like to thank Purolite International Ltd (Mr. Brian Windsor and the late Dr. Jim Dale) for supplying the ion-exchange catalyst, GreenFuel Oil Co Ltd., UK for supplying the UCO and Novozymes UK. Ltd. (Dr. David Cowan) for supplying the enzyme catalyst and his help and advice with using Novozyme 435 for this project.

5. References


[20] D. Ganesan, A. Rajendran, V. Thangavelu, An overview on the recent advances in
the transesterification of vegetable oils for biodiesel production using chemical and
biocatalysts, Reviews in Environmental Science and Bio/Technology. 8 (2009) 367-
394.

Biodiesel via Enzymatic Hydrolysis Followed by Chemical Esterification, Energy &


[23] Y. Watanabe, T. Nagao, Y. Nishida, Y. Takagi, Y. Shimada, Enzymatic Production of
Fatty Acid Methyl Esters by Hydrolysis of Acid Oil Followed by Esterification, Journal
of the American Oil Chemists' Society. 84 (2007) 1015-1021.

synthesis of biodiesel from used palm oil and ethanol in a solvent-free system,

via esterification of feedstock with high content of free fatty acids., Applied

catalysis for transesterification of high free fatty acid oil (waste cooking oil) to

[27] Y. Shimada, Enzymatic alcoholysis for biodiesel fuel production and application of the
reaction to oil processing, Journal of Molecular Catalysis B: Enzymatic. 17 (2002)
133-142.