New High-throughput reactor for biomass valorisation

Deasyl

UNIVERSIDAD DE MÁLAGA

2020

What is Mechanochemistry ?

For Academics

- **Planetary Ball Milling**
- **Dry Milling or Liquid assisted**
- **Run at ambiant temperature, never controlled heating**
- **Mostly Bacth however trends to make it continuous in last publications**

For Industrials

Grinding
Mixing
Mechanical Alloying for metallurgists

Mechanochemistry, is a chemical transformations initiated or sustained by mechanical force

Do, Jean-Louis & Friscic, Tomislav. (2016). Mechanochemistry: A Force of Synthesis. ACS Central Science

FEED the NEED

A+B -> C+D

A,B,C,D: Solid, Liquid or Gas

Breakthrough Innovation for Green Chemistry Reactors

High-throughput Reactor®

Breakthrough Innovation for Green Chemistry Reactors

- Continuous flow
- Heating controlled up to 200°C
- In Situ Induction
- Scale-up industrial

Our first innovation

High-throughput Reactor®

(patented)

WAB Deasyl

Advantages

- Micro-Emulsion
- Relevant for heterogeneous catalysisis
- Surface Regeneration
- Temperature increases reactants activity

- Stoichiometric ratios
- Avoid excess
- Solvant amount can be reduced

- Increase selectivity and yield
- Increase kinetic
- Decrease energetic cost
- Save energy versus batch Reactors

Combination of heating, catalyst and local pressure

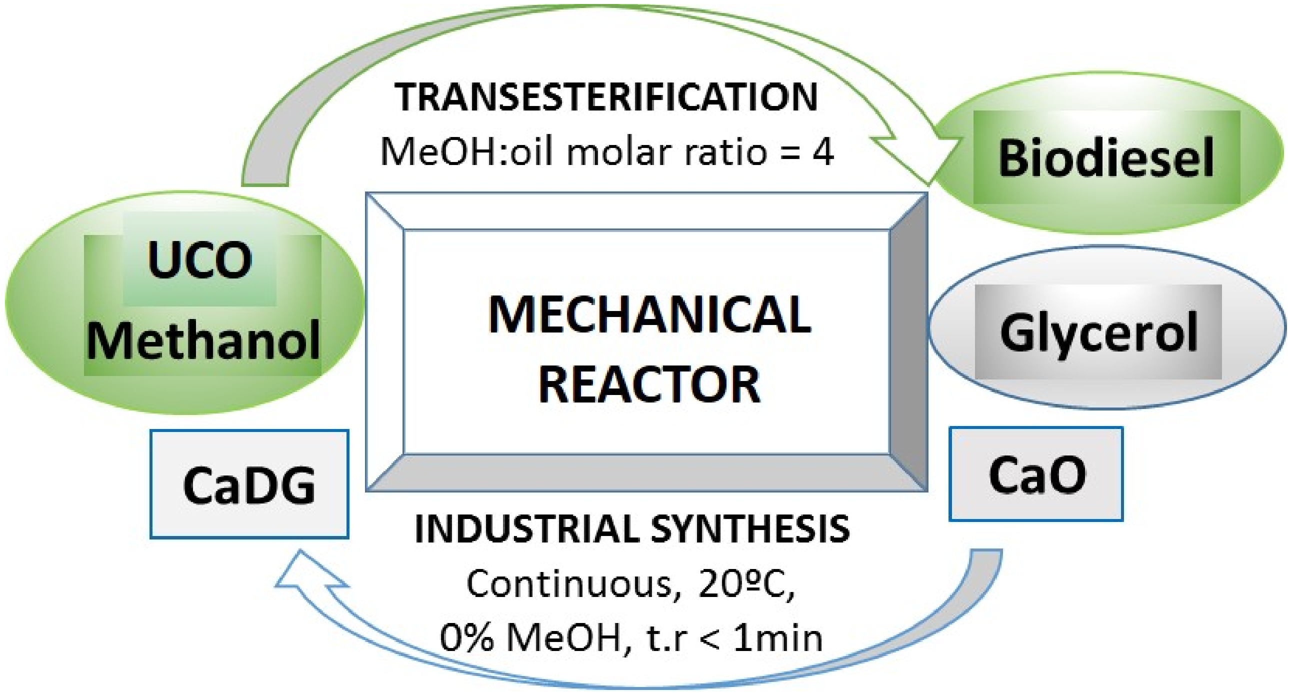
Deasyl

Why ?

Family	Temp	Type of reaction	Advantage	Catalyst	Carrier	Patent
Mineral	20°C	S + S -> S	Output 10t/h No other industrial process	No	Water	Calcium Zincate
Mineral	20°C	S + S -> S	Mechanical activation Decrease calcination temperature	No	Water	Aluminate
Mineral	20°C	S + S -> S	Mechanical activation Decrease calcination temperature	No	Water	Zincate
Organic	**20°C**	**L + S -> L + S**	**Yield, no solvents, decrease time** **Increase ROI**	**No**	**Glycerol**	**Calcium Diglyceroxide CadG**
Organic	**20-60°C**	**L + L -> L + L**	**Save energy vs conventional process,** **Decrease Mass Transfer Limitations** **Increase ROI**	**Heterogeneous CaDG**	**No need**	**Transesterification**
Organometallic	85°C	L + S -> L + S	Save energy vs conventional process Increase ROI	No	Glycerol	Zinc Glyceroxide
Organic	56°C	L + L + L -> L + L	Save energy vs conventional process Increase ROI	Yes	Yes	Pending
	Up to 200°C	*More to come!* *S+G, L+G*	*Free test for user to estimate ROI*		*Neutral liquid*	*More to come!*

Deasyl

1. Optimisation of CaDG



Formation reaction:

$CaO + 2\ C_3H_8O_3 \dashrightarrow Ca(C_3H_7O3)_2 + H_2O$

Reaction time: 2 h, 4h, 12h
Temperature: 50º C- 120º C
Batch condition, laboratory scale

Esipovich A. et al. J Mol Catal A Chem 2014; Lisboa FdaS. et al. J Braz Chem Soc.2014; Reyero I. et al.Chem Eng Res Des 2014; León-Reina et al., J. Catal. 300 (2013) 30;

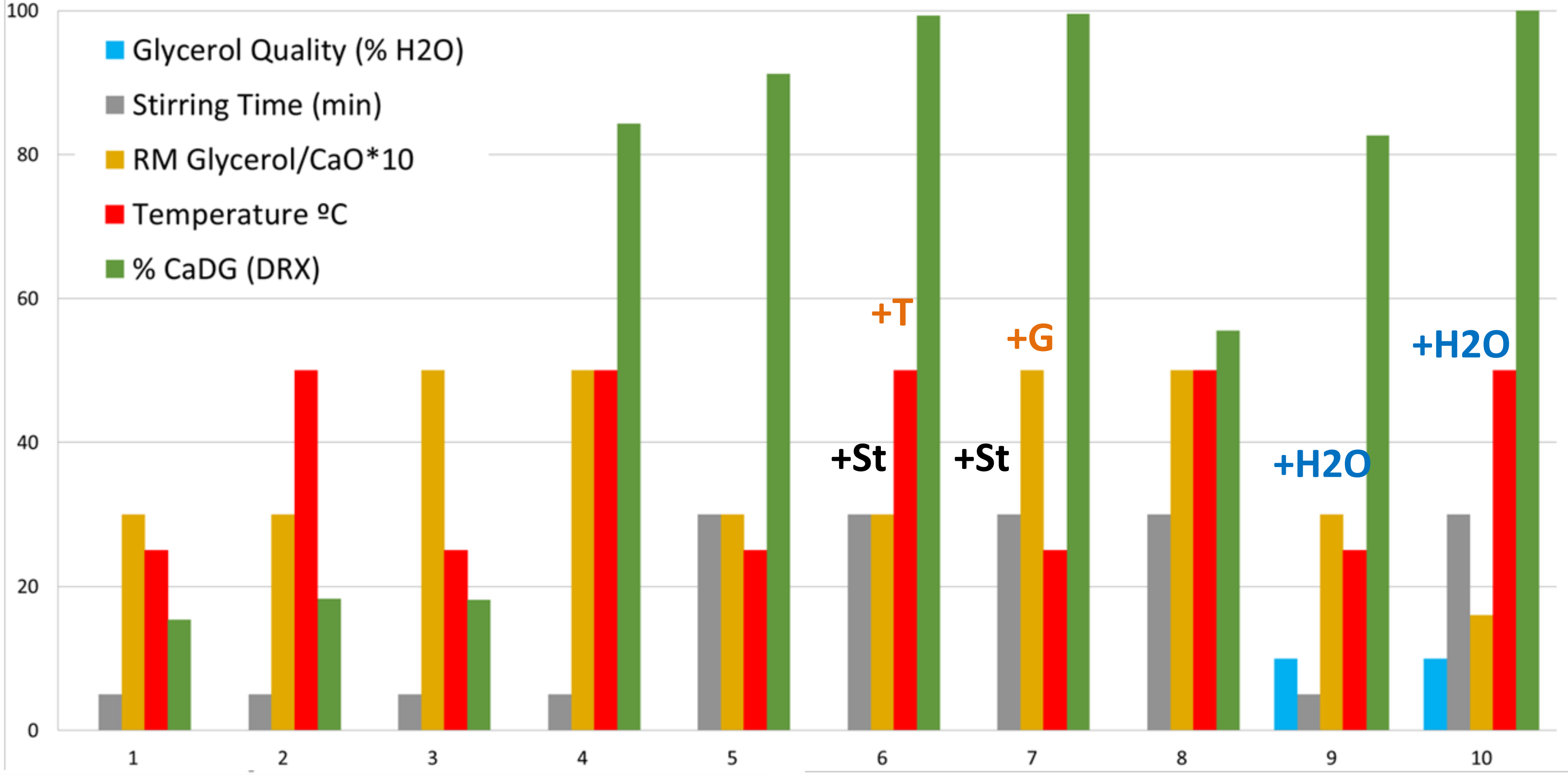
Deasyl

Optimisation of CaDG

Stirring Time, Glyc/CaO Molar ratio, Temperature and water presence
ATD-TG, Elemental Analysis and X-Ray difraction

Excess of glycerol → Increases CaDG formation (5-7)
50 ºC → Increases CaDG formation (5-6)
- No synergic effect with 30 min of stirring (5-8)

Higher stirring time, increases CaDG formation (2-6, 3-7)



With Low stirring time, excess of glycerol and temperature is needed to increase % of CaDG

Addition of water, increases % of CaDG (1-9, 4-10)

UNIVERSIDAD DE MÁLAGA
Deasyl

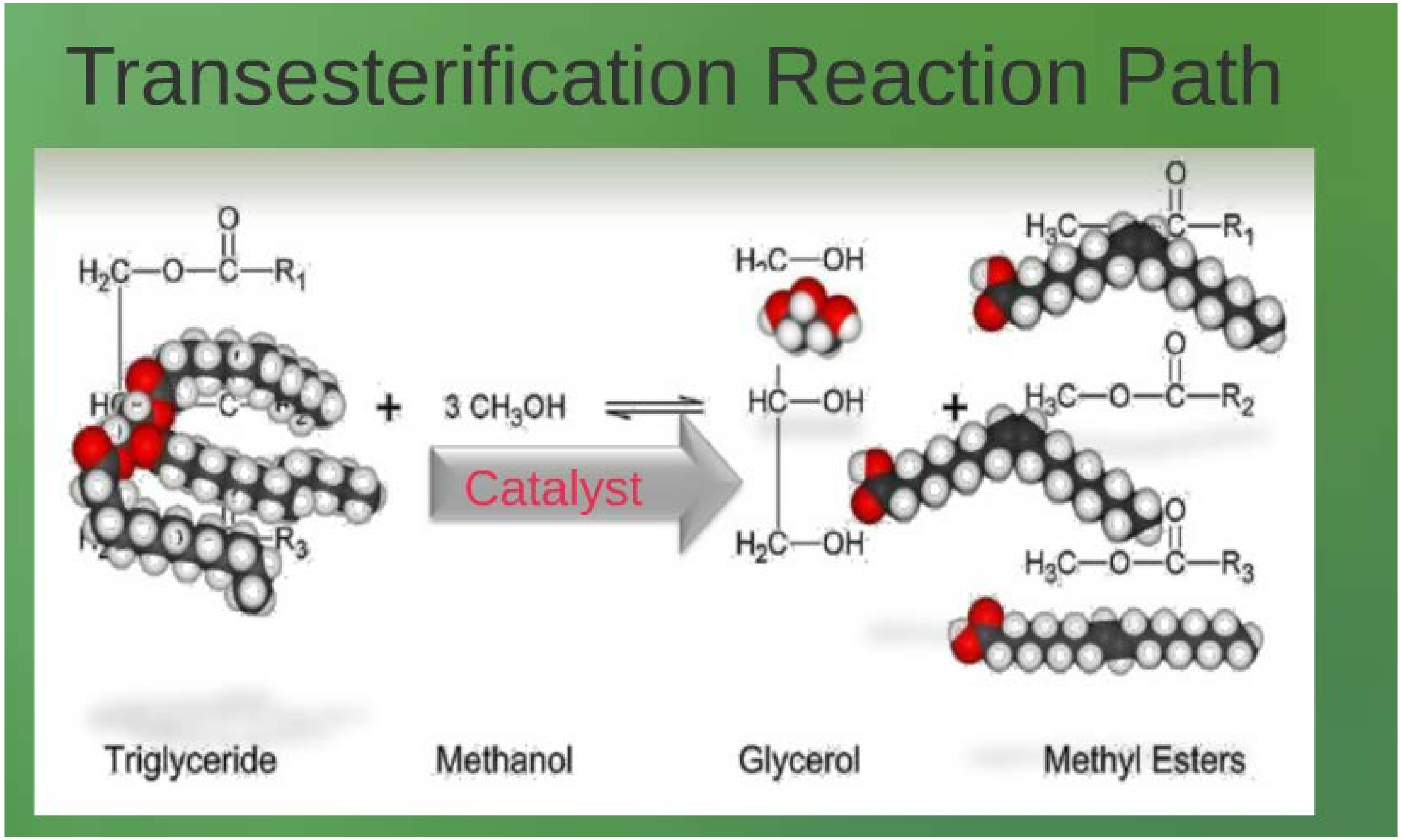
Optimisation of CaDG

Stirring Time, Glyc/CaO Molar ratio, Temperature and water presence
ATD-TG, Elemental Analysis and X-Ray difraction

Entry	Glycerol Quality (wt.% H_2O)	Stirring time (min)	Glyc/CaO MR*	Temp (ºC)	% CaDG (XRD)
1	0	5	30	25	15.40
2	0	5	30	50	18.30
3	0	5	50	25	18.10
4	0	5	50	50	84.30
5	0	30	30	25	91.20
6	**0**	**30**	**30**	**50**	**99.30**
7	**0**	**30**	**50**	**25**	**99.50**
8	0	30	50	50	55.50
9	10	5	30	25	82.60
10	10	30	50	50	100

Industrial Calcium Diglyceroxide Synthesis Protocol PATENTED (PCT/FR2017 052675):
Continuous Temperature 25º C
Glycerol / CaO molar ratio = 5
Residence Time = 20 s
Stirring Time = 30 min
No methanol

2. Biodiesel production



REACTIONS CONDITIONS:
Temperature: 50 ºC
Methanol:oil molar ratio of 4:1
1.5% of weight of catalyst by oil.

High-throughput REACTOR
vs
CLASSIC 3-NECK

UNIVERSIDAD DE MÁLAGA

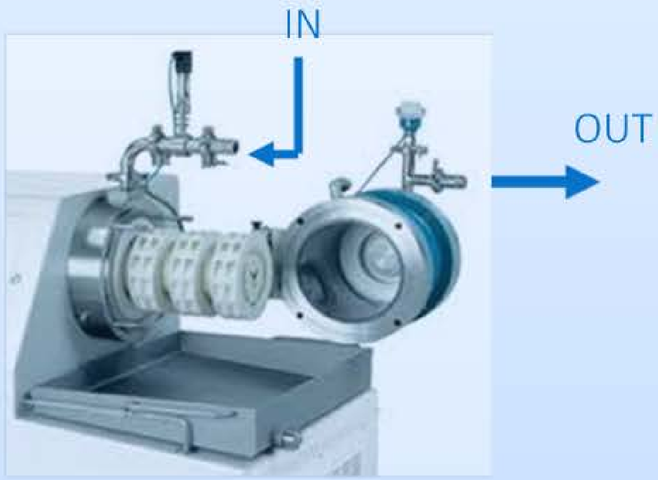
Deasyl

2. Biodiesel production

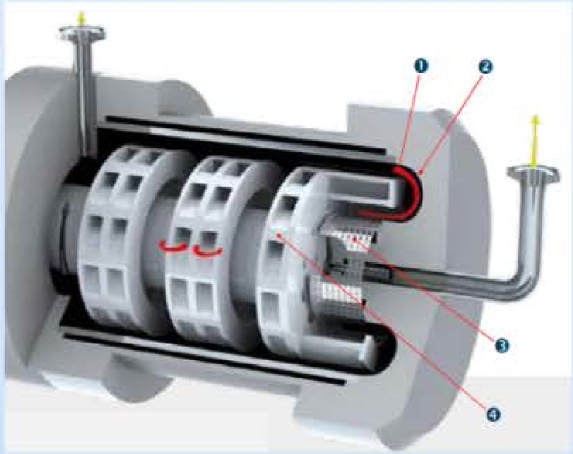
Reaction condition & Machine Parameters

Parameters	Grinding bead	Diameter (mm)	Rotation (tour/min)	Input Flow rate (L/h)	Reactor's technology // grinding chamber volume	% wt catalyst	Molar Ratio MeOH:Oil
Possibilities tested	SiLibeads, Zirmil	0.2 -0.5 - 0.75 - 1	2000 - 5000	4 – 10 – 30 – 45 – 90 - 150	ECM or KD agitator discs // 0.3L - 0.6L	1.5 – 10	4 – 5 – 10
Selection	**Zirmil**	**0.5**	**2986**	**45**	**ECM agitator discs // 0,5L**	**1.5 - 5**	**4**

Zirmil Chemical Analysis	
ZrO2	93%
Y2O3	5%
Others	2%

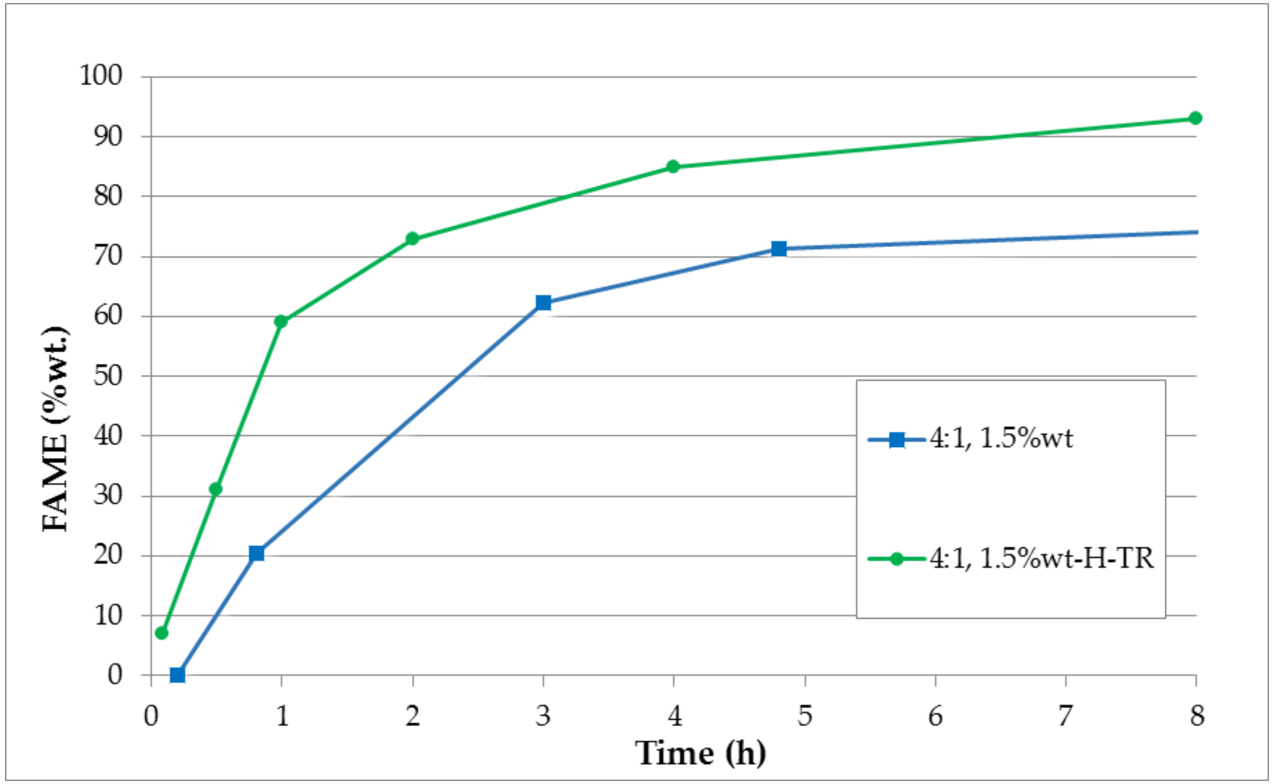


ECM



2. Biodiesel production

Kinetics of FAME yield under conventional and high-throughput reactor (H-TR) at 50 ºC, 4/1 methanol:oil molar ratio and 1.5% of weight percentage of catalyst by oil weight.c



the high-throughput reactor is very promising, since both low temperature and methanol:oil molar ratio have been used

Conclusions

This breakthrough technology will open new opportunities for greener and more efficient chemical processes:

as it is demonstrated, in biodiesel production and catalyst preparation to:

i) shorten reaction times (from h to min) as a result of the activation by mechanical energy;
ii) decrease the reaction temperature, since mechanical activation takes place under non-equilibrium conditions;
iii) improve reactions kinetics as mass transfer limitations are reduced, while the collision between beads and reactants increases the probability of contact between them;
iv) minimize the use of reactants (methanol);
v) increase volume treated (from mL to L), enabling a real scale-up; and
vi) enhance the yields and/or selectivity, as regeneration of catalyst surface takes place simultaneously to the reaction.

Deasyl

THANK YOU!