Lee Men Quan, Derrick Toh Yong Seng, Khoo Chun Yuet

ABSTRACT

Five types of transesterification processes (acid-catalysed, base-catalysed, acid-base catalysed, iron(III) sulfate-base-catalysed and prawn shell-catalysed) were evaluated in terms of yield, bound glycerol content, density, viscosity and heat of combustion. The base-catalysed transesterification was carried out with methanol and sodium hydroxide as a catalyst while the acid-catalysed transesterification was carried out with methanol and 98% w/w concentrated sulfuric acid as a catalyst. The acid-base-catalysed transesterification was carried out by 2 hours of acid pretreatment followed by base-catalysed transesterification. The iron(III) sulfate-base-catalysed transesterification was carried out by 3 hours of iron(III) sulfate pretreatment followed by base-catalysed transesterification. The prawn shell-catalysed transesterification was carried out by carbonizing the prawn shells and allowing it to undergo reflux with the waste vegetable oil and methanol. For all processes, reflux was carried out at 65-70°C. Reflux time was kept at 3 hours except for acid-catalysed transesterification which requires 56 hours of reflux time. Results show that the conversion of waste vegetable oil to biodiesel was the highest through acid-base-catalysed transesterification and acid-catalysed transesterification (56 hours) and lowest in acid-catalysed transesterification (21 hours). Acid-base-catalysed transesterification produces biodiesel of the best quality, in terms of glycerol content and kinematic viscosity.

1 INTRODUCTION

Majority of the world energy needs are supplied through petrochemical sources, coal and natural gases. These sources are finite and the oil reserves in the world are predicted to be used up in 35–84 years at the rate it is being exploited (PUPPÁN. 2002). Augmented with the fact that fuel from crude oil produces numerous pollutants, such as sulfur dioxide and oxides of nitrogen, there is a pressing need to find alternative sources of energy, of which one possible source is biodiesel.

Biodiesel are fatty acid methyl esters derived from vegetable oil or animal fat. Biodiesel is a good alternative to diesel because it is renewable, biodegradable, produces fewer pollutants such as carbon monoxide, sulfur dioxide and unburnt hydrocarbon and does not contribute to a net rise in the amount of CO_2 (Akers, 2006.).

The most widely used method for commercial production of biodiesel is base-catalysed transesterification. The equation for transesterification is shown in Figure 1.
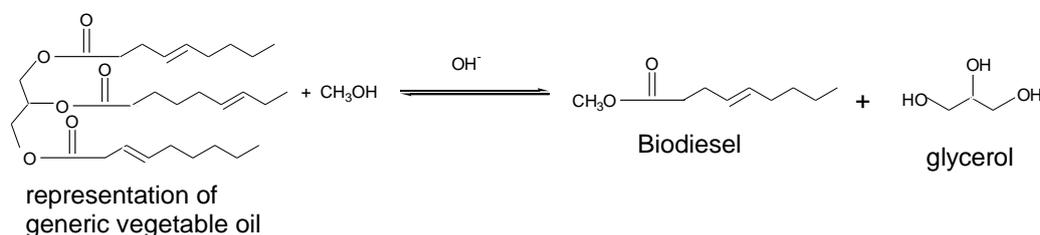

Figure 1 Equation representing transesterification reaction

Base-catalysed transesterification is sensitive to the purity of reactants and needs well-refined vegetable oil as raw material. As vegetable oil is used to fry food, moisture in the food combined with high heat tends to hydrolyze triglycerides to free fatty acids. These free fatty acids can account for up to 15% of the total weight of waste vegetable oil. In cases where free fatty acid content is greater than 1%, they can neutralize the base used in the transesterification reaction, leading to poor yield of conversion and increasing the cost of production (Yong, 2006). Hence, alternative methods need to be developed to improve the conversion and lower the cost of production of biodiesel.

In the current study, five methods of synthesising biodiesel, namely base-catalysed transesterification, acid-catalysed transesterification, acid-base-catalysed transesterification, iron (III) sulfate-base-catalysed transesterification and prawn shell-catalysed transesterification were evaluated in terms of yield and quality of biodiesel produced.

2   MATERIALS AND METHODS

The waste vegetable oil (WVO) was obtained from a local food stall which sells fried banana. The same type of waste vegetable oil was used for the five methods of synthesizing biodiesel. Prawn shells were obtained from prawns from local supermarket. Chemicals comprising 98% w/w sulfuric acid (Reagent grade, Dickson), sodium hydroxide (G.C.E Chemicals), iron(III) sulfate (G.C.E Chemicals) and methanol (reagent grade, Dickson) were used in the transesterification experiments.

2.1   Synthesis of biodiesel

2.1.1   Base-catalysed transesterification

A 200.00g sample of WVO was heated till 55°C, when 2.00g of sodium hydroxide and 58.60g of methanol were then added and the mixture refluxed at 65- 70°C for 3 hours. The biodiesel was then separated from the glycerol with a separating funnel, washed with deionised water until neutrality, and dried using anhydrous sodium sulfate.

2.1.2   Acid-catalysed transesterification

The conversion of triglyceride to biodiesel in acid-catalysed transesterification was monitored at every 3 hour intervals using HPLC. The HPLC chromatograms (figure 2) were shown on page 10 of appendix. As the triglyceride peak corresponding to the WVO was barely visible for the acid-catalysed transesterification at 21 hours (figure 3, pg 10), the optimum time for acid-catalysed transesterification was initially determined to be 21 hours. However, subsequent tests show that biodiesel synthesised from 21 hours of reflux was out of specification, indicating that conversion

was still incomplete after 21 hours. Thus, it was concluded that HPLC could not determine the optimum time of reflux accurately.

Hence, another test, known as the bound glycerol test was carried out to determine the conversion of the waste oil to biodiesel. Bound glycerol is the intermediate of transesterification, thus the lower the percentage of bound glycerol, the greater the conversion. As seen from figure 4 (appendix, page 10), the acid-catalysed transesterification was most complete at 56 hours as the % bound glycerol was the lowest. Hence subsequent acid-catalysed transesterification were carried out at 56 hours.

A 200.00g sample of WVO was first mixed with 10.00g of concentrated sulfuric acid and 73.25g of methanol. The mixture was refluxed at 65- 70°C for 56 hours. Biodiesel was separated from glycerol and acid using a separating funnel. The biodiesel was washed with deionised water till neutrality and dried using anhydrous sodium sulfate.

2.1.3 Acid-base-catalysed transesterification

WVO was titrated with $0.1mol/dm^3$ KOH to determine the concentration of free fatty acid (FFA) present in it. From the titration results, the mass of 98% w/w sulfuric acid needed was determined (mass of acid= 5% of weight of FFA). The WVO was refluxed with 0.22g of concentrated sulfuric acid and 19.66g of methanol at 65- 70°C for 2 hours. The oil was separated from the acid and subjected to base-catalysed transesterification for another 3 hours. The biodiesel obtained was then separated from the glycerol by a separating funnel, washed with deionised water till neutrality and dried using anhydrous sodium sulfate.

2.1.4 Iron(III) sulfate-base-catalysed transesterification

19.66g of methanol and 2.16g of anhydrous iron(III) sulfate were added to a 200.00g sample of WVO. The mixture was refluxed at 65- 70°C for 3 hours. The mixture was then centrifuged to remove the iron(III) sulfate residue and subjected to base-catalysed transesterification for another 3 hours. The biodiesel obtained was then separated from the glycerol by a separating funnel, washed with deionised water till neutrality and dried using anhydrous sodium sulfate.

2.1.5 Prawn shell- catalysed transesterification

Prawn shell was ground to powder form. The catalyst was activated by carbonizing the prawn shells through heating in furnace loaded with KF (25% mass of carbonized prawn shell) at 245°C. 200.00g of WVO was refluxed with 5.00g of prawn shell catalysts and methanol at 65-70°C for 3 hours. The biodiesel obtained was then separated from the glycerol by a separating funnel, washed

with deionised water till neutrality and dried using anhydrous sodium sulfate. Reaction was monitored by the use of HPLC (High performance liquid chromatography).

2.2   Quality of biodiesel

2.2.1   Glycerol test (total and free glycerol)

The determination of total, free and bound glycerol in the final biodiesel sample was carried out utilizing a modification of American Oil Chemists' Society Method Ca 14-56 Total, Free and Combined Glycerol (Iodometric-Periodic Acid Method) (AOCS Official Test Method Ca 14-56. 1991) by oxidation of glycerol with periodic acid and subsequent periodate titration.

2.2.1.1   Free Glycerol Test

A sample of 5.00g of biodiesel was transferred to a 100ml volumetric flask. 9.0ml of dichloromethane was added, followed by 50.0 ml of water. The mixture was shaken for 60 seconds, while venting it. The solution was made up to 100ml with deionised water. On standing the mixture separated into 2 layers, the aqueous and oil layer. A volume of 25.0ml of periodic acid and 25.0ml of the aqueous layer were transferred into another conical flask. After half an hour, 10ml of potassium iodide was added and mixture was allowed to stand for 60 seconds. The mixture was topped up to 125ml with deionised water and the mixture titrated with 0.1 N sodium thiosulfate using starch as indicator. A blank was prepared with the same reagents, but without the sample. The volume of sodium thiosulfate required was used to calculate the percentage of free glycerol. The following formula was used to calculate the percentage of glycerol:

$$\text{Glycerol \%} = \frac{[B-S][M][0.0230]}{[W]*0.294}*100\%$$

Where B = ml of thiosulfate to titrate the blank, M = normality of thiosulfate, S= ml of thiosulfate to titrate the sample, W = weight of sample extracted in g

2.2.1.2   Total Glycerol Test

A 5.00g sample of biodiesel was refluxed with 15.0ml of 0.7 mol/dm^3 potassium hydroxide in 95% ethanol for 30 minutes. The reflux condenser was washed down with 5ml water. The mixture was quantitatively transferred to a 100ml volumetric flask and 9ml of dichloromethane followed by 2.5ml of acetic acid were added. The glycerol content was determined as described in the free glycerol test.

The percentage of combined or bound glycerol was obtained by subtracting % of free glycerol from the % of total glycerol.

2.2.2 NMR analysis

^{1}H NMR was used to monitor the transesterification reaction. ^{1}H NMR spectrum was recorded on a Bruker AMX 500 MHz spectrometer at the National University of Singapore. The sample solvent was $CDCl_3$. All spectra were referenced to TMS, 0.00 ppm.

2.2.3 Density

Mass of 25ml of biodiesel was determined and the density calculated using the formula Density = M/V where M = mass in g and V= volume in cm^3.

2.2.4 Kinematic viscosity

Kinematic viscosity was determined according to ASTM D445-06.

2.2.5 Heat of combustion

10.00g of biodiesel was weighed into a crucible. Wick was fitted into the crucible and the whole set up weighed. The biodiesel was used to heat up 10ml of DI water at room temperature. Flame was extinguished when temperature reached 90°C and the set up weighed to find out the mass of biodiesel combusted. Heat of combustion was determined by using the formula: $\Delta H = mc\theta$, where m=10g, c= specific heat capacity of water= $4.186 Jg^{-1} K^{-1}$, θ= change in temperature

3.   RESULTS AND DISCUSSION

3.1   Prawn shell-catalysed transesterification
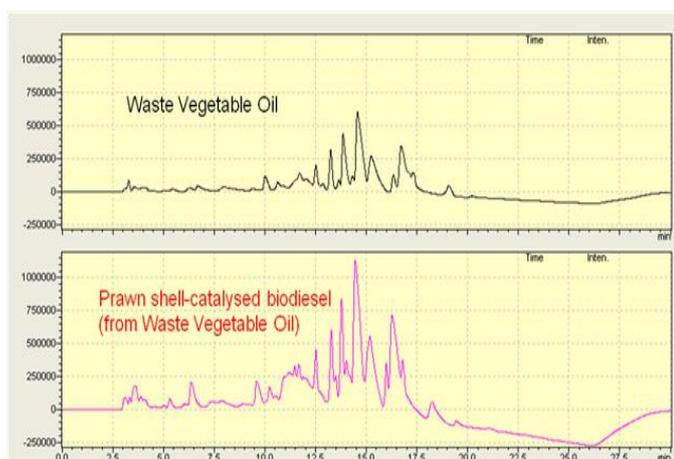
Figure 5 HPLC chromatogram of WVO versus biodiesel from prawn shell-catalysed transesteification
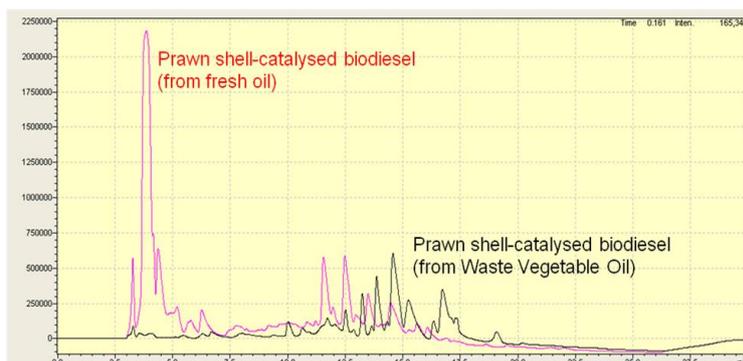
Figure 6 HPLC chromatogram of prawn shell biodiesel from fresh vegetable oil and waste vegetable oil

From figure 5, it can be seen that the activated prawn shell catalyst failed to produce biodiesel from WVO. Spectrum of prawn shell-catalysed biodiesel shows that the triglyceride peak from WVO

was still present and there was barely any biodiesel peak visible. It was hypothesised that it could be due to poisoning of catalyst by impurities in WVO.

From figure 6, it is evident that the prawn shell catalyst was able to convert fresh oil to biodiesel as a peak corresponding to biodiesel can be observed, proving the hypothesis right. Prawn shell catalyst was hence abandoned as it cannot be used on WVO.

3.2   NMR spectra of biodiesel

The ^{1}H NMR spectra of WVO and the biodiesel obtained from the various transesterification processes other than the prawn-shell-catalysed transesterification are shown on appendix, pg 11-12.

The region of the proton NMR spectra for the oil and biodiesel indicating transesterification lies between 3-7 ppm. The most important part of the spectra is the region that indicates that the glycerol group of the waste vegetable oil has been replaced by the methyl group of the biodiesel. In the spectrum of the waste cooking oil (Figure 7 of pg 11) the glycerol group is indicated by a complicated set of doublets (H[b]) ranging from 4.277 to 4.309 ppm. In the base-catalysed, iron(III) sulfate-base-catalysed and acid-base-catalysed biodiesel, it is clear that a methyl group has replaced the glycerol and hence the doublets in figure 7 are replaced with a sharp CH_3 singlet (H[a]) at about 3.650 ppm in figure 8 to 10. Hence the conversions for base-catalysed, iron(III) sulfate-base-catalysed and acid-base-catalysed transesterification are complete. However, this is not the case for acid-catalysed transesterification at 21 hours as seen from figure 12 which shows peaks corresponding to both the glycerol group and CH_3, indicating that the conversion is relatively incomplete. However, for acid-catalysed transesterification (56 h), the conversion is complete, as the peaks corresponding to the glycerol group of WVO was absent, as seen from figure 13 of pg 12.
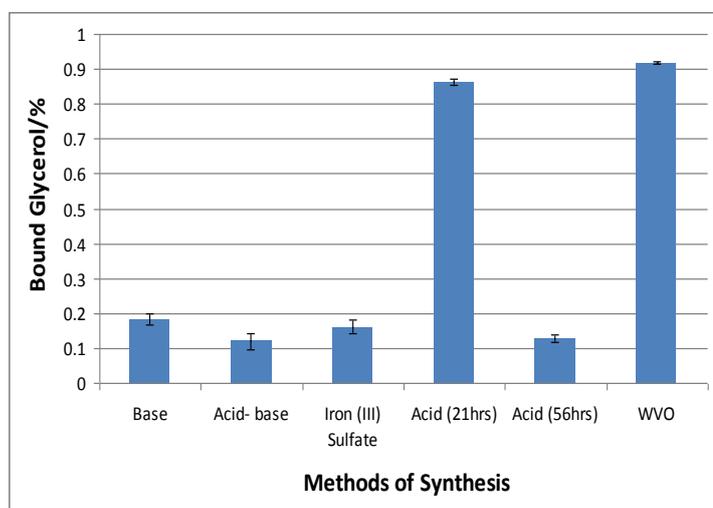
3.3   Percentage of total and bound glycerol

Bound glycerols are intermediates of the transesterification process. Hence the higher the % of bound glycerol, the lower is the conversion. In Figure 14, acid-catalysed biodiesel (56 hours) shows a great decrease in % of bound glycerol as compared to the acid-catalyed biodiesel (21 hours). The % of bound glycerol in biodiesel from acid-catalyed transesterification (56 hours) is also comparable with that from acid-base-catalysed transesterification. These two methods have the highest conversion of WVO into biodiesel.

Figure 14 Bound glycerol content of biodiesel from different transesteification processes (n=3)
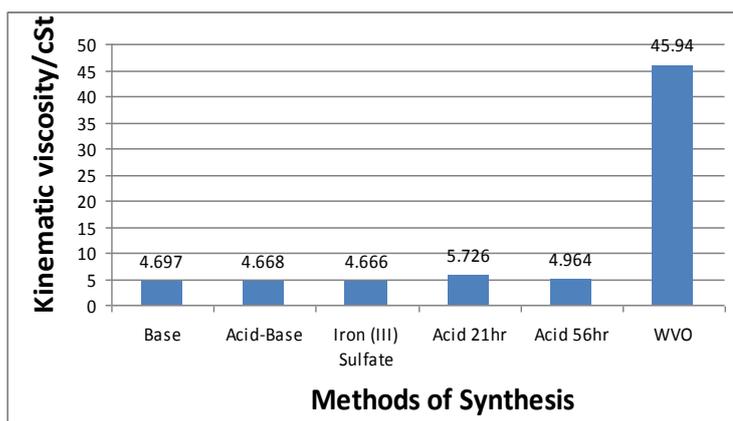
3.4 Kinematic viscosity

Figure 15 Kinematic viscosity of biodiesel from different methods

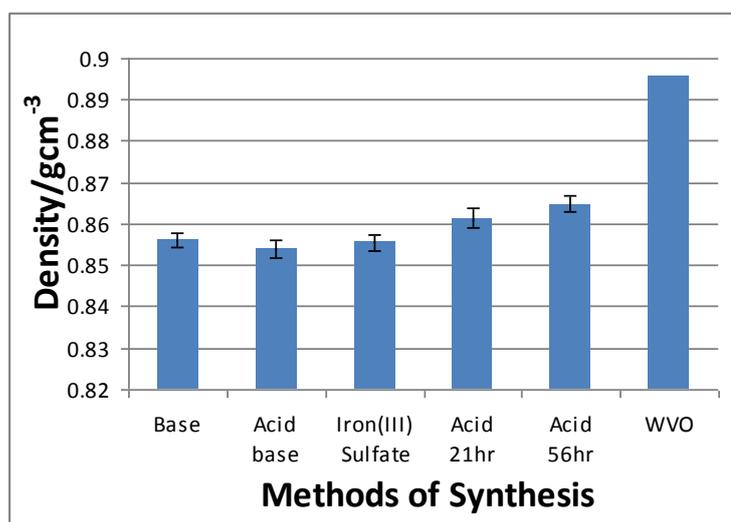## 3.5 Density of biodiesel

Figure 16 Density of biodiesel from different methods (n=3)
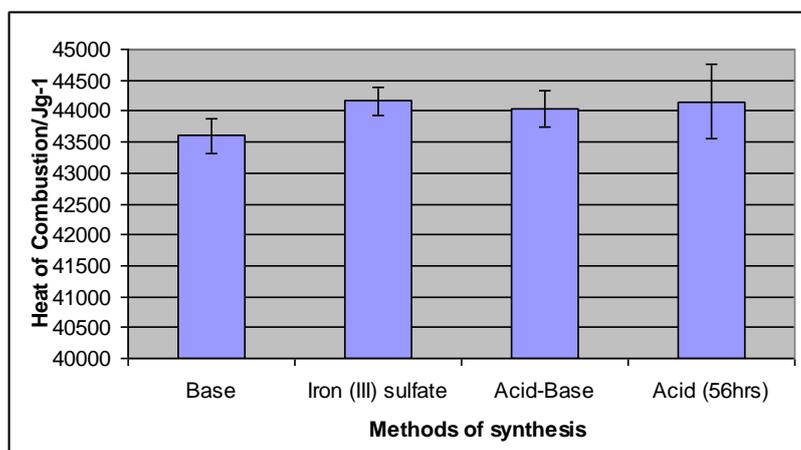
3.6 Heat of combustion

Figure 17 Heat of combustion of biodiesel from different methods (n=3)

As indicated in Figure 15, the viscosities of biodiesels obtained from all methods are within the biodiesel specification, ASTM D 6751 (1.9 to 6.0 cSt). The viscosity of acid-catalysed (56 hours) biodiesel was much lower than acid-catalysed (21 hours) biodiesel, showing higher conversion at 56 hours. The viscosities of biodiesel synthesized from acid-catalysed transesterification were higher than viscosity of biodiesel synthesised from other methods.

The standard for biodiesel density for most countries lies between 0.850 and 0.900 g/cm^3 (Meher. et al, 2006). This property is important mainly in airless combustion systems because it influences the efficiency of atomization of the fuel (Ryan, 1984). The results obtained showed that the densities of biodiesel produced by all the methods of synthesis are within the range of standard (Figure 16). The density of biodiesel from acid-catalysed transesterification is the highest among all the biodiesels, similar to the trend for the viscosity data.

The heat of combustion is comparable for biodiesels synthesised from all the above methods (Figure 17). The values for heat of combustion for the biodiesels were consistently close to the reported value of 41000J/g (Akers, 2006).

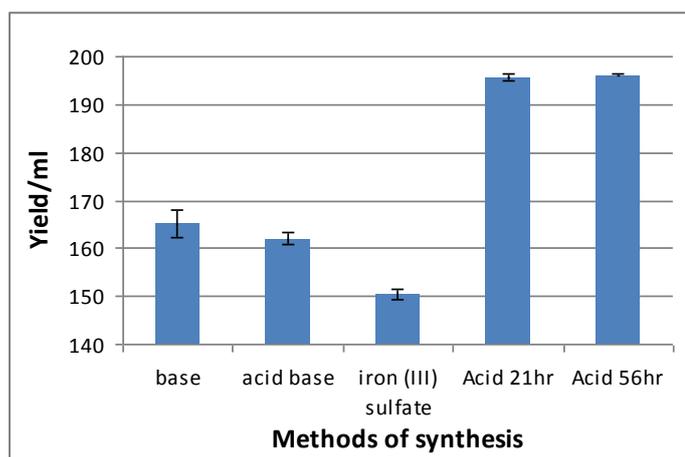Lee Men Quan, Derrick Toh Yong Seng, Khoo Chun Yuet

Figure 18 Yield of biodiesel from different methods (n=3)

From figure 18, acid-catalysed transesterification has the highest yield among the 4 synthesis methods as no soap is formed during acid reaction. The other methods produce soap as a by-product, due to the side reaction of sodium hydroxide with fatty acid. Iron(III) sulfate-base-catalysed transesterification has the lowest yield, which is believed to be due to an intermediate step involving centrifuging which leads to loss of biodiesel.

4.   CONCLUSION

Five types of transesterification (acid-catalysed, base-catalysed, acid-base-catalysed, iron(III) sulfate-base-catalysed and prawn shell-catalysed transesterification) were evaluated in terms of yield and quality. Prawn shell catalysts were not able to convert WVO into biodiesel due to poisoning of catalyst by impurities present in WVO. Conversion of WVO to biodiesel is lower in acid-catalysed transesterification (21 hours) and highest in acid-base-catalysed transesterification and acid-catalyed transesterification (56 hours). In most of the tests conducted, biodiesel synthesised from acid-base-catalysed transesterification shows the best qualities, most notably in terms of bound glycerol content and kinematic viscosity.

Acid-base-catalysed transesterification has the greatest efficacy (highest conversion of oil to biodiesel, good quality of biodiesel produced and moderately high rate of conversion). This method does not have a major drawback, unlike base-catalysed transesterification, which produces a very large amount of soap especially if the oil is of poor quality. Therefore, it is very time consuming to wash the biodiesel. Acid-catalysed transesterification has highest yield as it does not produce soap but reflux duration is far too long at 56 hours. Iron(III) sulfate-base-catalysed transesterification also produces biodiesel of good quality but has much lower yield due to an additional centrifuging step needed to remove iron(III) sulfate. Hence acid-base-catalysed transesterification method has the potential to be commercialised to manufacture biodiesel in large scale.

ACKNOWLEDGEMENT

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Yong. W., Ou S., Tang S., Liu P., Feng, X. (2006). Comparison of two different processes to synthesise biodiesel by waste cooking oil. *Journal of Molecular Catalysis A: Chemical,* 252, 107-112.

APPENDIX
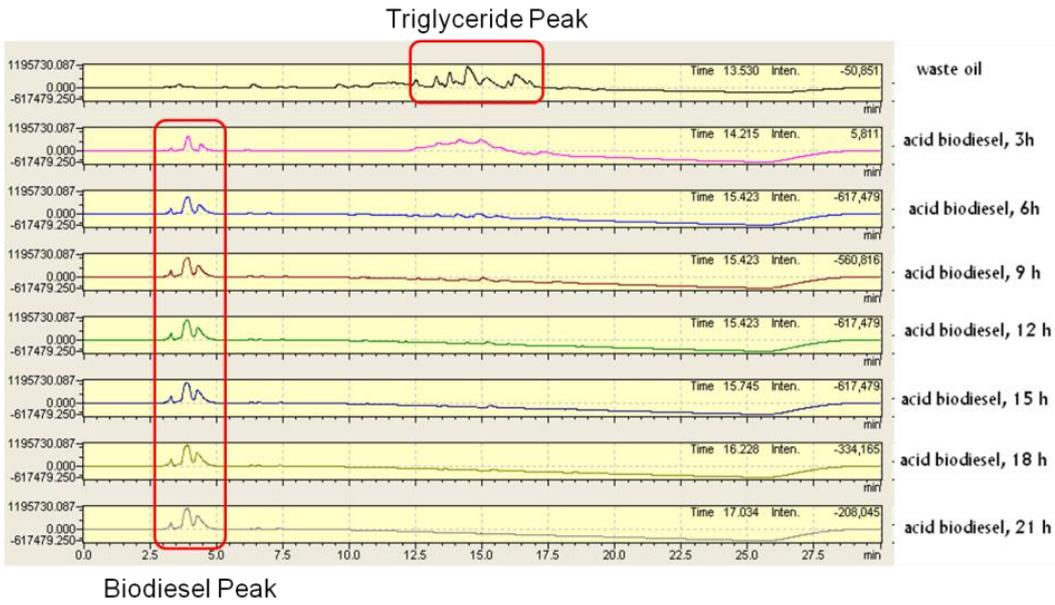
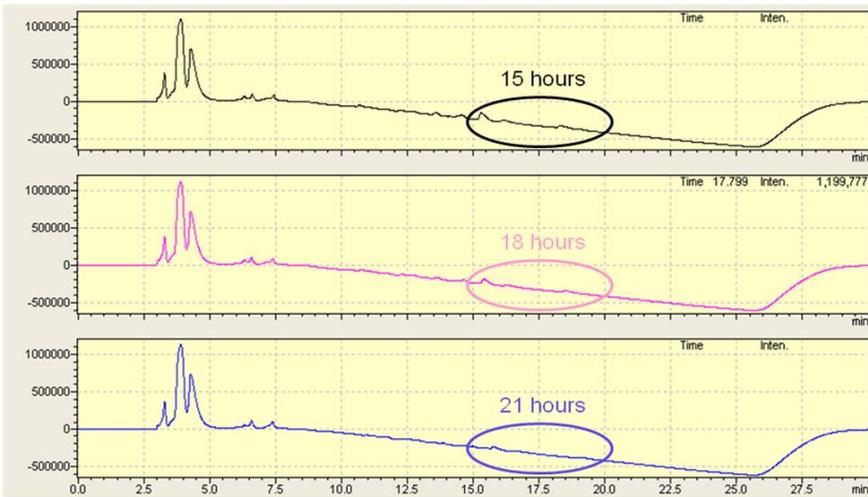Figure 2 HPLC chromatogram of the acid- catalysed biodiesel at 3 hour intervals.

Figure 3 HPLC chromatogram of the acid- catalysed biodiesel from 15- 21 hours.
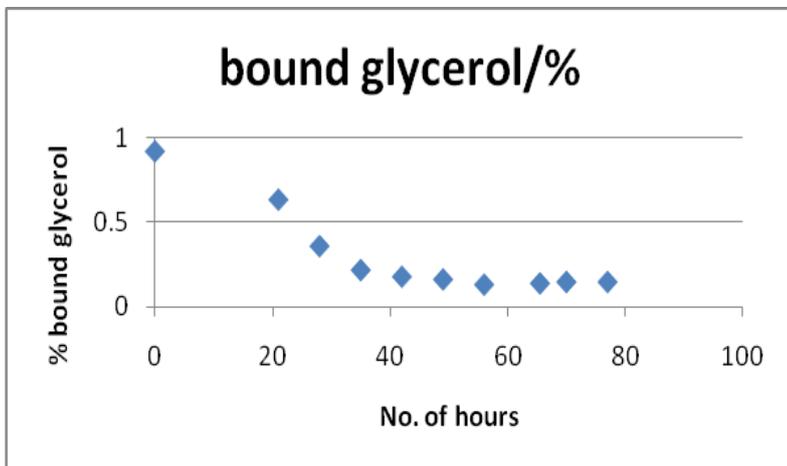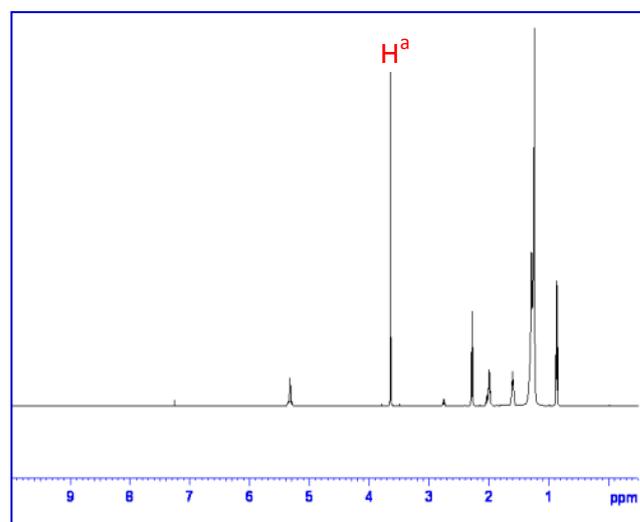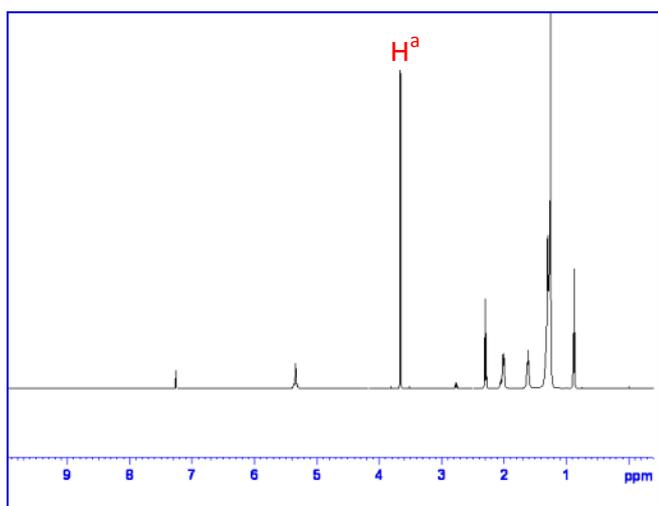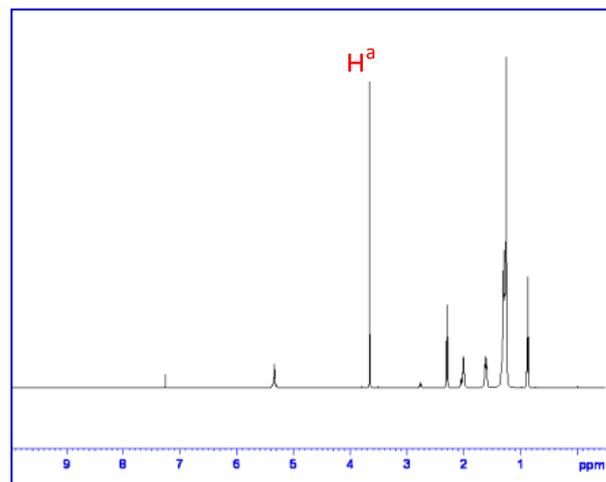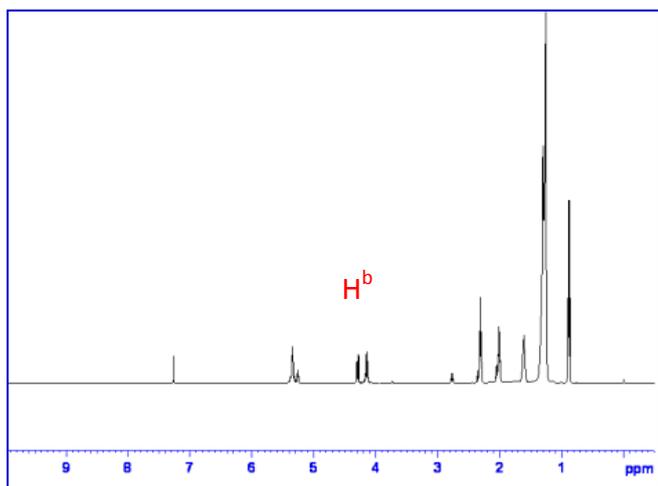

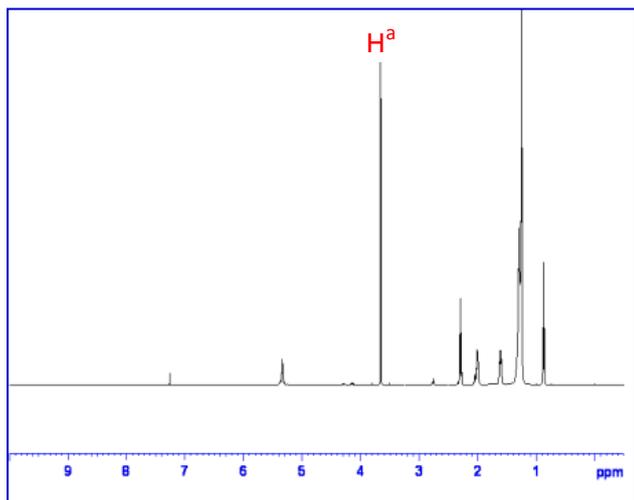Figure 4 Bound glycerol for acid- catalysed biodiesel at 7 hour interval.

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Structure of vegetable oil

Structure of biodiesel

Figure 7 ^1H NMR spectrum of WVO

Figure 8 ^1H NMR spectrum of base-catalysed biodiesel

Figure 9 ^1H NMR spectrum of acid- base catalvsed biodiesel

Figure 10 ^{1}H NMR spectrum of iron (III) sulfate catalysed biodiesel.
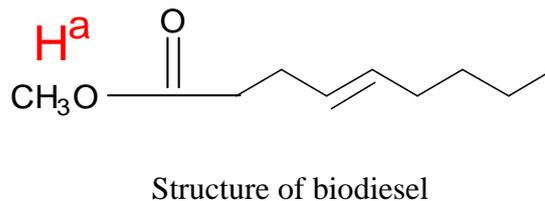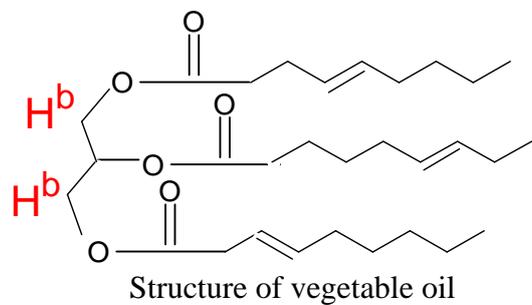
Figure 11 ^1H NMR spectrum of acid-catalysed biodiesel (21 hour)
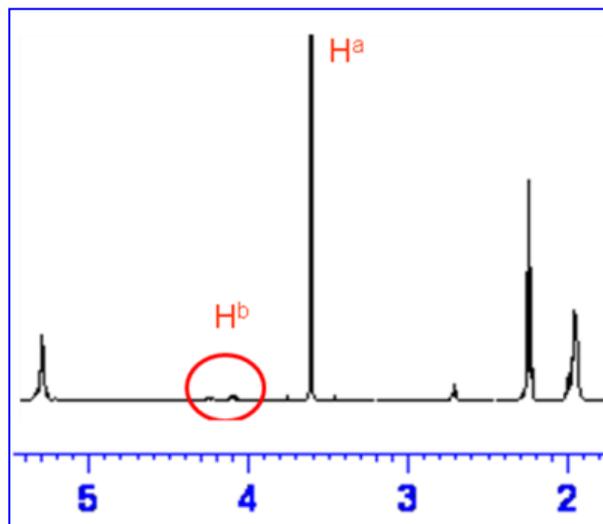

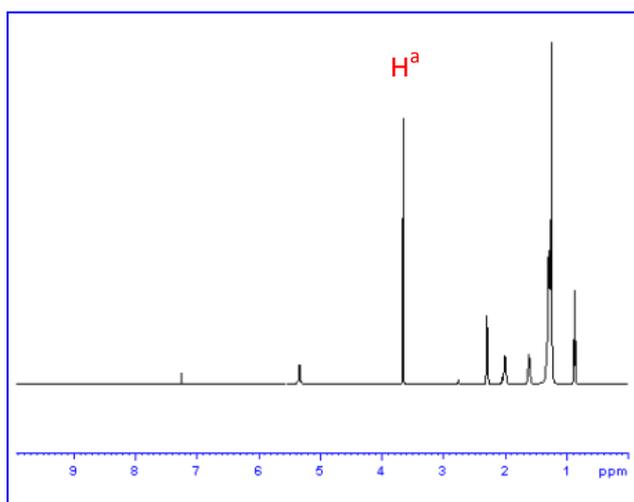Figure 12 Close-up view of ^1H NMR spectrum of acid-catalysed biodiesel (21 hour)

Figure 13 ^1H NMR spectrum of acid-catalysed biodiesel (56 hours)