CAMPUS MARE NOSTRUM
de Excelencia Internacional

III Encuentro Ingeniería Energía CMN

Red Mediterránea de Investigación:

QUÍMICA SOSTENIBLE

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QUİMICA SOSTENIBLE

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1. UNIVERSIDAD DE MURCIA

Grupo de Investigación: Biotecnología (E-060-04).

1.1. Pedro Lozano Rodríguez. Catedrático de Bioquímica y Biología Molecular

1.2. Susana Nieto Cerón. Profesora Asociada

1.3. Juana María Bernal Palazón. Profesora Asociada.

1.4. Celia Gomez. Colaboradora-Estudiante de Doctorado.

1.5. Angel Nicolas. Colaborador-Estudiante de Máster

Grupo de Investigación: Química de la Coordinación-Bioinorgánica (E-046-01)

1.6 Gregorio Sánchez Gómez. Catedrático de Química Inorgánica

2. UNIVERSIDAD POLITÉCNICA DE CARTAGENA

Grupo de Investigación: Aplicaciones Químico-Industriales

2.1. José Pérez Pérez. Prof. Titular Universidad Química Inorgánica

2.2. José Luis Serrano Martin. Prof. Titular Universidad Química Inorgánica

2.3. Luis García González. Prof. Titular Universidad. Química Inorgánica

2.4. Eduardo Pérez Pardo. Prof. Titular Universidad. Química Inorgánica

3. UNIVERSIDAD JAUME I – CASTELLON.

Grupo de de Investigación: Química Sostenible y Química Supramacromolecular (021)

3.1 Santiago V. Luis Lafuente. Catedrático de Química Orgánica.

3.2. M. Isabel Burguete Azcarate. Catedrática de Química Orgánica

3.3 Eduardo García-Verdugo Cepeda. Prof. Titular Química Orgánica

3.4. Belen Altava Benito. Prof. Titular Química Orgánica.

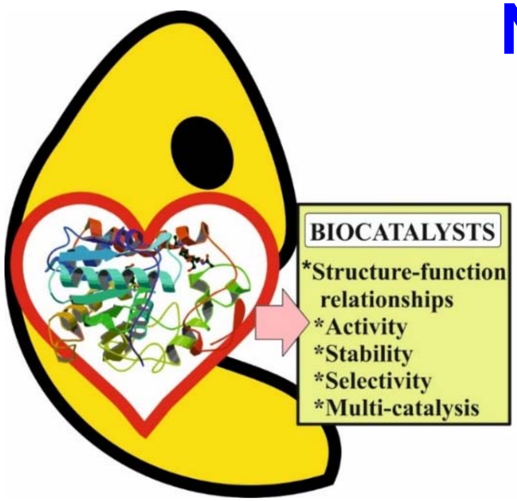
3.5. Raul Porcar García. Post Doctoral

4. INSTITUTO DE CATALISIS Y PETROLQUUÍMICA - CSIC

Grupo de Investigación: Optimización de biocatalizadores y bioprocesos enzimáticos

4.1 Roberto Fernandez Lafuente. Profesor de Investigación

AIMS: CLEAN CHEMICAL PROCESS IN NON-AQUEOUS MEDIA



S ⟶ **P**

100% Yield
100% Steroselectivity

- No by-products
- No air emissions
- No wastes
- Full recovery and reuse of biocatalysts, solvents, etc.
- Direct obtention of nearly pure produts

- **SUPERCRITICAL FLUIDS**
- **IONIC LIQUIDS**

P. Lozano 2016

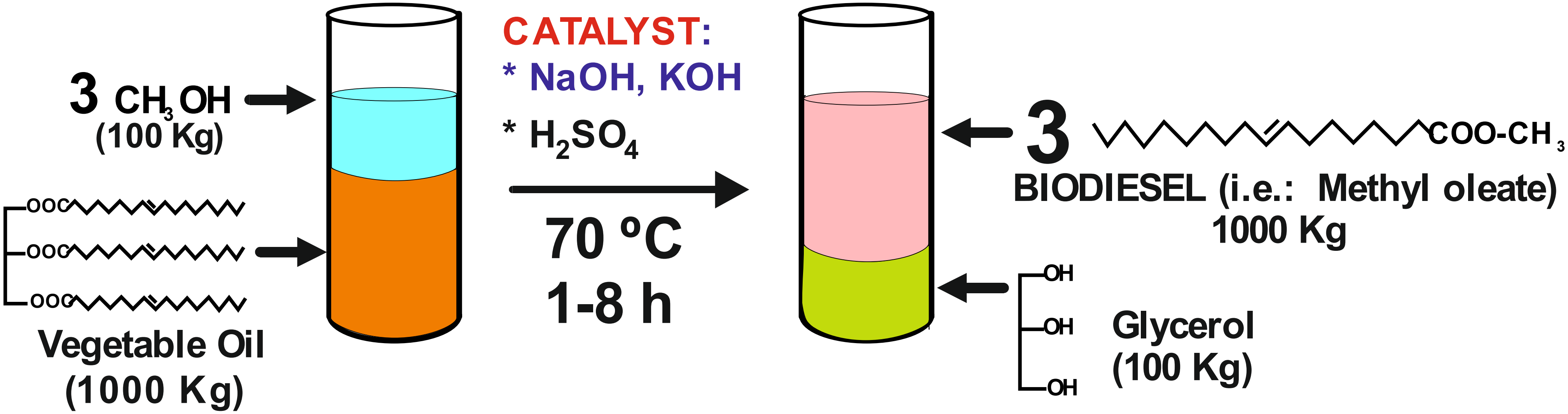
Example:

BIOCATALYTIC SYNTHESIS OF BIODIESEL IN IONIC LIQUIDS

A Green Technology for Producing Green Biofuels

THE PRODUCTION OF BIODIESEL

Transesterification reaction



BIPHASIC REACTION MEDIUM

TOO MUCH PROBLEMS!!:

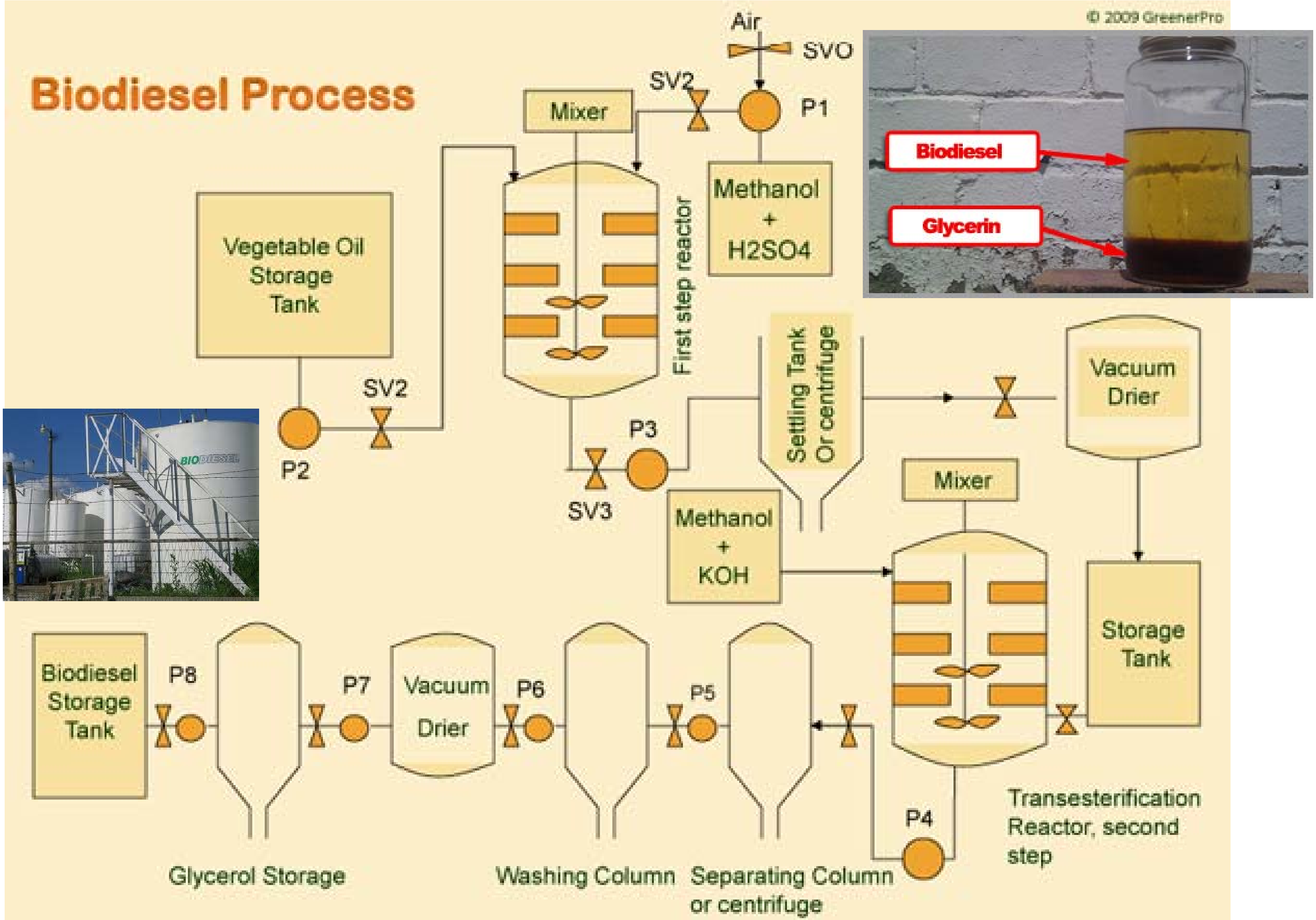
<u>Biphasic systems</u>, Low selectivity, catalyst recovery, water content, soaps, etc.

2. Separation of glycerol: Centrifugation

3. Washing of biodiesel with water : WASTEWATER !!

4. Drying of biodiesel

The Industrial Production of Biodiesel



THE PRODUCTION OF BIODIESEL

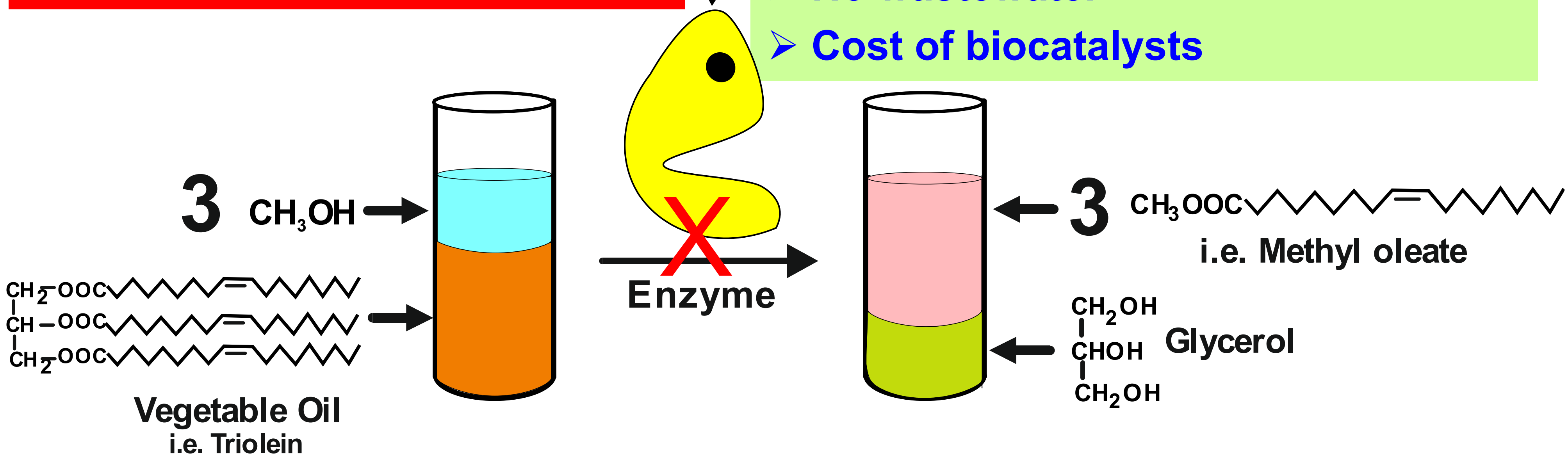
Fatty acid methyl esters (i.e. methyl oleate)

Obtained by transesterification between triacylglycerides and 1-alkanols catalyzed by:

Biocatalysts

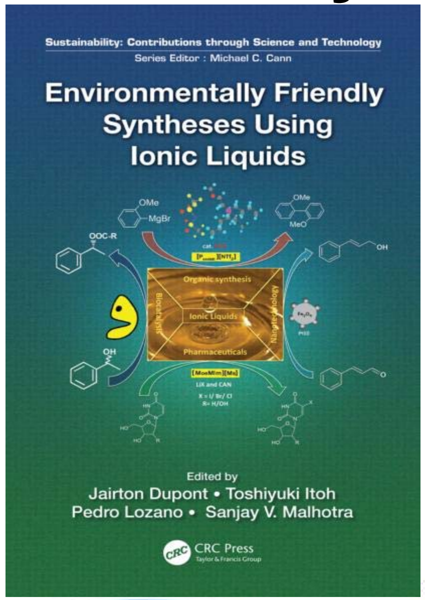
BIPHASIC REACTION MEDIUM

- Low activity !!
- Very high reaction selectivity
- Fast enzyme deactivation by MeOH
- No wastewater
- Cost of biocatalysts



IONIC LIQUIDS: Liquid comprised entirely by IONS

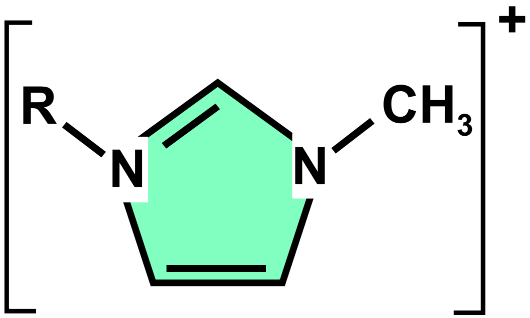
- **NON-VOLATILE, Non-flammable, High thermal stability**
- **Wide temperature range for liquid phase**
- **Good solvents**
- **Tunable solvent properties**



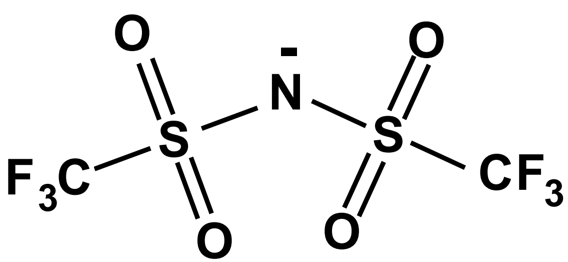
IONIC SOLVENTS vs MOLECULAR SOLVENTS

Example:

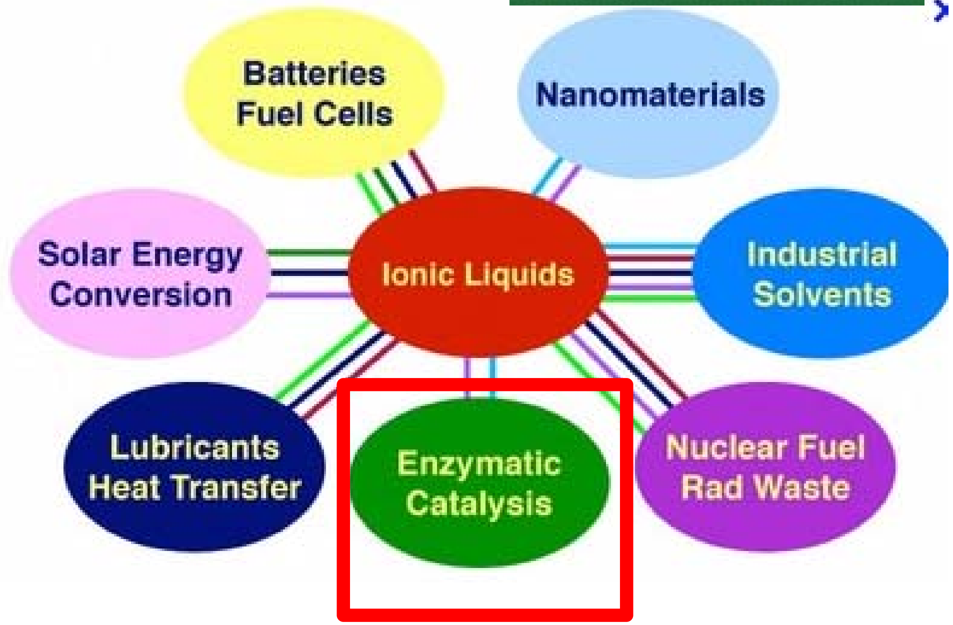
Cation



Anion



NTf_2^-

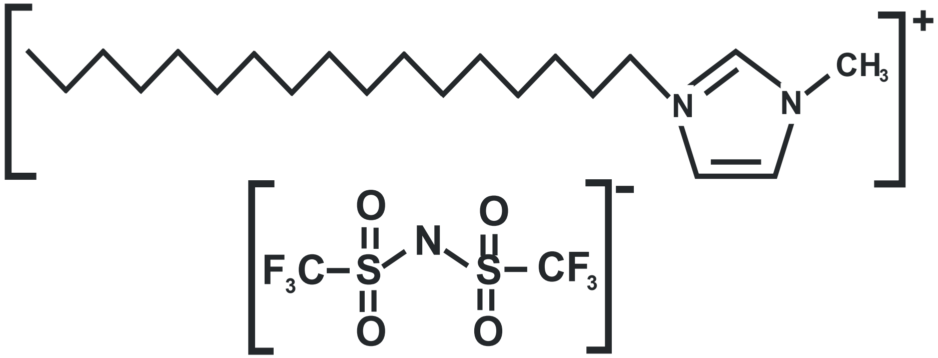


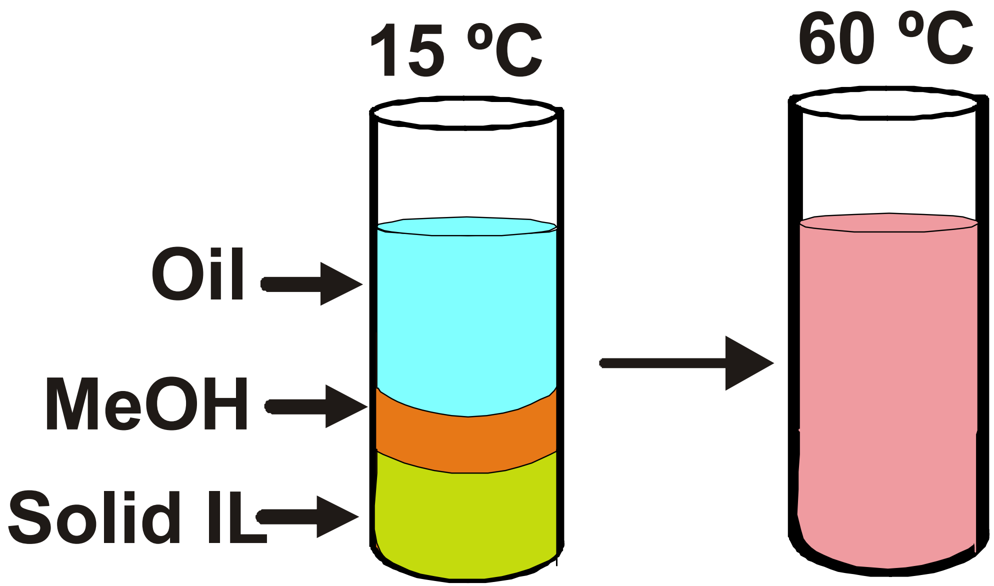
Green Solvents? ⇨ FULL RECOVERY AND REUSE

SLILs ABLE TO DISSOLVE VEGETABLE OIL AND MeOH

ILs based on large alkyl-side chain in cation

i.e. [C18mim] [NTf_2], [C18tma] [NTf_2],

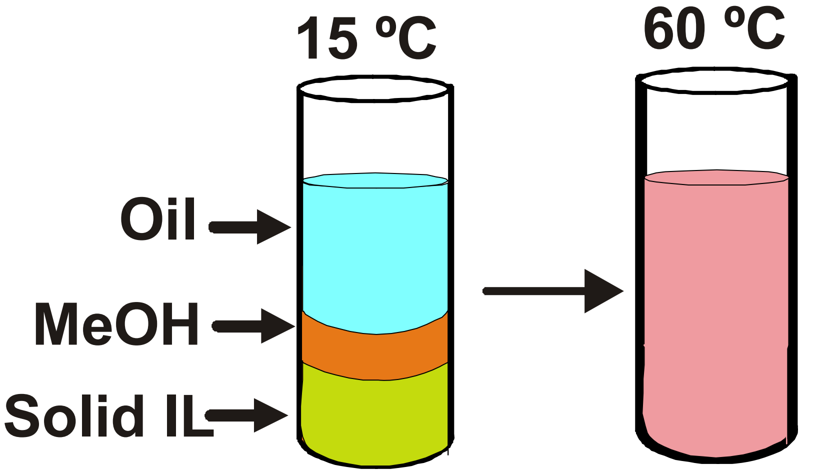


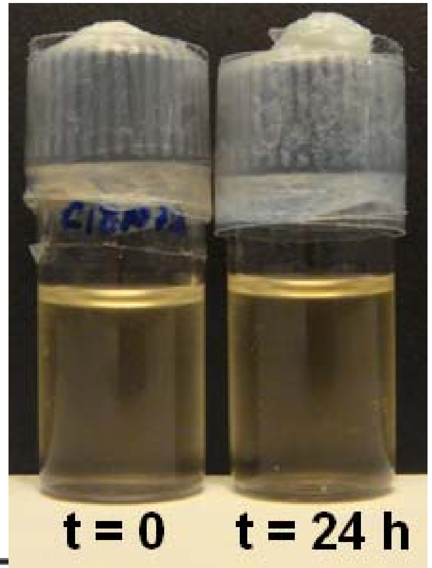


IL	Melting Point (ºC)
[C18mim] [NTf_2]	53
[C18mim] [PF_6]	82
[C18mim] [BF_4]	60
[C16mim] [NTf_2]	46
[C14mim] [NTf_2]	33
[C12mim] [NTf_2]	< 20

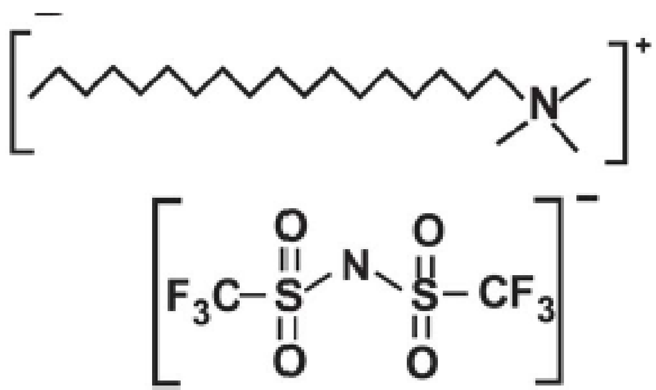
Lozano *et al*. *ChemSusChem*. 2010, 3, 1359 – 1363

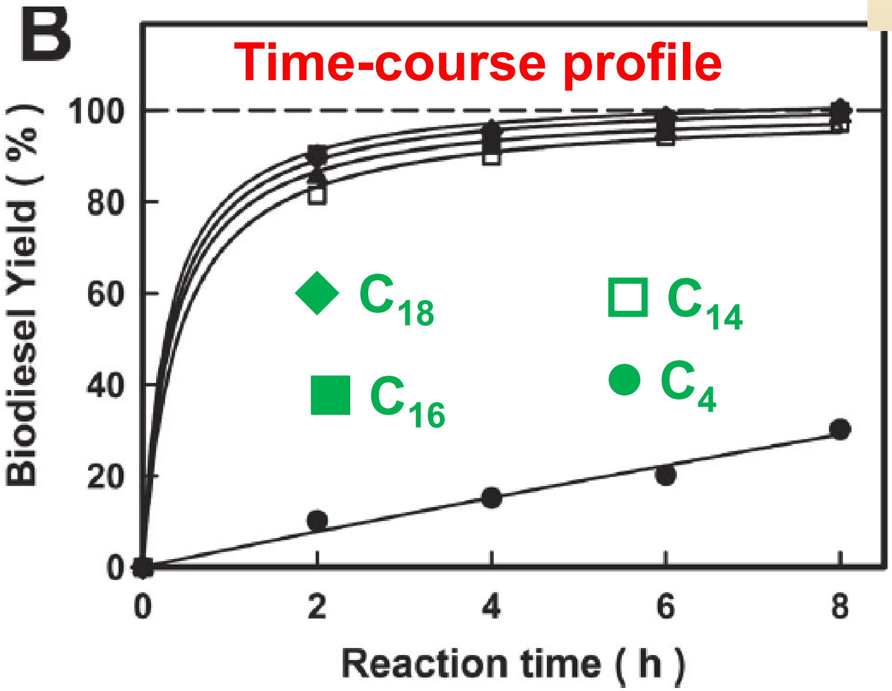
Exp. 1. BIOCATALYTIC SYNTHESIS OF BIODIESEL IN SLILs

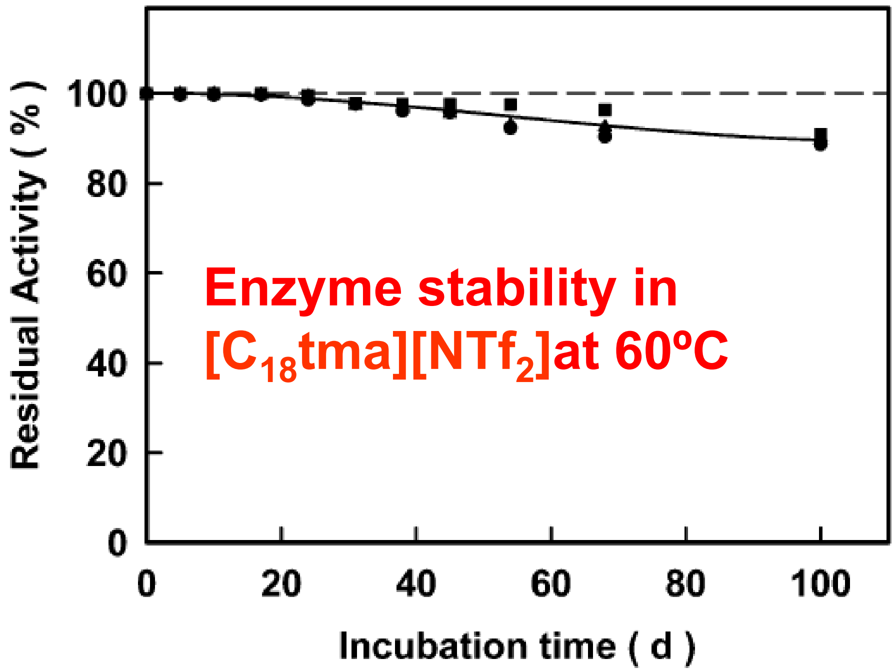




$[C_{18}tma][NTf_2]$



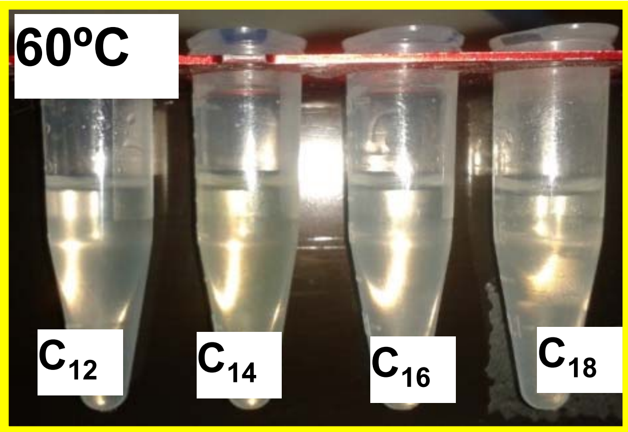




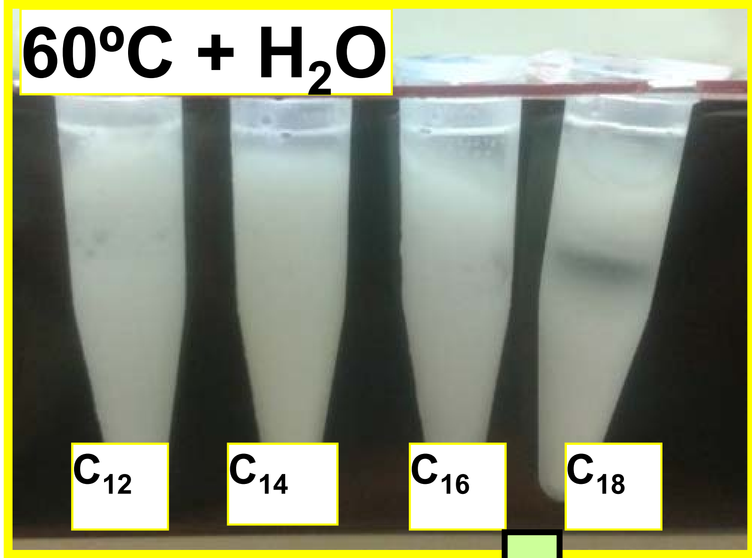
Lozano *et al*.. *ChemSusChem*. 2010, 3, 1359 – 1363

SEPARATION OF BIOFUELS AND GLYCEROL FROM SLILs

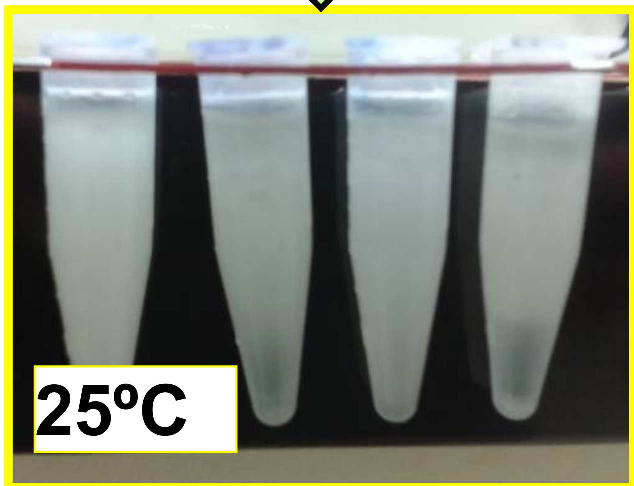
Substrate: TRIOLEIN



Addition of water



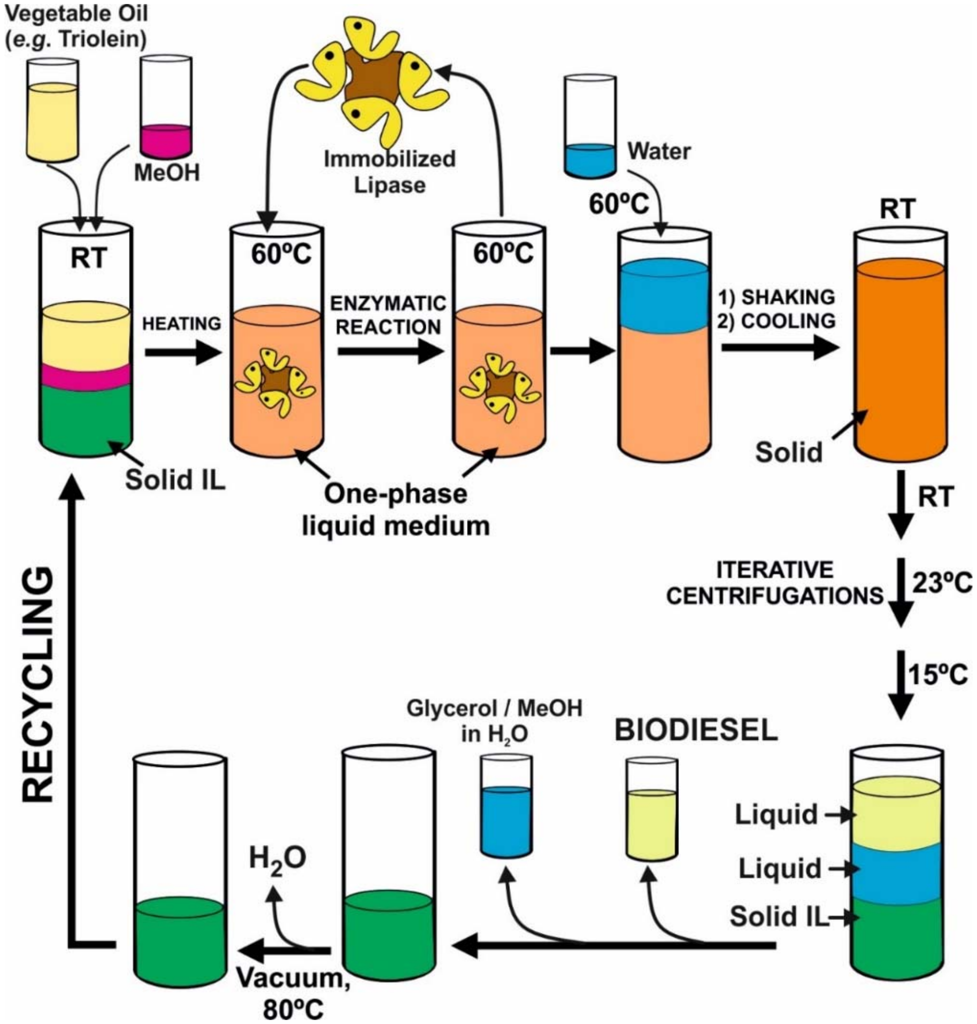
COOLING

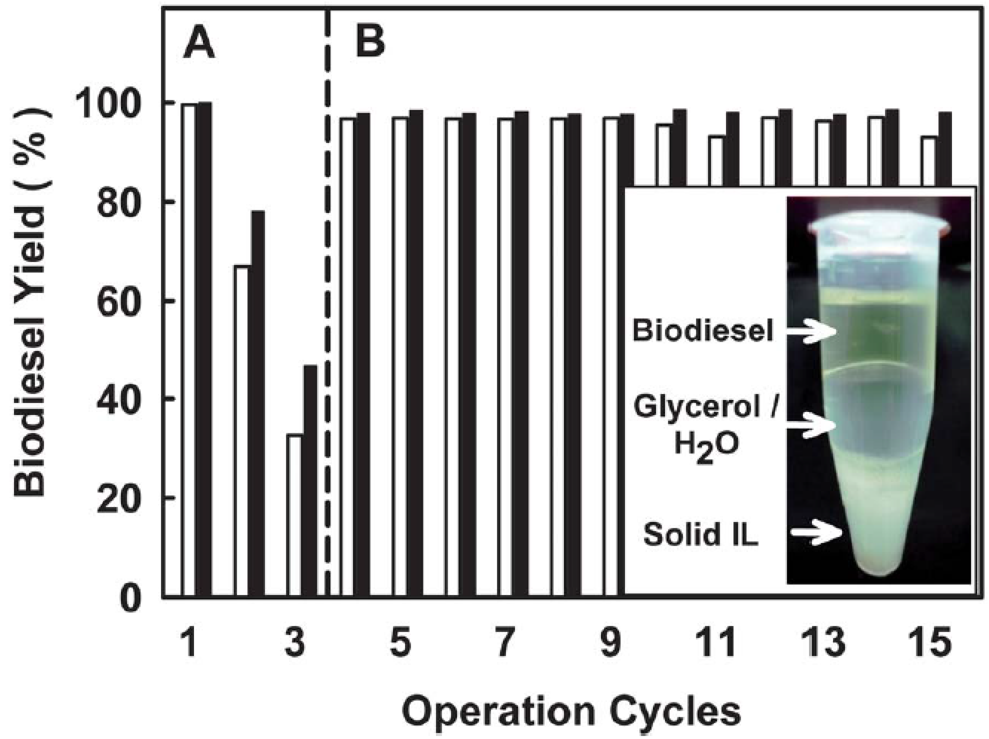


Three centrifugation steps (15 min) at 25, 20 and 15 ºC

Lozano *et al.*, How to produce biodiesel easily using a green biocatalytic approach in sponge-like ionic liquids *Energy Environ. Sci.* 2013, 6, 1328-1338

RECOVERY AND REUSE OF SLILs



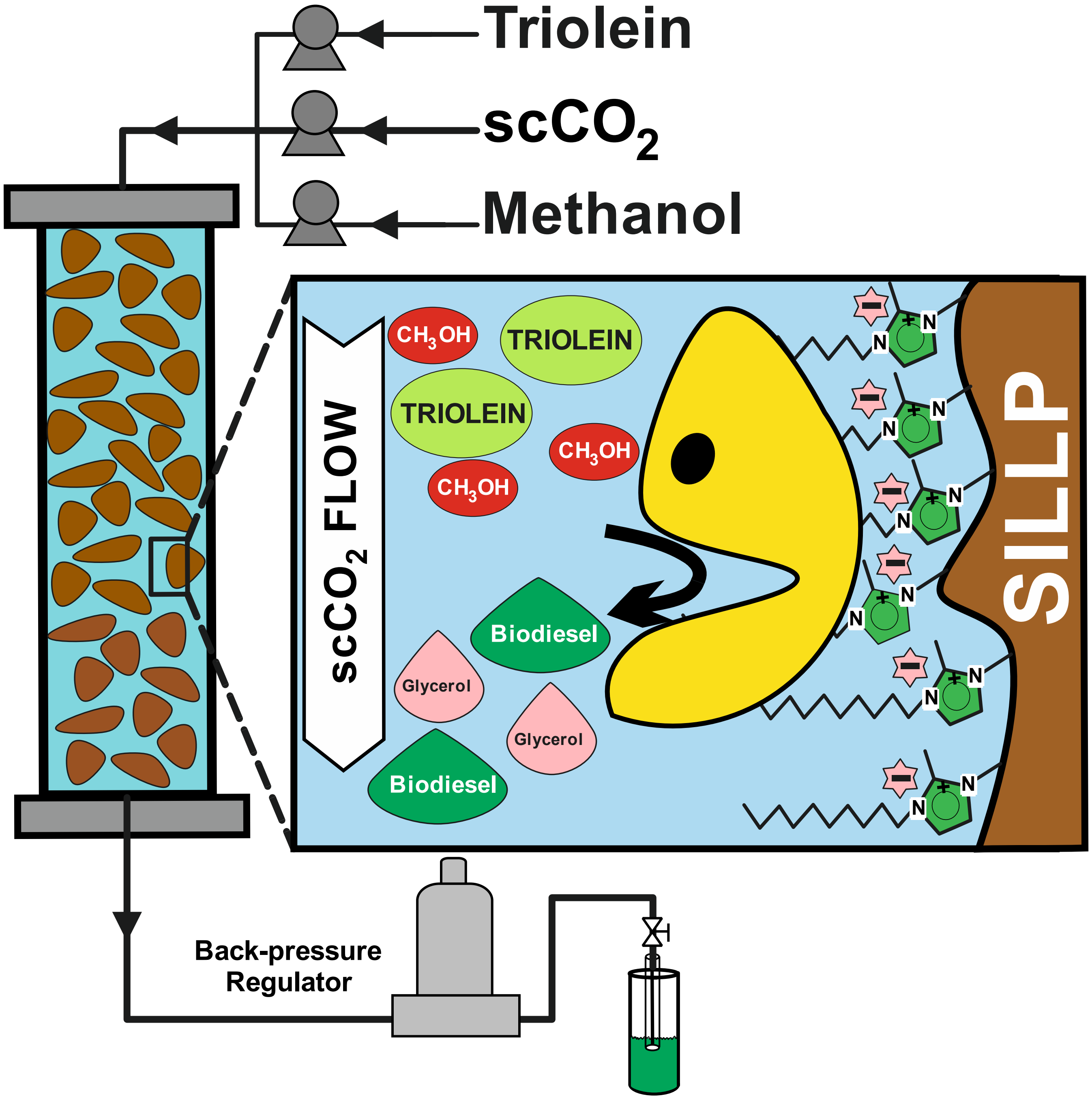


A: No washing biocatalyst particles with *t*-BuOH

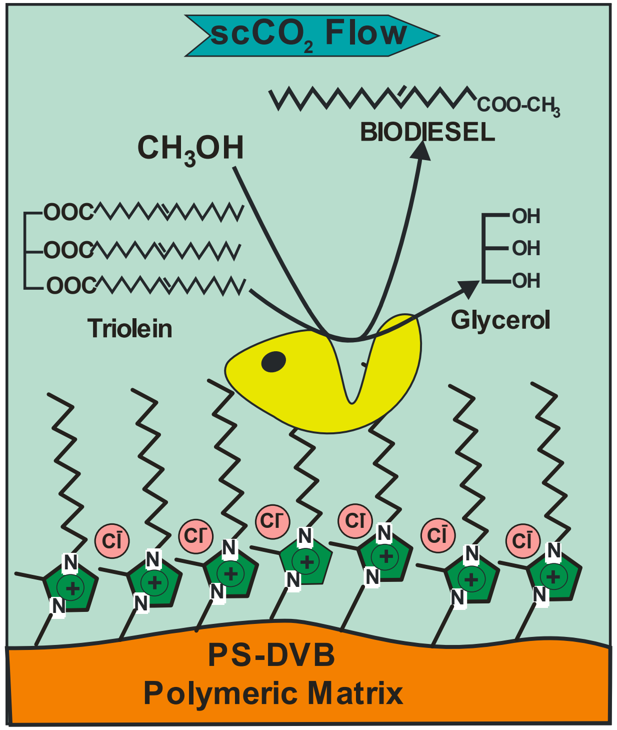
B: WASHING biotatalyst particles with *t*-BuOH

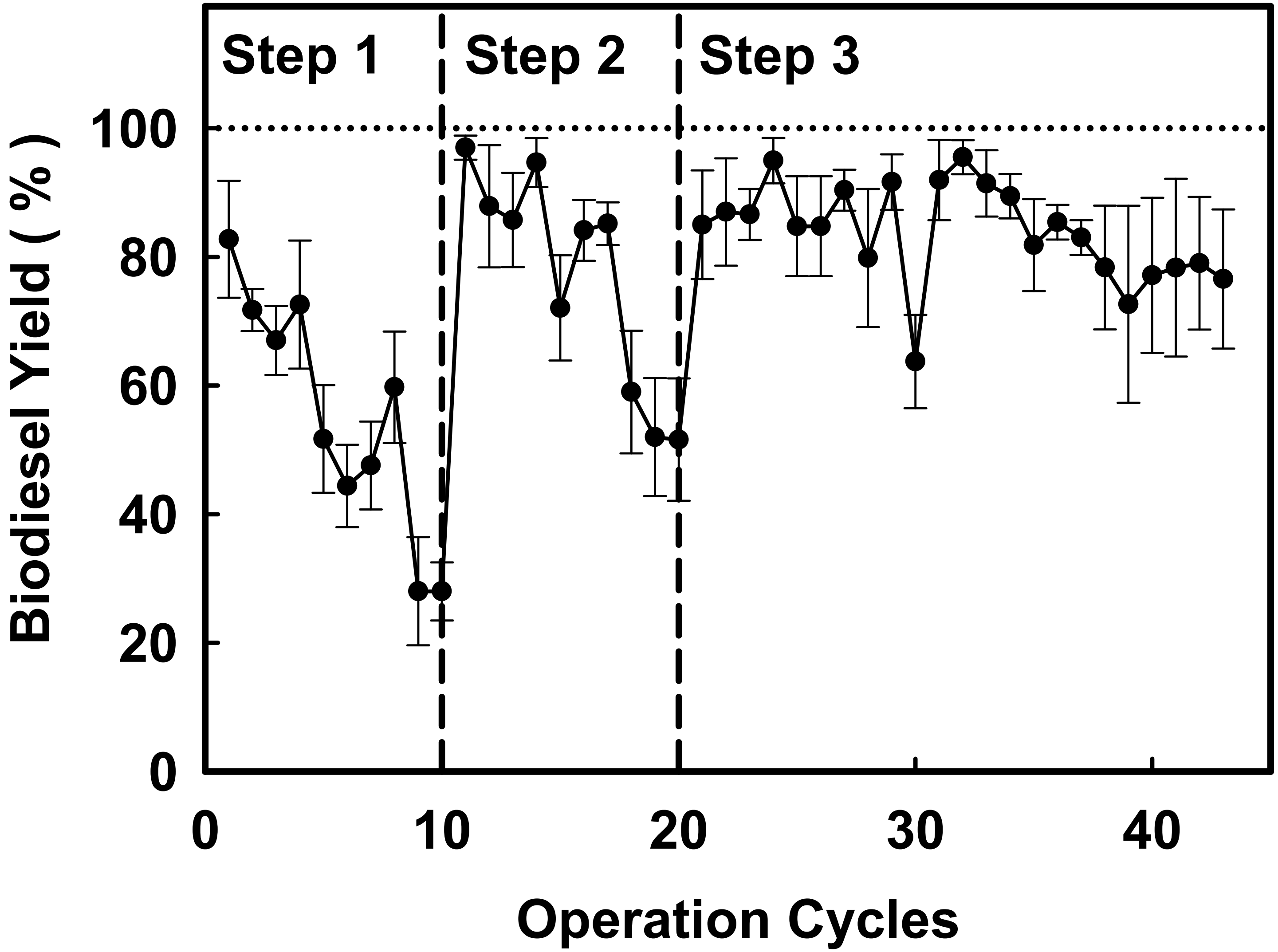
Lozano *et al.*,
How to produce biodiesel easily using a green biocatalytic approach in Sponge-Like Ionic Liquids. *Energy Environ. Sci.* 2013, 6, 1328-1338

Exp. 2 BIOREACTOR BASED ON LIPASE - SILLP FOR BIODIESEL SYNTHESIS IN $scCO_2$



Continuous BIODIESEL production by lipase-SILLP in $scCO_2$





Steps 1 and 2: Lipase-SILLPs washed with t-BuOH at the end of the step.

Step 3: Continuous feed of *t*-butanol (10.5 mmol/min).

Lozano, García-Verdugo *et al*., *ChemSusChem*, 2012, 5, 790 – 798

P. Lozano 2016

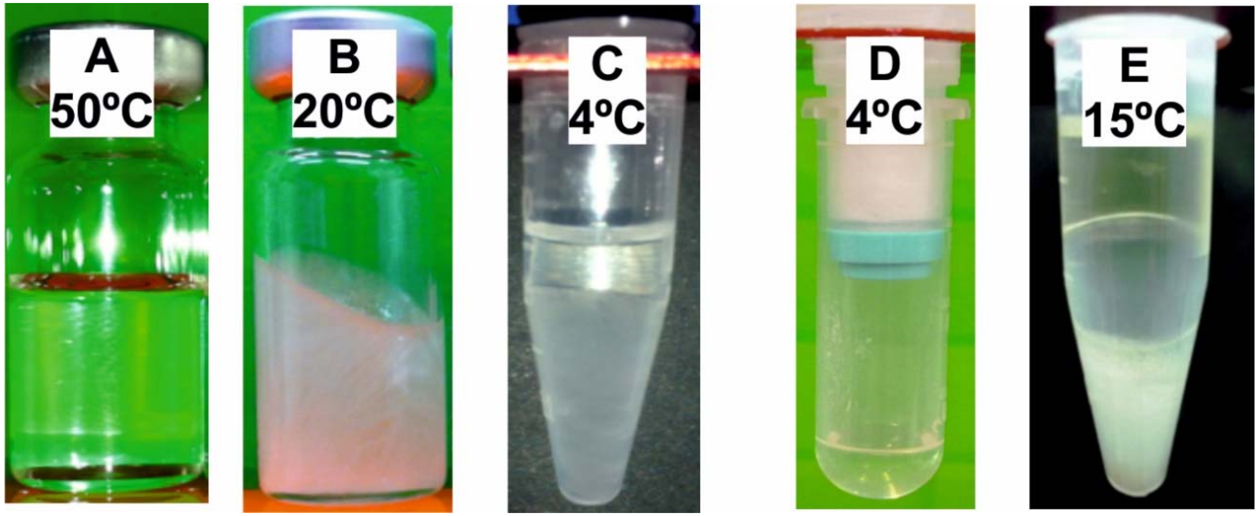
CONCLUSIONS

1. Excellent monophasic reaction media for BIOCATALYSIS

- **HIGH ACTIVITY AND OPERATIONAL STABILITY**

2 SLILs: Temperature switchable solid/liquid phases

- **Easy separation of pure products and SLILs for recovery and reuse**



A new clean and sustainable platform for synthesis and separation of pure products is demonstrated. !!

ACKNOWLEDGEMENTS

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- **CTQ2015-67927-R (MINECO/FEDER, Spain)**
- **08616/PI/08 (F (Fundación SENECA, CARM, Spain)**
- **Ramiro Martinez (Novozymes) for gift of enzymes**

GOBIERNO DE ESPAÑA | MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

REFERENCIA: CTQ2015-67927-R

ENTIDAD BENEFICIARIA: UNIVERSIDAD DE MURCIA

CENTRO: FACULTAD DE QUIMICA

INVESTIGADOR PRINCIPAL: PEDRO LOZANO RODRIGUEZ

TÍTULO: PROCESOS QUIMIO-ENZIMATICOS SOSTENIBLES DE INTERES INDUSTRIAL EN LIQUIDOS IONICOS TIPO ESPONJA Y FLUIDOS SUPERCRITICOS

PLAZO DE EJECUCIÓN: DEL 01/01/2016 AL 31/12/2018

f SéNeCa(+)
Agencia de Ciencia y Tecnología
Región de Murcia
Región de Murcia

Referencia: 19278/PI/14

Investigador principal: Lozano Rodriguez Pedro

Organismo: Universidad de Murcia

Título del proyecto: PROCESOS QUIMIO-ENZIMATICOS BASADOS EN LA QUIMICA VERDE: Aplicaciones para la obtención de biocombustibles de 2º generación y la valorización de glicerol

Fecha de inicio: 01/07/2015 al 30/06/2018
Duración: 3 AÑOS