Synthesis, characterization and applications of carbon-based calcium catalysts deriving from avocado seeds for biodiesel production

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7TH INTERNATIONAL CONFERENCE ON SUSTAINABLE SOLID WASTE MANAGEMENT

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Fossil fuels vs Biofuels

Fossil fuels

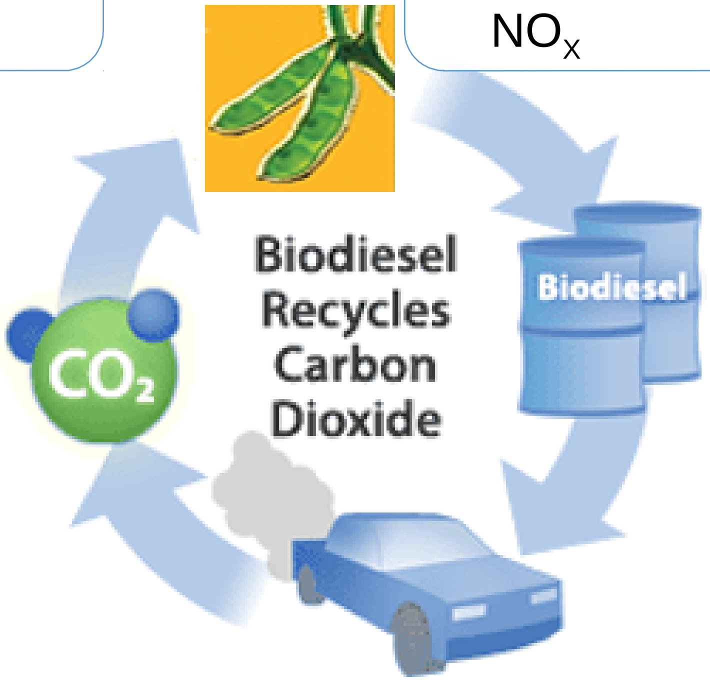
- Petroleum;
- Coal;
- Natural gas

disadvantages

- Exhaustible resources;
- Greenhouse gases emission: CO_2, CO, SO_X E NO_X

Biofuels

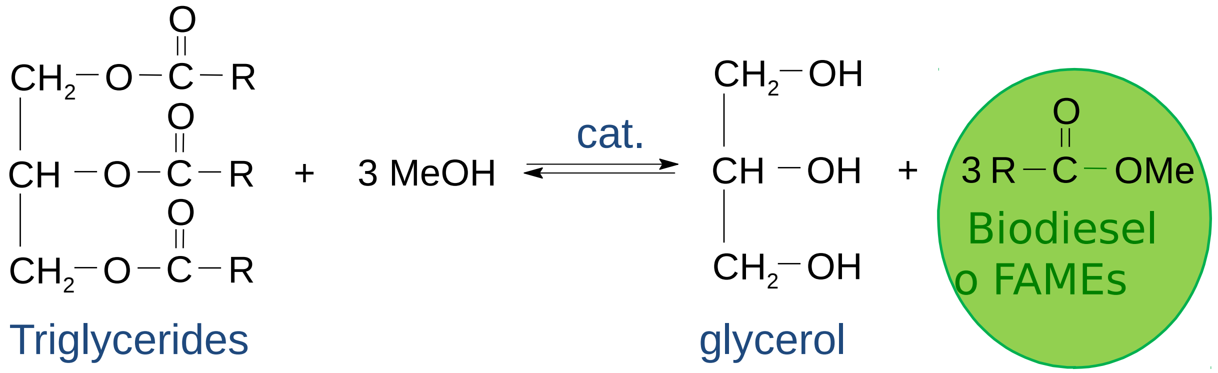
- Vegetable oil
- **Biodiesel**
- Biogas
- Bioethanol



Eco-sustainable

Renewable resources

Biodiesel



Earth biomass

Aquatic biomass

Animal fats

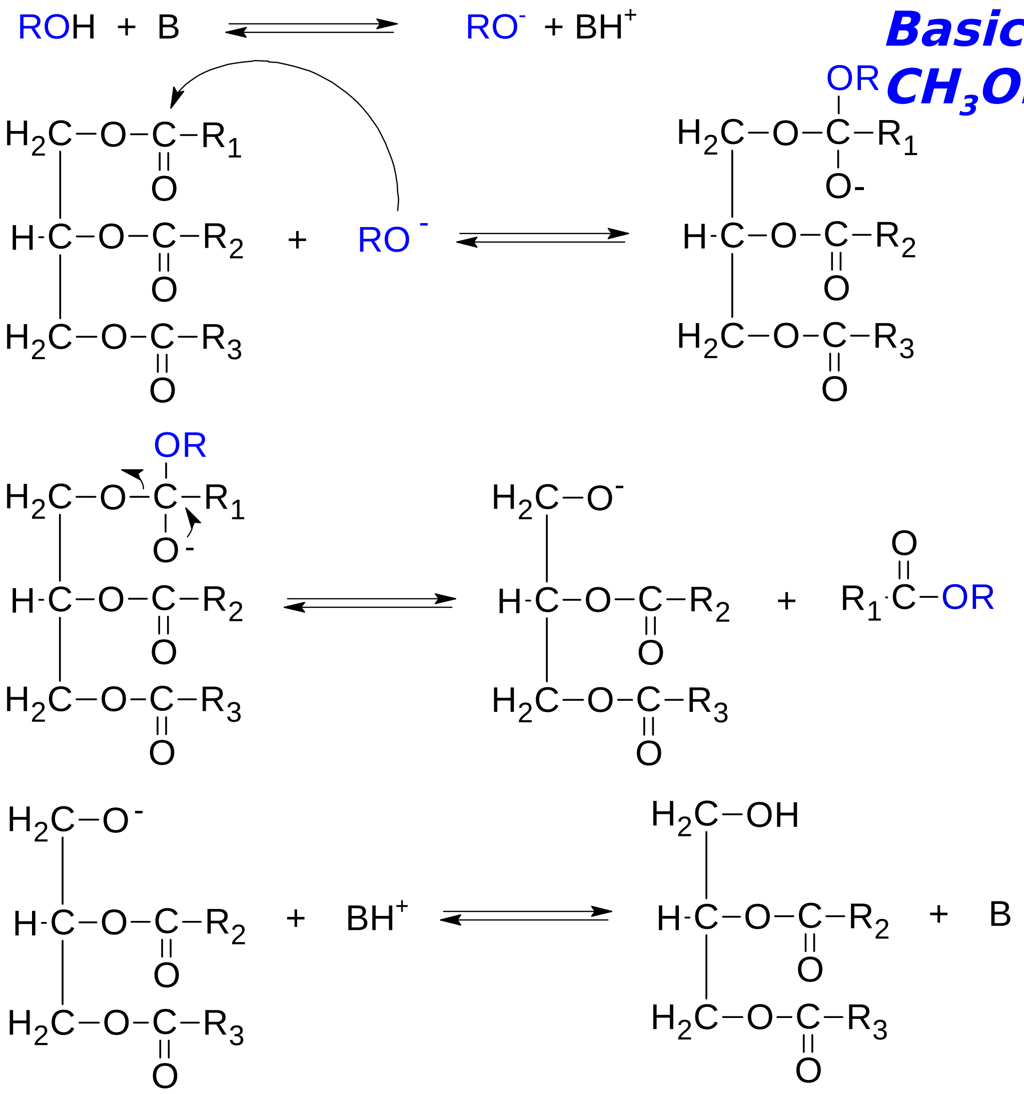
Triglycerides + MeOH ⇄ Diglycerides + RCOOMe

Diglycerides + MeOH ⇄ Monoglycerides + RCOOMe

Monoglycerides + MeOH ⇄ Glycerol + RCOOMe

F. Ma, M. A. Hanna, Bioresource Technologies, vol. 70, pp. 115-118, **1999**

Homogeneous basic catalysts



Basic catalysts ***NaOH*** ***KOH*** ***CH_3ONa***

Advantages

- Lower ratio methanol to oil(18-30:1)
- Cost of catalysts
- Temperature (50-70 °C)
- Time of reaction (< 3h)

Drawbacks

- Production of water
- Lower concentration of **FFAs** (< 0.5%w)
- Production of waste

M. Kouzu, T. Kasuno, Appl. Catal. A ***2008****, 334, 65*

Homogeneous catalysis

- Corrosion of the plants used derived from the use of strong acids and bases
- Loss of the catalyst
- Neutralization and removal of water from chemical products

Heterogeneous catalysis

- Lower cost in plant management
- Recovery of the catalyst
- Thermal and chemical resistance of catalysts
- Easy purification of the products

CaO

- Cheap
- Abundant
- Efficient
- Leaching

Why not supporting?

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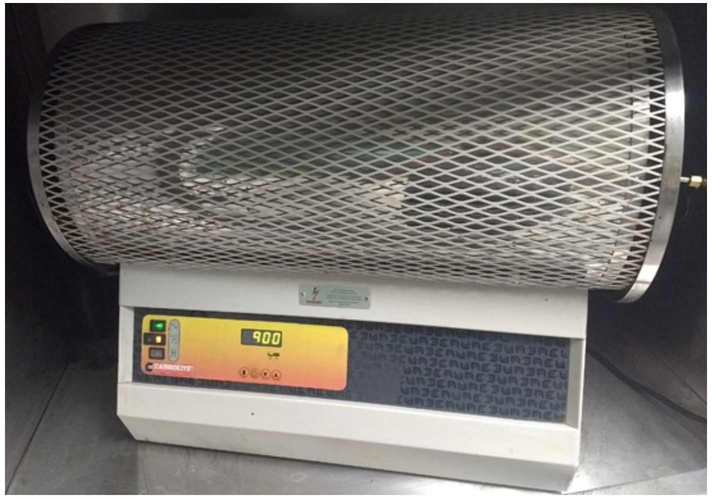
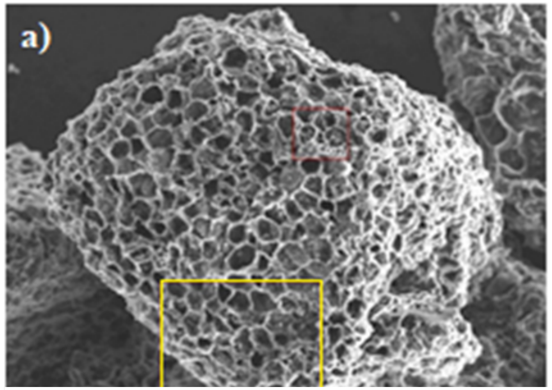
Part 1. Preparation of CaO-deposited on biochar

- Preparation of biochar
- Deposition of Ca onto the biochar

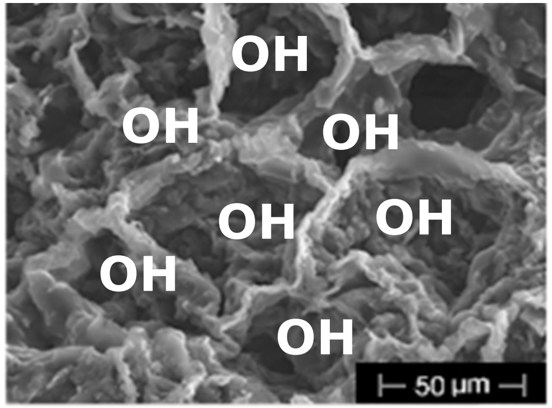
Preparation of biochar



900 °C, 2h
under nitrogen flow



Average pore diameter (nm)	Pore volume (cm^3/g)	Surface area (m^2/g)
4.29	0.03	12



Carbon avocado seeds

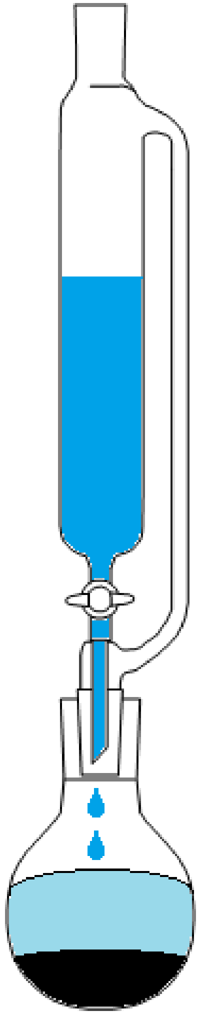
C	H	N	S	O
85.03	2.15	1.99	0.05	10.78

Deposition of Ca onto avocado-char

1.5 N NaOH solution

1h, 25 °C
under stirring

Metal salts solution



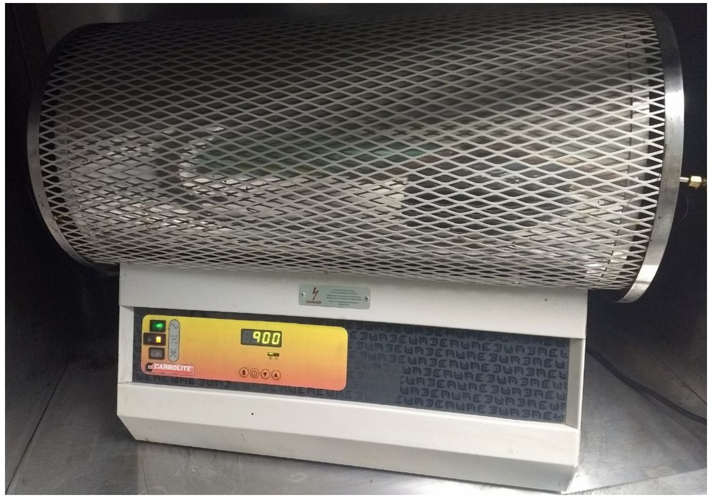
Avocado seed carbon char

1) 1h, 80 °C

2) washing with water

3) dried in oven 100 °C, 24 h

Activation



900 °C, 2h
under nitrogen flow

Calcium carbon-based materials

Metals supported
20%wt Ca
10%wt Ca
5%wt Ca

CaO

$Ca(OH)_2$

Part 2. Characterization of Ca carbon-based materials

- Elemental analysis
- Determination of acid and basic sites, piezoelectric point
- FT-IR analysis
- XRD analysis
- SEM analysis

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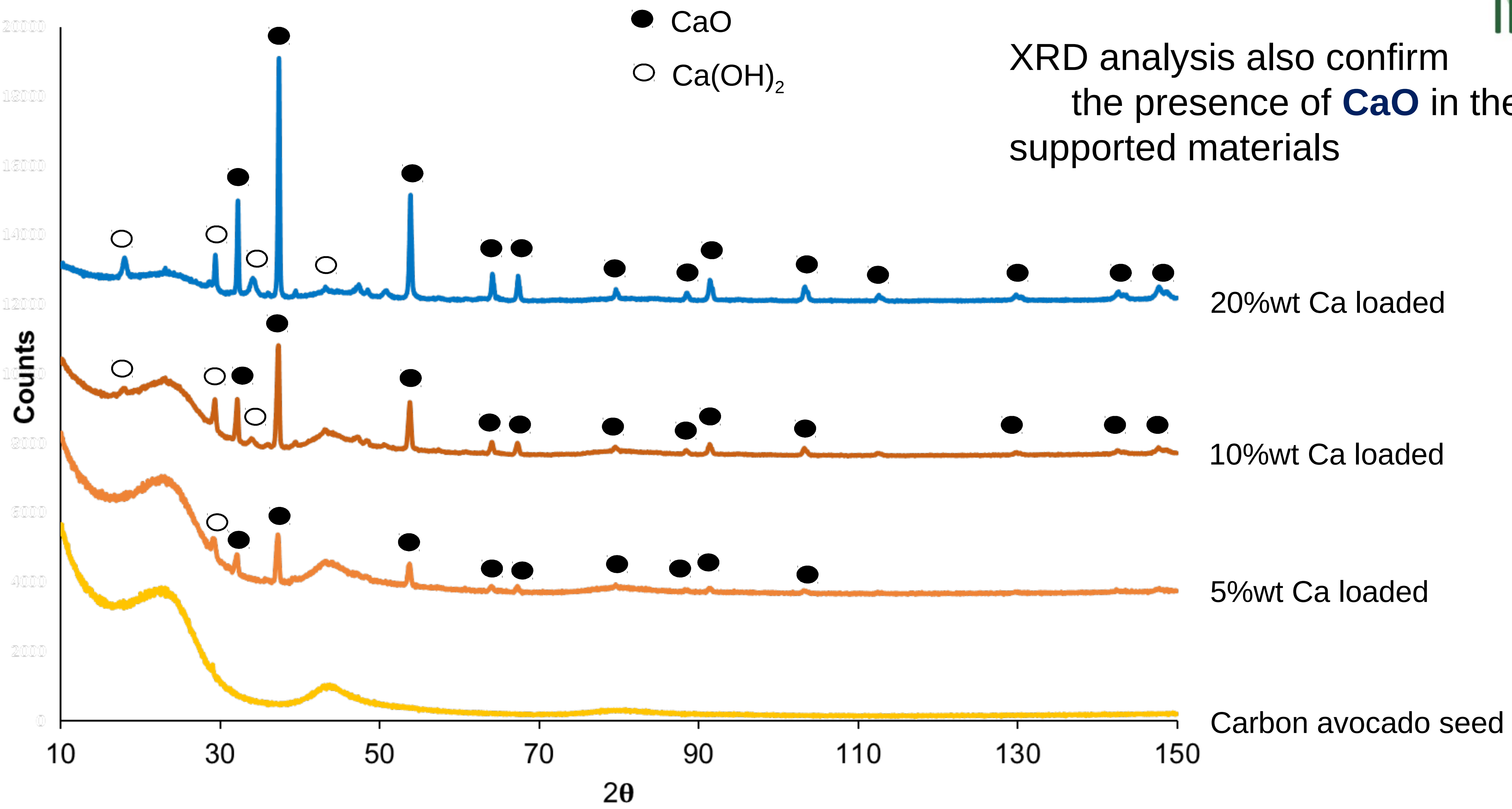
Elemental analysis

Table 1. Elemental analysis for determination of Ca content for pure and Ca-carbon supported materials.

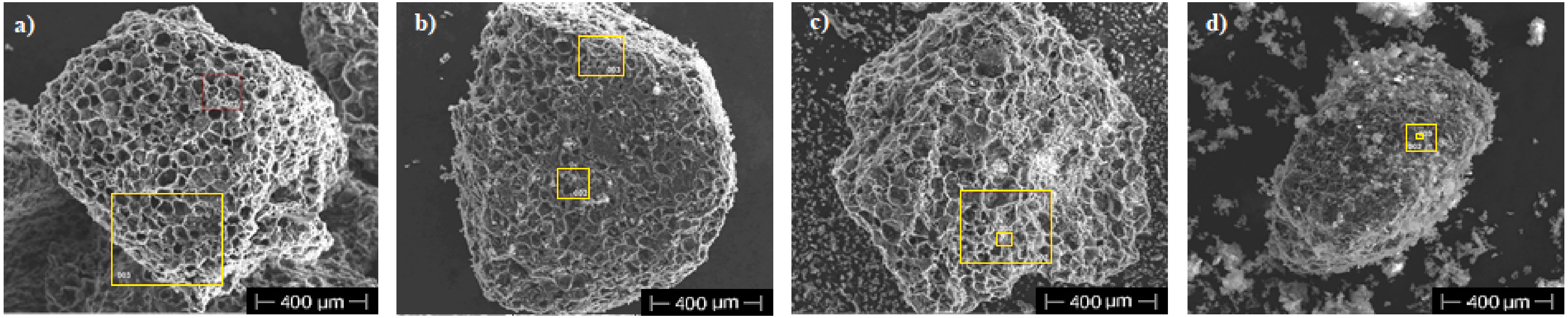
Catalysts	**Theoretical value (%wt)**	**Experimental Value (%wt)**
20%wt Ca carbon avocado seed	20	14.3 ± 0.5
10%wt Ca carbon avocado seed	10	7.9 ± 0.2
5%wt Ca carbon avocado seed	5	3.4 ± 0.1
CaO	71.5	64.1 ± 2.1
$Ca(OH)_2$	54.1	52.7 ± 1.8

XRD analysis: calcium compounds (supported materials)

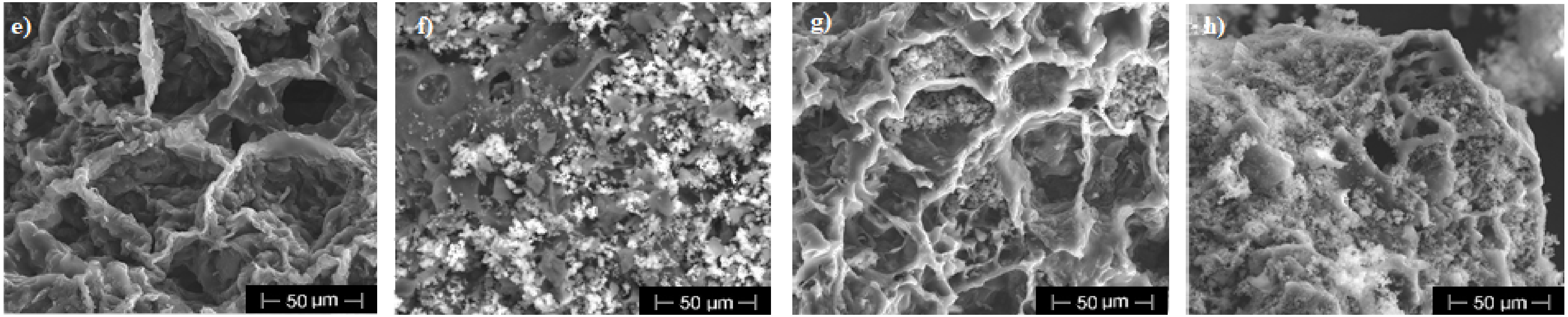


XRD analysis also confirm the presence of **CaO** in the supported materials

SEM analysis



Carbon avocado seeds | 5%wt Ca loaded | 10%wt Ca loaded | 20%wt Ca loaded



Carbon avocado seeds | 5%wt Ca loaded | 10%wt Ca loaded | 20%wt Ca loaded

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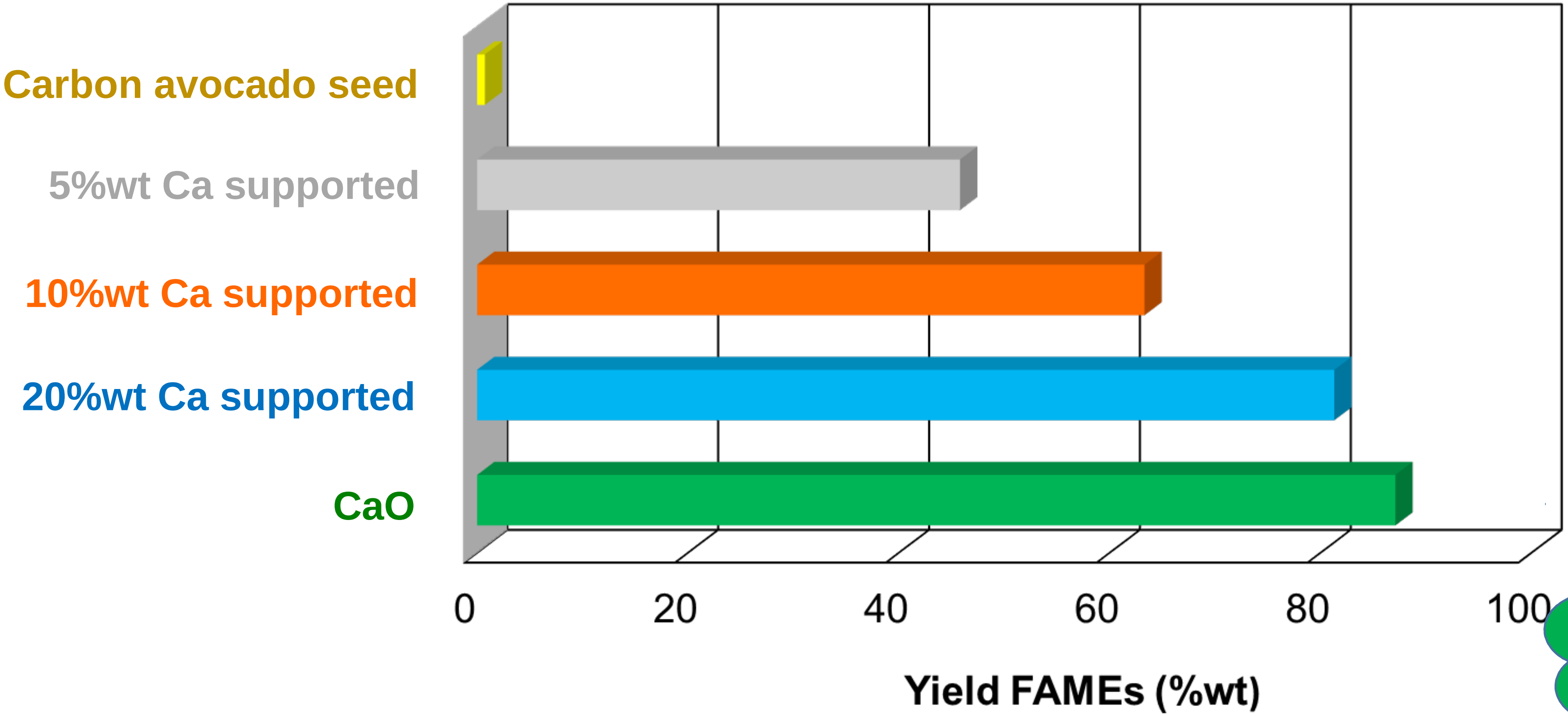
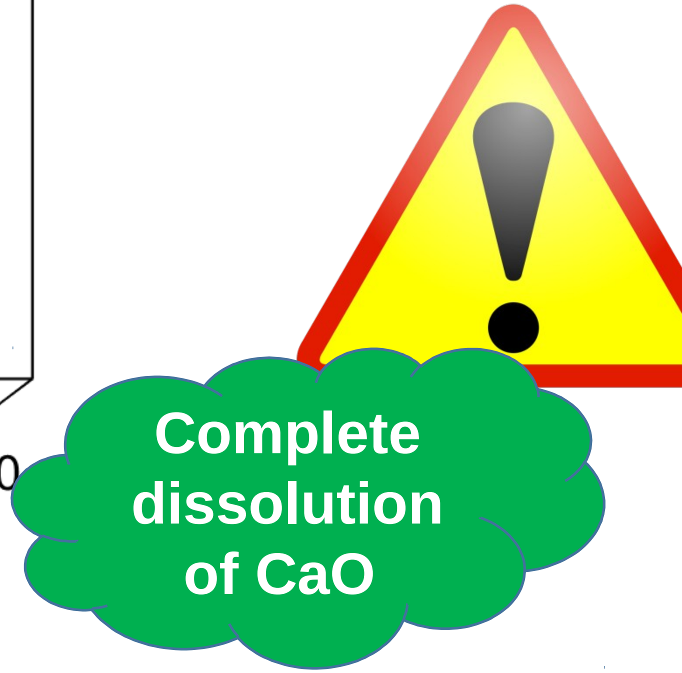
Part 3. Catalyst reactivity for biodiesel production on refined oils

- Reactivity tests of pure metal compounds and supported catalysts
- Kinetic studies
- Optimization of reaction conditions
- Recycling tests
- Reactivity tests with other bio-oils

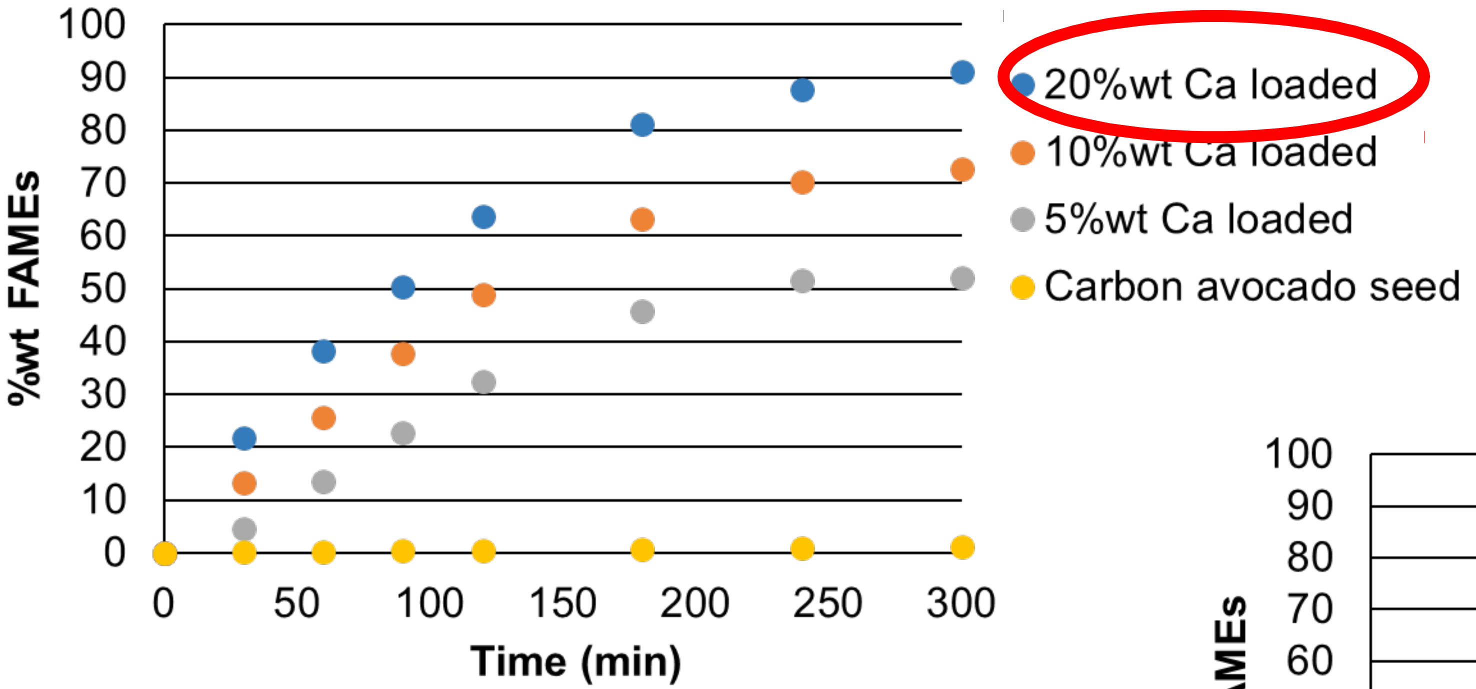
Reactivity of supported catalysts on refined oils





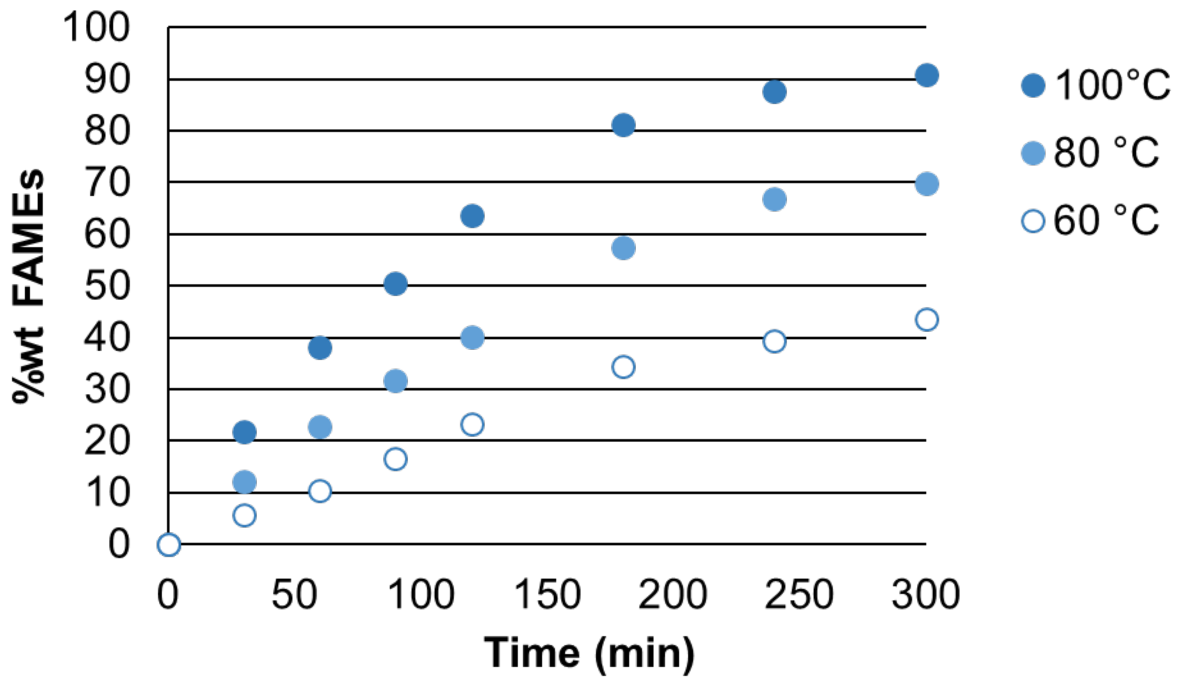
Trans-esterification using Ca-supported materials as catalysts. Reaction conditions: weight ratio catalyst to oil = 5%, molar ratio methanol to oil = 15:1, temperature = 100 °C, time = 3 h. Sunflower oil

Kinetic studies



Reaction conditions: weight ratio catalyst to oil = 5%, molar ratio oil to methanol = 15:1, temperature = 100 °C, time = 300 min. Sunflower oil

Effect of Temperature



$$TG + 3\ MeOH \rightleftharpoons 3\ FAMEs + Gly$$

Pseudo first-order

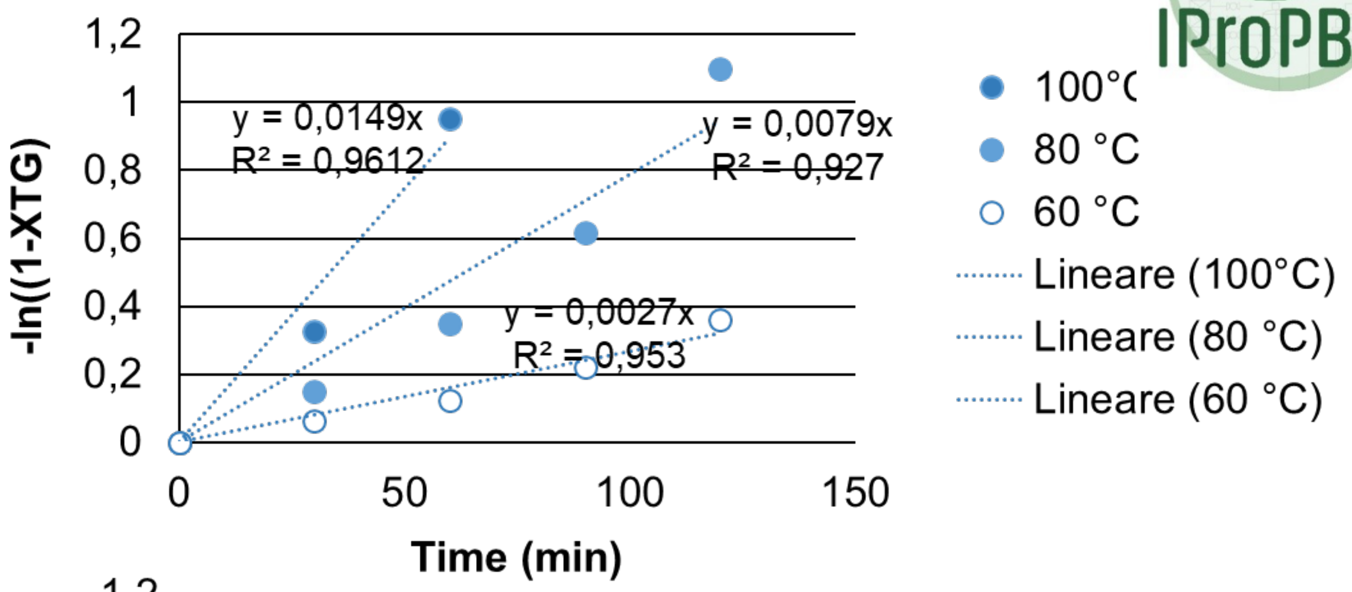
$$\ln[TG] - \ln[TG]_0 = -k_1 t$$

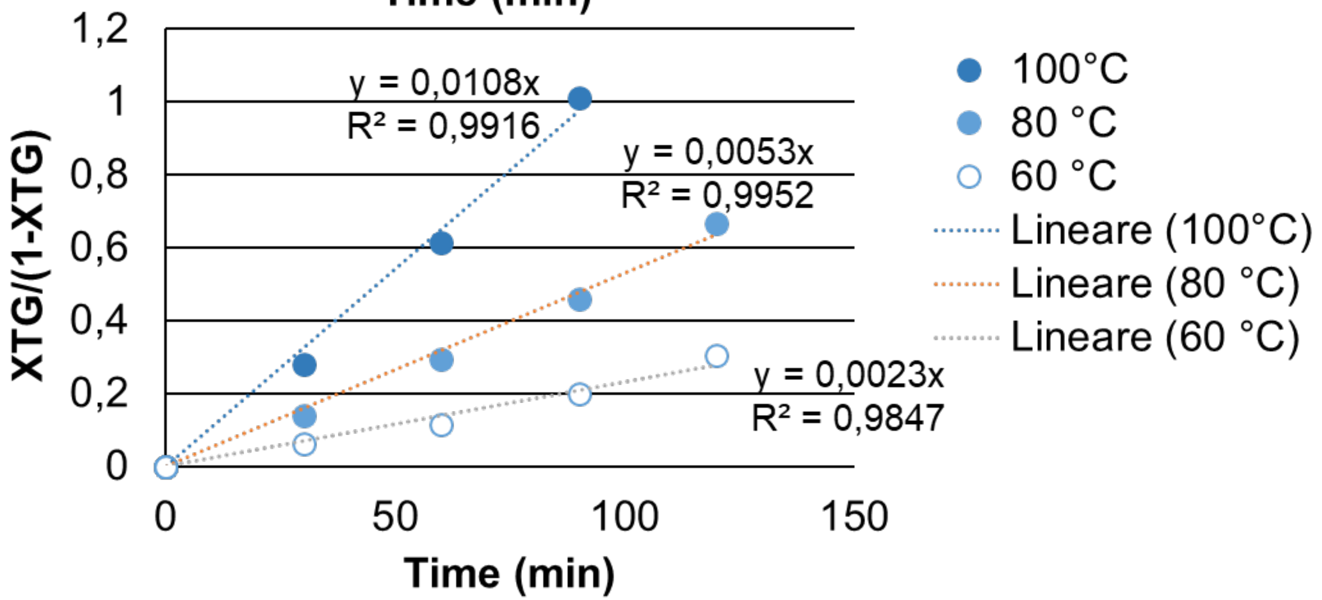
$$-\ln(1-\alpha_{TG}) = k_1 t$$

Pseudo second-order

$$\frac{1}{[TG]} - \frac{1}{[TG]_0} = k_2 t \qquad \frac{\alpha_{TG}}{1-\alpha_{TG}} = k_2 t$$

Bioresource Technology 100 (2009) 1203–1210



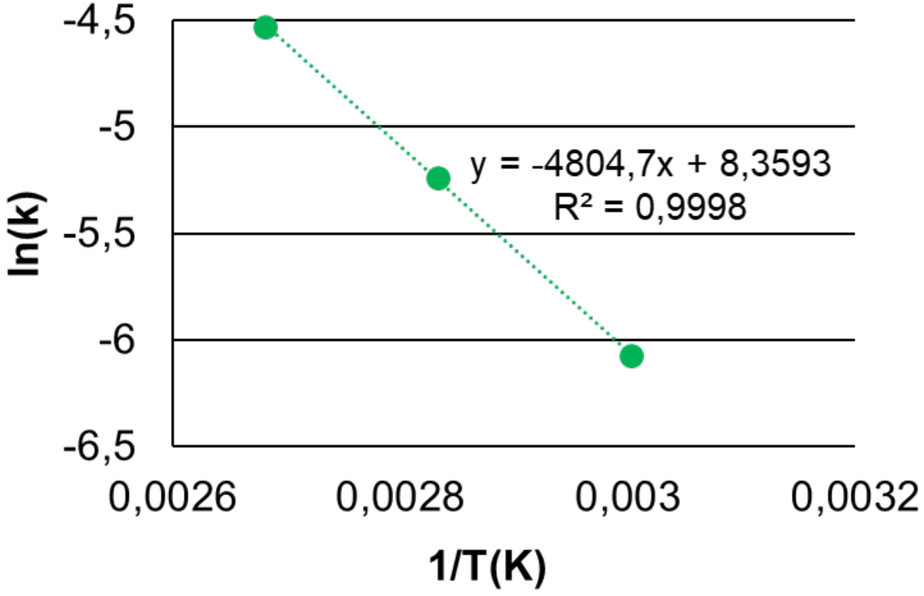


Kinetic studies

$$k_2 = A\,e^{-\frac{Ea}{RT}} \qquad \ln k_2 = \ln A - \frac{Ea}{RT}$$

Kinetic constants

T (K)	k_2 (L/mol min)
373	$1.8*10^{-2}$
353	$5.3*10^{-3}$
333	$2.3*10^{-3}$



Linear interpolation for Ea determination.

80-100 kj K^{-1} mol^{-1}

Ea = 39.94 kJ $K^{-1}mol^{-1}$

20-30 kj K^{-1} mol^{-1}

Optimization of reactive conditions

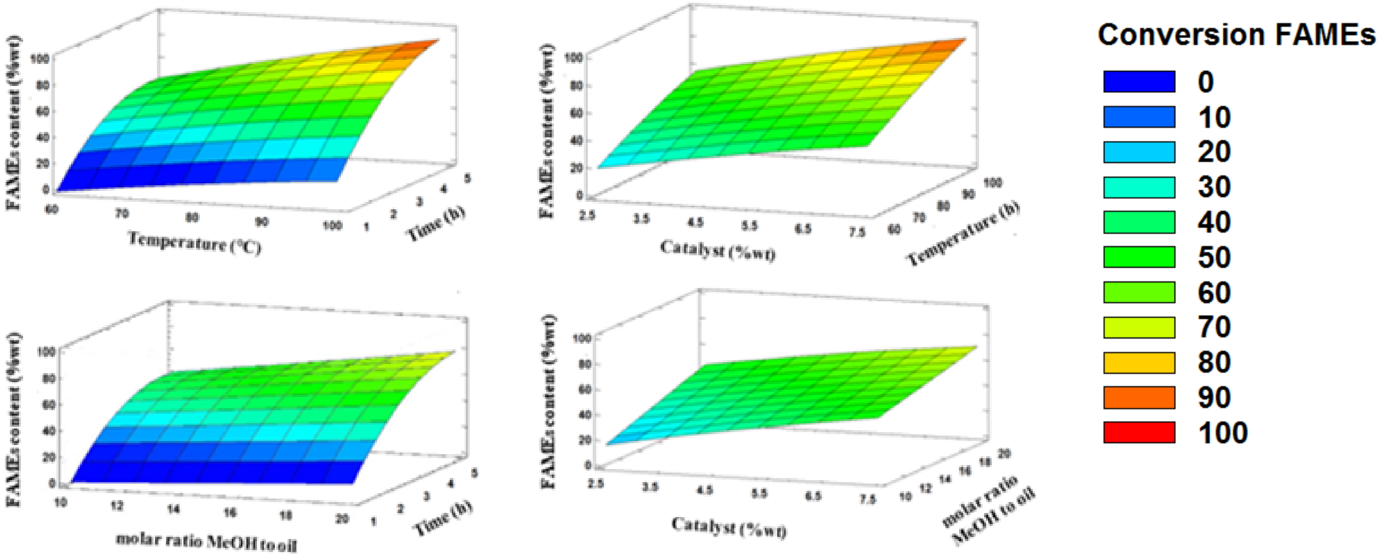
Box-Behnken design matrix for the four independent variables for the production of FAMEs (27 experiments).

Catalyst (%wt)= 2.5, 5, 10 (cat)

Methanol (molar ratio to oil): 10, 15

Temperature (°C) = 60, 80, 100 (T)

Time (h) = 1, 3, 5 (t)



Fitting equation:

$$\textbf{Yield FAMEs} = -162.71 + 4.46733\,cat + 4.50325\,C + 1.82206\,T + 7.69187\,t - 0.230933\,cat^2 - 0.139\,cat\,C + 0.0362\,cat\,T + 1.156\,cat\,t + 0.00551667\,C^2 - 0.03785\,CT + 0.40475\,Ct - 0.00518333\,T^2 + 0.131688\,T\,t - 2.97052\,t^2$$

Recycling tests and mechanism

Reactive conditions

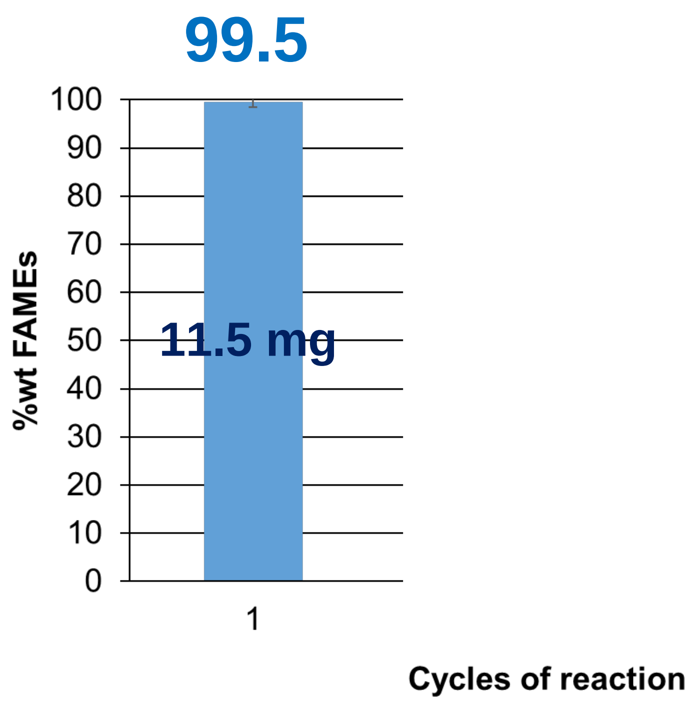
Sunflower oil (Acidity = 0.21 mg KOH/g)

Weight ratio catalyst to oil = 7.3%

Molar ratio methanol to oil = 15.6:1

Temperature = 99.5 °C

Time = 5 h



Recovery and reuse of catalyst

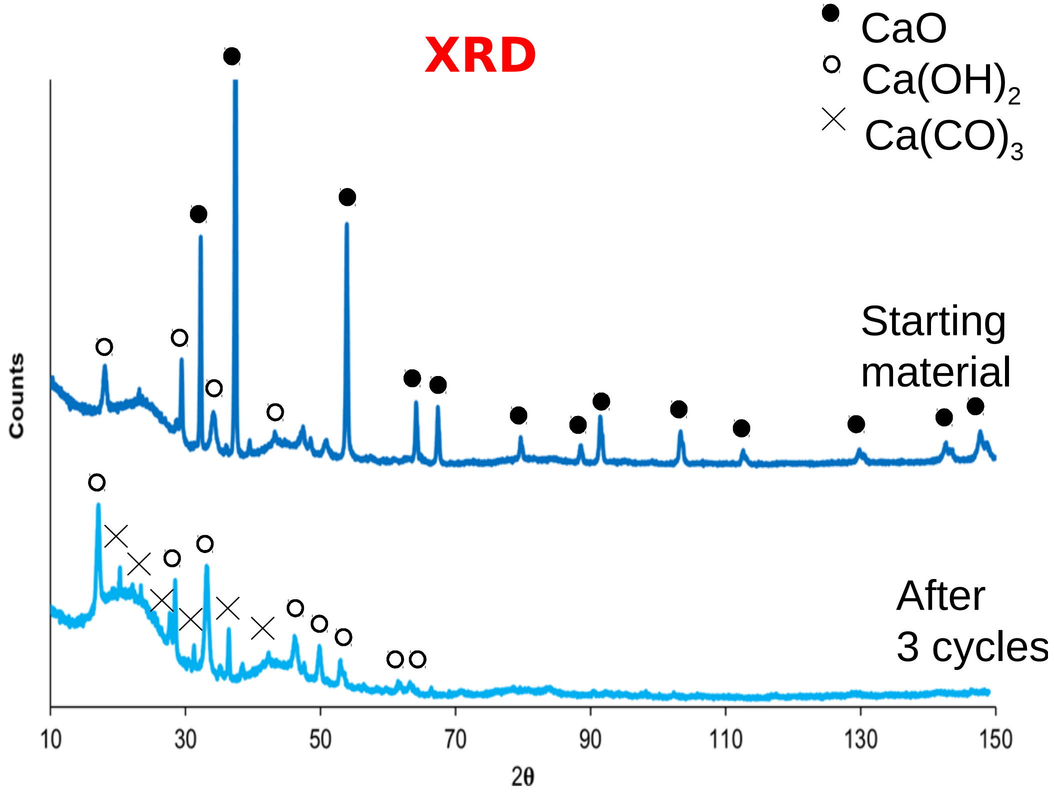
- Separation from organic mixture by centrifugation
- Washing with methanol
- Dried in oven (100 °C, 3 h)

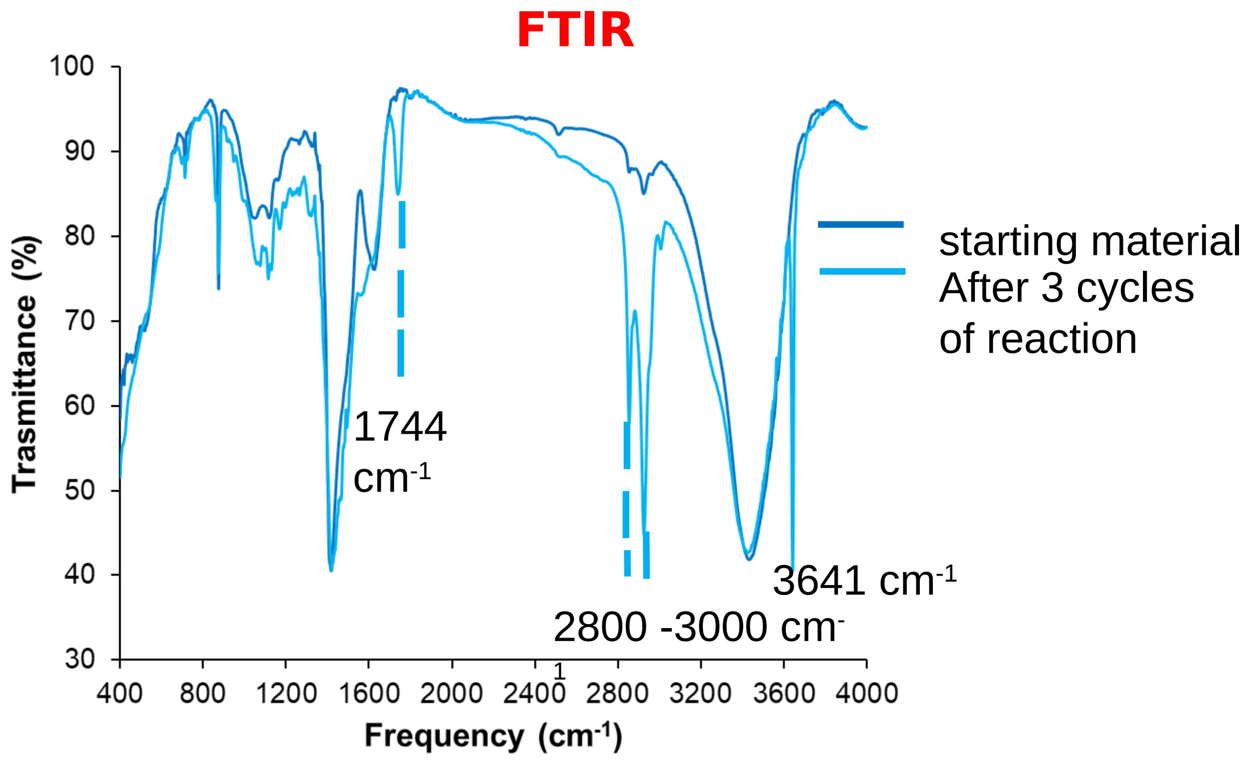
11.5 mg Ca lost = 16.1 mg CaO

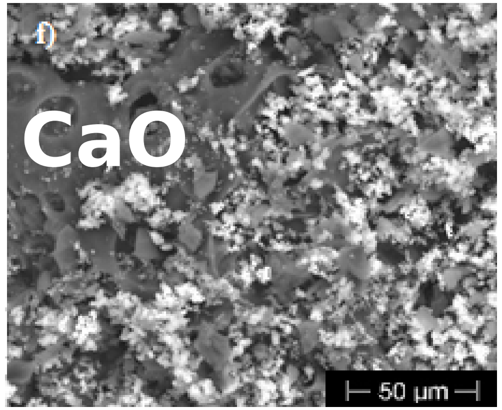
Reacting an equivalent amount of the Ca lost during the 1° cycle under the same experimental conditions

Yield FAMEs = 31.4 ± 0.4 %wt

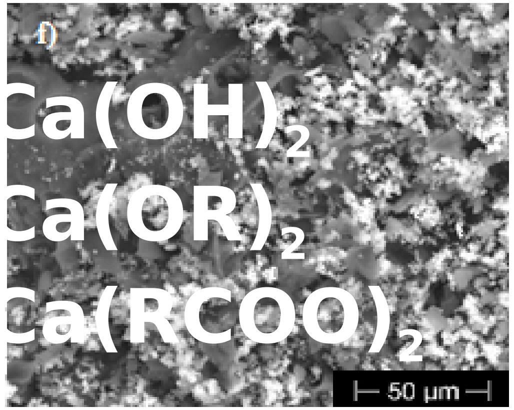
Catalysis occurred mainly onto the surface

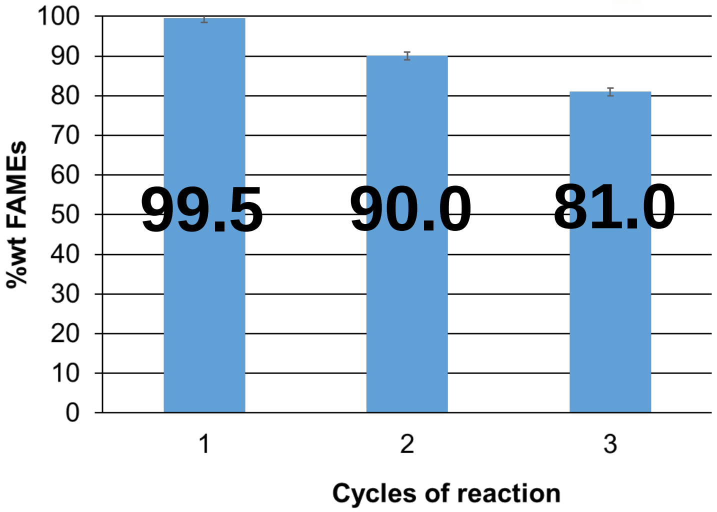

XRD
CaO
Ca(OH)2
Ca(CO)3
Starting material
After 3 cycles
Counts
2θ
10
30
50
70
90
110
130
150


FTIR
starting material
After 3 cycles of reaction
1744 cm-1
2800 -3000 cm-1
3641 cm-1
Trasmittance (%)
Frequency (cm-1)
100
90
80
70
60
50
40
30
400
800
1200
1600
2000
2400
2800
3200
3600
4000

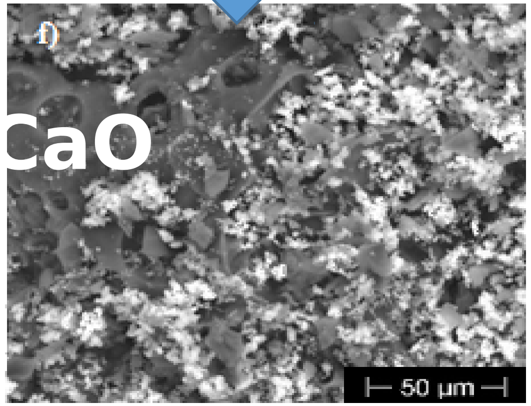


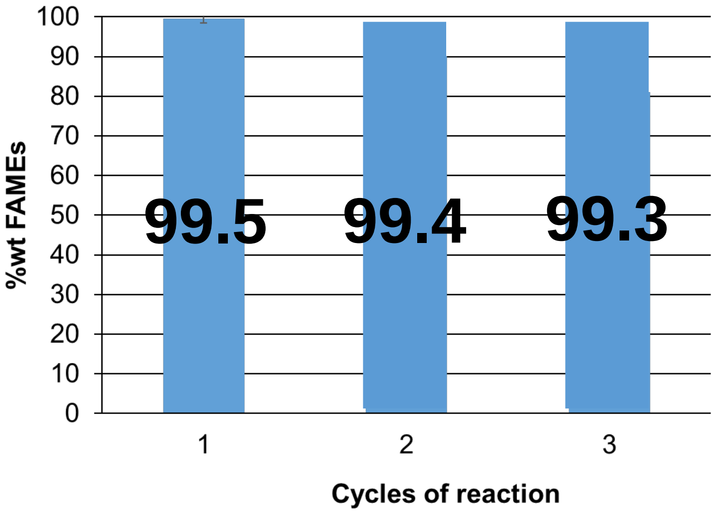
1. Centrifugation
2. Washing with methanol
3. Dried in oven (100 °C, 3 h)





under N_2





se of waste cooking oil

MeOH

$AlCl_3\ 6H_2O$

Chemical composition	Waste cooking oil	Pretreated Oil
Water content (ppm)	701 ± 8	100 ± 6
Acid value (mg KOH/g)	8.05 ± 0.04	1.05 ± 0.03
FAMEs	Traces	3.5 ± 0.2
Monoglycerides	0.8 ± 0.1	0
Diglycerides	3.9 ± 0.1	2.8 ± 0.1
Triglycerides (%wt)	90.9 ± 0.3	93.2 ± 0.4
SN (mg KOH/g)	194 ± 1	190 ± 1
Ashes (ppm)	100 ± 11	Nd
Metal content (ppm)		
Na	-	-
Ca	13.3 ± 0.2	-
Mg	9.2 ± 0.3	-
P	-	-

MeOH

20% CaO

Avocado cha

Biodiesel

di Bitonto, L., Pastore, C. (2019) Renewable Energy, 143, pp. 1193-1200.

Conclusions

1. *A new catalyst was prepared and characterized*
2. *Reaction conditions were optimised*
3. *Kinetics was studied*
4. *Procedures to recover and recycle were critically studied and optmized*
5. *Application to waste cooking oil was positively verified*

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