TRANSESTERIFICATION OF RAPESEED OIL BY SOLID OXIDE CATALYSTS

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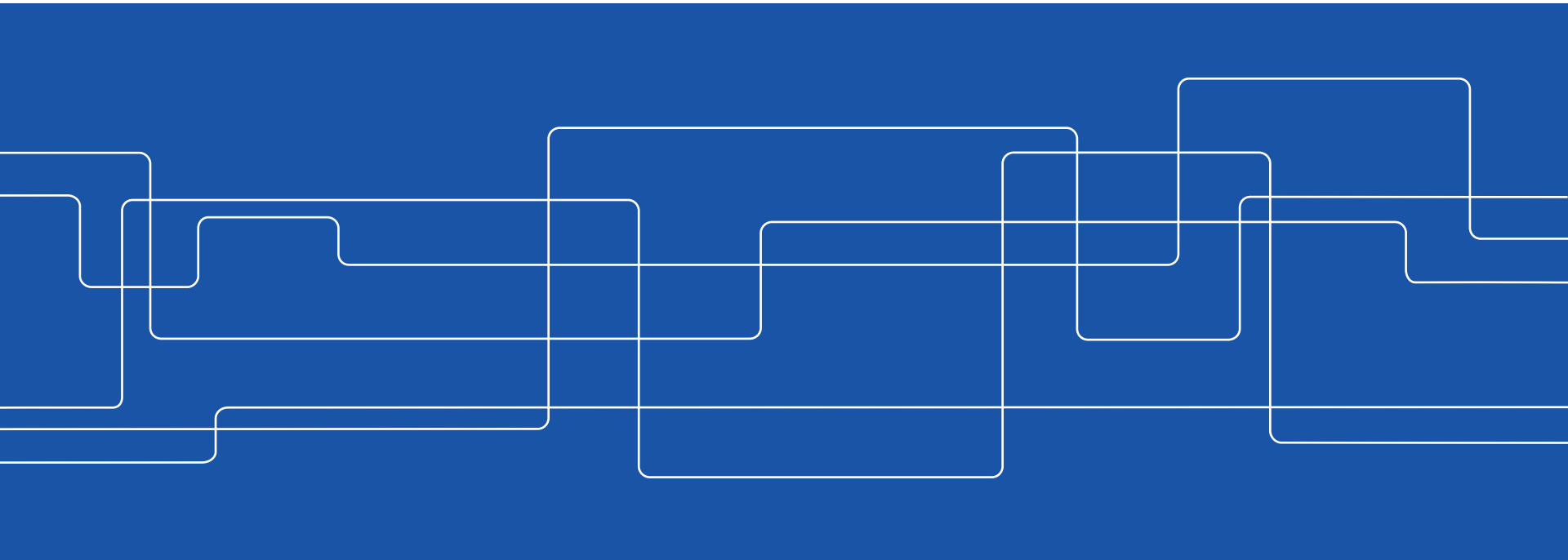


OUTLINE

- INTRODUCTION
- BACKGROUND
- EXPERIMENTAL METHOD
- RESULTS AND DISCUSSION
- CONCLUSIONS
- FURTHER STUDIES

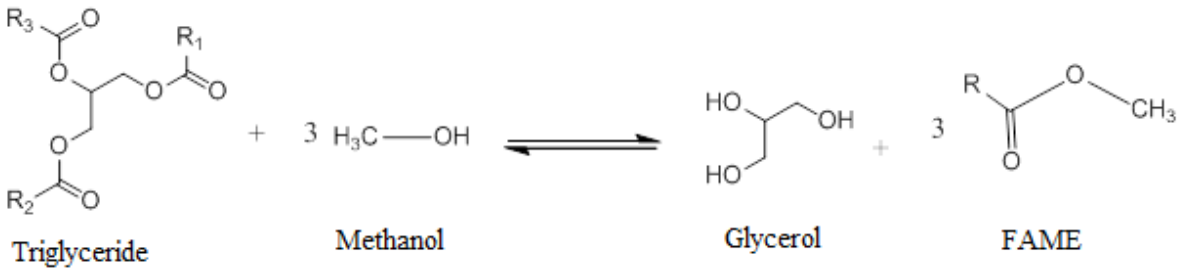
INTRODUCTION

- ✓ Biodiesel production through transesterification is industrially done using acid or base homogeneous catalysts. Improvement could be achieved with other catalysts offering an environmental friendly process.

- ✓ This work describes the preparation of a novel catalyst to run the reaction at mild conditions.

BACKGROUND

TRANSESTERIFICATION REACTION



Triglyceride Methanol Glycerol FAME

CATALYST!

Homogeneous Heterogeneous

FAME = Fatty acid methyl esters.

BACKGROUND

FEEDSTOCK

First generation feed stocks such as corn oil, palm oil, rapeseed oil and soy bean oil, are commonly used for biodiesel because of their availability. But food and economic issues turn the biodiesel production unsustainable through time.

BACKGROUND

HOMOGENEOUS CATALYST

- ✓ High yields.
- ✓ Fast reaction rates[1].
- ✗ Difficulty on catalyst separation step.
- ✗ Commonly as a two step reaction.

HETEROGENEOUS CATALYST

- ✓ One step reaction.
- ✓ Simple catalyst separation step.
- ✓ Possibility of regeneration and recycling.
- ✗ Lower yields and harder reaction conditions.

BACKGROUND

CATALYST CARRIERS

Mayenite ($Ca_{12}Al_{14}O_{33}$)

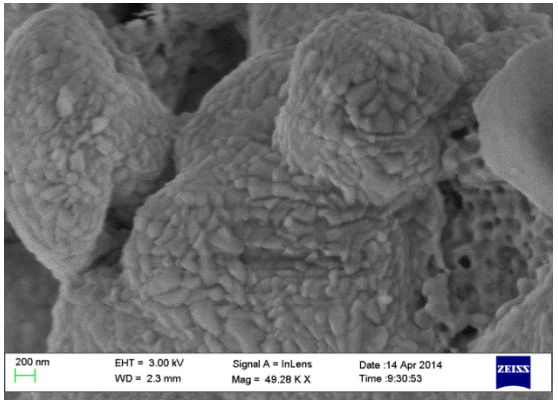
2θ: 17-33° [2]

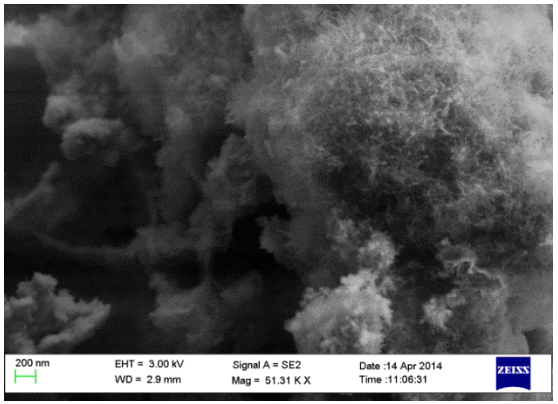
Mesoporous [3]

Alumina (Al_2O_3)

2θ: 26-35-43-57° [2]

Mesoporous [3]





BACKGROUND

CATALYTIC MATERIAL

Magnesium oxide (MgO)

2θ: 43-62° [2]

Largely used in solid catalysts for biodiesel production.

Lithium oxide (Li_2O)

2θ: 33-39-56-67° [4]

Less reported.

EXPERIMENTAL METHOD

CATALYSTS SYNTHETIZED

The prepared catalysts (support-impregnating oxide):

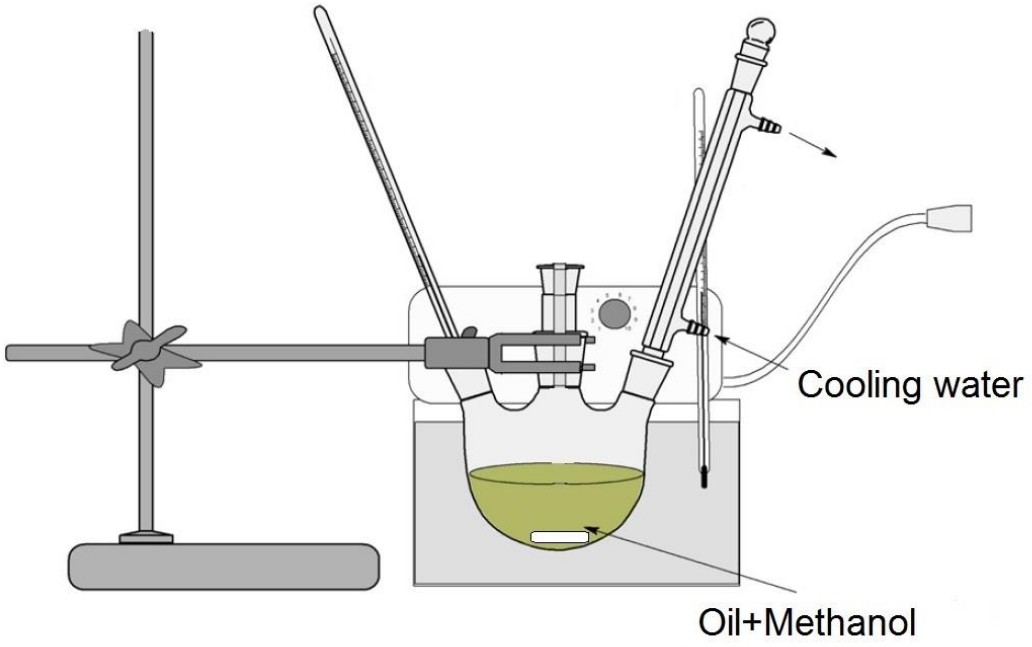
1. Alumina-MgO (5 – 30 wt.%)
2. Alumina-Li_2O (5 – 10 wt.%)
3. Mayenite-MgO (5 – 30 wt.%)
4. Mayenite-Li_2O (5 – 10 wt.%)

Stoichiometric quantities of the species are mixed with isopropanol, dried at 100 ºC and calcinated at 650 ºC for 2 h.

EXPERIMENTAL METHOD

TRANSESTERIFICATION

The experimental set up:



EXPERIMENTAL METHOD

TRANSESTERIFICATION

The conditions:

Methanol to oil ratio 6:1, heated up to 60 °C and stirred at 180 rpm for 2 h.

The variables:

- Oxide impregnation over catalyst (5 – 10 – 30 wt.%)
- Amount of used catalyst relative to oil (2.5 – 5.0 – 10.0 wt.%).
- Reusability for a second time for the catalyst with the best biodiesel production.

EXPERIMENTAL METHOD

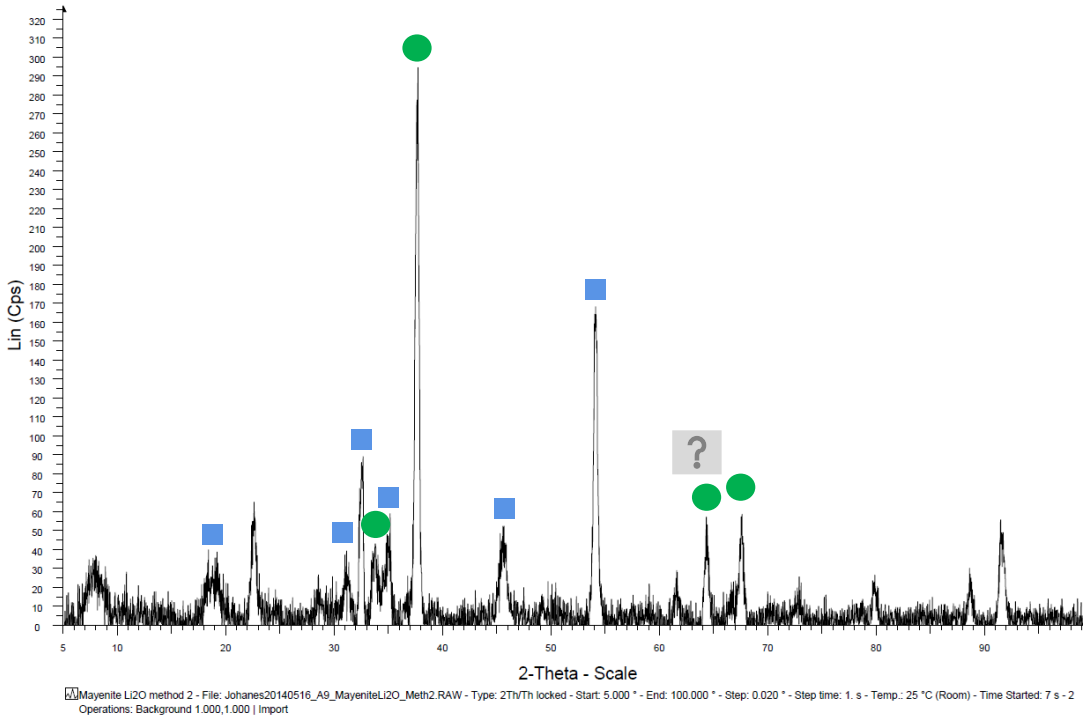
- ✓ Catalyst characterization: N_2 adsorption Brunauer–Emmett–Teller (BET), powder X-ray diffraction (XRD) and Scanning electron microscope (SEM).

- ✓ Catalyst performance: The product is analysed on Gas Chromatography.

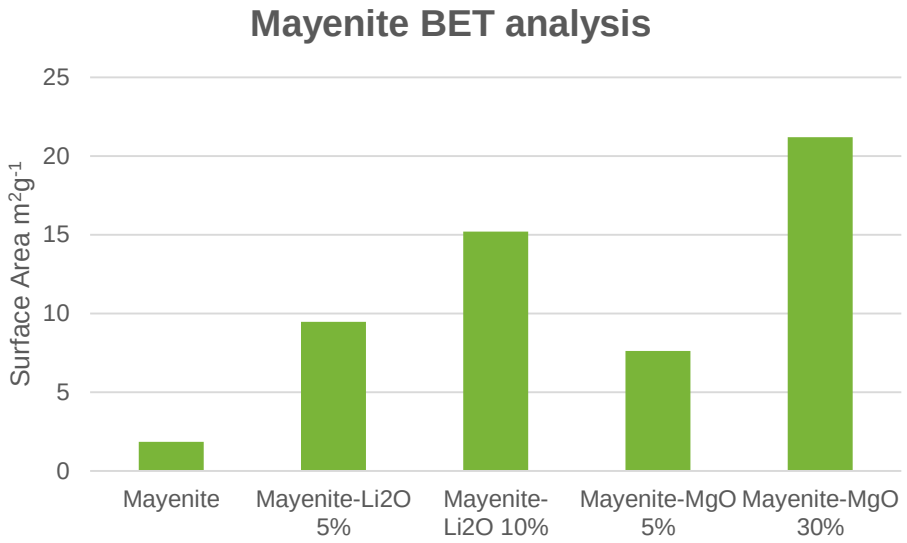
RESULTS AND DISCUSSION

✓ XRD analysis, qualitatively confirms the presence of the expected species. The case of Mayenite-Li_2O 10%

- Mayenite
- Li_2O



RESULTS AND DISCUSSION



- ✓ Reported catalysts like Mg/MCM-41 that have 1289 m^2g^{-1} of surface area but achieve a maximum of 89 % biodiesel yield [5], also using low frequency ultrasonic waves and high rate stirrer.

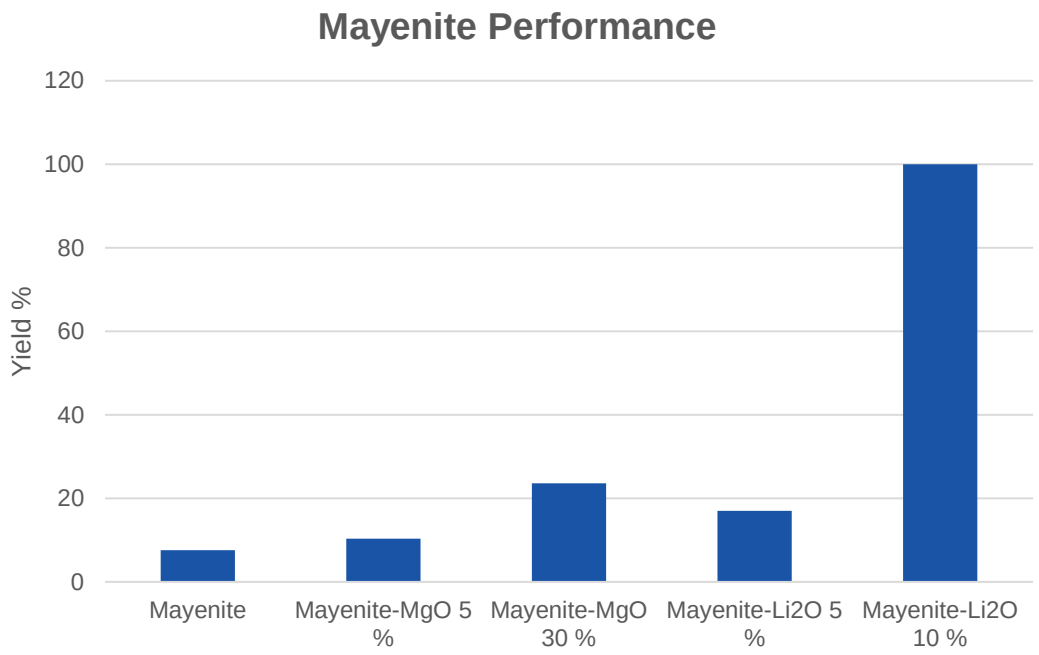
RESULTS AND DISCUSSION

- ✓ Mayenite alone and oxide impregnated show BET porosity from 11.9 to 40.1 Å placing them as mesoporous. The lowest is Mayenite-MgO 30% and the highest Mayenite-Li_2O 10%

- ✓ Alumina alone and oxide impregnated show BET porosity between 16.5 and 18.3 Å, suggesting that they are also mesoporous.

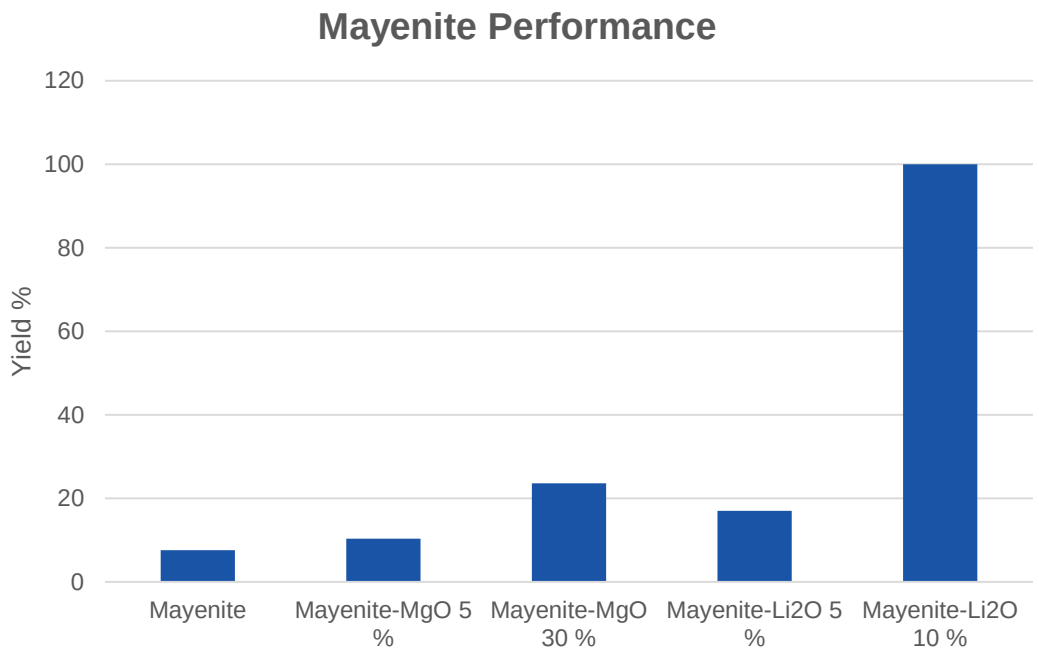
RESULTS AND DISCUSSION

- ✓ The best catalyst for biodiesel production is Li_2O 10% impregnated mayenite charged up to 5 wt.% relative to oil.



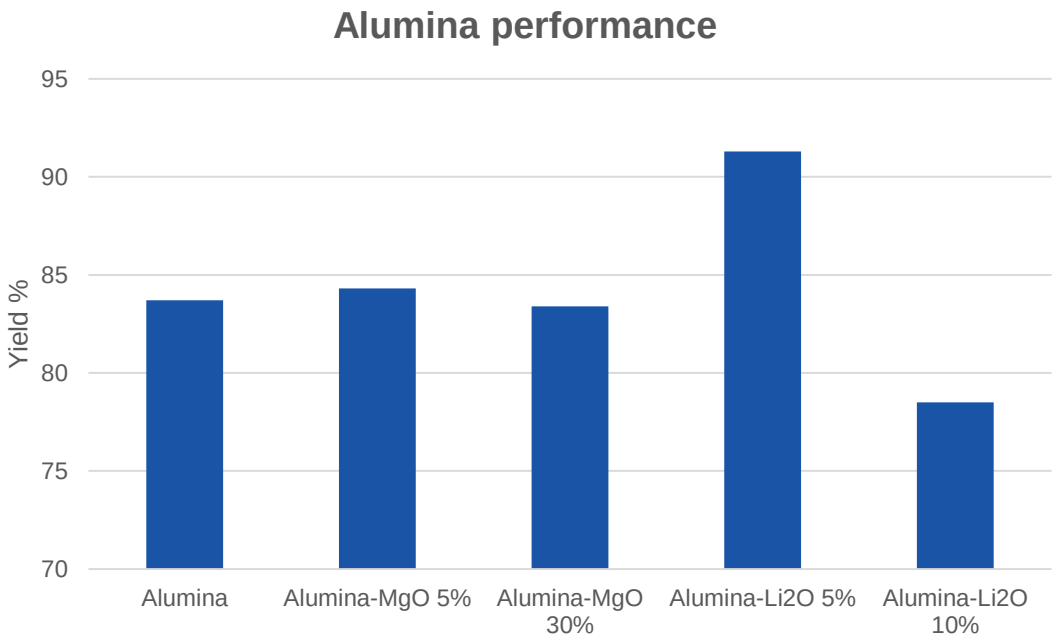
RESULTS AND DISCUSSION

- ✓ The patent granted to Delfort et al., 2006 reports [6], achieve a yield of 94 % at 200 °C and 50 bar.



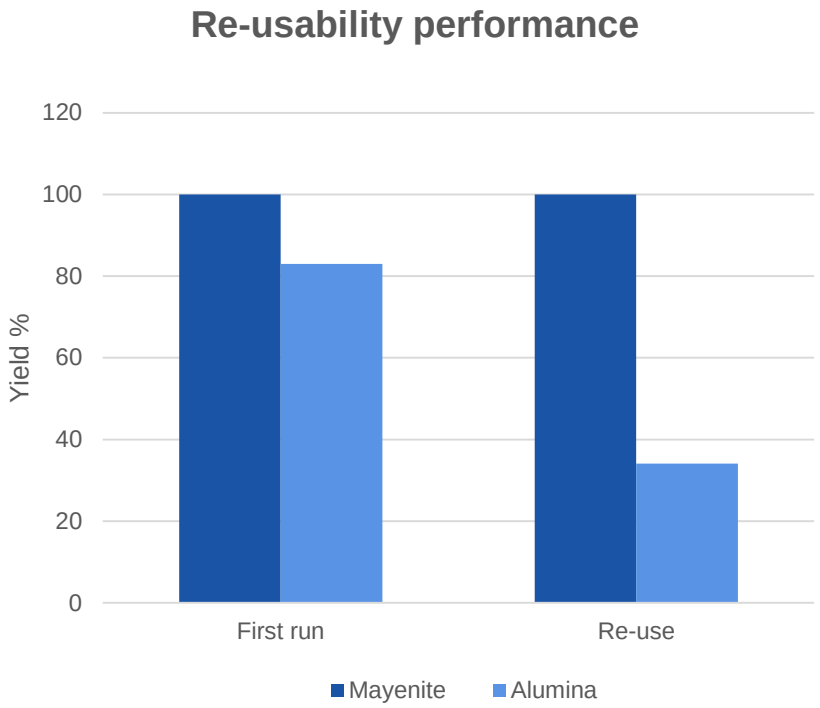
RESULTS AND DISCUSSION

- ✓ Alumina alone used as a catalyst in the transesterification reaction has a relatively high biodiesel yield.



RESULTS AND DISCUSSION

- ✓ Re-usability tests have shown that Mayenite-Li_2O 10% can be used twice.



CONCLUSIONS

- ✓ Mayenite-Li_2O 10% catalyst has a yield of 100 % at 60 °C 180 rpm and at atmospheric pressure.
- ✓ Magnesium oxide impregnated over both studied carriers has a poor catalytic activity.
- ✓ Reusability is feasible for two times usage with Mayenite-Li_2O 10% catalyst, further studies must be carried to determine maximum reuse.

FURTHER STUDIES

- ✓ Transesterification nowadays is based in first generation feedstocks, such as soy bean oil, palm oil and canola oil[7]. For further studies, 2nd generation feedstock oils must be studied, e.g., from castor oil[8].

- ✓ Maximum reuse and the best recovery method for Mayenite-Li2O 10% catalyst must be determined.

THANKS FOR YOUR ATTENTION!

ANY QUESTIONS?

REFERENCES

[1] Schuchardt, U., Sercheli, R., Vargas, M., 1998, Transesterification of vegetable oils: a review: Journal of Brazilian Chemistry Society, v. 9, p. 199-210

[2] http://www.mineralienatlas.de/. Visited on August, 2014

[3] Kaneko, K., 1994, DETERMINATION OF PORE- SIZE AND PORE- SIZE DISTRIBUTION . 1. ADSORBENTS AND CATALYSTS, J. Membr. Sci., p. 59-89.

[4] Kessinger, G. F., Jurgensen, A. R., Missimer, D. M., Morrell, J. S., 2009, The High Temperature Chemical Reactivity of Li2O

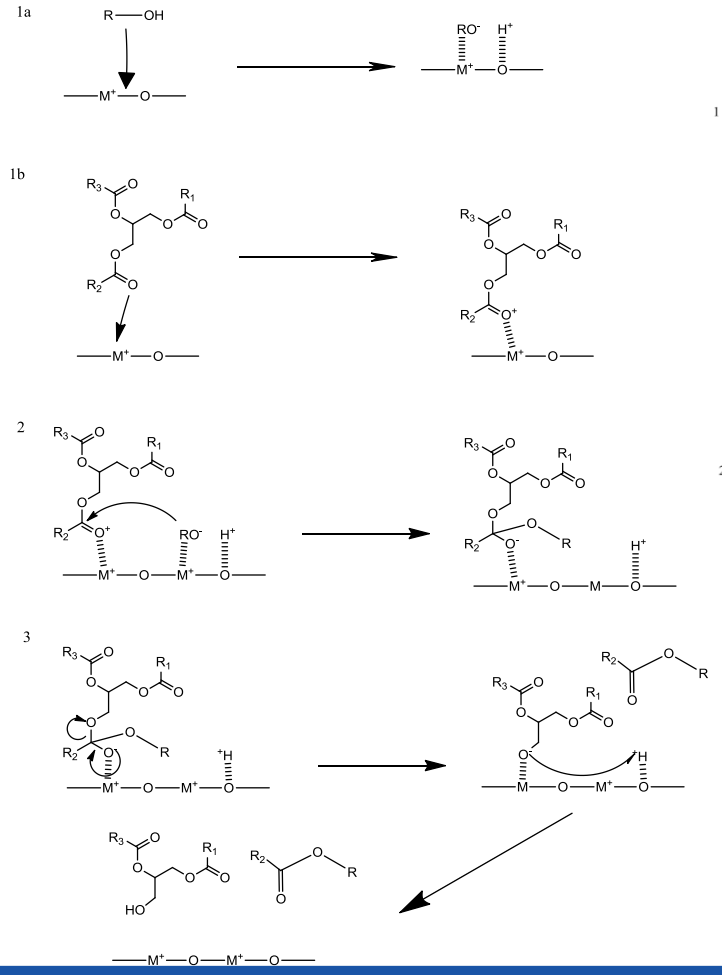
[5] Georgogianni, K. G., A. P. Katsoulidis, P. J. Pomonis, and M. G. Kontominas, 2009, Transesterification of soybean frying oil to biodiesel using heterogeneous catalysts: Fuel Processing Technology, v. 90, p. 671-676.

[6] B. Delfort, D. Le Pennec, C. Lendresse, Process for transesterification of vegetable oils or animal oils by means of heterogeneous catalysts based on zinc or bismuth, titanium and aluminum. United State patent 7,151,187 B2 (2006).

[7] Jahirul, M. I., R. J. Brown, W. Senadeera, I. M. Hara, and Z. D. Ristovski, 2013, The use of artificial neural networks for identifying sustainable biodiesel feedstocks: Energies, v. 6, p. 3764-3806.

[8] Jahirul, M. I., R. J. Brown, W. Senadeera, I. M. Hara, and Z. D. Ristovski, 2013, The use of artificial neural networks for identifying sustainable biodiesel feedstocks: Energies, v. 6, p. 3764-3806.

Base Catalyst Mechanism



Acid Catalyst Mechanism