Fatty Acids esterification with ethanol and heavy alcohols using layered zinc carboxylates – Kinetics Modeling and Process Evaluation.

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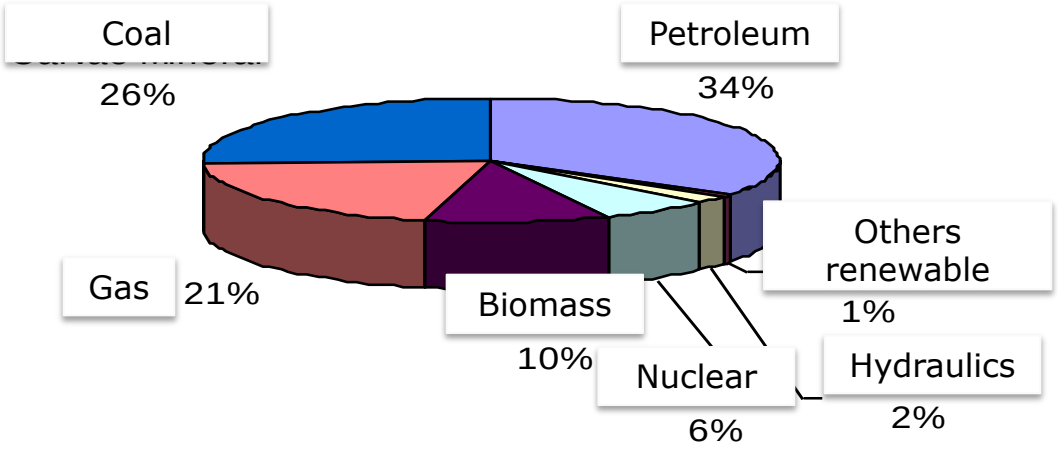
Introduction

World Energy Matrix (WEM) (MME, 2009)



Feature: Except hydraulics, geothermal and nuclear, all other sources of energy are limitated.

Introduction

WEM enhancing and fine chemicals obtainment through catalytic esterification of biomass

Advantages: reuse and recovery of catalyst, shortening of process steps and reduction of energy consumption.

Some research in the field:

- Zeolites (KARMEE e CHADHA, 2005);
- Inorganic oxides (MACEDO et. al, 2006; GONÇALVES et. al, 2010)
- Ion exchange resins (NI e MEUNIER, 2007);
- Sulfonated carbohydrates (LOU et. al, 2008);
- Metallic soaps (CORDEIRO, et. al, 2008, LISBOA, 2012);

Introduction

Metallic Carboxylates

Group results review: Cordeiro (2008) employing Layred Double Hidroxides (LDH) and Lisboa (2012) with different metal carboxylates.

- 97.4 % methyl esters conversion (molar ratio 4:1 methanol to oil, at 140 ºC, 4% wt. catalyst and 2 h of esterification)
- Co-product glycerol with assay around 93% (transesterification)
- "in situ" transformation layered double hidroxides into zinc laurate (DRX, FTIR)
- Catalyst reuse up to 11 cycles without loosing the activity.
- 20% of equilibrium conversion gain compared to blank experiment (140 ºC, 2h, manganese laurate in the esterification)

Introduction

Precursors – Lamellar compounds (HDLs)

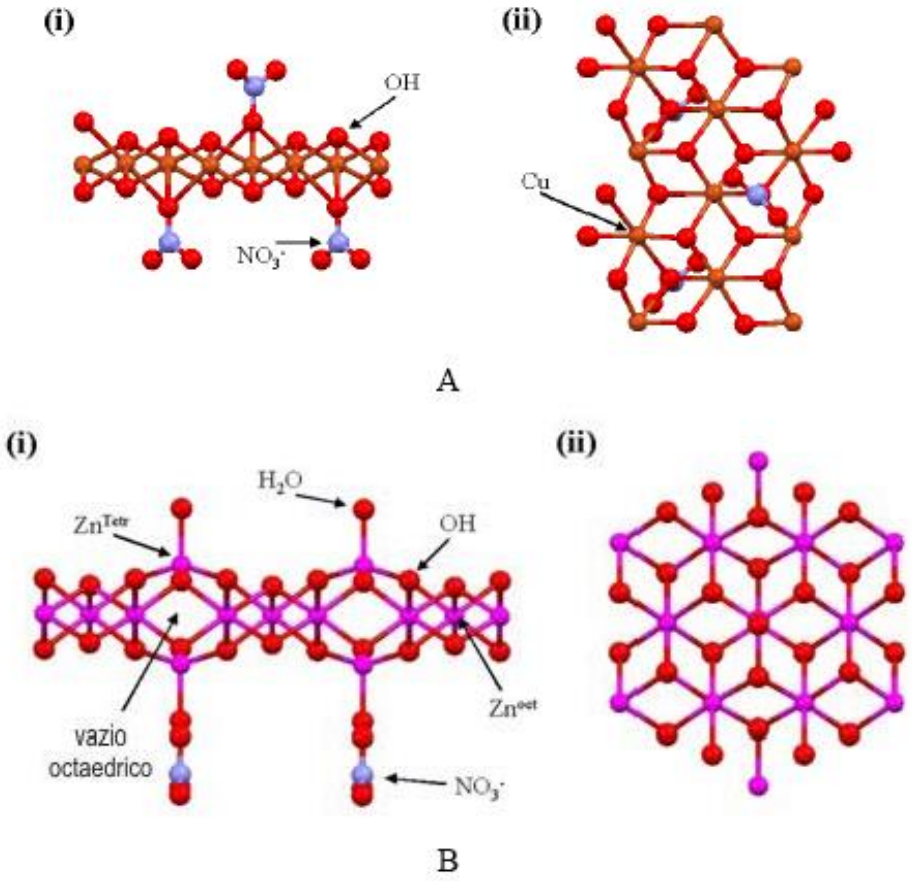


Figure 1. Cooper Hydroxide nitrate structure (a) ($Cu_2(OH)_3NO_3$) and (b) Zinc hydroxide nitrate ($Zn_5(OH)_8(NO_3)_2.2H_2O$). i) side view and ii) top view (layer) (ARIZAGA; GUNDAPPA; WYPYCH, 2007)

Introduction

Metallic Carboxylates (Lewis acid catalysts)

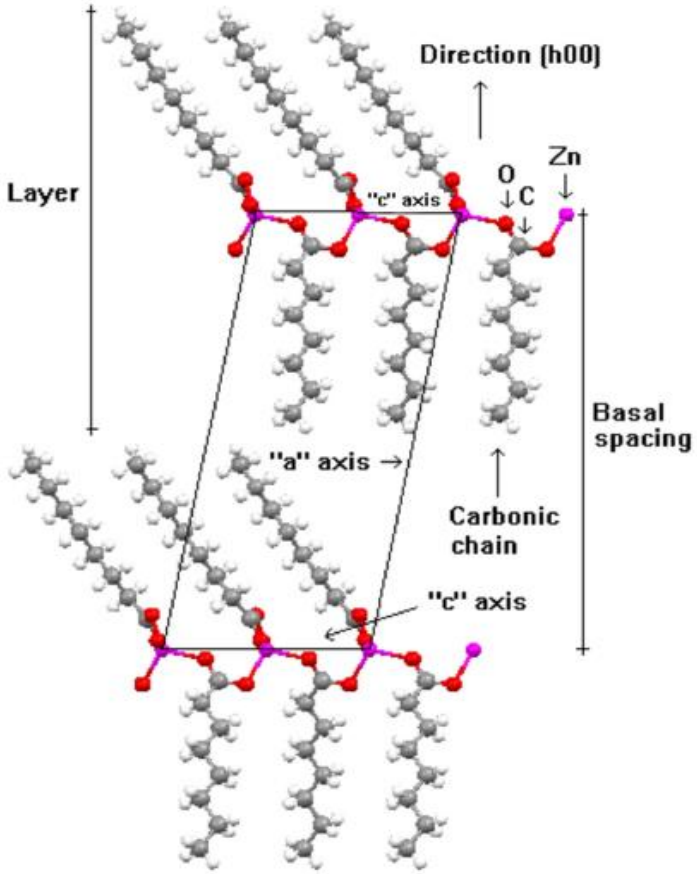
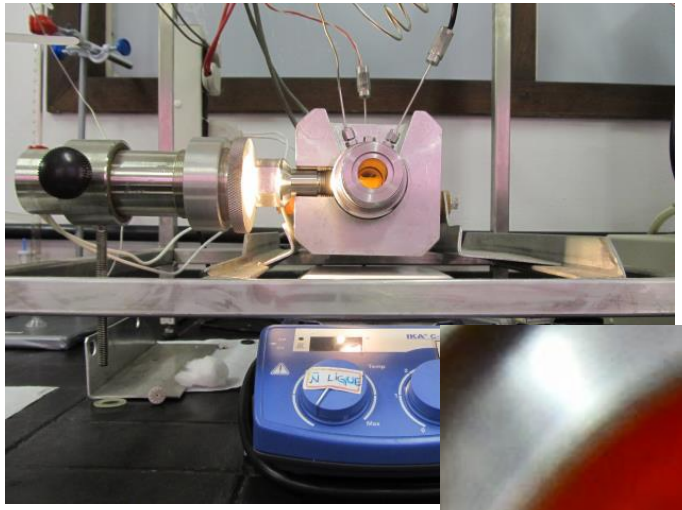
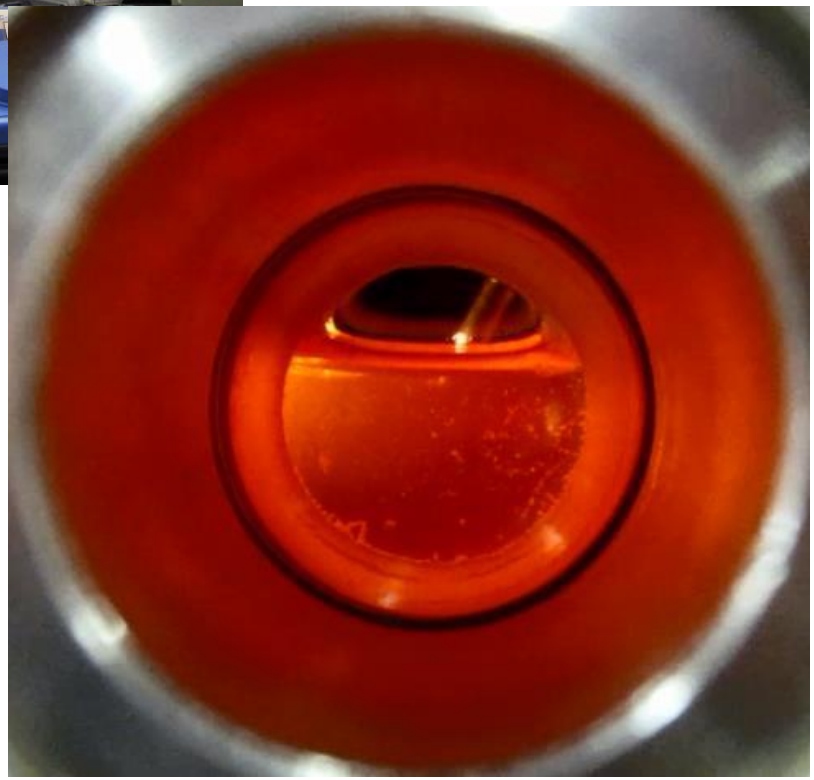


Figure 2. Zinc octanoate structure (LISBOA et. al, 2012).

Introduction

Reaction medium visualized by a pressure cell T150 9bar in the laboratory of high pressure and thermodynamics in Brazil





Objectives

- The main objective is the enhancement of alkyl esters production using metallic carboxylates and raw materials with high FFA content and water.

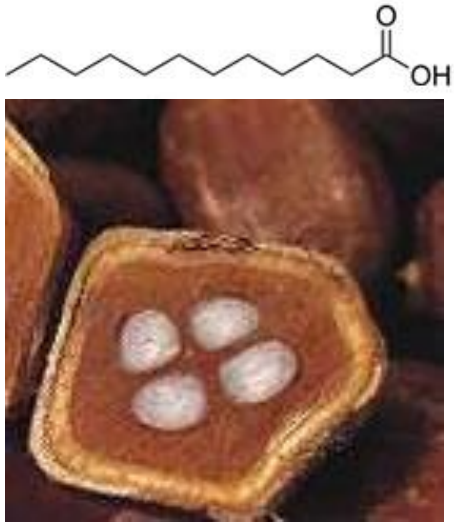
Specific Objectives

- Esterification kinetics evaluation and modeling of main saturated and unsaturated free fatty acids with ethanol and heavier alcohols;
- Catalyst recovering and leaching evaluation;
- To study the catalyst surfactant influence on the reaction medium;
- To provide thermodynamic data concerning the esterification reactions with ethanol and heavy alcohols.

Development Strategy

Raw Material

- Lauric acid (C12:0) – Babassu oil (64% C12)
- Commercial mix with oleic (92%), linoleic (4.5%), stearic (2.5%) (C18:1, C18:2 and C18:0, respectively)
- Anhydrous ethanol (99,8%)
- Hydrated ethanol (93 - 95%)



Characterization

Methods

- The analysis of all components was performed by GC in a suitable column for fatty acids and esters (60 m with polar mobile phase).

- The calibration was made based on the Internal Standard method proposed by Konstatine Sychev (1998).

- Esterification of 4 fatty acids (FA) (90% oleic mix Sigma) was performed in excess of ethanol, n-butanol and n-hexanol (molar ratios of 3,8 and 12 related to FA), 3 temperatures and 2 different amount of catalyst.

- A summation of 41 experiments with 7 kinetics points was generated.

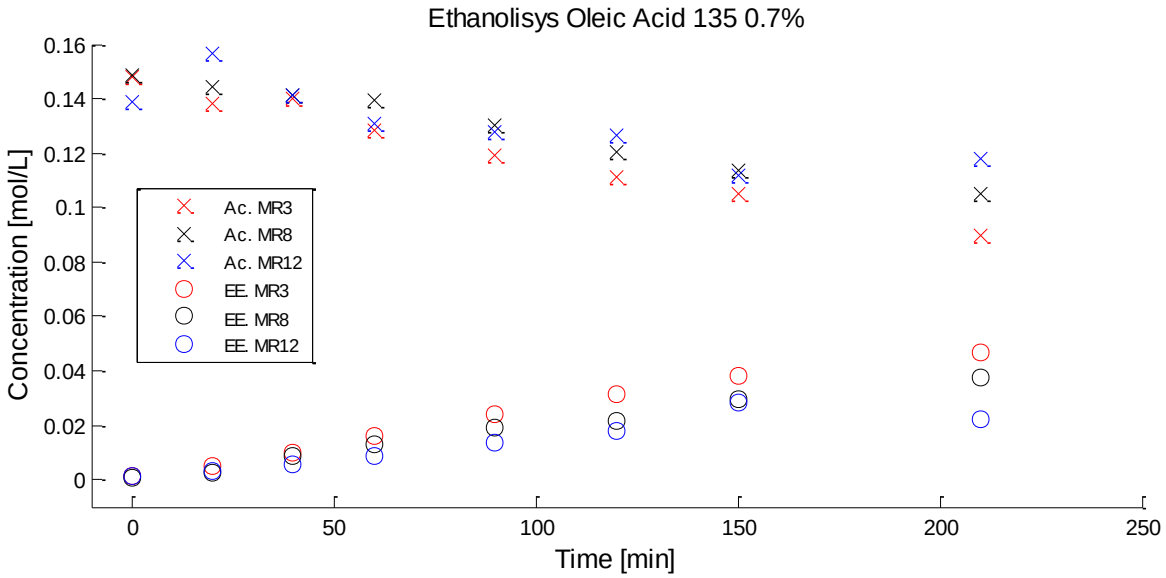
Table 1. Summary of the conditions employed in the kinetic experiments.

MR alcohol:FA	Reactor fraction	Temp. Celsius	Cat. %
1:3	0.51	135	0.70
1:8	0.48	150	5.00
1:12	0.48	165	-

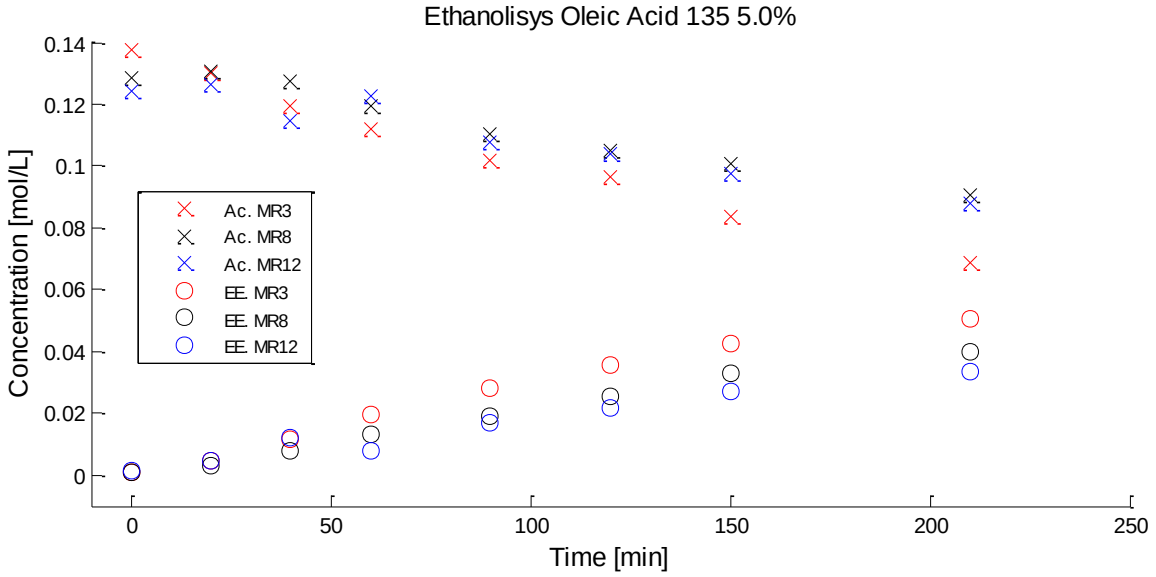
Konstantine Sychev available at: http://www.rasxodniki.ru/jurnal/arhiv/32

Experimental results - Ethanol

Excess of ethanol and catalyst amount influence



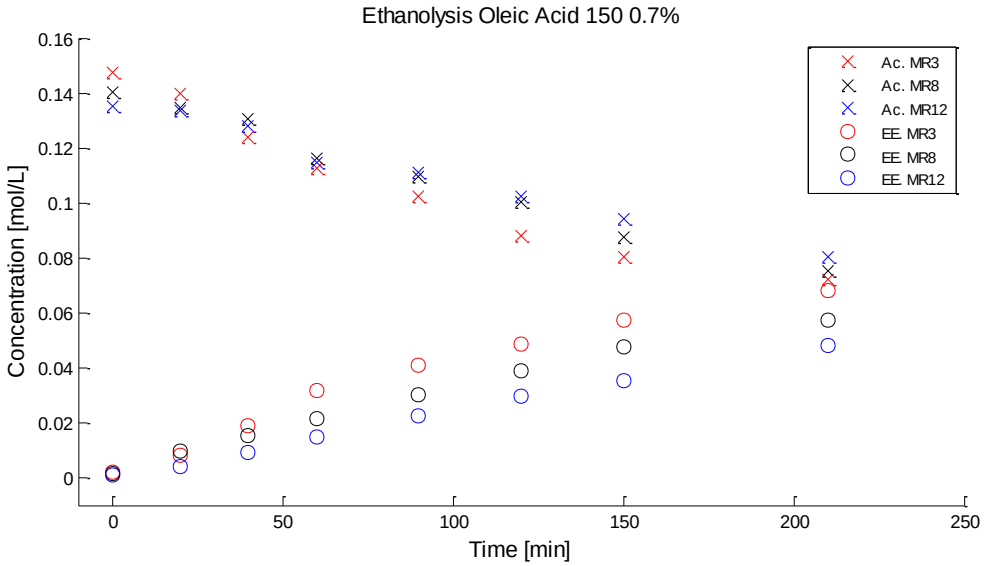
- 135 ℃



- OA – Oleic acid (92% of the mix)
- EtOH.O – Ethyl oleate
- MR [molar ratio acid:ethanol]

Experimental results - Ethanol

Excess of ethanol and catalyst amount influence



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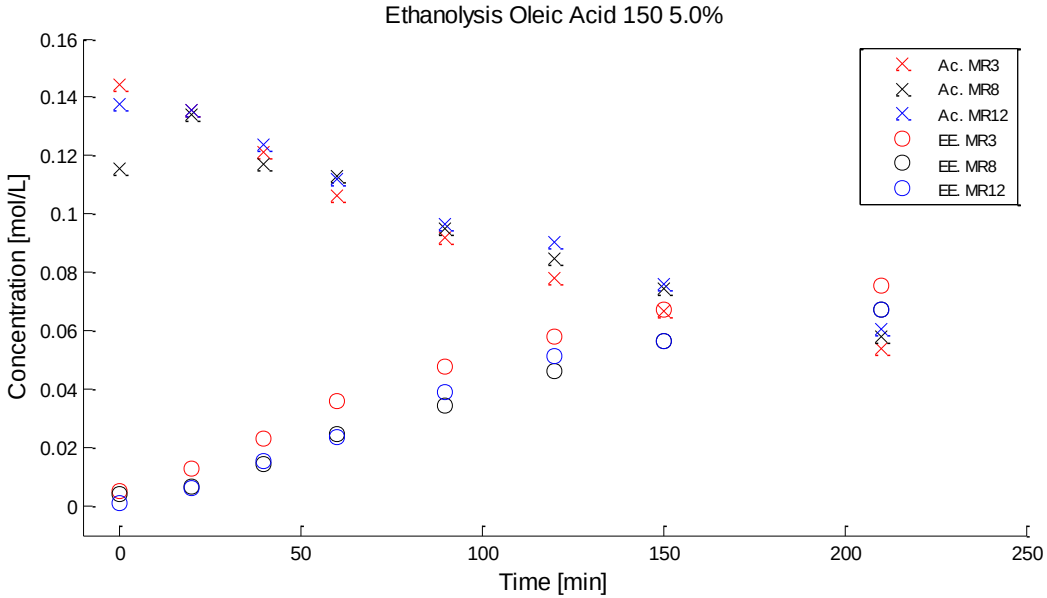

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Experimental results - Ethanol

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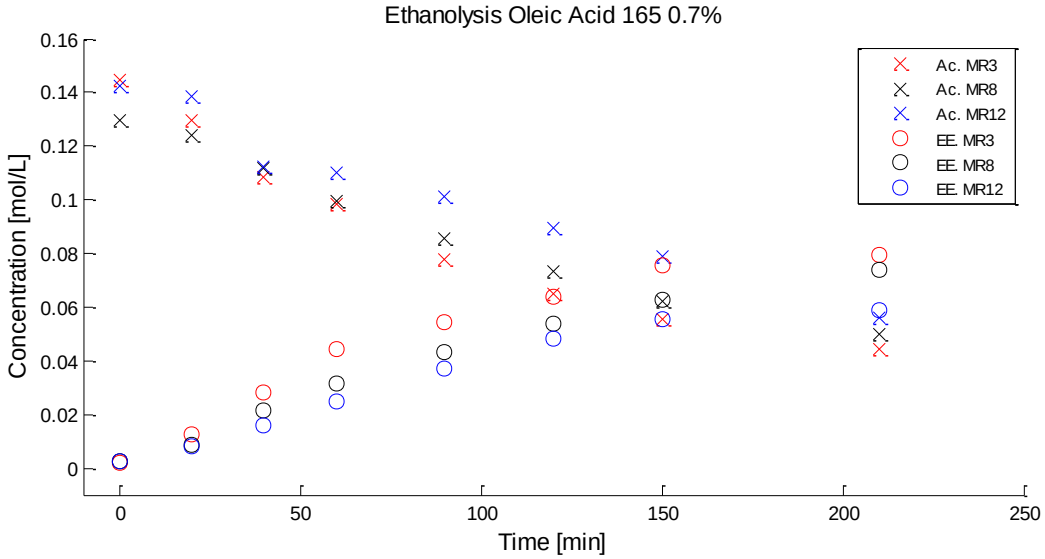

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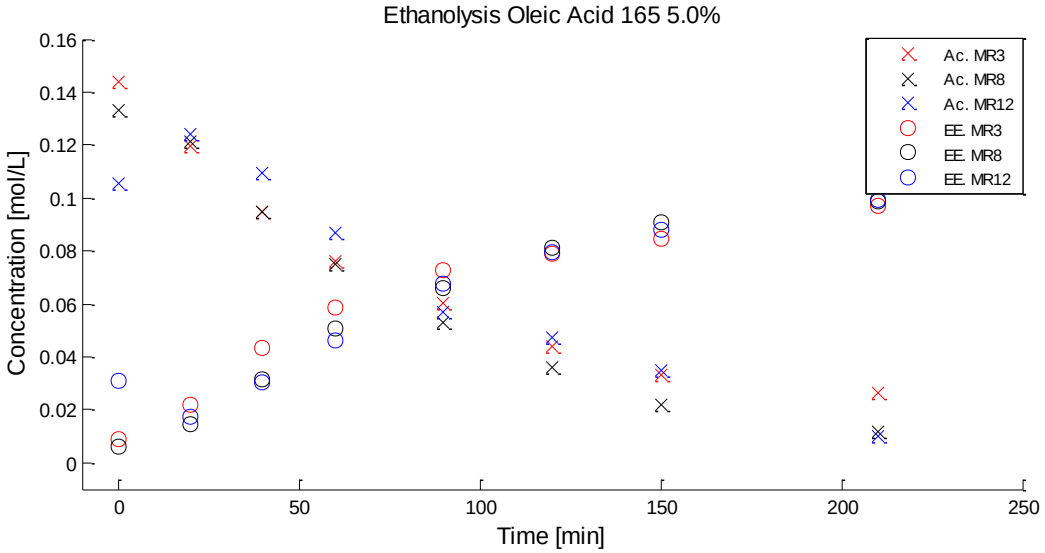

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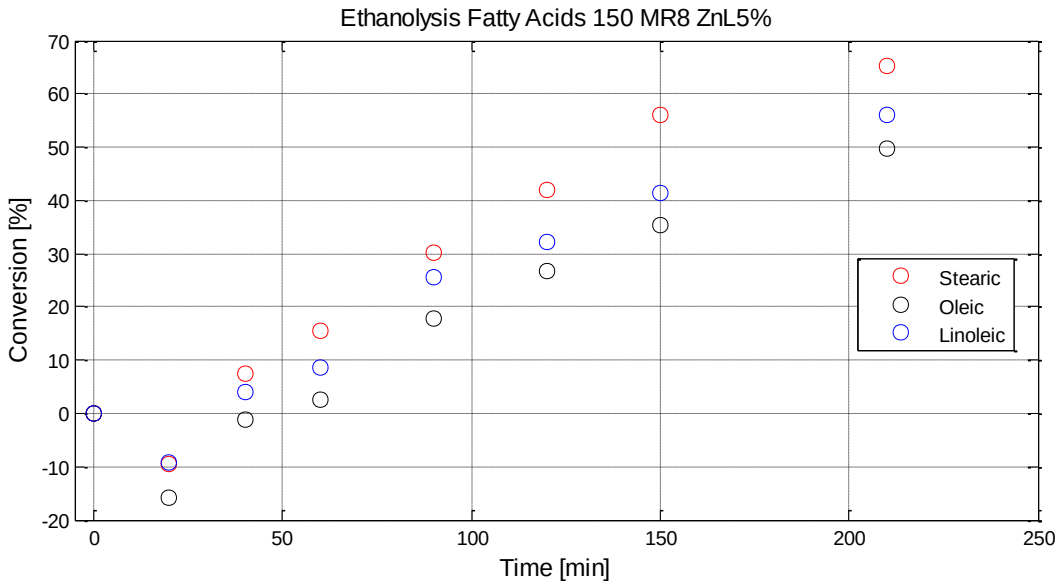
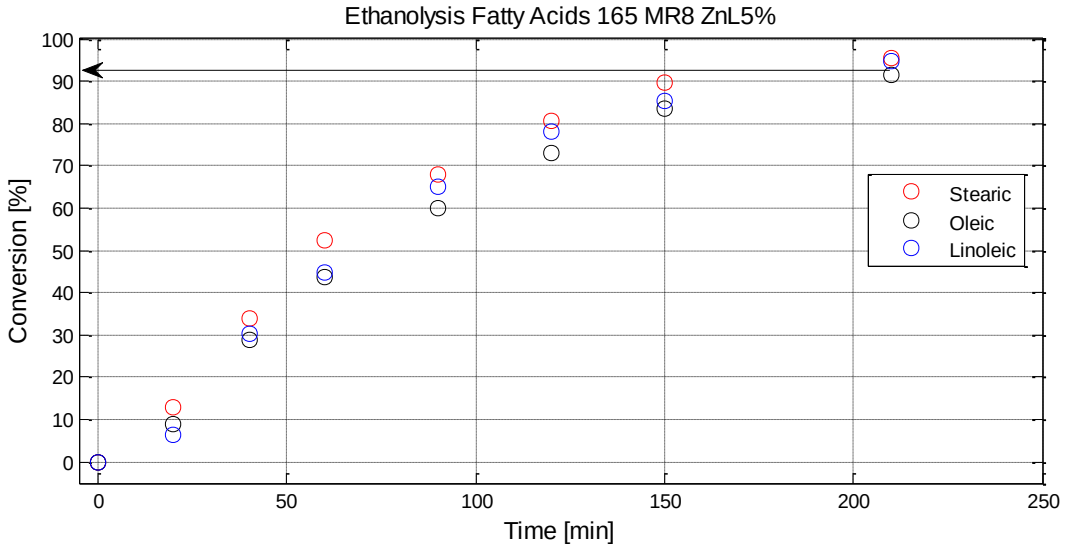
- MR [molar ratio acid:ethanol]

Experimental results - Ethanol

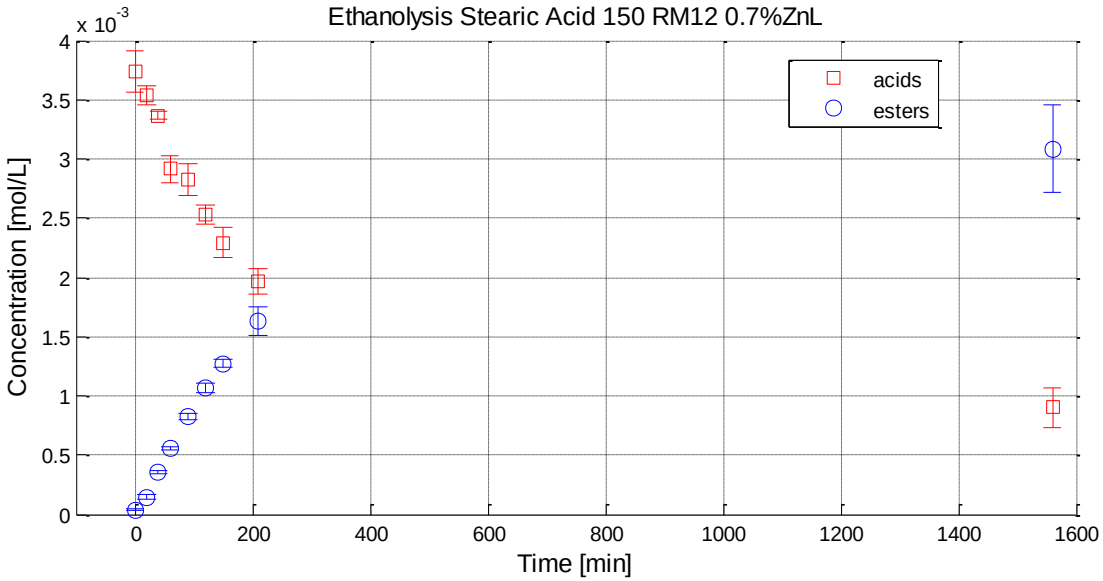
Temperature influence and conversion

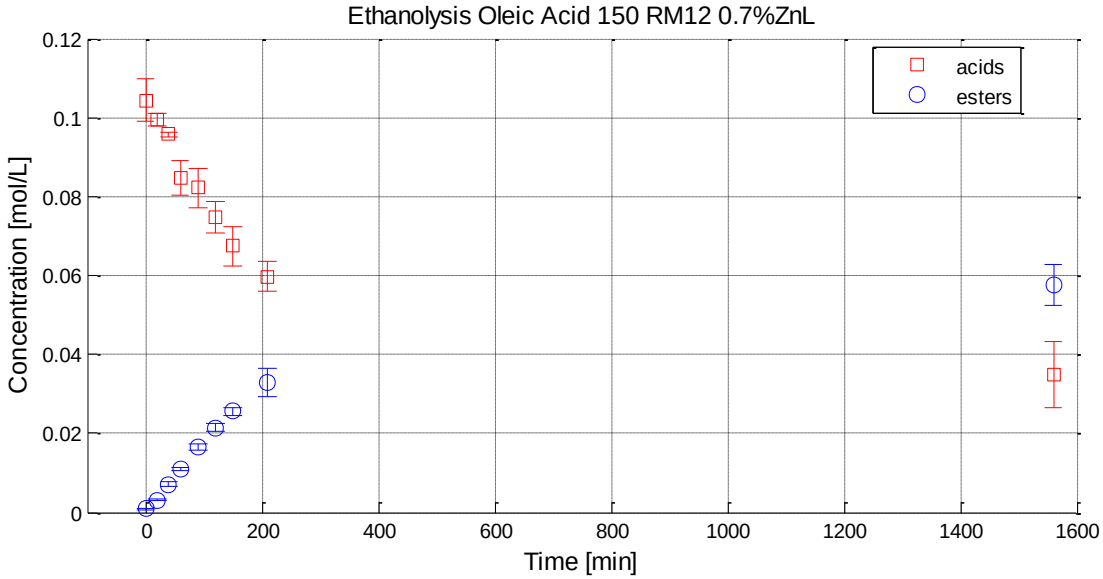




Experimental results - Ethanol

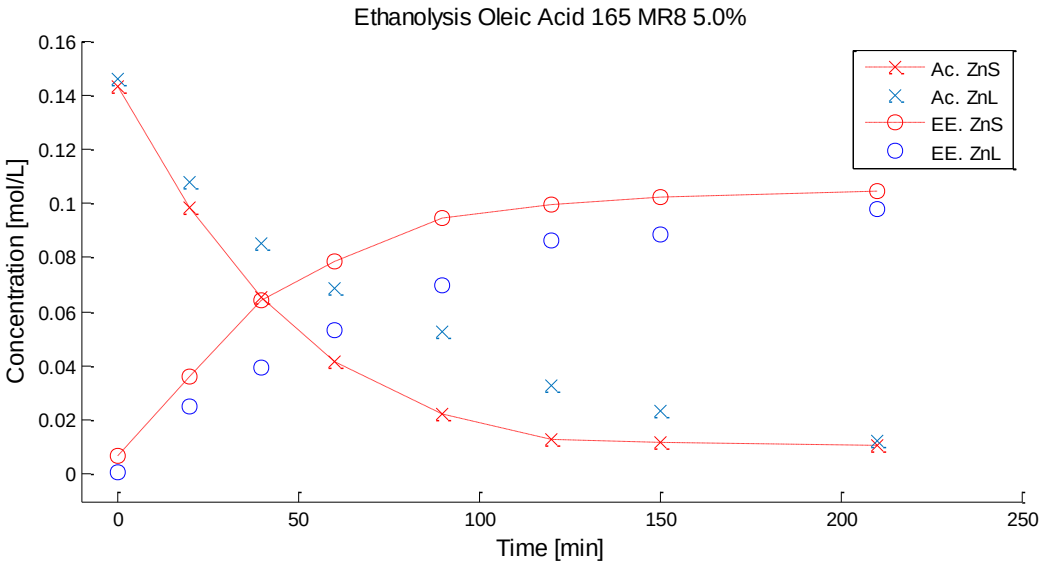
Reproducibility

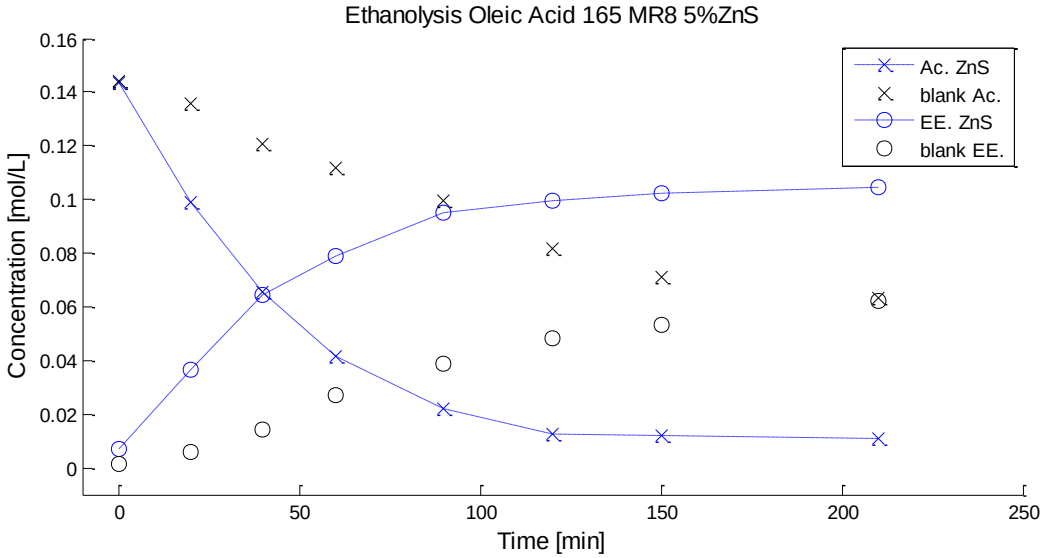




Experimental results - Ethanol

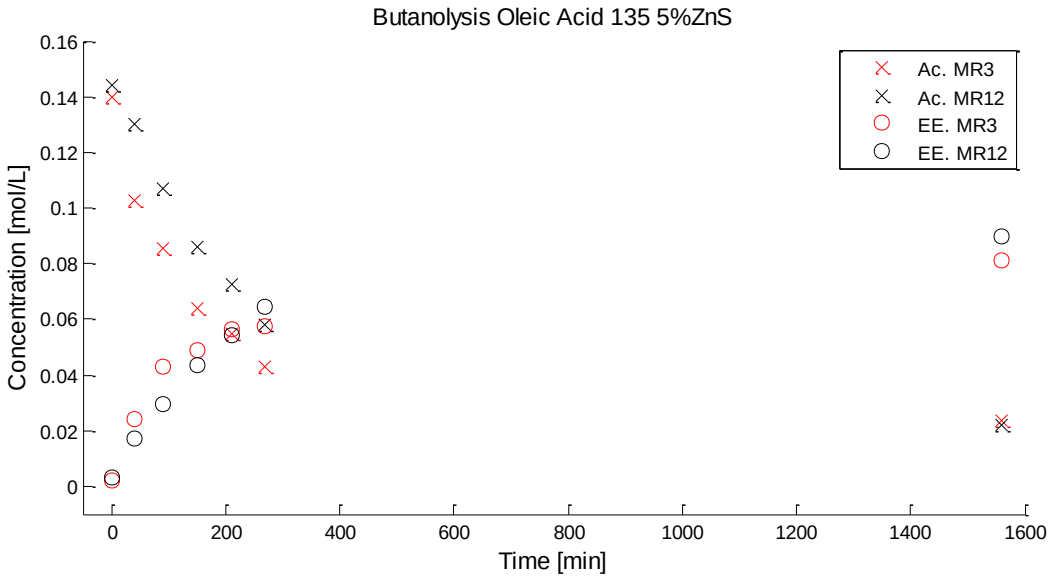
Zinc Laurate vs Zinc Stearate





Experimental results – (n)butanol

Excess of butanol and catalyst amount influence



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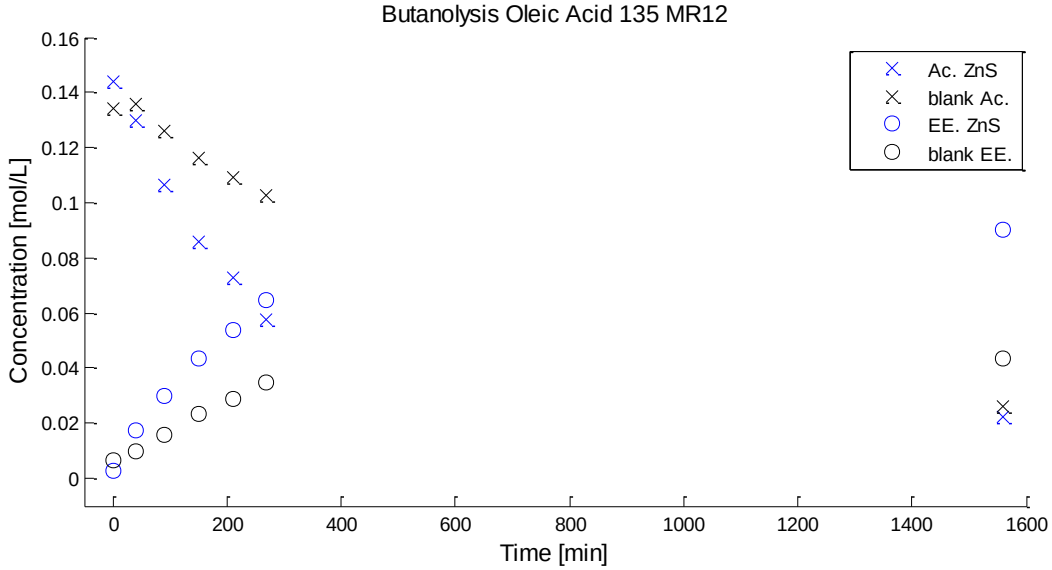

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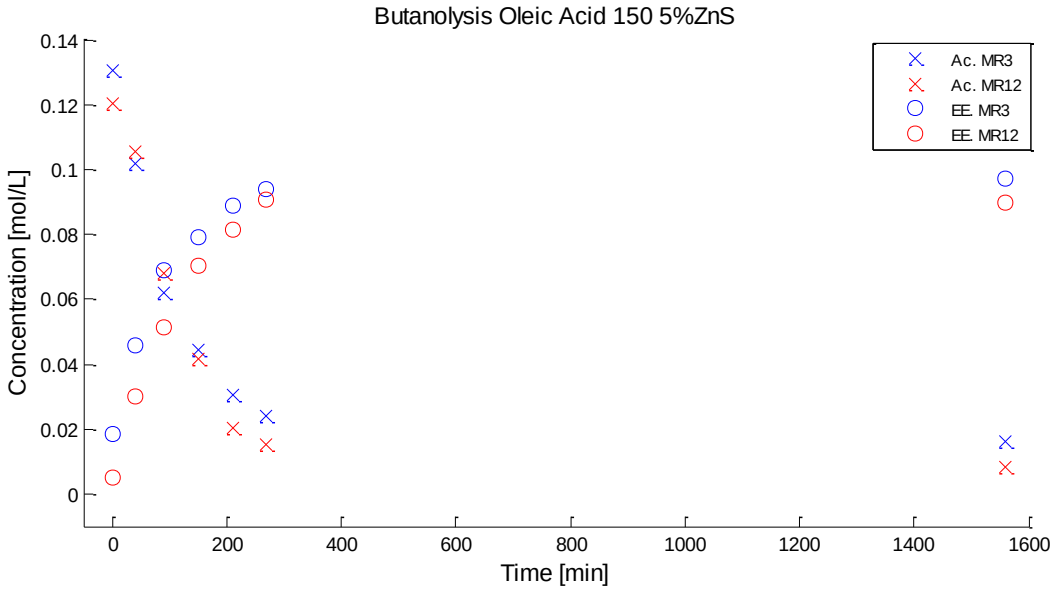

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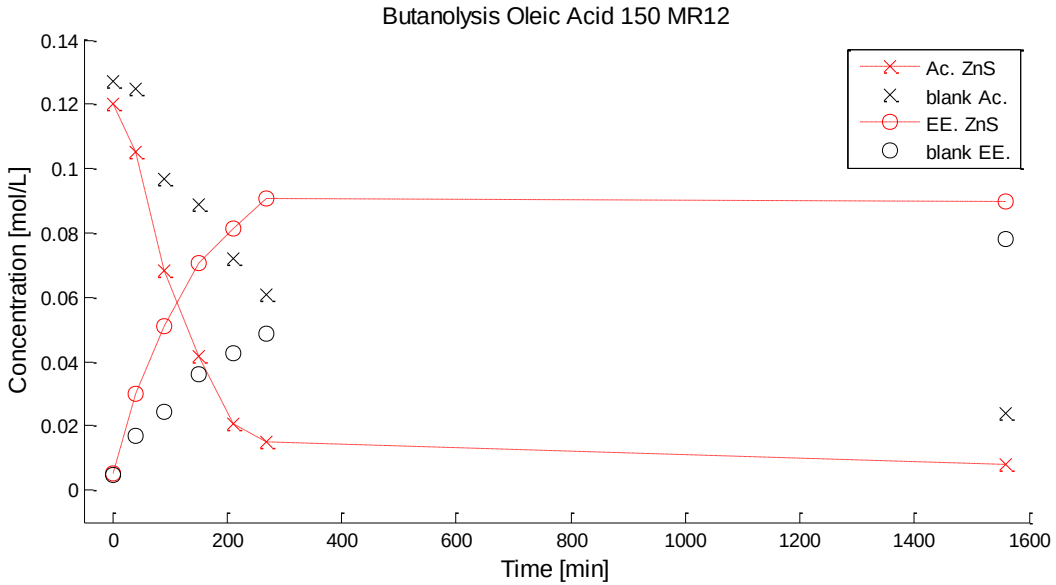
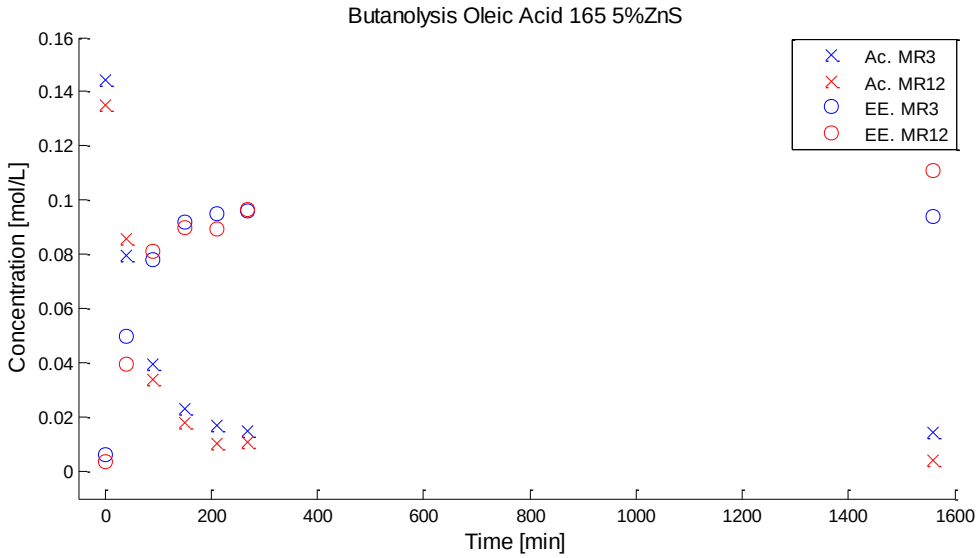
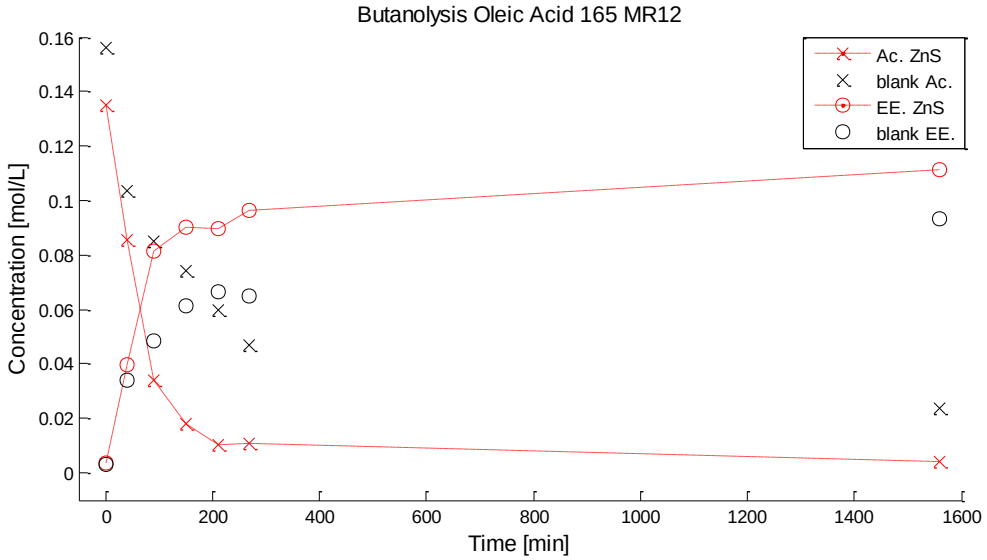


Experimental results – (n)butanol

Excess of butanol and catalyst amount influence

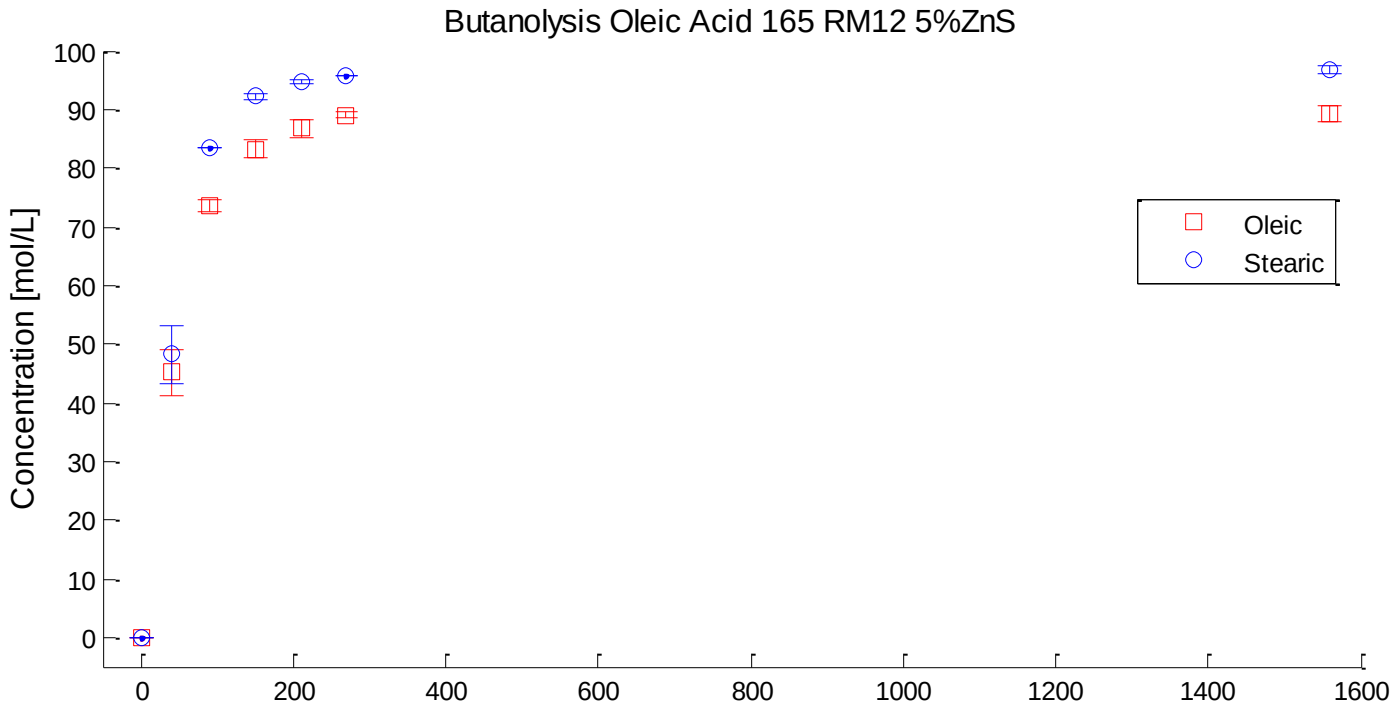


- 165 ℃



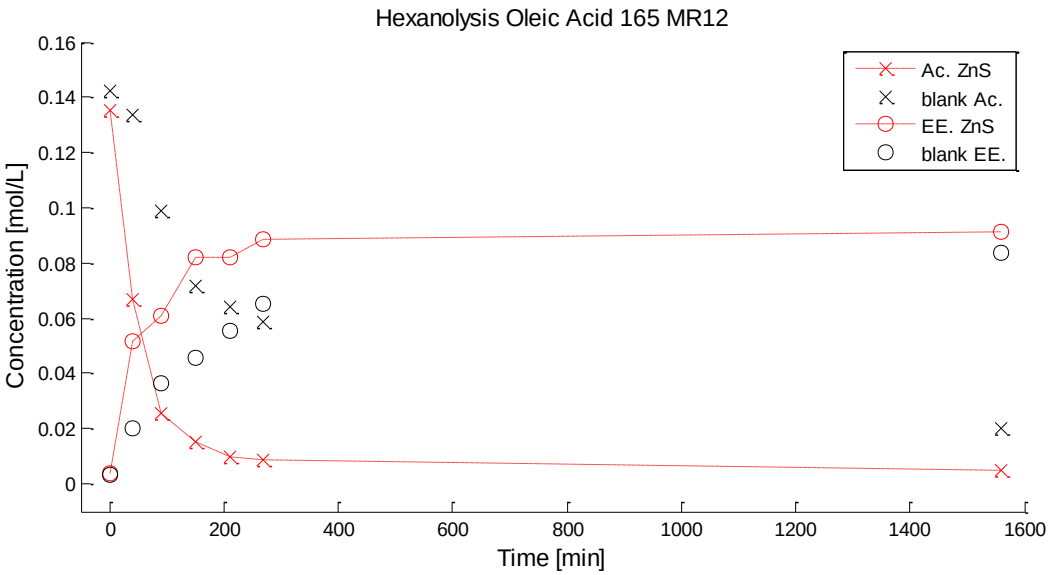
Experimental results – (n)butanol

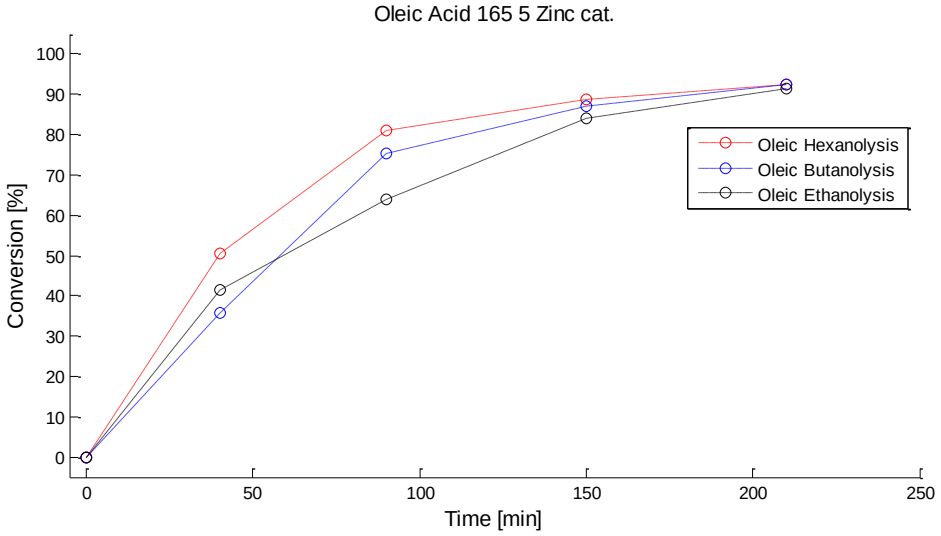
Reproducibility butanolysis



Experimental results – (n)hexanol

Comparative plots - Hexanolysis





First results

Proposed kinetics – based mechanism

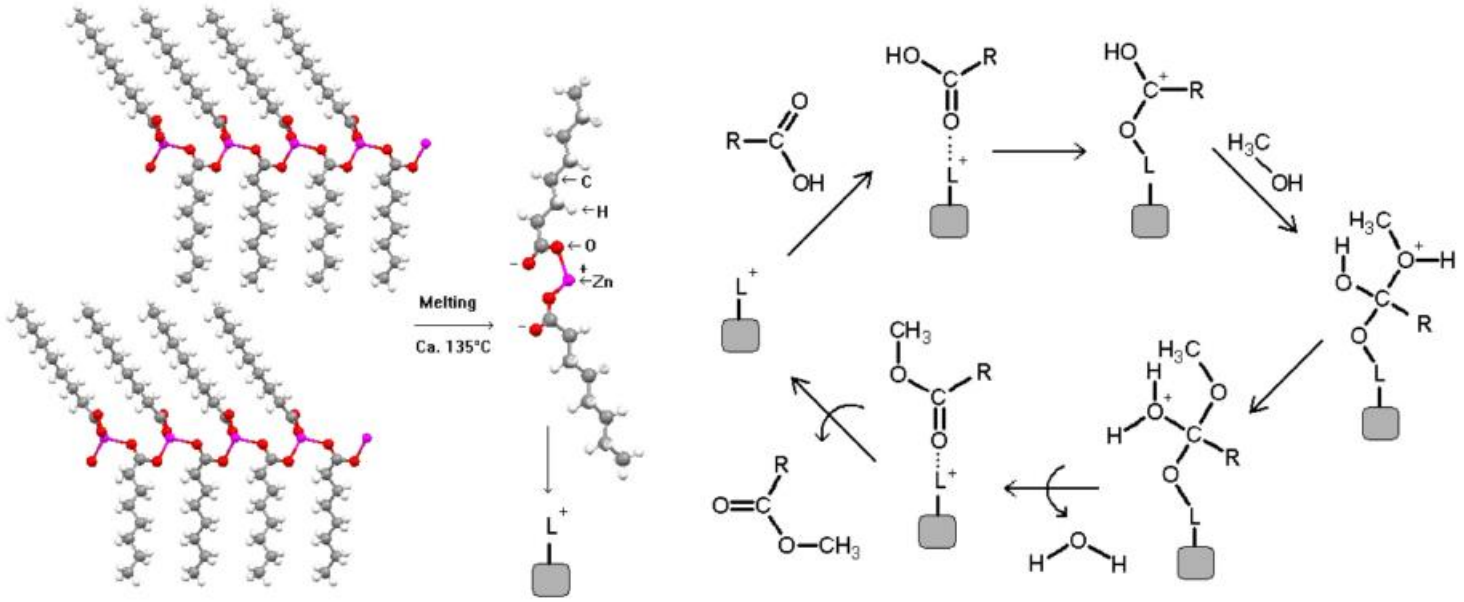


Figure 1. Schematic representation of the zinc octanoate structure and the proposed catalytic mechanism involving layered metal laurates (adaptation from Lisboa et. al, 2012).

The overall kinetics can be simplified to the following scheme and step 2 is assumed to be the rate determining step (RDS) of the reaction:

$$\underset{(A)}{RCOOH} + \underset{(cat)}{ZnL_2^+} \underset{1}{\longleftrightarrow} ZnL_2\left[RCOOH\right]^+ \xleftrightarrow[2]{+(B)} \underset{(C)}{RCOOR'} + \underset{(D)}{H_2O} + ZnL_2^+$$

First results

Proposed kinetics

Based on pseudo-homogeneous catalysis with no diffusion effects.

$$r = \frac{k''\left(C_A C_B - C_E C_W / K_c\right)}{1 + \alpha C_A + \beta C_E C_W + \gamma C_E}$$

$$\frac{dn_i}{dt} = \nu_i \times r \times m_{cat}$$

$$-\frac{dC_A}{dt} = \frac{k''\left[C_A{}^2 - a_0 C_A - \left(C_{A0} - C_A\right)^2 / K_c\right]}{1 + \alpha C_A + \beta\left(C_{A0} - C_A\right)^2 + \gamma\left(C_{A0} - C_A\right)} \times \rho_{cat}$$

where; vi = 1 and rho = bulk catalyst

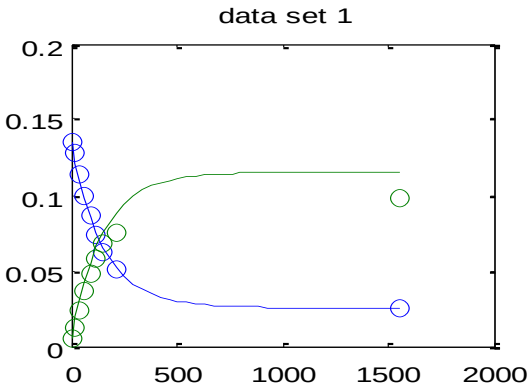
Vliq can be considered constant.

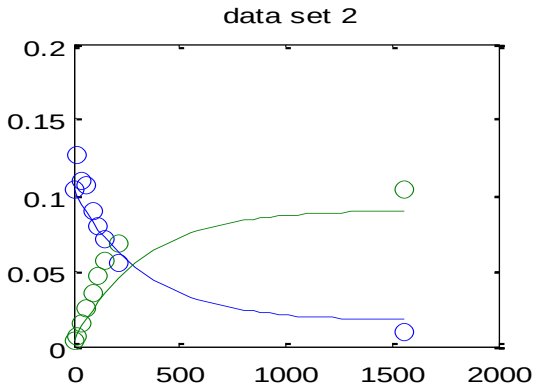
Ethanolysis modeling

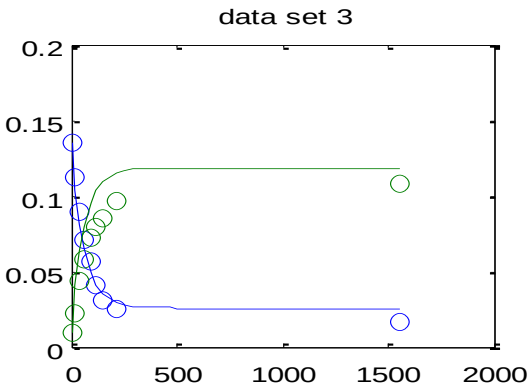
Oleic Acid – Main compound (92%)

Based on this first approach:

$$r = \frac{k''\left(C_A C_B - C_E C_W / K_c\right)}{1 + \alpha C_A}$$







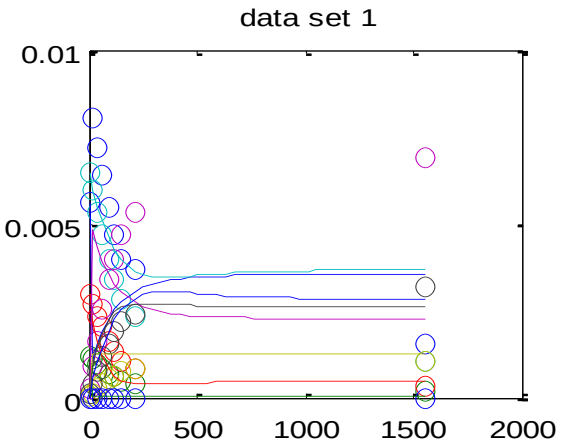
datafile(1) = 150C MR 3 5% ZnL

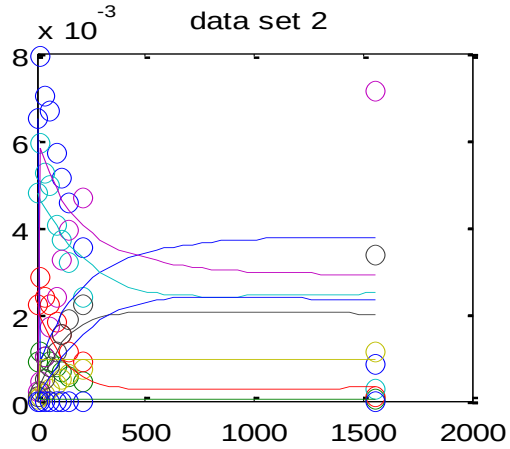
datafile(2) = 150C MR8 5% ZnL

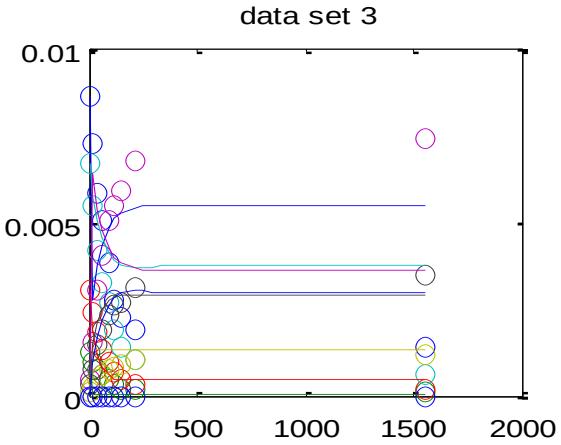
datafile(3) = 165C MR3 5% ZnL

Ethanolysis modeling

Others compounds (8%)







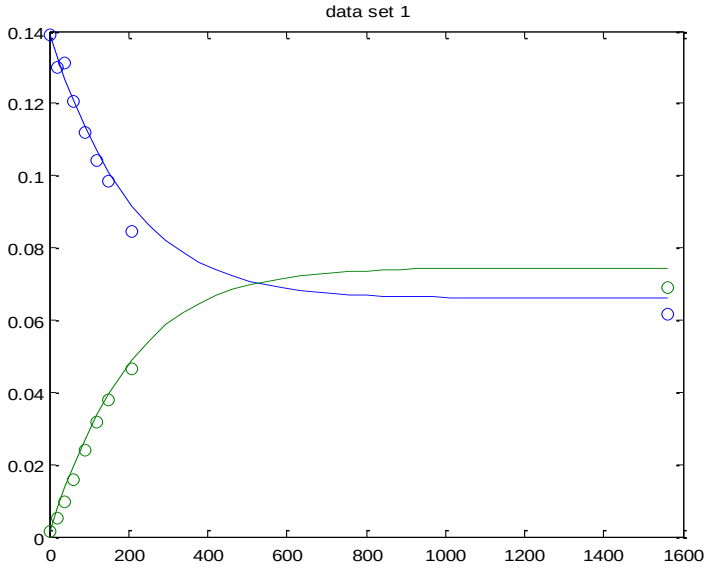
datafile(1) = 150C MR 3 5% ZnL

datafile(2) = 150C MR8 5% ZnL

datafile(3) = 165C MR3 5% ZnL

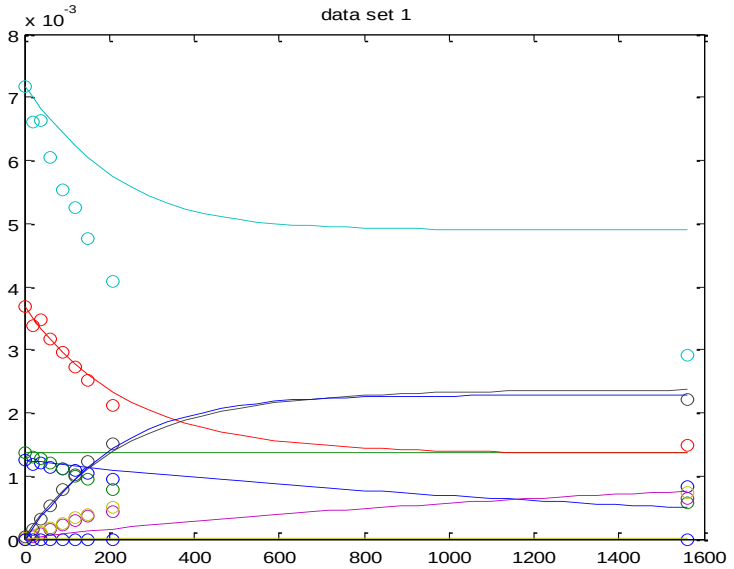
Ethanolysis modeling

Statistics first results - Modest



Dataset:135C MR3 0.7% ZnL

Total SS (corrected for means): 0.8600E-01
Residual SS: 0.2288E-03
Std. Error of estimate:0.1747E-02
Explained (%): 99.73



First results

Next steps

- As supported by the results its clearly that the catalyst fatty acid matrix (lauric acid) is being exchanged by other types available on the reaction.
- Continue experiments with hexanol (next matrix)
- Open the catalyst to investigate the acids profile and establish rate exchanging of FA. Seems that stearic is most preferable from a entropic point of view.
- Use the blanks reactions to survey thermodynamic data.
- Improve model.

Publications:

I. DE PAIVA, EDUARDO JOSE MENDES ; GRAESER, VALERIA ; WYPYCH, FERNANDO ; CORAZZA, MARCOS L. . Kinetics of non-catalytic and ZnL2-catalyzed esterification of lauric acid with ethanol. Fuel (Guildford), v. 117, p. 125-132, 2014.

II. ZATTA, L. ; DE PAIVA, EDUARDO JOSE MENDES ; CORAZZA, MARCOS L. ; WYPYCH, FERNANDO . The use of acid activated montmorillonite as a solid catalyst for the production of fatty acid methyl esters. Energy & Fuels (Online), 2015.

First results

Acknowledgments

Thank you for your attention!

Results

Catalyst Characterization

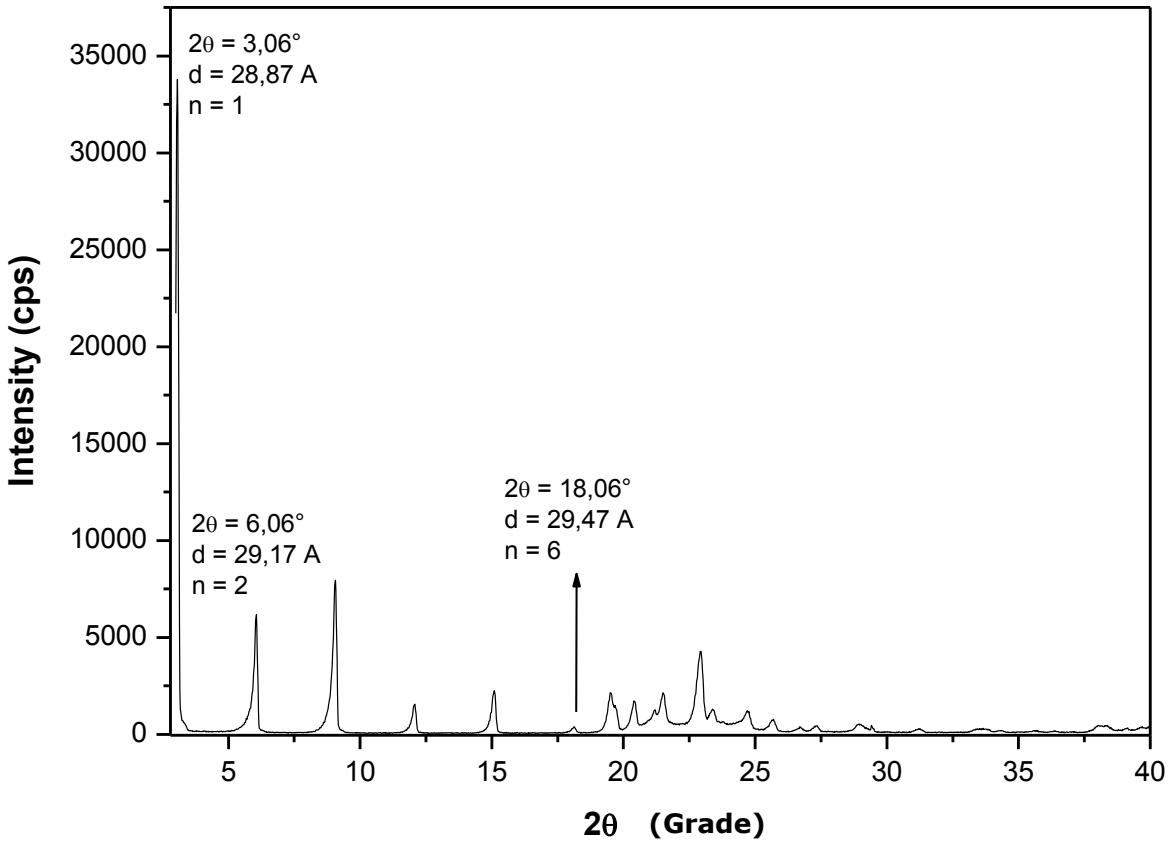


Figure 3 . X-Ray powder diffraction patterns of the layered zinc laurate.

Results

Catalyst Characterization

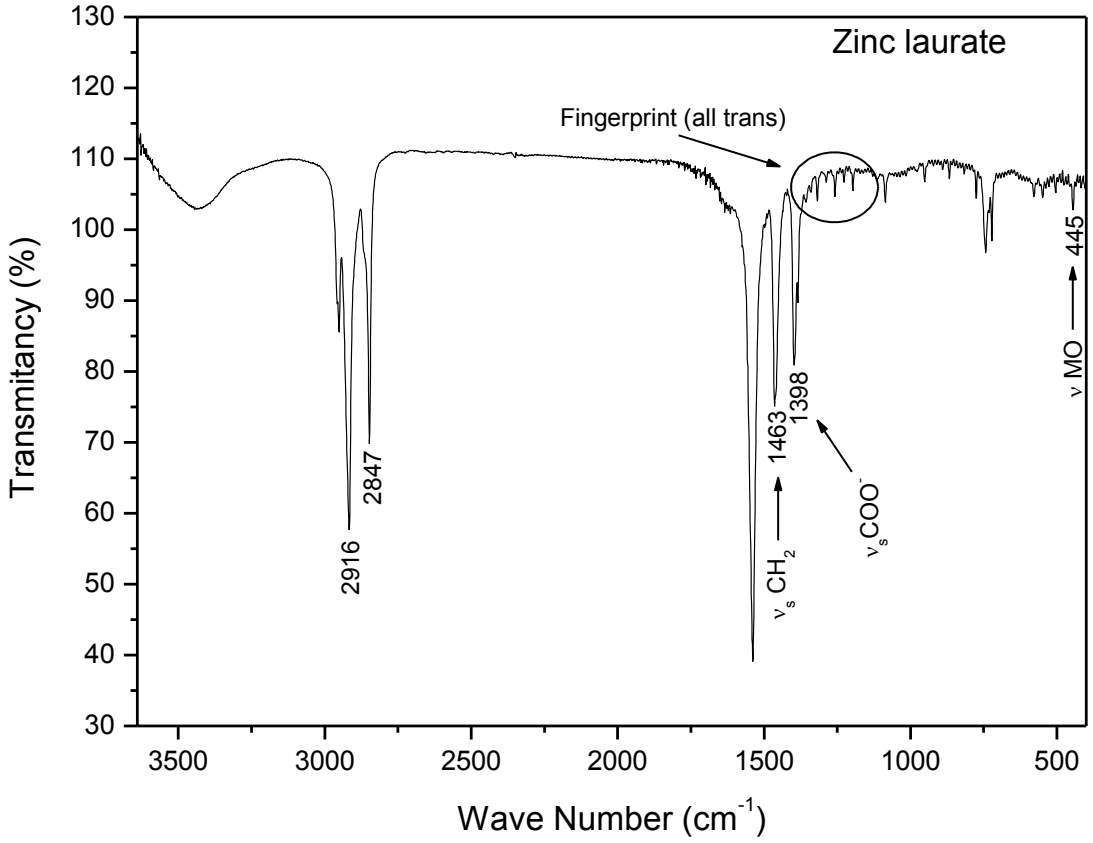


Figure 4 . FTIR spectra of the layered zinc laurate.

Raw material composition

Raw material characterization

Table 2. Oleic acid - technical grade (Aldrich) characterization by GC

Main Comp.	code	Resp. Area	%
Palmitic Acid	C16:0	15.30	0.77
Stearic Acid	C18:0	45.80	2.30
Oleic Acid	C18:1	1835.90	92.08
Linoleic Acid	C18:2	86.60	4.34
others		10.20	0.51
		1993.90	

Parallel results

Recovering of the catalyst after several washings with acetone.

Exp. 14		purged mass(g)	
t(min)	mass(g)	estim.	recov.
0	0,028	0,269	0,272
20	0,026		
40	0,023		
60	0,022		
90	0,023		
120	0,022		
150	0,026		
210	0,027		
Average	0,025		