FIRST2RUN

Flagship demonstration of an integrated biorefinery for dry crops sustainable exploitation towards biobased materials production

WP2: Chemical and Biochemical conversion of vegetable oils into biodegradable esters.

Oxidative cleavage of glycols.

Team:

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Porto Torres

15th July 2016

This project has received funding from the Bio Based Industries Joint Undertaking under the European Union's Horizon 2020 research and innovation programme under grant agreement No 669029

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Subtask 2.1.2 Catalyst for oxidative cleavage

Activity carried out:

- **February 2016**: delivery of the starting substrate by Novamont S.p.a for the catalytic tests of oxidative cleavage with our catalysts.
- **March – April 2016**: development of the analytical method for the determination of conversions and yields
- **May – June 2016**: catalytic tests

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Starting material: **DSA Novamont**

(9,10-dihydroxystearic acid)

- Obtained from Sunflower oil with H_2O_2/H_2WO_4
- Composition after transmethylation of triglyceride

Methyl esters from sunflower oil*:	Methyl oleate	Methy linoleate	Methyl palmitate	Methyl stearate
%wt	92	1	4	3

- Problem → **viscosity** ($T_f \cong 57$ °C)

*arising from **PATENT US 2008/024595 A1**

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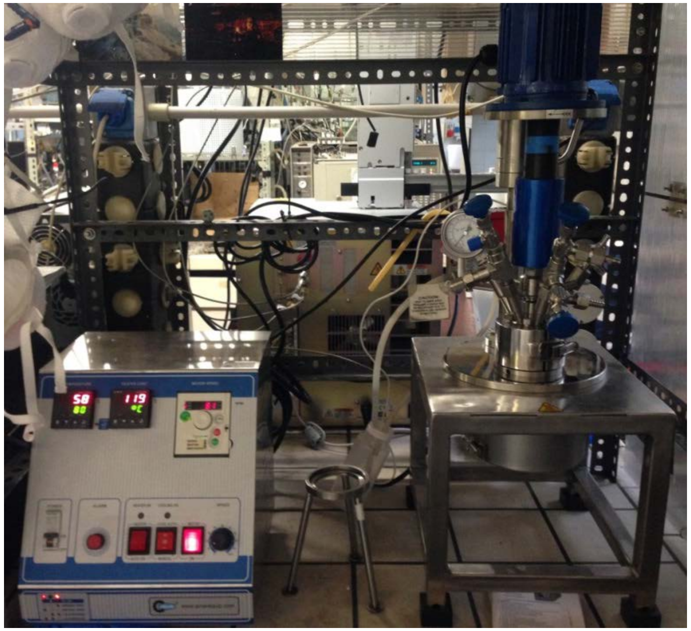
Activity & Results

Catalytic tests were conducted in bench scale reactor under the same conditions for each catalyst tested



Reaction conditions*:

- T = 80 °C
- Stirring = 500 rpm
- P_{O_2} = 25 bar
- t = 5 h

*arising from **PATENT US 2008/024595 A1**

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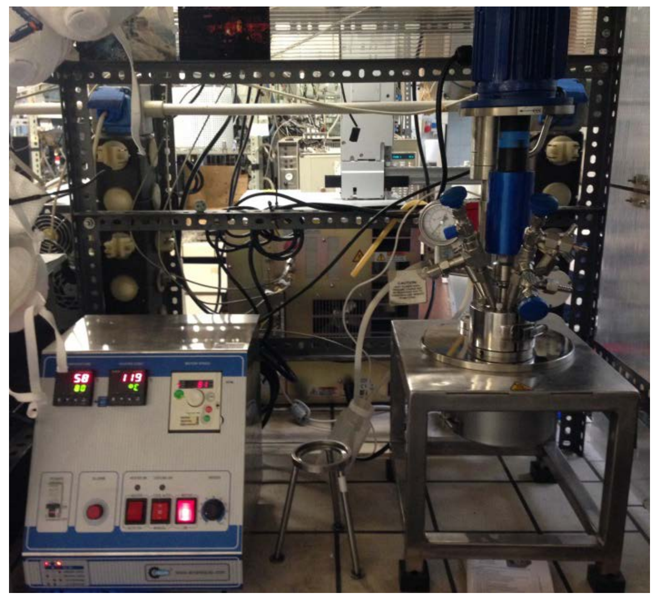
Example Reactivity test on DSA

Reaction Conditions from **PATENT US 2008/024595 A1**

- DSA + cat. system (next slide)
- T = 80 °C
- Stirring = 500 rpm
- P_{O_2} = 25 bar
- t = 5 h



Oily phase

Aqueous phase (with the Novamont catalyst)

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Catalytic System of Novamont patent: **preparation**

Na_2WO_4 (colourless) + $CoAc_2$ (pink)

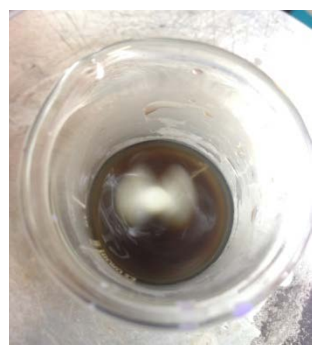
1 →

Na_2WO_4 + $CoAc_2$ (<u>complete mixing)</u>

2 ←

Na_2WO_4 + $CoAc_2$ + H_2O_2

3 →



Na_2WO_4 + $CoAc_2$ + H_2O_2 + HCl

Example 1*:

1. A solution of $CoAc_2$ in H_2O was added to a solution of Na_2WO_4 in H_2O.
2. H_2O_2 (30 %wt.) was added in order to oxidize Co (II) to Co (III).
3. The precipitate was solubilized by means of HCl (3 M).

* C. Bastioli, T. Milizia, G. Borsotti, *Patent: US 2008/0245995*

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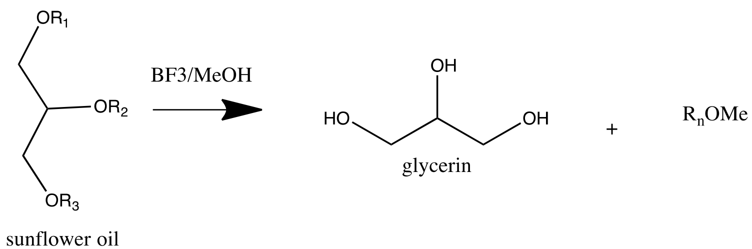
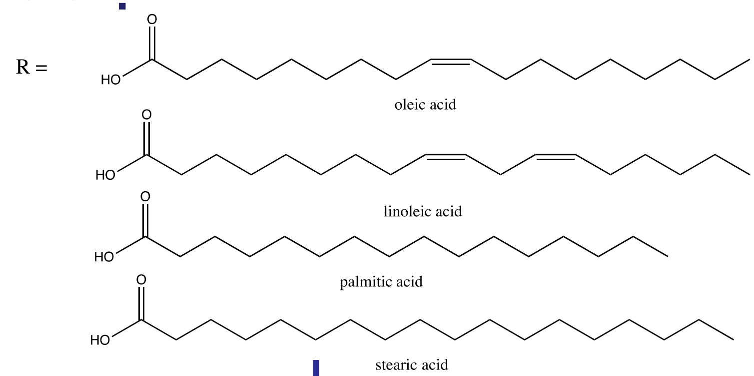
Products analysis

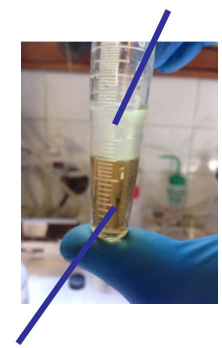
Transmethylation (typical procedure)[1., 2., 3.]:





1. 0,1 g of sample, previously dryed with Na_2SO_4, was dissolved in 1 mL of toluene
2. Add 450 μL of STD Int (solution prepared dissolving 1%wt. of 10-undecenoic acid and 0,8%wt. of nonadecanoic acid in 10 mL of MeOH)
3. Add 2,8 mL BF3/methanol (10% w/w) and 150 μL 2,2-dimethoxypropane can be added at this point.
4. Heat at 80 °C for 1h
5. Cool, then add 1mL of water and 1 mL of $CHCl_3$.
6. Carefully remove the lower (organic) layer, and dry it over anhydrous Na_2SO_4.

Aqueous phase (with glycerin)



Organic phase (with products of reaction)

[1.] K. Blau and J. Halket Handbook of Derivatives for Chromatography (2nd ed.) John Wiley & Sons, New York, 1993.
[2.] D.R. Knapp Handbook of Analytical Derivatization Reactions John Wiley & Sons, New York, 1979.
[3.] Bailey's Industrial Oil and Fat Products, fifth edition, Vol. 5, John Wiley & Sons, New York (1995).

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Products analysis: ***Gas Chromatography***

Shimadzu GC-2025 (arrived 27/04/16) equipped with:

- auto-injector AOC-20i with syringe (10 μL)
- Split injector
- Hydrogen flame ionization detector (**FID**)

Column DB-23 J&W

Max Temperature: 250 °C
Length: 60 m
Diameter: 250 μm
Film thickness: 0,25 μm

<u>Operation Method</u>

Column

Max Temperature: 250 °C
Mode: constant linear velocity

Detector

Temperature: 250 °C

Injector*

Temperature: 250 °C
Mode: constant linear velocity
Pressure: 337,3 kPa
Flow:158,8 mL/min
Flow: 3,8 mL/min
Linear velocity: 46,6 mL/min
Purge Flow: 3,0 mL/min
Split ratio: 40,0

*Method delivered by Novamont S.p.a.

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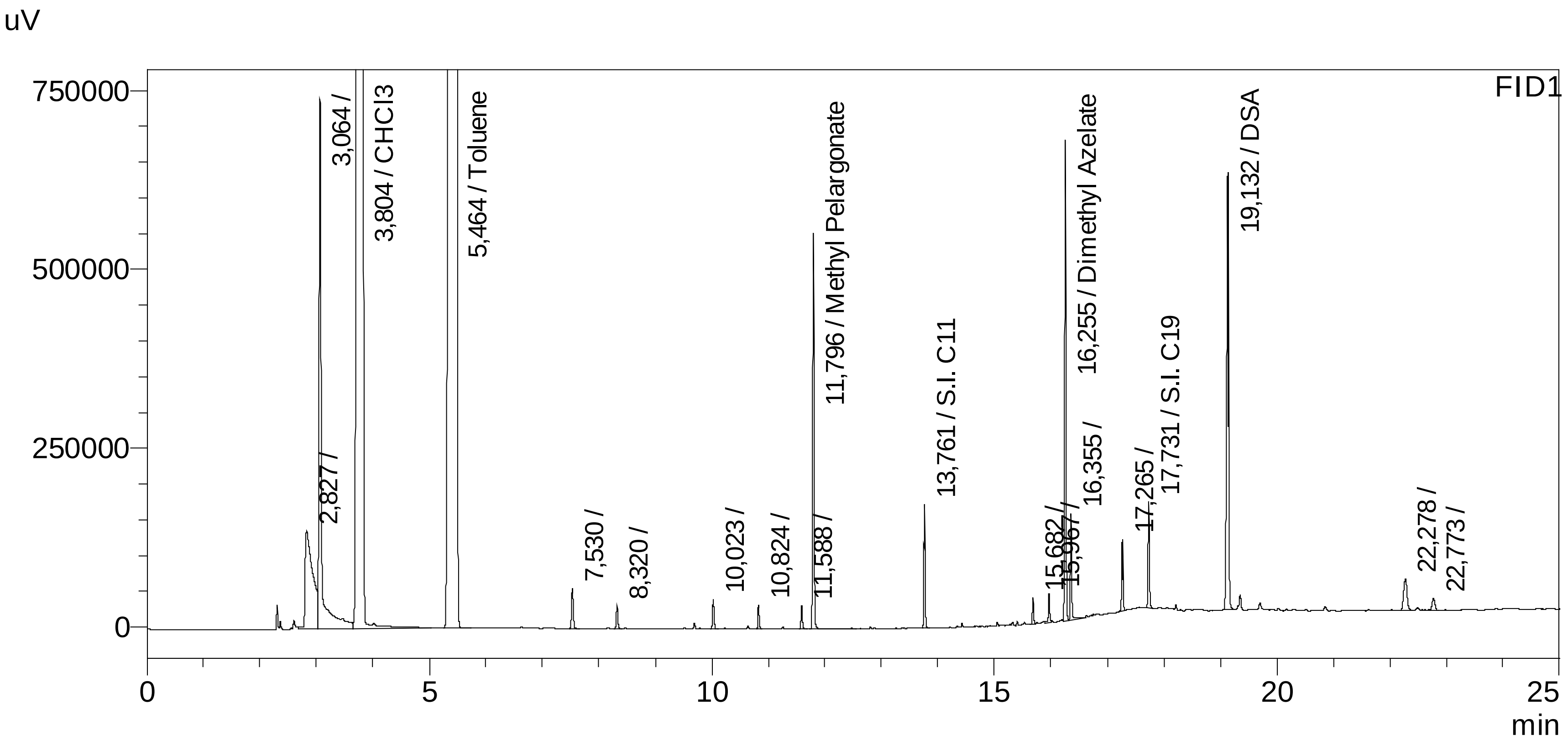
Products analysis: ***chromatograms***

Typical chromatogram of scissed oil (batch Reaction) Test



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Products analysis: ***chromatograms***

Problems:

- ***Several products***

Determination **only** of products of interest for conversions & yields evaluation:

- ***Methyl pelargonate***
- ***Methyl azelate***
- ***9,10 – dimethoxymethylstearate***

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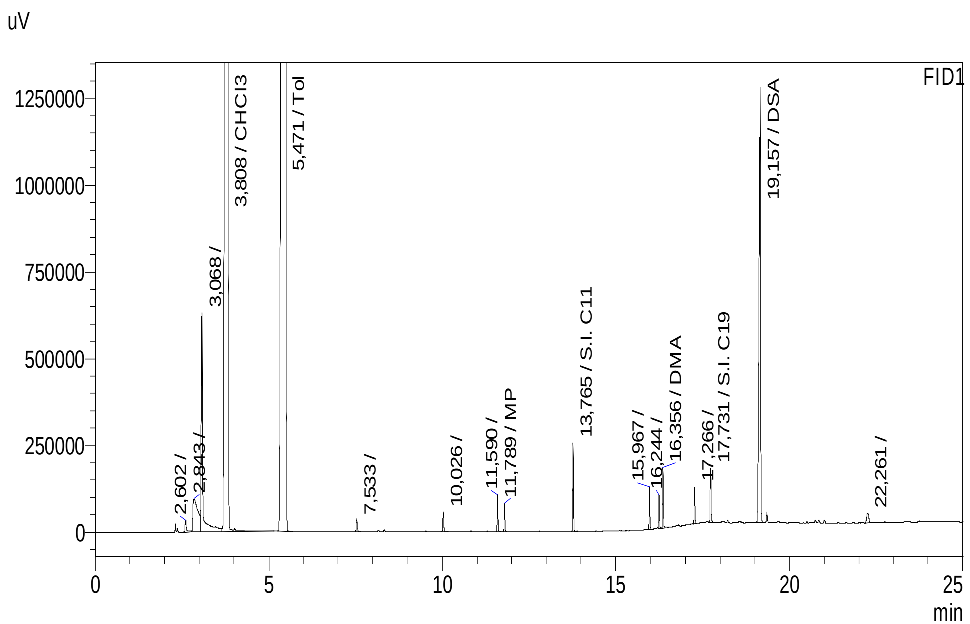
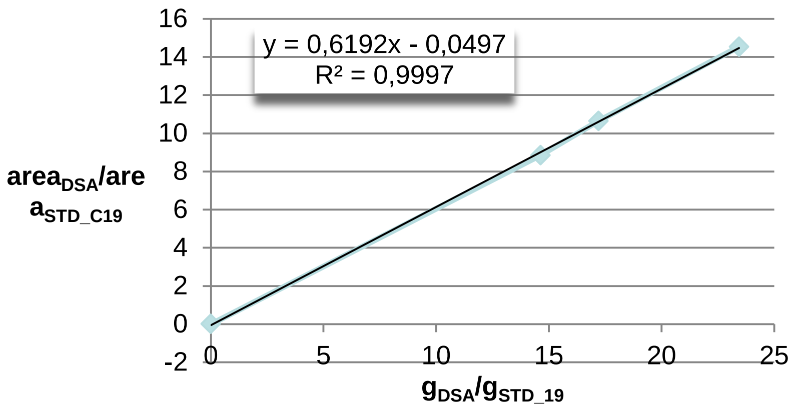
Calibration

DSA Novamont (9,10-dimethoxymethylstearate):

g_{DSA}/g_{STD_19}	$area_{DSA}/area_{STD\_C19}$
0	0
14,63021092	8,849167136
17,20324708	10,64171978
23,43862995	14,53458703





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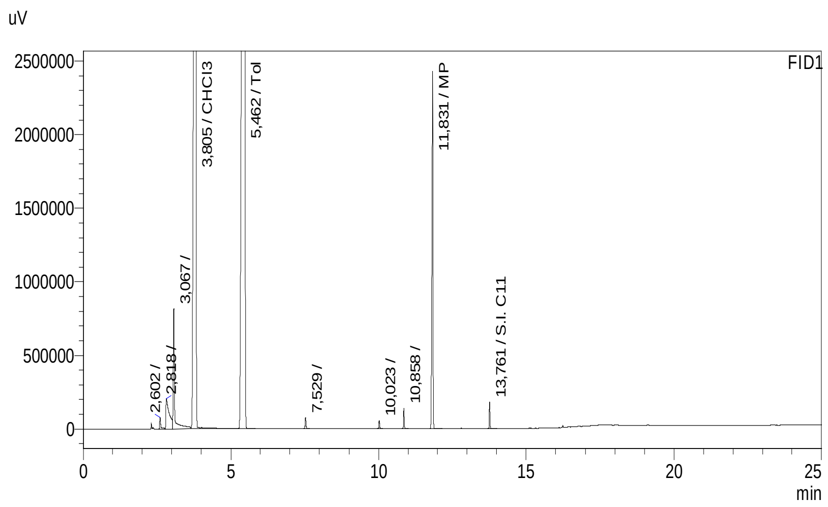
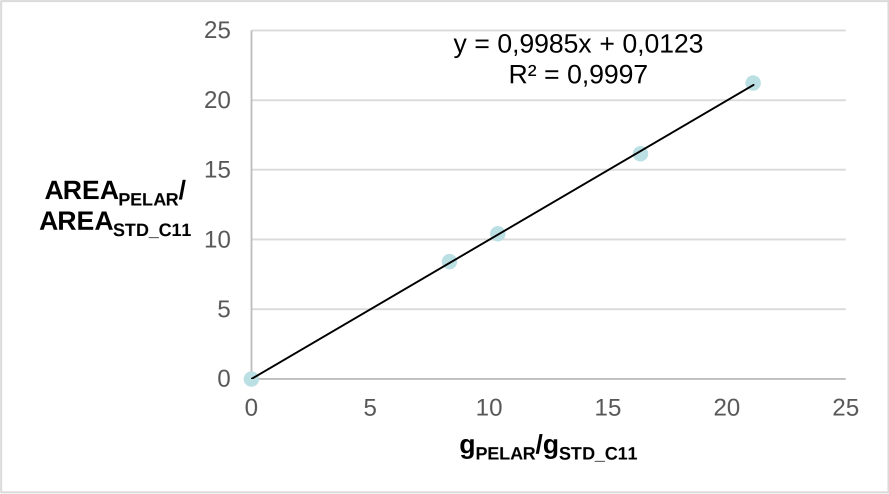
Calibration

Methyl Pelargonate:

g_{PELAR}/g_{STD_C11}	$AREA_{PELAR}/AREA_{STD\_C11}$
0	0
21,1150614	21,22217984
10,3685592	10,41447768
8,34048398	8,4030506
16,3787232	16,14129687





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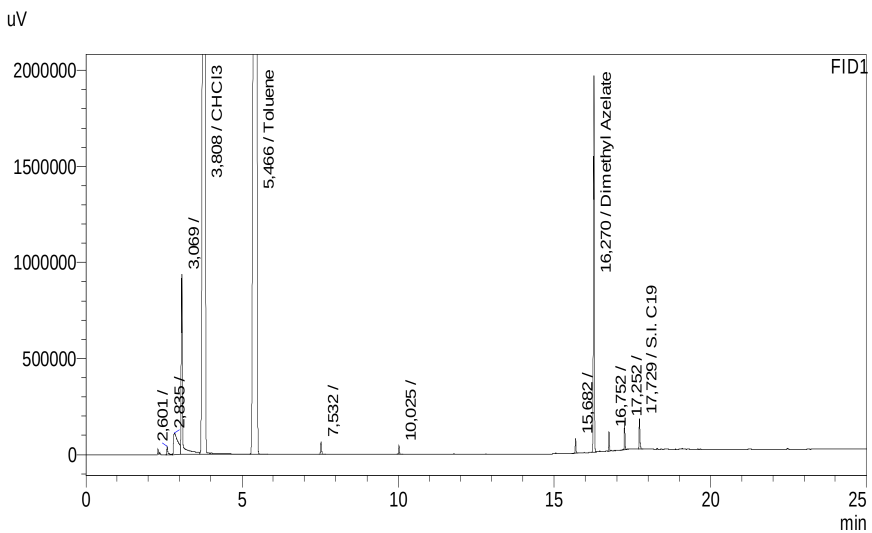
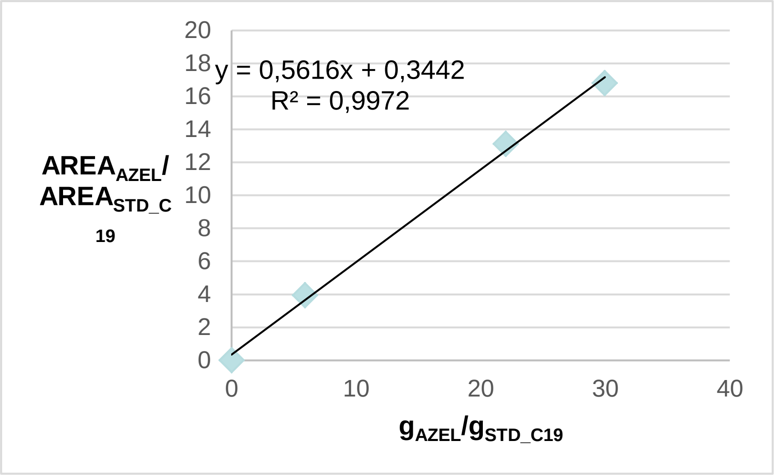
Calibration

Dimethyl Azelate:

g_{AZEL}/g_{STD_C19}	$AREA_{AZEL}/AREA_{STD\_C19}$
0	0
5,89613972	3,946013554
22,0062238	13,12062388
29,9590944	16,80569477





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Catalysts Tested

- Blank Test
- $CoAc_2/Na_2WO_4$
- Au/TiO_2 (Au = 1,5 % wt.)
- $CoFe_2O_4$ (ovo-016)
- Fe_3O_4 (ovo-036)
- Fe_3O_4 (ovo-036) + $Na_2WO_{4(aq)}$
- $CuFe_2O_4$ (ovo-017)
- $CuFe_2O_4$ (ovo-017) + $Na_2WO_{4(aq)}$
- $NiFe_2O_4$ (ovo-029)
- $NiFe_2O_4$ (ovo-029) + $Na_2WO_{4(aq)}$
- $H_3PW_{11}\mathbf{Fe}O_{40}$ (POM4)
- CuO (Merck)
- CuO/Al_2O_3 (Sigma Aldrich Pcode:1001502365)

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FIRST 2RUN

Catalyst Tested: **CATALYSTS**

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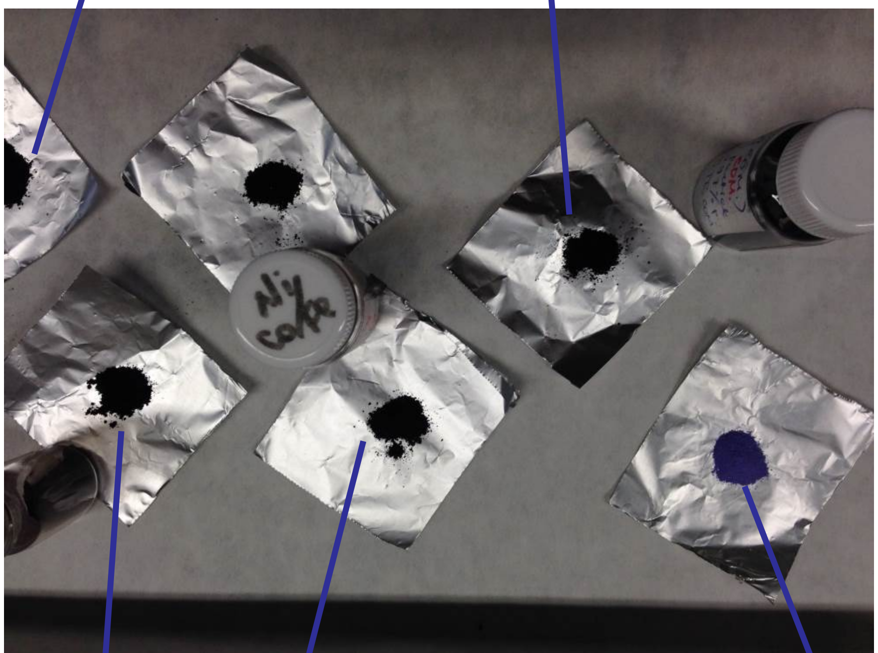

Au/TiO_2

Fe_3O_4

$CoFe_2O_4$

$NiFe_2O_4$

$CoAc_2/Na_2WO_4$

$CuFe_2O_4$

CuO/Al_2O_3

CuO

POM4

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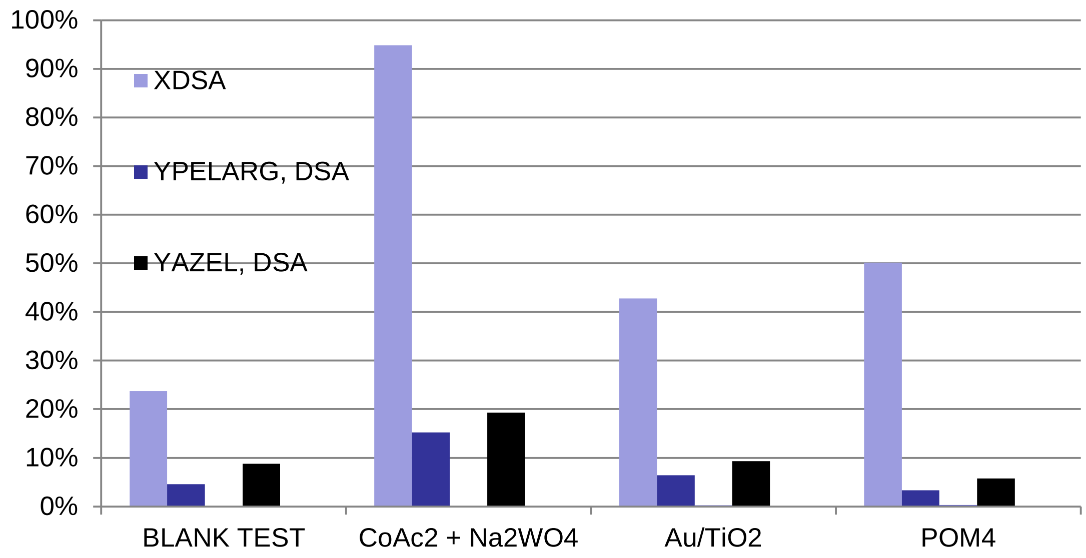
Activity & Results

- Au/TiO_2 (Au = 1,5 % wt.)
- H_3PW_{11}**Fe**O_{40} (POM4)



$$\text{CONVERSION} = X_{DSA} = \frac{m^i{}_{DSA} - m^f{}_{DSA}}{m^i{}_{DSA}}$$

$$\text{YIELDS} = \mathrm{Y}_{\mathrm{i},DSA} = \frac{m^f{}_i}{m^i{}_{DSA}}$$

$$\text{PRODUCTIVITY} = \mathrm{P}_{\mathrm{i},DSA} = \frac{m^f{}_i}{t_{BATCH} \cdot m_{\mathrm{CAT}}}$$

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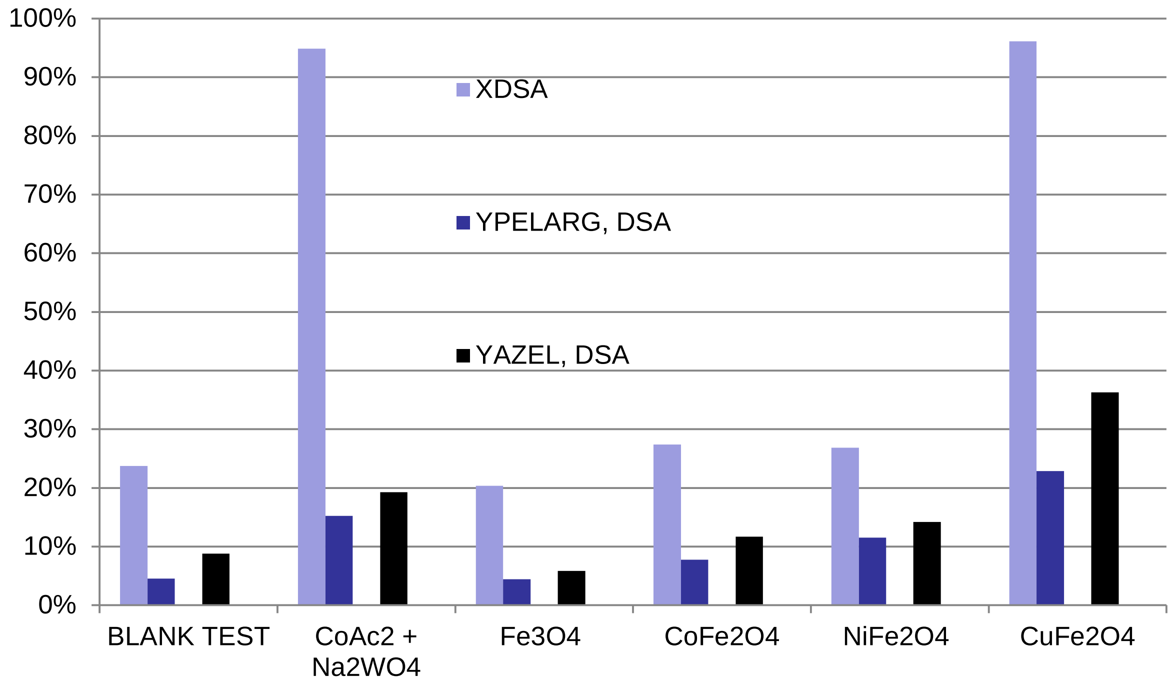
Activity & Results

Ferrites:

- Fe_3O_4 (ovo-036)
- $CoFe_2O_4$ (ovo-016) → is the cobalt the active metal? No!
- **$CuFe_2O_4$ (ovo-017)**
- $NiFe_2O_4$ (ovo-029)



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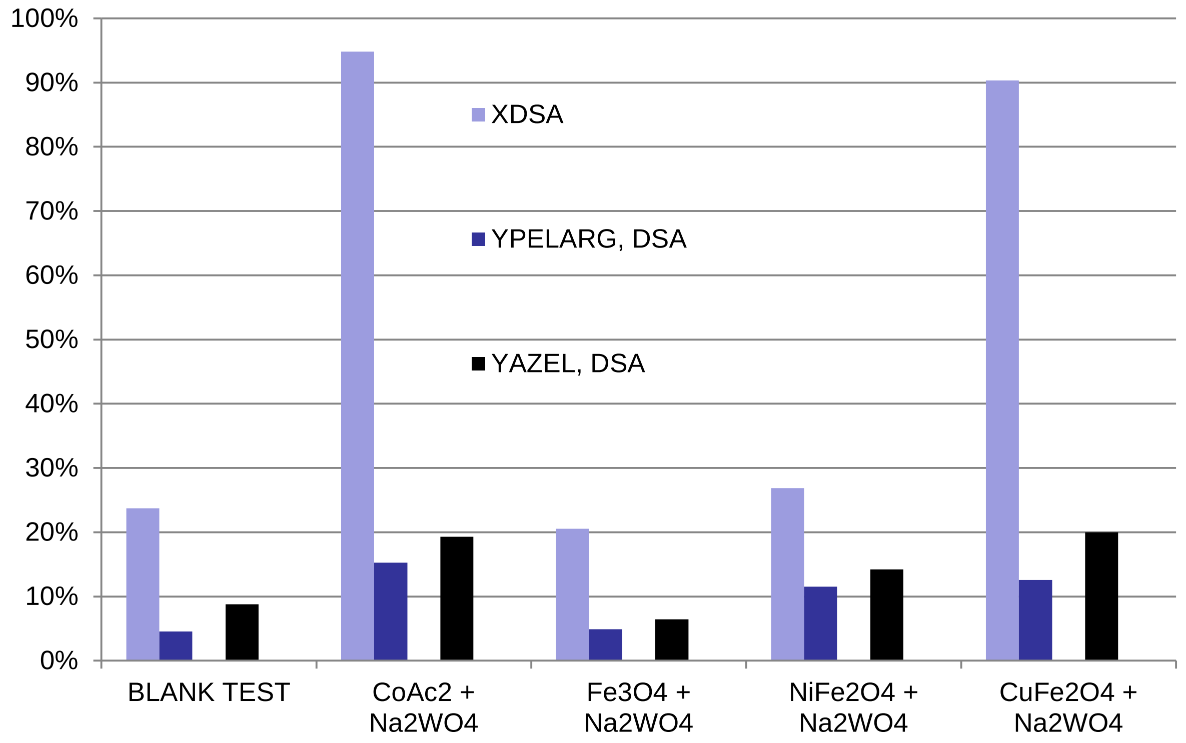
Activity & Results

Ferrites with Tungstate → Synergic effects??

- F_3O_4 (ovo-036) + $Na_2WO_{4(aq)}$
- CuF_2O_4 (ovo-017) + $Na_2WO_{4(aq)}$
- NiF_2O_4 (ovo-029) + $Na_2WO_{4(aq)}$

In this case, we added an aqueous solution of WO_4^{2-} to the system.



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Catalyst Tested

$CuFe_2O_4$ (ovo-017) → **Copper as active phase**

- CuO (Merk) — $ASS_{B.E.T.} = 30\ m^2/g$
- CuO/Al_2O_3 (Sigma Aldrich) — $ASS_{B.E.T.} = 170\ m^2/g$

Problem:

- leaching of Cu^{2+} from the oxide

Role of the **support**:

- avoid leaching of the Cupper
- increase the surface area

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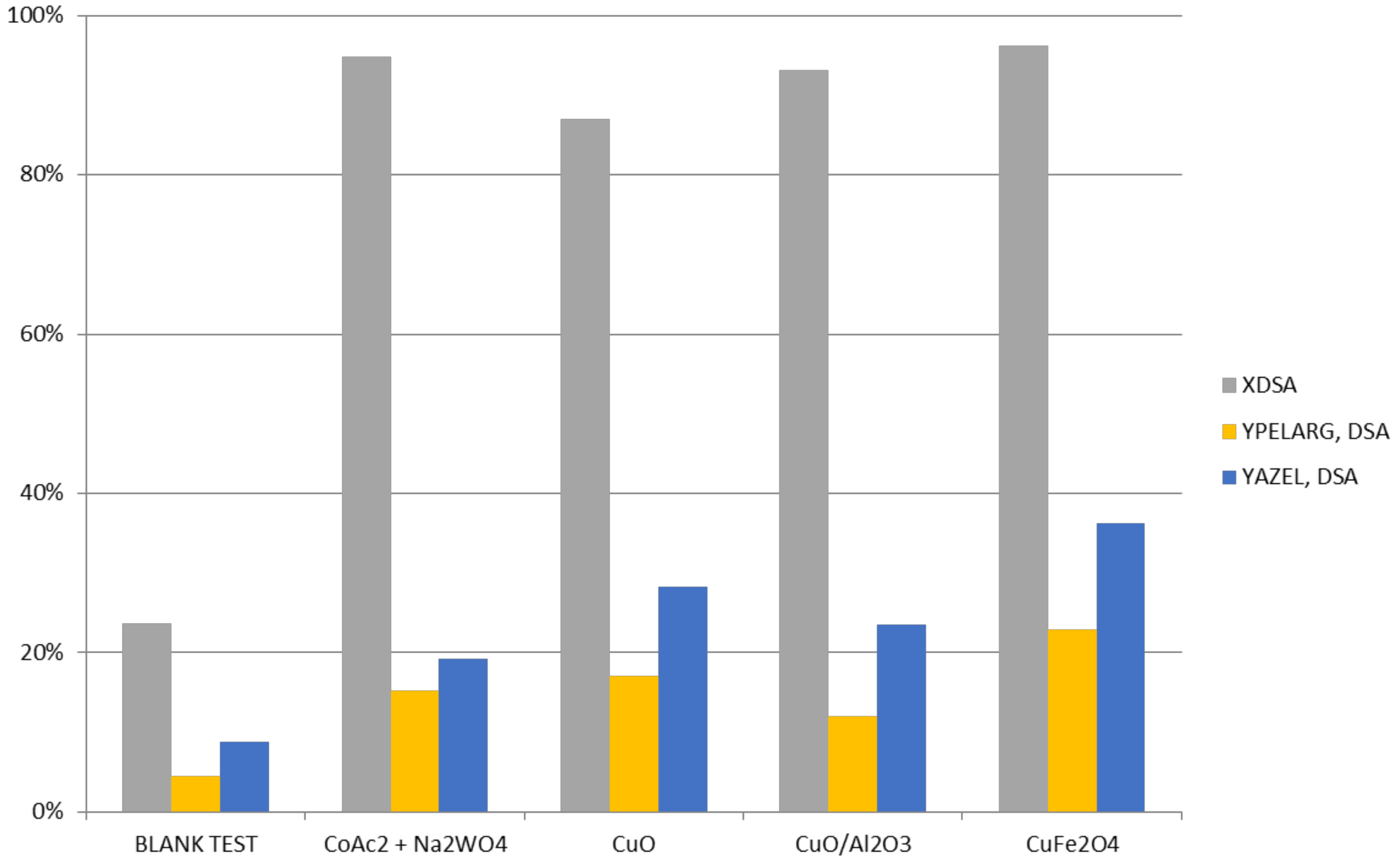
Catalysts Tested



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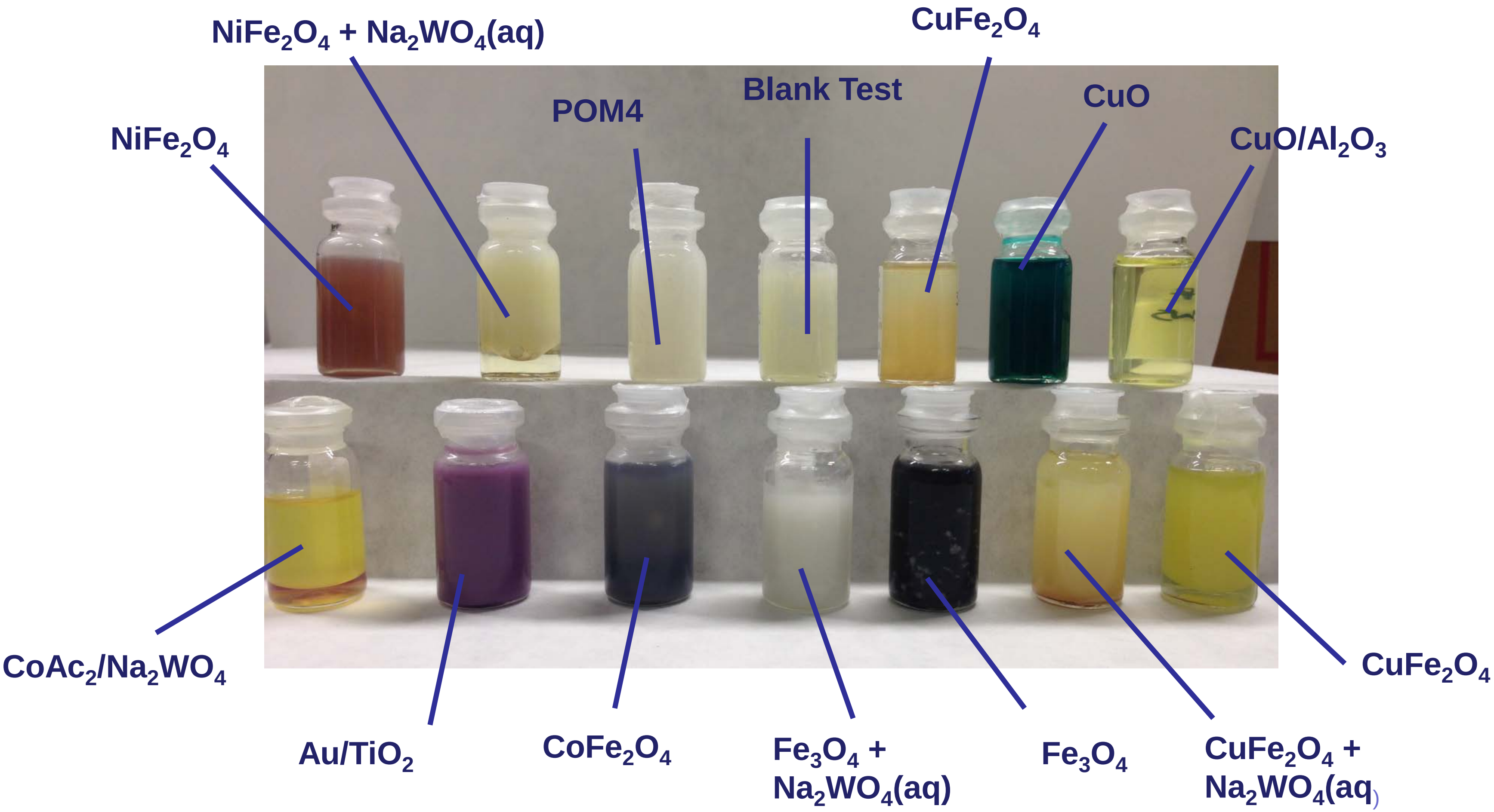
Catalyst Tested: **PRODUCTS**



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Next Steps

TASK 2.1.2. – Next steps:

- Optimise the analysis (close the mass balance): precise determination of DSA RF from a pure reference; identification and calibration of main by-products.
- Catalysts: identification of the "best catalyst" (based on CuO): amount of Cu loading ? Support ? Sinergy with Fe oxide ?
- Catalyst recyclability and reuse (regeneration necessary ?)
- Effect of reaction conditions (T, time, catalyst/oil ratio, O_2 pp)

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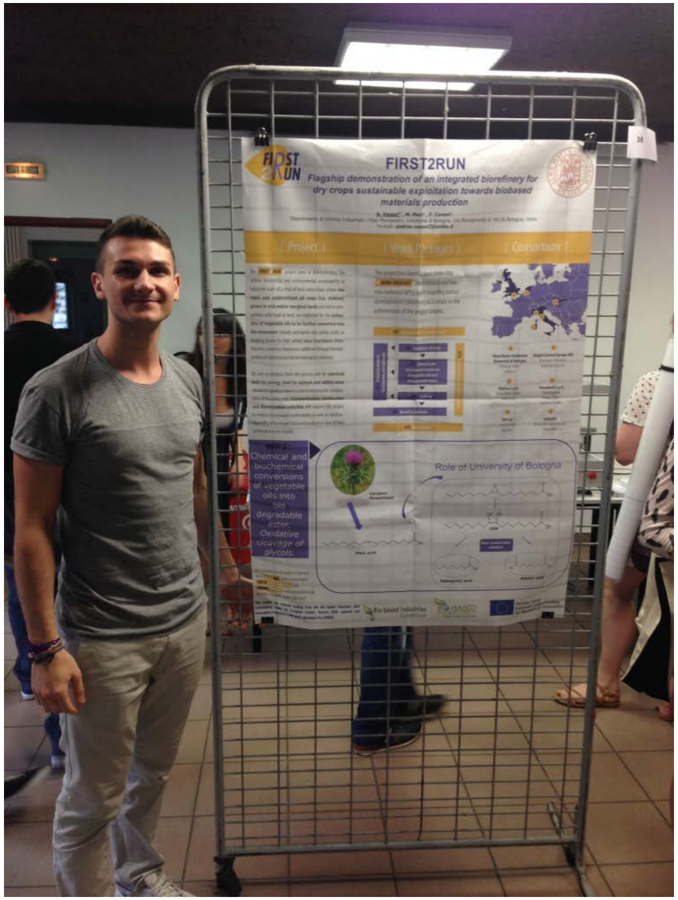
Dissemination activity.
Participation to
CatPrep2016 :
2nd EFCATS - CNRS EUROPEAN SUMMER SCHOOL ON CATALYST PREPARATION

Vogüe (F) 12-17 June 2016



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