Tunable and efficient catalysts for the simultaneous trans-esterification of lipids and esterification of free fatty acids from bio-oils for an effective production of FAMEs

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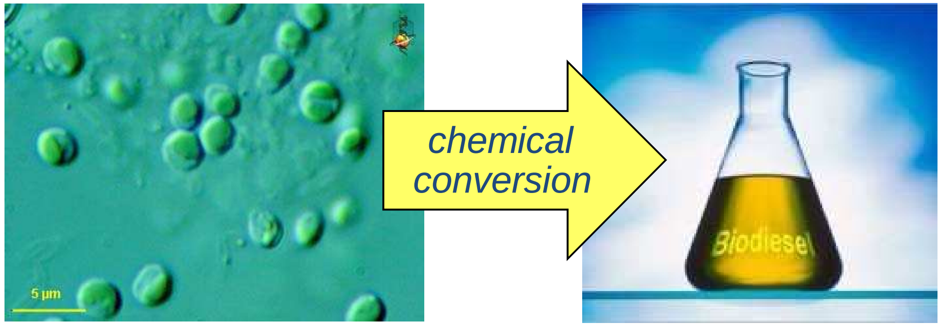
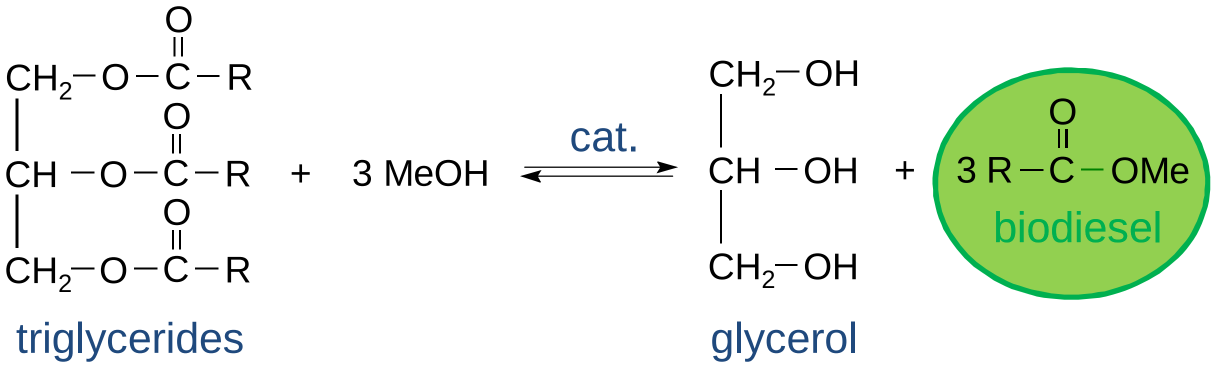
Introduction

Utilization of aquatic biomass



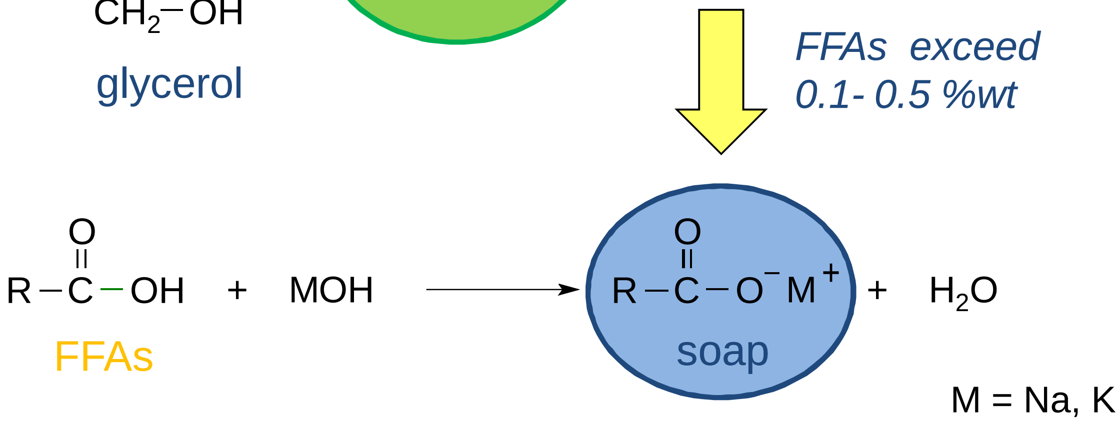
Disadvantages

- may contain up to 20% of free fatty acids-FFAs
- it is formed by a mixture of poly-unsaturated fatty acids-PuFAs



Basic catalysts

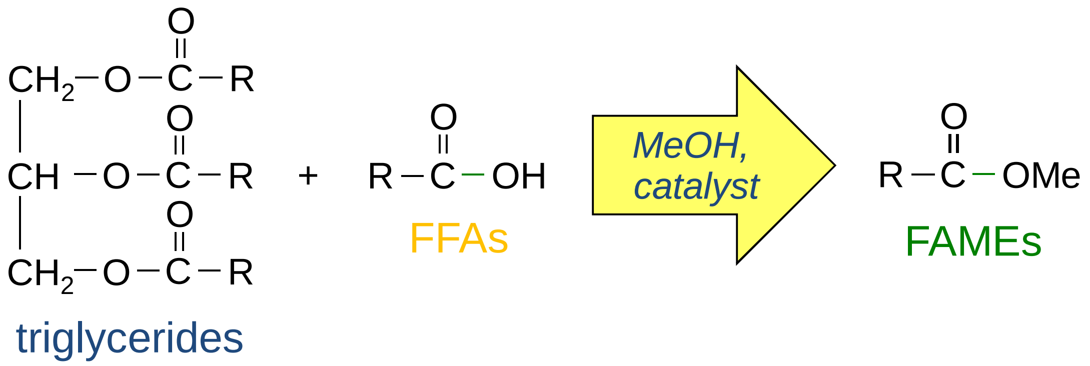
NaOH, KOH, carbonate or alkoxides



- formation of gels
- increase of viscosity
- high cost of separation

Scope of study

Our approach to the treatment of bio-oil is based on the use of solid bifunctional catalysts that are able to catalyze the simultaneous trans-esterification of lipids and esterification of FFAs



Catalysts

- $CaCO_3$
- $xCaO \cdot yAl_2O_3$
- Al_2O_3
- $xCaO \cdot zCeO_2$
- CeO_2
- $yAl_2O_3 \cdot zCeO_2$
- $xCaO \cdot yAl_2O_3 \cdot zCeO_2$

Preparation method: solid state synthesis

- Reagents: $Ce(NO_3)_3 \cdot 6\ H_2O$, $CaCO_3$ and γ-Al_2O_3
- Anidrification
- Mixing and homogenization in a High Energy Milling HEM apparatus for 1 h at a speed of 700 rpm
- **Calcination for 3 h at 823 and 1373 K**

Characterization

- Elemental analysis
- DRIFT
- BET Surface Area
- Acid and basic sites

Catalytic tests 1

New mixed oxides based on calcium, cerium and aluminium have been used as catalysts in the reaction of trans-esterification of *extra-virgin oil* as test case

Extra-virgin oil

Table 1. Trans-esterification of extra-virgin oil using several mixed oxides (Bold characters evidentiate biodiesel responding to EU regulations)

Catalyst	% Composition organic phase				Saponifiable matter
	FAMEs	MG	DG	TG	
Oil used	0	1.07	2.71	93.45	97.23
$CaCO_3$	7.6	1.55	8.20	72.37	89.72
Al_2O_3	15.1	3.69	8.66	62.93	90.38
CeO_2	11.1	0.90	6.00	75.63	93.63
$CaO{\cdot}CeO_2$	**97.0**	**0.79**	**0.07**	**0.11**	**97.97**
$12CaO{\cdot}7Al_2O_3$	50.4	11.16	8.75	20.17	90.48
$12CeO_2{\cdot}7Al_2O_3$	5.7	0.31	3.71	84.56	94.28
$12CaO{\cdot}7Al_2O_3{\cdot}3\ CeO_2$	**96.8**	**0.80**	**0.02**	**0.05**	**97.67**
$12CaO{\cdot}7Al_2O_3{\cdot}7\ CeO_2$	**96.7**	**0.65**	**0.01**	**0.01**	**97.37**
$12CaO{\cdot}7Al_2O_3.\ 12\ CeO_2$	**96.1**	**0.80**	**0.01**	**0.01**	**97.92**

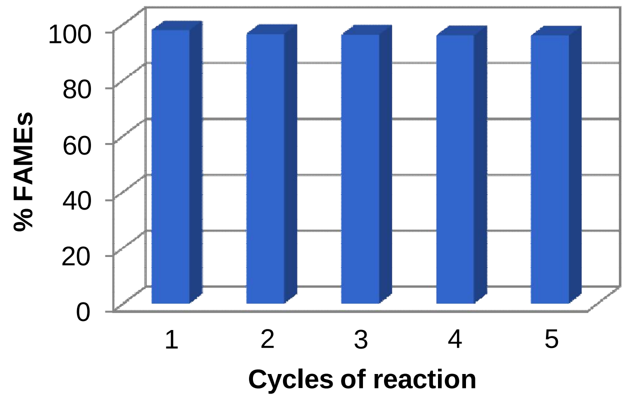
M. Aresta, A. Dibenedetto, M. Ricci ENI patent H10008, 2010

Trans-esterification tests

- Reagents - 1.8 g of starting oil
  - 0.05 g of catalyst
  - 5 mL of methanol
- Pressure 5 MPa of N_2
- Temperature 453 K for 3 h

The catalysts calcinated at 823 K show the best catalytic activity in trans-esterification process: with **$12CaO{\cdot}7Al_2O_3{\cdot}7CeO_2$** shows a very good stability without any loss of activity over 5 cycles

Figure 1. Recycling test of $12CaO\ 7Al_2O_3\ 7CeO_2$



Catalytic tests 2

Lampante olive oil

Ceria alone has good catalytic properties for the direct esterification of FFAs into methyl-esters

Mixed oxides composed by calcium and ceria show a good activity in both the trans-esterification of TG and direct esterification of FFAs, aluminium does not improve the catalytic activity but increases the stability of catalyst

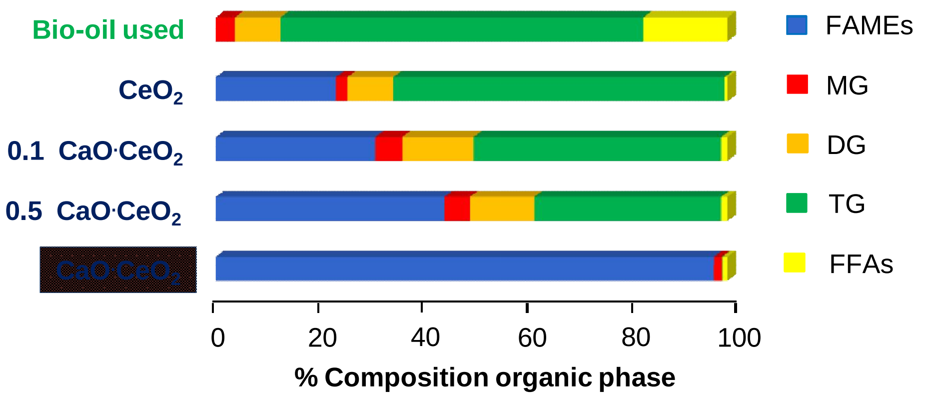
Table 2. Reactivity of mixed oxides in the trans-esterification of lampante olive oil.

Catalyst	% Composition organic phase					Saponifiable matter
	FAMEs	MG	DG	TG	FFA	
Oil used	0	1.24	5.83	72.92	18.68	98.67
$CaCO_3$	17.92	3.85	13.52	47.17	14.57	97.03
Al_2O_3	13.22	2.61	11.96	54.88	15.70	98.37
CeO_2	26.49	0.55	7.67	63.23	0.32	98.26
$CaO \cdot CeO_2$	**95.62**	**0.91**	**0.02**	**0**	**0.68**	**97.23**
$CaO \cdot Al_2O_3$	28.57	5.85	13.98	35.97	13.45	97.82
$12CaO \cdot 7Al_2O_3 \cdot 7\ CeO_2$	**95.48**	**0.88**	**0.01**	**0.01**	**0.70**	**97.08**

Bio-oil extracted from microalgae

The catalytic activity of mixed oxides Ca/Ce is connected to the calcium content correlated to the increase of acid and basic sites

Figure 2. Trans-esterification of bio-oil extracted from microalgae (Operative conditions: 1h at 353 K, MeOH/oil = 150:1)



Biodiesel composition

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Conclusion

In this work, new mixed oxides have been used as catalysts in the conversion of bio-oil with different lipids-FFA composition

- extra-virgin oil
- lampante olive oil
- oil extracted from aquatic biomass

$CaO \cdot CeO_2$ and $12CaO \cdot 7Al_2O_3 \cdot 7CeO_2$ show the best catalytic activity in both the trans-esterification of lipids and esterification of FFAs with the resulting biodiesel being well within the EU specifications

A. Dibenedetto, C. Pastore, L. di Bitonto, A. Colucci and M. Aresta,
"Bifunctional catalysts: tunable and efficient agents for the simultaneous trans-esterification of lipids and esterification of free fatty acids from bio-oils", submitted