Investigation of KI impregnated chicken, oyster shells and calcium oxide as catalysts for transesterification of sunflower oil into biodiesel.

Group 1-31

Abstract

Our project aims to investigate the effect of different catalysts on the transesterification process of sunflower oil to biodiesel. We used chicken shells, oyster shells and calcium oxide as catalysts. The effects of KI on the catalysts were tested out by impregnating KI onto the base catalysts. Iodine value tests, acid value and free fatty acid content tests, biodiesel density tests, NMR spectroscopy, calculations of biodiesel yield were conducted to determine the best catalyst the best biodiesel, with quality and yield as factors. Based on the results collected, chicken egg shell catalyst is the best catalyst to produce the highest quantity and quality of biodiesel sample. It is also clear and evident throughout our experiments, that, contrary to our hypothesis, the impregnation of KI onto solid supports of catalysts does not actually improve the quality and yield of biodiesel during transesterification process.

Introduction

Fossil fuels have and will play a big role in our economic systems. However, there are two main areas of concern regarding our use of fossil fuels: their non-renewability and their contribution to climate change. Hence, there is a need for alternative sources of energy that are both environmentally-friendly and renewable.

Biodiesel has been touted as a potential alternative source of energy. Mainly used in car engines in place of traditional diesel, biodiesel offers numerous advantages over fossil fuels. Based on the French Institute of Petroleum, the carbon monoxide (CO) emissions, a toxic by-product gas, for biodiesel combustion in diesel engines are 40 to 50% lower than those for conventional diesel. It generates little carbon dioxide emissions. According to Coronado et al., 2009, although the combustion of biodiesel generates a comparable amount of carbon dioxide to fossil fuels, the plant feedstock used in the production of biodiesel would have absorbed the same amount of carbon dioxide released during combustion throughout its life. Given that road transportation represents 84% of the CO_2 emissions *(Coronado et al., 2009),* biodiesel has the potential to dramatically cut emissions. However, there are currently many roadblocks to the implementation of biodiesel on a large scale. Current methods of producing biodiesel rely on the use of homogenous acids or alkali catalysts to produce fatty acid methyl esters (FAMEs). These

catalysts are prone to causing contamination, which can be harmful to the environment. Furthermore, homogeneous catalysed reactions require higher reaction temperatures than heterogeneous catalysed reactions *(Talha & Sulaiman, 2016)*. These factors contribute to the high production cost of biodiesel. Consequently, the use of biodiesel remains low today. Therefore, cheaper, more efficient production methods will be necessary.

Calcium oxide has been suggested as an efficient heterogeneous catalyst for transesterification. It poses a strong cost advantage over traditional catalysts *(Xie et al. , 2006).* Shells like chicken egg and ashed oyster shells that contain calcium carbonate, are heterogeneous catalysts that are viable alternatives for homogeneous catalysts, and are also cheaper and more abundant.

Xie et al. (2006) tested several potassium salts and concluded that potassium iodide has the highest activity in soybean oil transesterification. We hypothesise that there would be similar effects on catalysts derived from different shells. Eggshells are one of the widely used food processing and manufacturing plants by-products. Therefore, we aim to investigate the effectiveness of transesterification of soybean oil with KI impregnated chicken shell, clam shells and commercial calcium oxide.

Objectives

1. To impregnate KI into the chicken egg shell, oyster shell and calcium oxide.
2. To synthesise biodiesel using our various solid catalysts (with KI and without KI)
3. Study the effectiveness of the catalyst in transesterification.
4. Analyse the biodiesel samples/ products of transesterification to determine the best catalyst to produce good biodiesel.

Hypothesis

1. KI can be impregnated on our solid support.
2. KI impregnated shells can be used as catalyst for transesterification.
3. All the heterogeneous catalysts (KI and non-KI) can function properly and result in successful transesterification.
4. The addition of KI onto various catalysts will improve biodiesel quality and increase biodiesel quantity produced.
5. KI impregnated oyster shell will have the highest yield and quality.

2. Materials and methods

2.1 Preparation of KI and non-KI impregnated catalyst

Materials:

- Calcined chicken egg shells
- Ashed Oyster shells
- Commercial Calcium Oxide (GCE)
- Potassium Iodide (KI) (GCE)
- Furnace (Carbolite AAF1100)

Methods:

Calcined Chicken Egg shells and Ashed Oyster shells was obtained from the laboratory. Industrial Calcium Oxide was activated by calcination at 800 °C for 4 hours. It was then stored in a dry cabinet and kept well to prevent oxidation by the environment. (The catalyst were then prepared using incipient wetness impregnation.) An aqueous Potassium Iodide solution was prepared by mixing 9.96g of KI in 30 mL of Deionised water. 10g of the support was added to the solution and stirred for 2 hours using a magnetic stirrer. The mixture was filtered using a filter funnel and the residue was collected. The residue was dried overnight in the oven. The solid obtained was then calcined at 300 °C for 4 hours and kept in an airtight environment to prevent oxidation. Non KI-impregnated Chicken Egg, Ashed Oyster and Calcium Oxide, along with KI-impregnated Chicken Egg, Ashed Oyster and Calcium Oxide was prepared as catalysts.

2.2 Transesterification of sunflower oil into biodiesel

Materials:

- Sunflower oil
- Methanol (scharlau)
- Heating mantle
- 2-neck flask

Methods:

50g of sunflower oil was placed in a 2-neck flask. Molar ratio of methanol to oil was set at 9:1. Molar mass of soybean oil was assumed to be 874g/mol, and methanol to be 32.04g/mol. 16.48g of methanol was added to 0.5g (1 wt%) of catalyst. The sunflower oil was poured in the 2-neck flask first. The 2-neck flask was attached to a reflux condenser and a thermometer, and was placed in a heating mantle. When the temperature reached 55 °C, methanol and catalyst mixture was then added immediately into the soybean oil. The reaction

was stopped after 3 hours. The mixture was put through a separating funnel to remove the solid catalyst. The bottom aqueous layer of glycerol was separated from the biodiesel layer. Deionised water was added to the remaining mixture and removed, until the pH was neutral. This was tested using a universal indicator paper. The biodiesel sample was transferred into a centrifuge tube, and centrifuged at 8000 rpm for 5 minutes. The biodiesel was removed and placed into another centrifuge tube. It was centrifuged again and removed. The biodiesel collected will be our sample. This process was repeated in triplicates per catalyst, and was done for both KI and non-KI impregnated catalysts for comparison.

2.3 Confirming validity of Biodiesel

Materials:

- Proton- Nuclear Magnetic Resonance (1H NMR)

Methods:

One sample from each catalyst type was sent for a 1H NMR spectroscopy. The parts-per-million (ppm) is noted, along with the integral values. It was compared to the various ppm of functional groups (ie. alkene groups, ester groups) to confirm it is biodiesel. The chemical shift (δ) was noted to determine the positions of the protons in the fatty acid chains . The neighbouring protons is also deduced by the formula: no. of neighbouring protons = no. of peaks - 1.

2.4 Determining effectiveness of catalyst and quality of biodiesel

2.4.1 Calculating biodiesel yield percentage

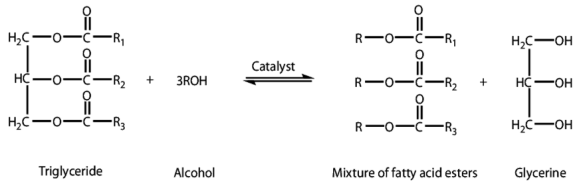
Materials:

- Biodiesel samples in various centrifuge tubes
- Beaker
- Weighing scale

Methods:

The biodiesel sample was extracted and weighed. The biodiesel yield was calculated by the equation : $Yield(\%) = \frac{Actual\ mass\ (g)}{Theoretical\ mass\ (g)}$ x 100%

The actual mass was calculated by using the molar ratio in the chemical equation for transesterification:



The fatty acid composition of Sunflower Oil was assumed to be 59% Linoleic Acid, 30% Oleic acid, 5% Palmitic acid and 6% Stearic Acid. Hence, the overall fatty acid molar mass was 280.096 g/mol. The theoretical mass was calculated to be 48.03g.

2.4.2 Checking of Free Fatty Acids (FFA) and Acid value (AV)

Materials:

- Absolute ethanol (GCE)
- Burette and Pipette
- 0.00825M potassium hydroxide (GCE)
- Thymol blue Indicator (GCE)

Methods:

20mL of Absolute ethanol solvent was added to 1g of biodiesel sample, with 5 drops of thymol blue. The solution should be yellow. Drops of 0.00825M potassium hydroxide (KOH) were titrated until the color of the solution changes colour from yellow. The volume of the potassium hydroxide added was derived by subtracting the initial volume by final volume. This was repeated in triplicate for each sample and the AV and FFA percentage is calculated. The average FFA and AV for each sample was deduced through these calculations:

$$\text{Acid Value [mg KOH/g]} = \frac{Volume\ of\ KOH\ added \times 56.11 \times Normality\ of\ KOH}{sample\ weight\ (g)}$$

$$\text{FFA [\%]} = \frac{Volume\ of\ KOH\ added \times 280.096^{*} \times Normality\ of\ KOH}{10 \times sample\ weight(g)}\ .$$

*The molecular weight of the fatty acid is taken to be that of the sum of the standard composition of fatty acids in Sunflower Oil , which is 280.096 g/mol.

2.4.3 Calculating Iodine value in Biodiesel

Materials:

- Spectrophotometer (Shimadzu UV-1800)
- Hexane (Labscan)
- Triiodide (from preparation)
- Centrifuge Machine

Methods:

A 1.2 mmol L-1 triiodide reference solution was prepared by dissolving 30 mg of I_2 in 15 mL of ethanol, followed by addition of KI to a final concentration of 0.210 mol L^{-1} and marking the volume up to 100 mL in a volumetric flask with deionised water. A calibration curve with various concentrations of triiodide solution was plotted. 1ml of biodiesel sample is diluted with 1ml hexane and 2.4ml of triiodide solution is added. The solution was shaken for 5 minutes before being centrifuged at 8000 rpm for 2 minutes. The 0.25ml of the aqueous layer was removed. The portion was diluted until it is able to fit in the calibration curve. The final concentration of triiodide was deducted from the initial concentration of the triiodide to find the concentration of iodine absorbed by the biodiesel. The iodine value can then be calculated.

2.4.4 Biodiesel Density

Materials:

- Micropipette
- 2 d.p Weighing Scale

Methods:

5.00 cm^3 of a biodiesel sample was measured using a pipette. The mass of the biodiesel was then measured in a beaker and recorded. This process was repeated 3 times with a new beaker each time and the average mass was obtained. The densities (g/cm^3) were evaluated by dividing the mass(g) by volume (cm^3). These steps are repeated for all the biodiesel samples 3 times each, allowing the average density of each sample to be determined and used for comparison.

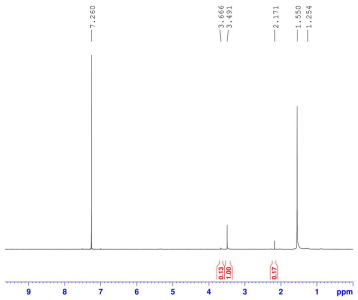
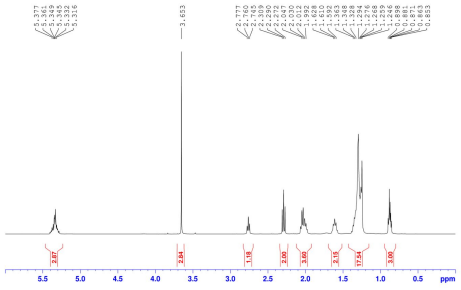
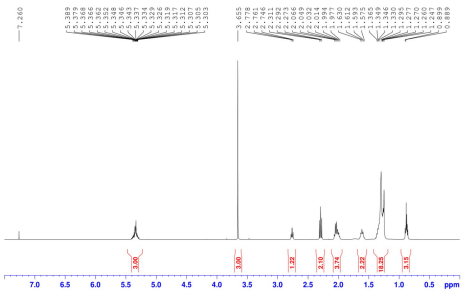
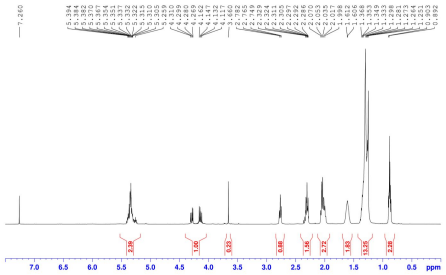
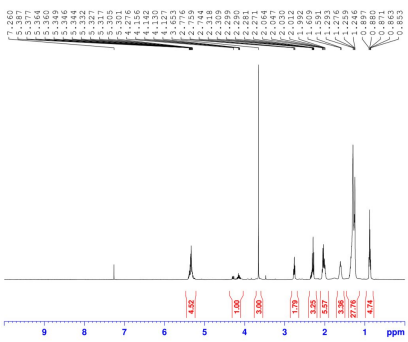
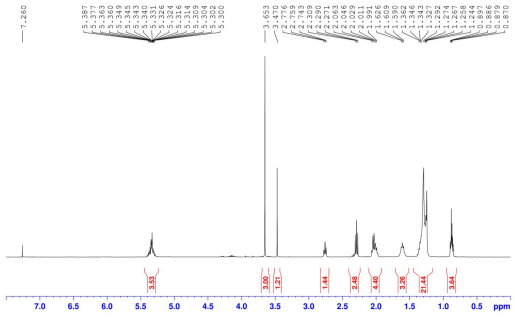
Note: The biodiesel sample was uncontaminated after each reading and can thus be reused.

3. Results and Discussion

3.1 Transesterification of sunflower oil into biodiesel

A series of transesterification set-ups were prepared with varying parameters. The methanol oil ratio, catalyst weight, reaction time and mass were varied and tested. The best parameters is as such in our methods. Non-activated CaO proved to have a lesser yield than activated one. We suspected it to be a decrease in effectiveness due to oxidation with the environment.

3.2 Confirming validity of biodiesel through 1H NMR Spectroscopy

	KI-impregnated	Non-KI impregnated
CE	 Fig. 1	 Fig. 2
AO	 *Fig. 3*	 *Fig. 4*
CaO	 *Fig. 5*	 *Fig. 6*

CE: Chicken Egg, **AO:** Ashed Oyster, **CaO:** Calcium Oxide

Figure 1-6: Screenshots of NMR results

NMR of all catalyst showed an intense singlet peak at around 3.5 ppm. This singlet peak indicates the presence of an ester bond. 2 messy peaks at around 4 - 4.5ppm indicate the presence of unreacted sunflower oil. KI/AO and CE catalyst did not have the unreacted oil peaks, hence we can conclude KI/AO and CE converted oil into biodiesel the most effectively.

3.3.1 Yield percent of biodiesel

Yield (%) of Chicken egg shell: 84.4%, KI-impregnated CaO at 81.5%, CaO at 76.1%, Ashed Oyster at 75.3%, KI-impregnated Ashed oyster shells at 75.1%, and lastly KI-impregnated chicken egg shell at 39.2% *(Fig. 8).*This data suggests that chicken egg shell catalyst may be the most efficient catalyst as it has high yield. We suspect the low yield for KI/CE to be perhaps the CE incompatibility with KI, that reduced its efficiency .

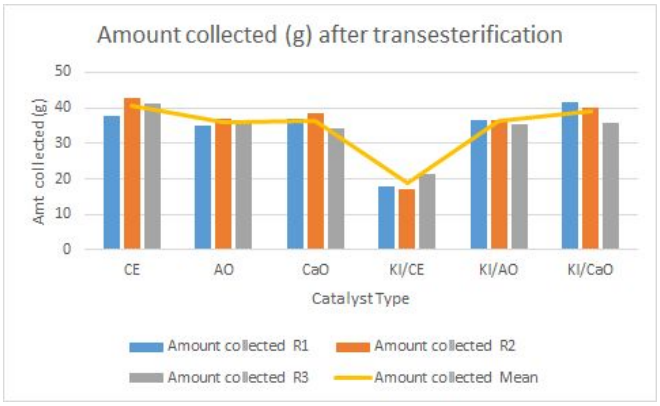


Fig. 7: Graph showing mass of sample

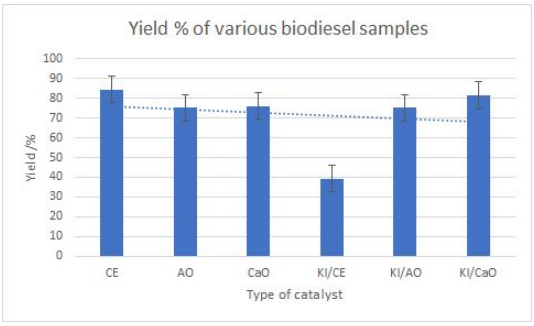


Fig. 8: Graph showing yield percent of biodiesel samples

3.3.2 Checking of Free Fatty Acids (FFA) and Acid value (AV)

Chicken Egg had the lowest AV and FFA%. Calcium Oxide and KI-Impregnated Calcium Oxide had the highest acid value and free fatty acid %, followed by KI-impregnated chicken egg shell *(Fig. 9)*. Chicken egg catalyst would have converted the most sunflower oil into biodiesel. The acid value is calculated by making use of the volume of KOH needed to neutralise the acid in the biodiesel samples. The higher acid value implies that the biodiesel would be less effective as there will be higher free fatty acid percentage in the sample, which results in lower percentage of biodiesel (FAMEs).

Thymol blue is used as the indicator for our experiments, which displays a range of colours. It is hard to determine the end point for thymol blue, thus our results may be slightly inaccurate, due to a limitation that is beyond our control. Phenolphthalein, the preferred choice because of the distinct color change, was prohibited from usage in the lab.

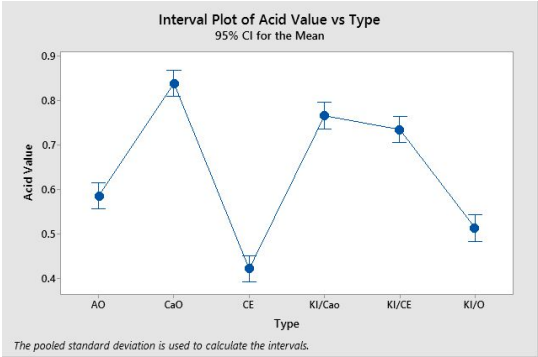


Fig. 9: ANOVA of Acid Value vs Catalyst Type

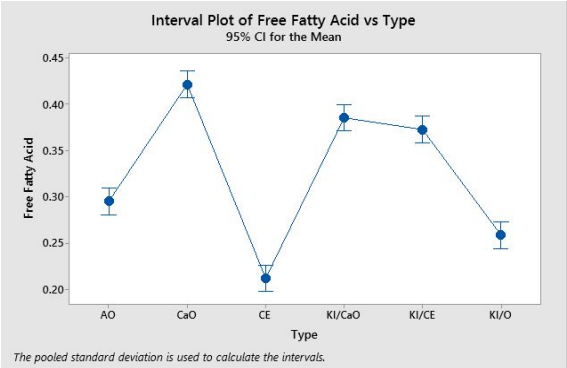


Fig. 10: ANOVA of FFA vs Catalyst Type

3.3.3 Biodiesel Density

The data for the density (g/cm³) of the various samples are presented below. The standard biodiesel density is ~0.87 g/cm³(EN ISO 3675, EN ISO 12185). Based on the ANOVA of densities below, CaO, CE and KI/AO was above the standard, while KI/CE was slightly below. AO and KI/CaO was significantly below the standard. A higher density has higher quality as its viscosity would increase during combustion at high temperatures, resulting in lower oil consumption and less wear. Based on our results, chicken egg shell catalyst produces the most dense biodiesel sample.

	Density (g/cm3)					
Catalyst	Reading 1	Reading 2	Reading 3	Mean	Standard Deviation	Standard Error
CE R1	0.886	0.884	0.884	0.885	0.00115	0.00067
CE R2	0.886	0.882	0.884	0.884	0.00200	0.00115
CE R3	0.884	0.884	0.886	0.885	0.00115	0.00067
AO R1	0.848	0.850	0.850	0.849	0.00115	0.00067
AO R2	0.852	0.850	0.852	0.851	0.00115	0.00067
AO R3	0.852	0.854	0.854	0.853	0.00115	0.00067
CaO R1	0.878	0.876	0.874	0.876	0.00200	0.00115
CaO R2	0.876	0.874	0.872	0.874	0.00200	0.00115
CaO R3	0.872	0.870	0.872	0.871	0.00115	0.00067
KI/CE R1	0.866	0.870	0.866	0.867	0.00231	0.00133
KI/CE R2	0.864	0.866	0.866	0.865	0.00115	0.00067
KI/CE R3	0.862	0.870	0.864	0.865	0.00416	0.00240
KI/ AO R1	0.874	0.880	0.882	0.879	0.00416	0.00240
KI/ AO R2	0.884	0.880	0.882	0.882	0.00200	0.00115
KI/ AO R3	0.878	0.876	0.880	0.878	0.00200	0.00115
KI/CaO R1	0.854	0.852	0.854	0.853	0.00115	0.00067
KI/CaO R2	0.852	0.856	0.856	0.855	0.00231	0.00133
KI/CaO R3	0.854	0.856	0.854	0.855	0.00115	0.00067

Fig. 11: Table showing the various density

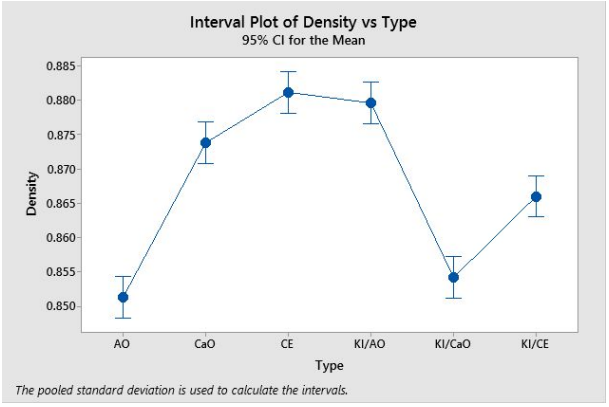


Fig. 12: ANOVA for densities vs catalyst type

3.3.4 Iodine Value Test

We were unable to produce results due to discrepancies in our researched methods as proposed by *Soares et al., 2018.* We suspected the preparation of Triiodide to be the main

cause. The method said to 'add until a final volume of 100 mL' *(under reagents and solutions),* but did not specify which solvent. We had tried using absolute ethanol, hexane and Deionised Water. KI was unable to dissolve in absolute ethanol and hexane despite mixing for more than 24 hours, but was able to dissolve in DI water. Hence we decided to use DI water as solvent. The absorbance unit for triiodide solution was the maximum *(Fig. 13)*, which contradicted the findings in the research paper (Less than 1.0 Abs. for 1.2 mmol/L Triiodide). After centrifuging, the aqueous layer that was directly present had too high absorbance unit. Some biodiesel samples also produced soap *(Fig. 14)*. We suspected it could be insufficient washing of biodiesel, yet they proved to be neutral when tested for pH. We tried diluting the aqueous layer and triiodide solution further to fit the range of the calibration curve, but the results were not accurate or precise at all.

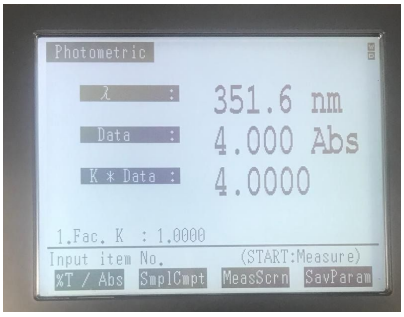


Fig. 13

Fig. 14

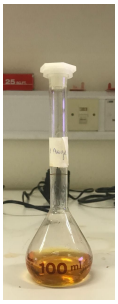


Fig. 15: Triiodide solution

Conclusion

Of all the catalysts tested, Chicken egg shell is the best catalyst as it consistently produces high quality biodiesel with high conversion rate as well. This can be seen through the NMR results, low acid value and free fatty acid content, high density and high yield%. KI-impregnated chicken egg shell is the worst catalyst as it has lowest yield%, high acid value and free fatty acid content compared to other catalysts. It is also evident that KI (Potassium Iodide) does not improve the quality of the catalyst at all, as KI-impregnated catalysts do not necessarily show higher yield% for biodiesel or produce higher quality of biodiesel. This research can serve as one of the many research papers on biodiesel, potentially being able to contribute useful data to the study and future production of biodiesel. Future work involving in-depth investigation on the reaction mechanism of various catalysts and catalyst reusability should be conducted.

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