Centro de Investigação de Montanha CIMO

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Optimization and kinetic study of esterification reaction of oleic acid using $[HMIM]HSO_4$ as catalyst

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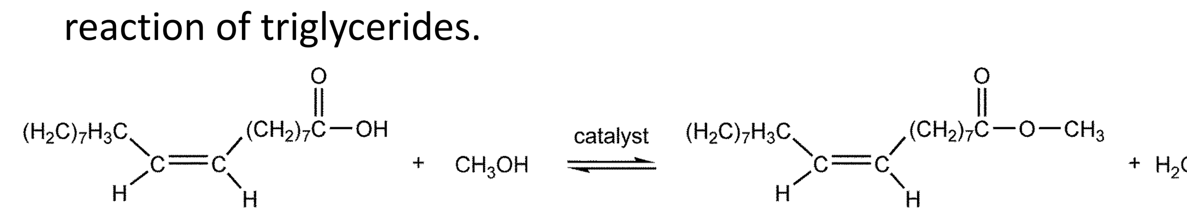
Background

Biodiesel Biodiesel is an alternative fuel to petrodiesel. It can be produced from a wide range of raw materials such as vegetable oils and animal fats. Yet, the use of sources that do not compete with the food market, such as waste cooking oils - which usually feature high levels of free fatty acids (FFA's), can lead to problems in the process of biodiesel production through alkaline transesterification. Therefore, new methodologies to successfully apply acidic oils need to be developed.

Ionic liquids Ionic liquids (ILs) could be employed in the biodiesel production to partially overcome these problems; since they are able to catalyze the esterification reaction of FFA's to biodiesel (FAMEs) as well as the transesterification reaction of triglycerides.



Esterification reaction of oleic acid with methanol

Goals Study the esterification reaction of oleic acid using the ionicl liquid *1-methylimidazolium hydrogen sulfate [HMIM]HSO4*, employing a Response Surface Methodology (RSM), in order to evaluate the influence of time, temperature, molar ratio between methanol and oleic acid and catalyst dosage on the conversion of oleic acid and on the FAME content, and to estimate optimal conditions, followed by a kinetic study to estimate kinetic parameters.

Methodologies

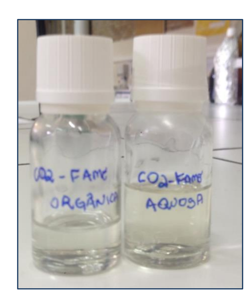
Oleic acid, Methanol, Catalyst, Temperature, Time

RSM: Box-Behken Design → 4 Factors, 3 levels → 27 experiments

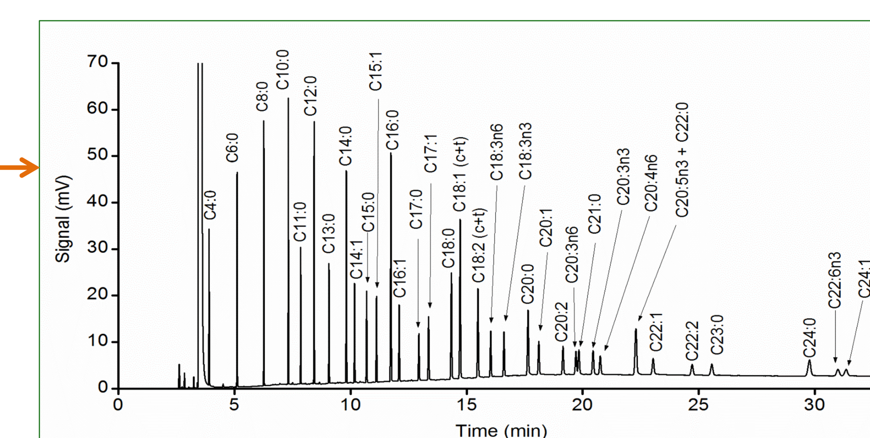
Esterification reaction → Biodiesel → FAME content EN 14103; Yield - Acidity EN 14104

Esterification reaction → Sample retrieving → Yield - Acidity EN 14104

Responses



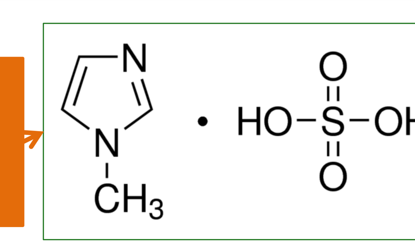
GC Conditions: Helium flow 1 mL/min. Initial oven temperature 50°C (held for 1 min). First ramp to 200°C at 25°C/min. Second ramp to 230°C at 3°C/min (held for 23 min). Injection temperature 250 °C, split ratio 1:25 and detector temperature 250°C.



GC of Standard Mixture containing 37 common FAMEs.

Acidity determined by titration

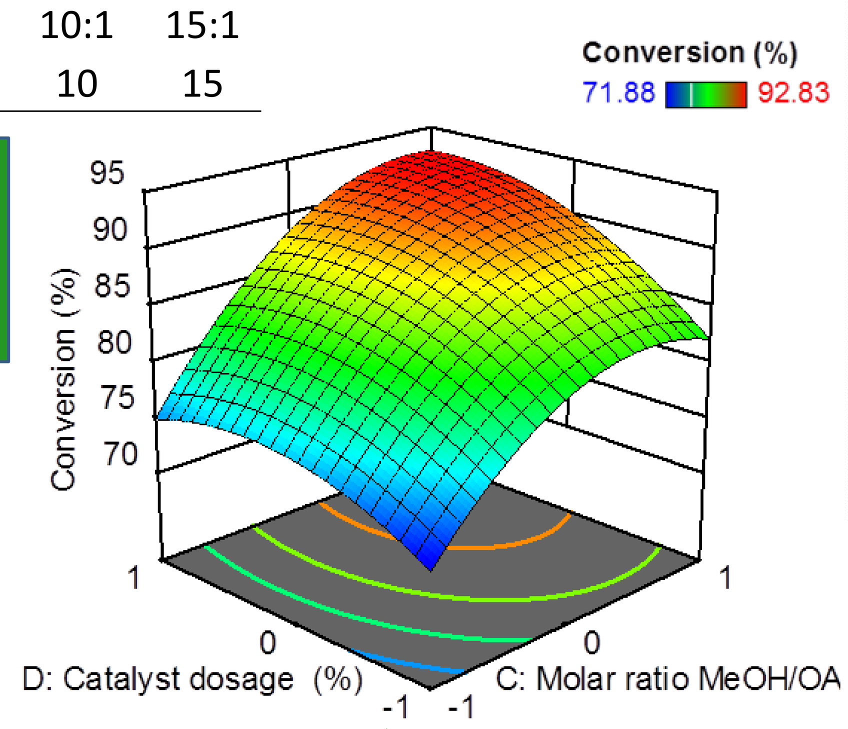
1-methylimidazolium hydrogen sulfate [HMIM]HSO4

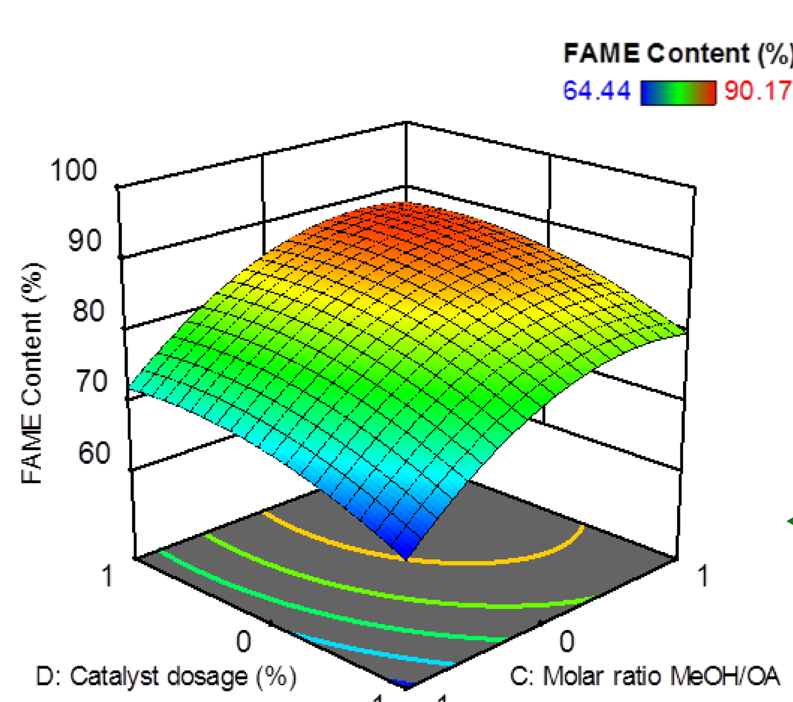


Results

Factor	Code	Level		
		-1	0	+1
Time (h)	A	4	6	8
Temperature (°C)	B	80	95	110
Molar ratio methanol/oleic acid	C	5:1	10:1	15:1
Catalyst dosage (%wt)	D	5	10	15

Box-Behnken Design (BBD) was used to evaluate the behaviour of the conversion and the FAME content for different levels of the factors.





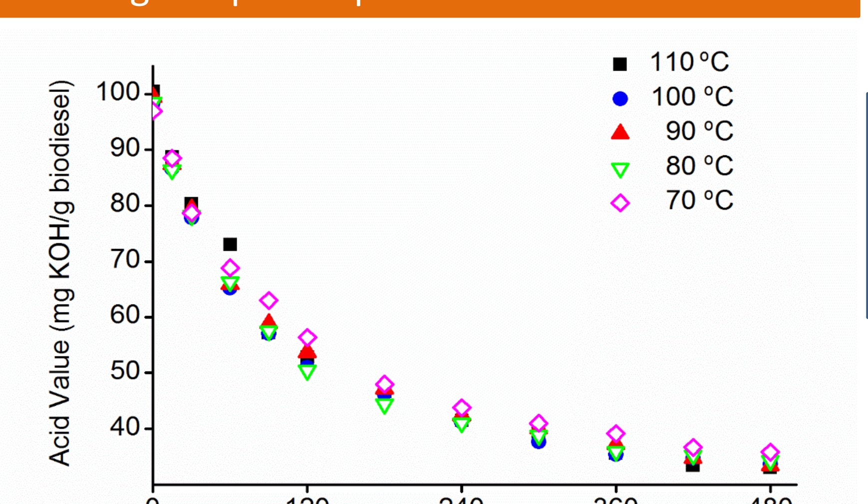
Response surfaces plotted for both responses, regarding the influence of molar ratio of methanol and oleic acid (C) and catalyst dosage (D).

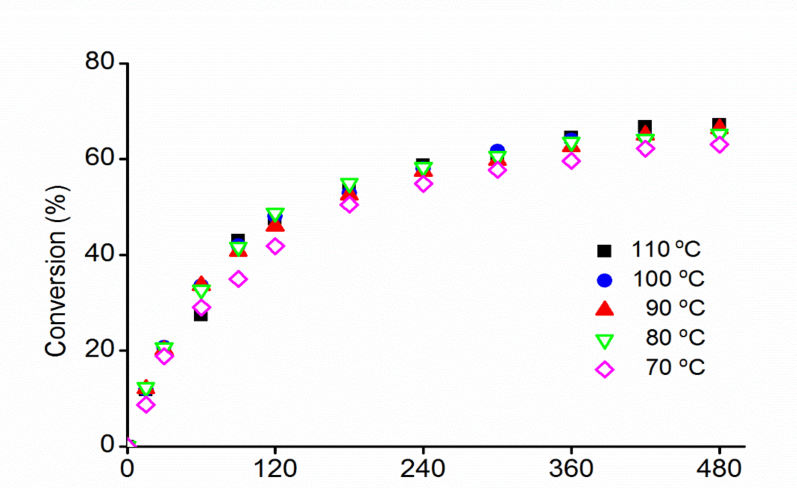
A model was adjusted for each response, and evaluated through ANOVA, allowing the estimation of the optimal conditions.

Parameters	Conversion	FAME content
A – Time (h)	8	8
B – Temperature (°C)	110	110
C – Molar ratio MeOH/OA	15:1	14:1
D – Catalyst dosage (wt%)	15	13.5
Predicted response (%)	97.96	92.86
Real response (%)	95.26	90.55

For both responses, the most important parameters were the **catalyst dosage** and **molar ratio**.
The **temperature** was the **least significant factor**.

The optimal conditions were then used to perform the kinetic study. Molar ratio and catalyst dosage were maintained at the optimal level and temperature was varied from 70 – 110 °C, retrieving samples at pre-determined times.





The activation energy was determined as 6.8 kJ/mol and the pre-exponential factor as 0.0765 $L^2.mol^{-2}.min^{-1}$, with a correlation coefficient of R^2=0.918.

The low activation energy reiterates the conclusion drawn in the RSM: the temperature does not show strong influence on the esterification reaction of oleic acid.

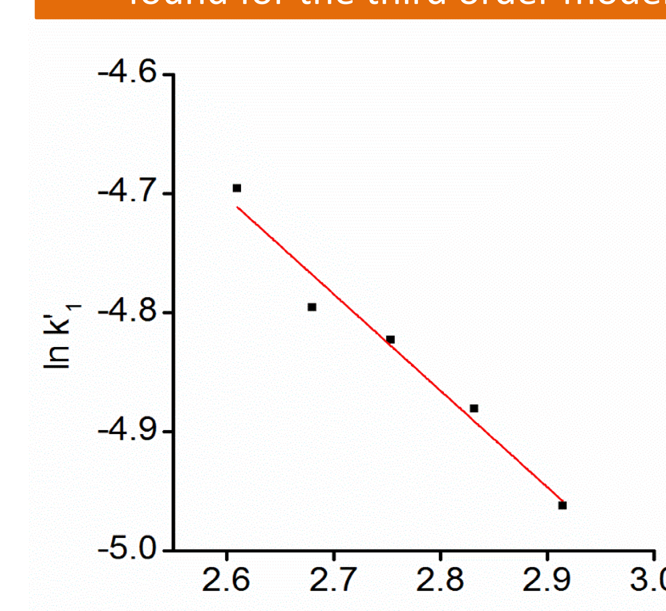
$$-r_{OA} = -\frac{dC_{OA}}{dt} = k_0 exp^{\frac{-Ea}{RT}} C_{OA}{}^{\alpha}$$

The goal was to estimate the reaction order (α) in relation to the oleic acid, the activation energy (E_a) and the pre-exponential factor (k_0).

$$\frac{1}{C_{OA}{}^2} = \frac{1}{C_{OA;0}{}^2} + 2k_0 exp^{\frac{-Ea}{RT}} t$$

Temperature (°C)	R^2 3rd order
110	0.99502
100	0.98604
90	0.99457
80	0.97686
70	0.99089

The reaction order was estimated according to the adjustment of the equation to the data. The best fit was found for the third order model.



Conclusions

The high conversion and high FAME content indicate that the IL displays a good catalytic activity in the esterification reaction of oleic acid. The RSM suggests that the most relevant factors are molar ratio and catalyst dosage.

The temperature does not seem to play an important role on the system studied. This conclusion is drawn based on the RSM and confirmed by the low activation energy estimated through the kinetic study.

Other studies with the same catalyst were performed to evaluate its catalytic activity in the transesterifcation reaction and also establish whether it can be recovered and recycled for further reaction cycles.