MICROWAVE-ASSISTED CONTINUOUS FLOW FOR THE SELECTIVE OLIGOMERIZATION OF GLYCEROL

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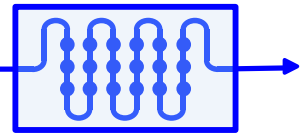
Chimie Paris ParisTech | PSL

BENIGN BY DESIGN PROCESSES & TECHNOLOGIES



WHAT ARE THE TOOLS & LEVERS ?

In term of the processes & technologies

CATALYSIS

Homogeneous catalysis & Heterogeneous catalysis from bio-based derivatives or not
Nanocatalysis
Micellar catalysis

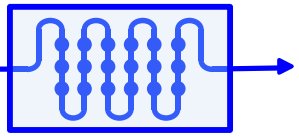
ALTERNATIVE ENERGY SOURCES

Continuous flow
Microwave irradiation in batch & in continuous flow
Ultrasound activation in batch & in continuous flow
Sunlight / UV in batch & in continuous flow
Electrochemistry in batch & in continuous flow
Ball Milling in batch & in continuous flow

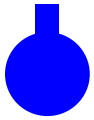
ALTERNATIVE REACTION MEDIA

Supercritical fluid (CO_2, MeOH, CH_3CN, H_2O…)
Ionic Liquids
Water
Polyethyleneglycol (PEG)
Solvent free « *Best solvent is no solvent* »

CONT. CHEMICAL PRODUCTION – A PARADIGM SHIFT



Current methods of synthesis for pharmaceuticals (APIs) and fine chemicals are entirely based on traditional batch manufacturing protocols.
Batch protocols have severe limitations compared to continuous flow processing.



- ✓ Slow temperature control
- ✓ Inefficient mass and heat transfer
- ✓ Dangerous temperature gradients
- ✓ Safety issues for many transformation

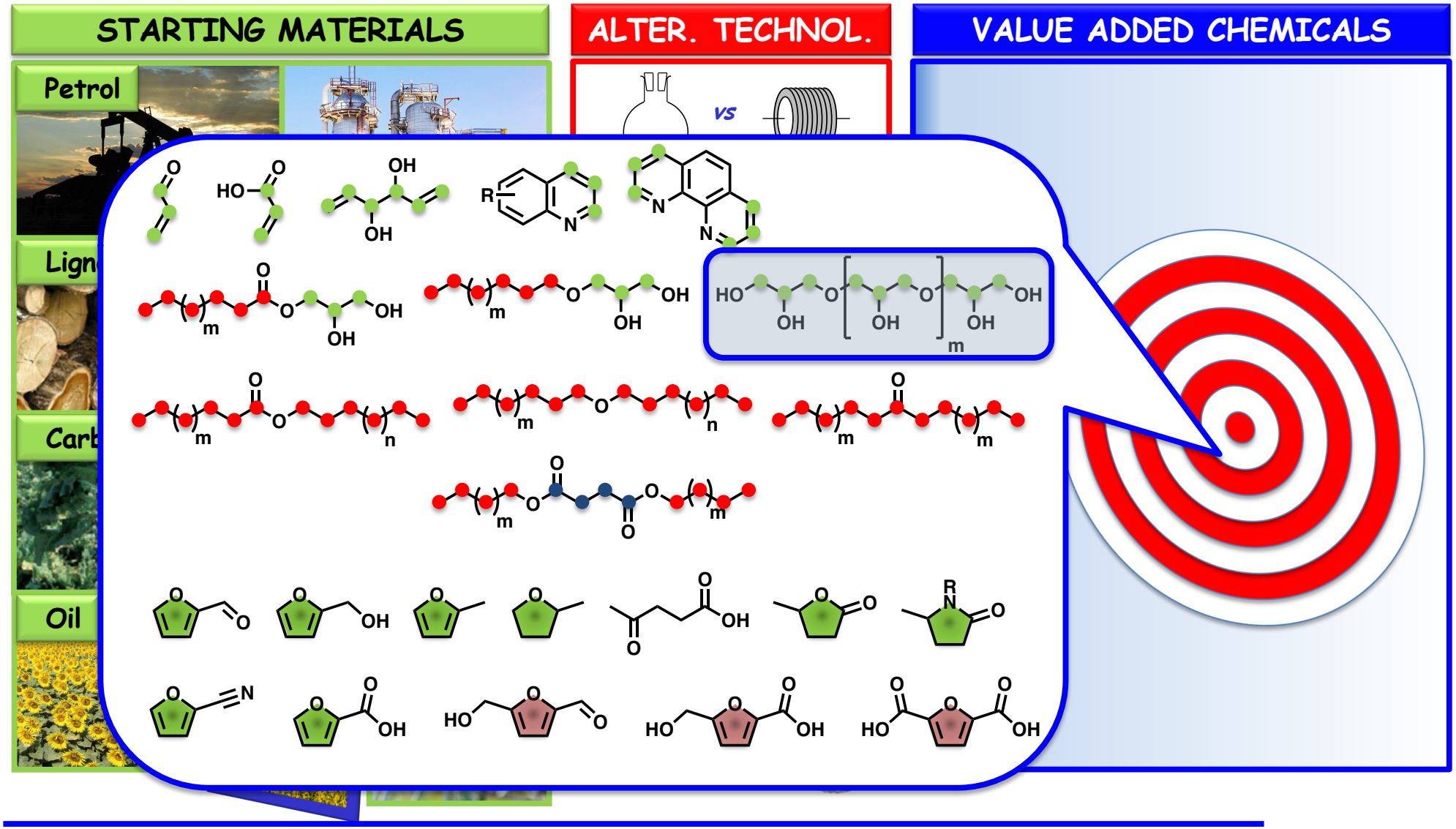
- ✓ Instantaneous heating/cooling
- ✓ Very fast mixing (<1s)
- ✓ No concentration/temperature gradients
- ✓ Inherently safe

- ✓ Segmented individual steps
- ✓ Processing a specific quantity
- ✓ Multi purpose equipment
- ✓ Quality managed by repetition and testing

- ✓ Integrated synchronized operations
- ✓ Continuous flow of product
- ✓ Equipment dedicated for purpose
- ✓ Quality managed by design and processes control of steady state

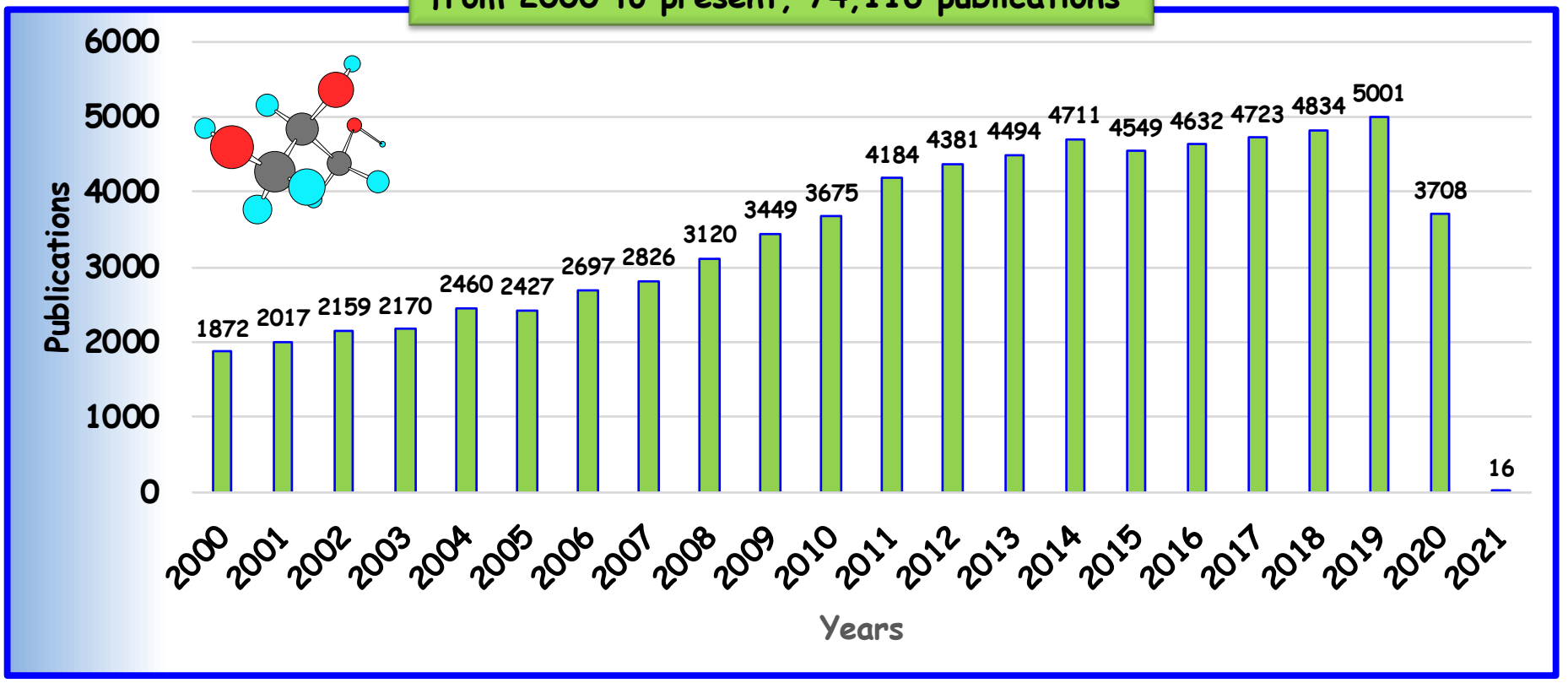
- ✓ Lower cost level (operational, invest)
- ✓ Increased productivity (small plant, low hold-up)
- ✓ Shorter throughput time (less inventory)
- ✓ Consistent quality (less off-spec, less by-products)

OUR EXPERTISES

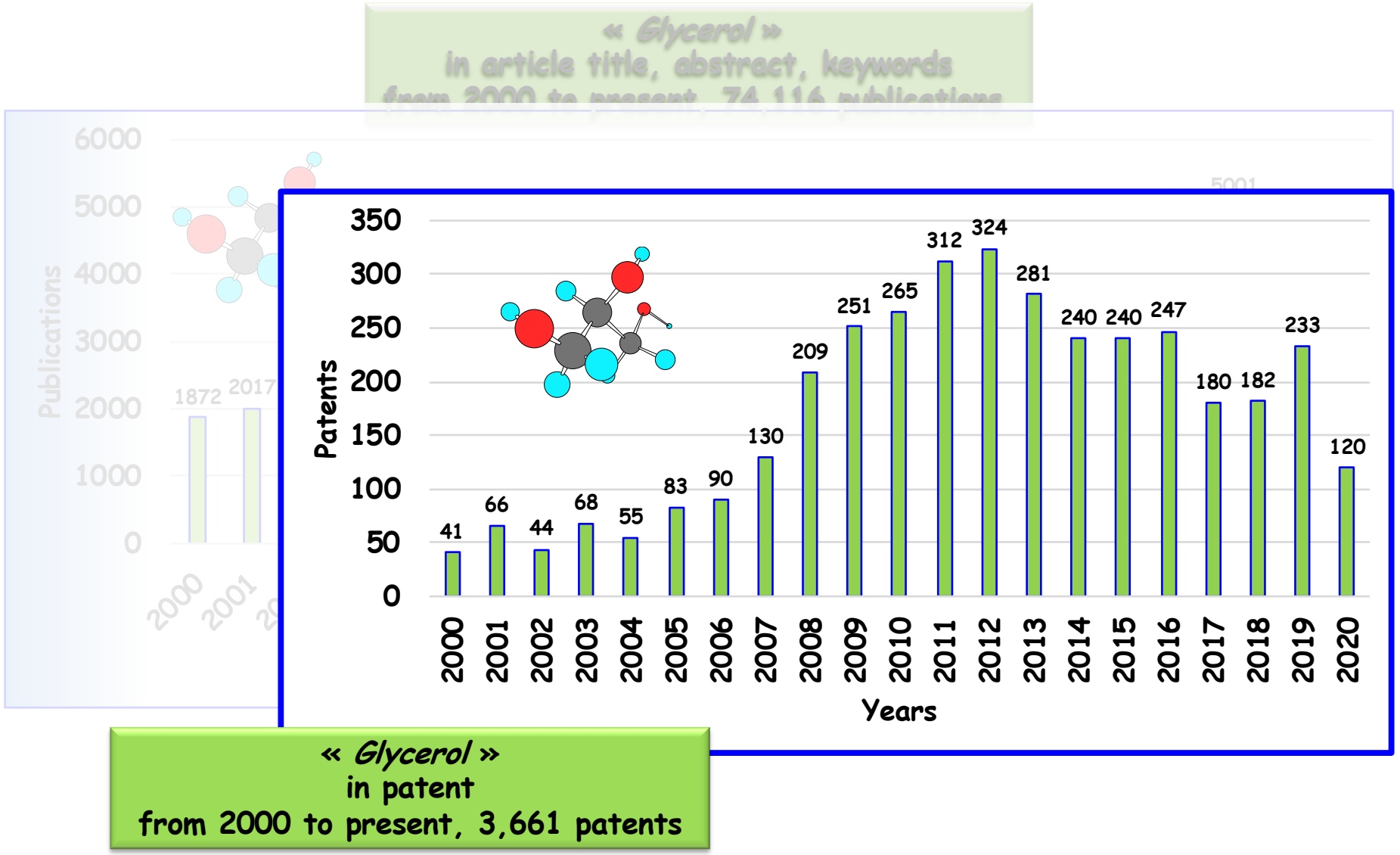


HIKE AROUND GLYCEROL

« *Glycerol* »
in article title, abstract, keywords
from 2000 to present, 74,116 publications



HIKE AROUND GLYCEROL



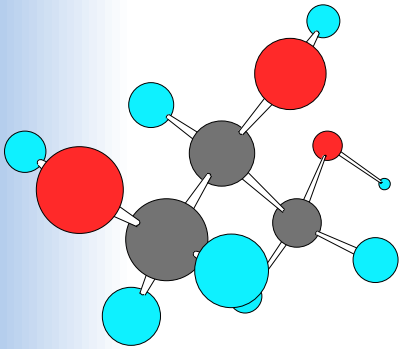
HIKE AROUND GLYCEROL

VEGETABLE OIL

RAPESEED

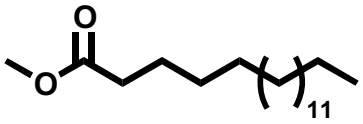
SUNFLOWER

(10 Tons)



CH_3OH
(1 Tons)

BIODIESEL



(10 Tons)

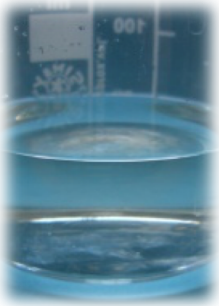
BLEND WITH DIESEL

GLYCERIN

(1.2 Ton)
Price: 270 €/Ton

Energy consuming process !

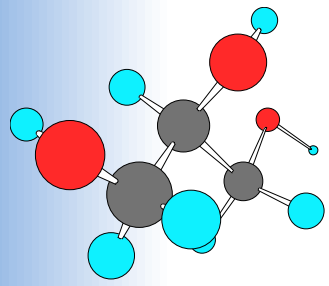
GLYCEROL



(1 Ton)
Price: 550 €/Ton

Sustainable Chem. Process. **2014**, *2*,1; *J. Chem. Technol. Biotechnol.* **2017**, *92*, 14; *Energy Convers. Manage.* **2017**, *149*, 355; *Synthesis*, **2018**, *50*, 723; *Curr. Opin. Green Sustain. Chem.* **2019**, *15*, 83.

HIKE AROUND GLYCEROL



CO + H_2
syngas

Biochemical paths

glycerol carbonate

propan-1,2-diol

cyclic acetals

propan-1,3-diol

glycidol

polyglycerols

epichlorhydrine

Mono- and polyethers

acrolein

Mono- and polyesters

reforming

hydrogenolysis

cyclization

cyclization

hydrogenolysis

cyclization

oligomerization

etherification

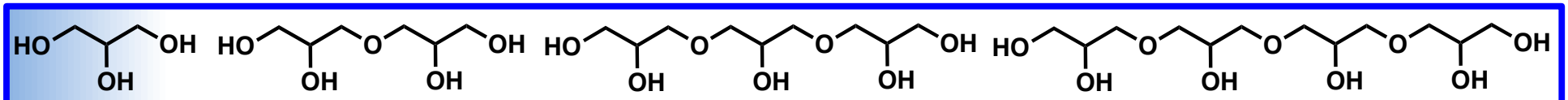
esterification

dehydration

cyclization

Sustainable Chem. Process. **2014**, *2*,1; *J. Chem. Technol. Biotechnol.* **2017**, *92*, 14; *Energy Convers. Manage.* **2017**, *149*, 355; *Synthesis*, **2018**, *50*, 723; *Curr. Opin. Green Sustain. Chem.* **2019**, *15*, 83.

INDUSTRIAL APPLICATIONS OF POLYGLYCEROLS



Glycerol Diglycerol Triglycerol Tetraglycerol

Polyglycerols for incorporation

- ✓ in polymers as plasticizer
- ✓ as ink ingredients
- ✓ in polyurethane production.

SOLVAY
asking more from chemistry®

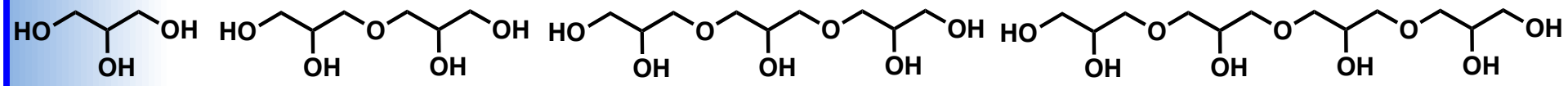
oleon
a natural chemistry

Esters of polyglycerol for incorporation

✓in food as an emulsifier
✓in polymers as antifogging and antistatic agents, or lubricants
✓in inks and agrochemical formulations as emulsifiers, stabilizers, dispersants or humectants
✓in the paper and wastewater industries as antifoaming agents …

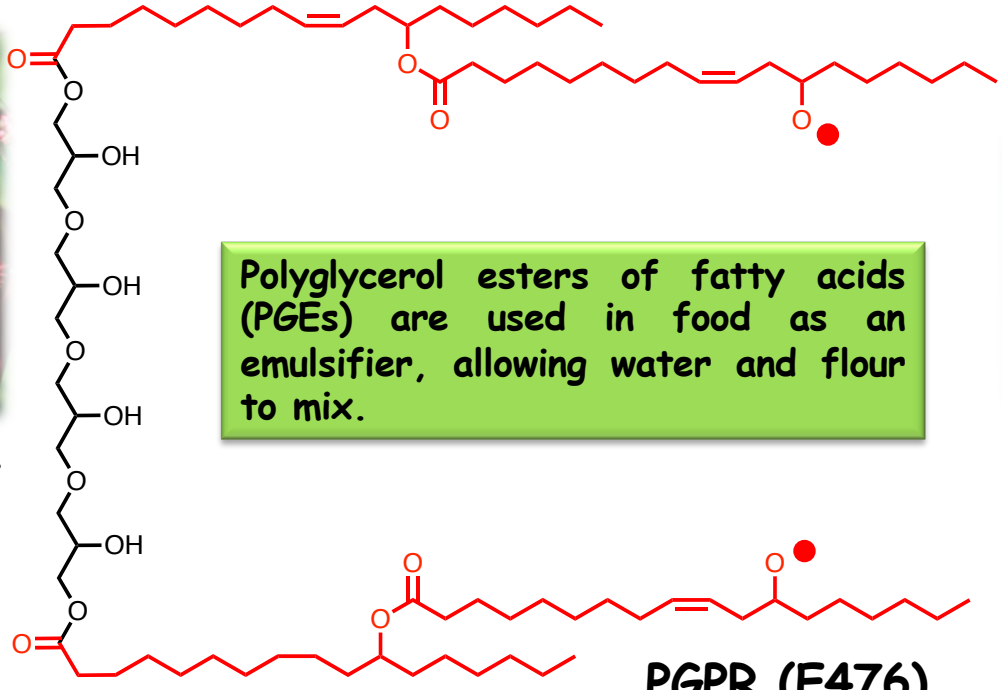
Molecules **2016**, *21*, 1038; *J. Ind. Eng. Chem.* **2017**, *51*, 312; *Catalysts* **2017**, *7*, 123; *J. Ind. Eng. Chem.* **2017**, *51*, 312; *Catalysts.* **2017**, *7*, 123.

INDUSTRIAL APPLICATIONS OF POLYGLYCEROLS



Glycerol Diglycerol Triglycerol Tetraglycerol

Castor bean plant
Ricinus communis



PGPR (E476)

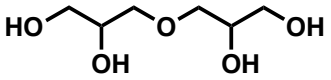
Polyglycerol esters of fatty acids (PGEs) are used in food as an emulsifier, allowing water and flour to mix.

Influence of PGPR addition (0.2%) to a molten chocolate (27% cocoa butter)

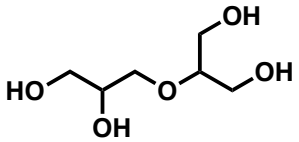
Molecules **2016**, *21*, 1038; *J. Ind. Eng. Chem.* **2017**, *51*, 312; *Catalysts* **2017**, *7*, 123; *J. Ind. Eng. Chem.* **2017**, *51*, 312; *Catalysts.* **2017**, *7*, 123.

ISOMERS PG2 AND PG3 AND CYCLIC ISOMERS cPG2

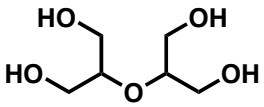
PG2



α,α-diglycerol

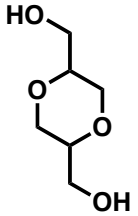


α,β-diglycerol

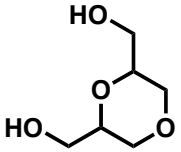


β,β-diglycerol

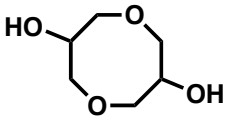
cPG2



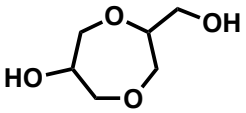
cyclic
α,β-α,β-diglycerol



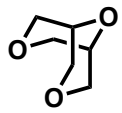
cyclic
α,α-β,β-diglycerol



cyclic
α,α-α,α-diglycerol

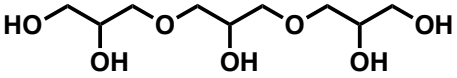


cyclic
α,α-α,β-diglycerol

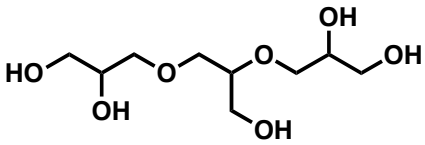


bicyclic
α,α-α,α-β,β-diglycerol

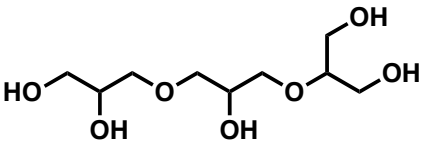
PG3



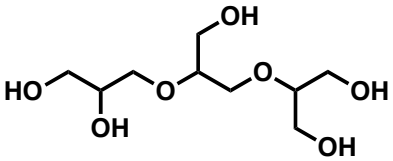
α,α-α,α-triglycerol



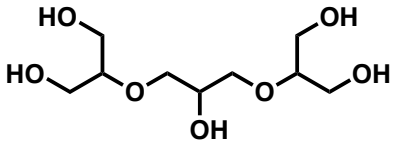
α,α-β,α-triglycerol



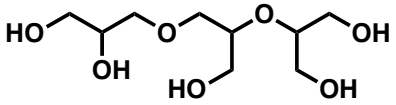
α,α-α,β-triglycerol



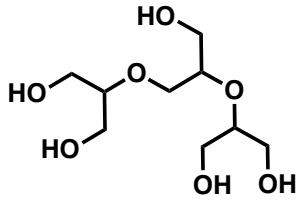
α,β-α,β-triglycerol



β,α-α,β-triglycerol

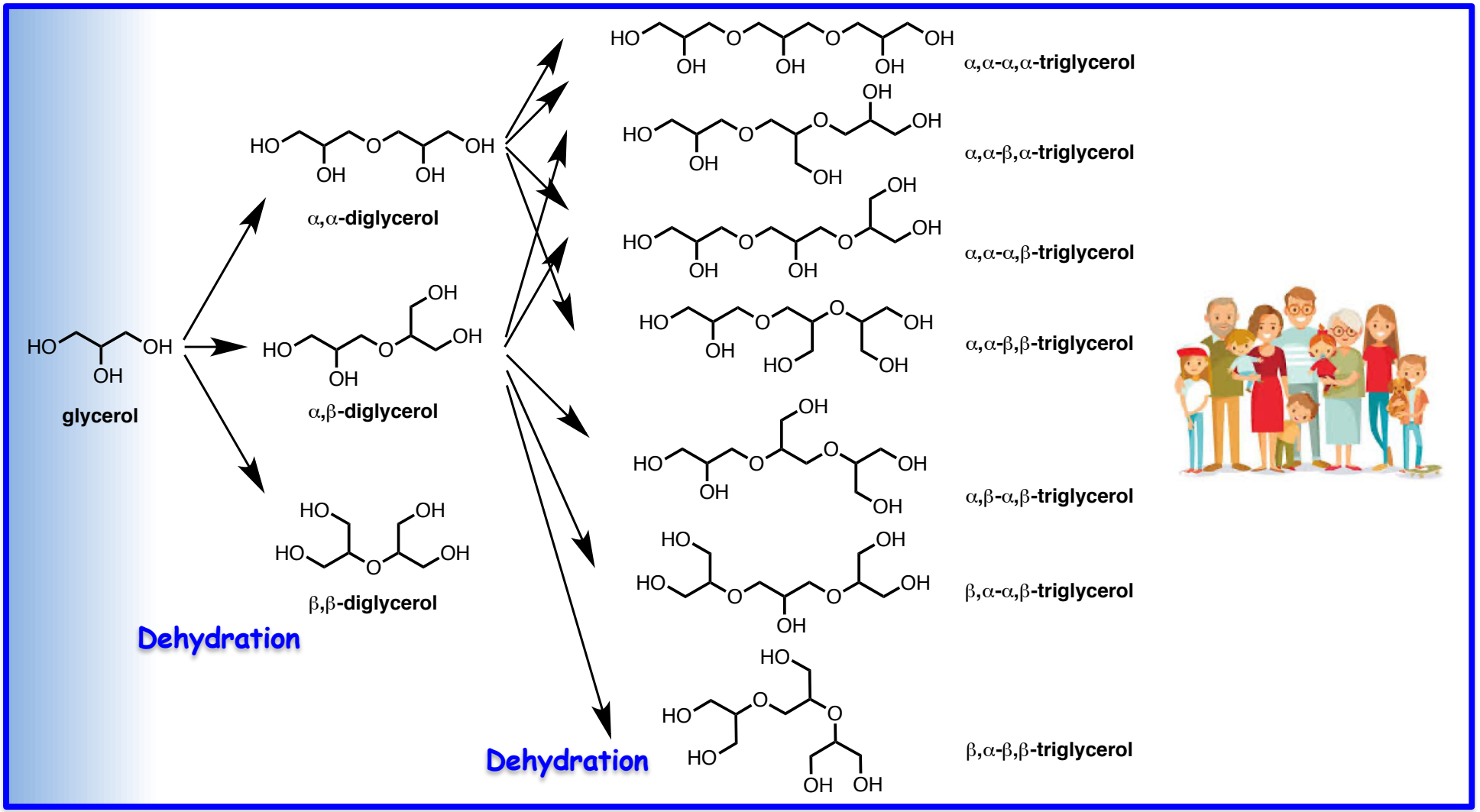


α,α-β,β-triglycerol



β,α-β,β-triglycerol

LINEAR/BRANCHED ISOMERS PG2 AND PG3



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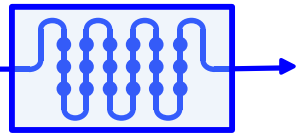
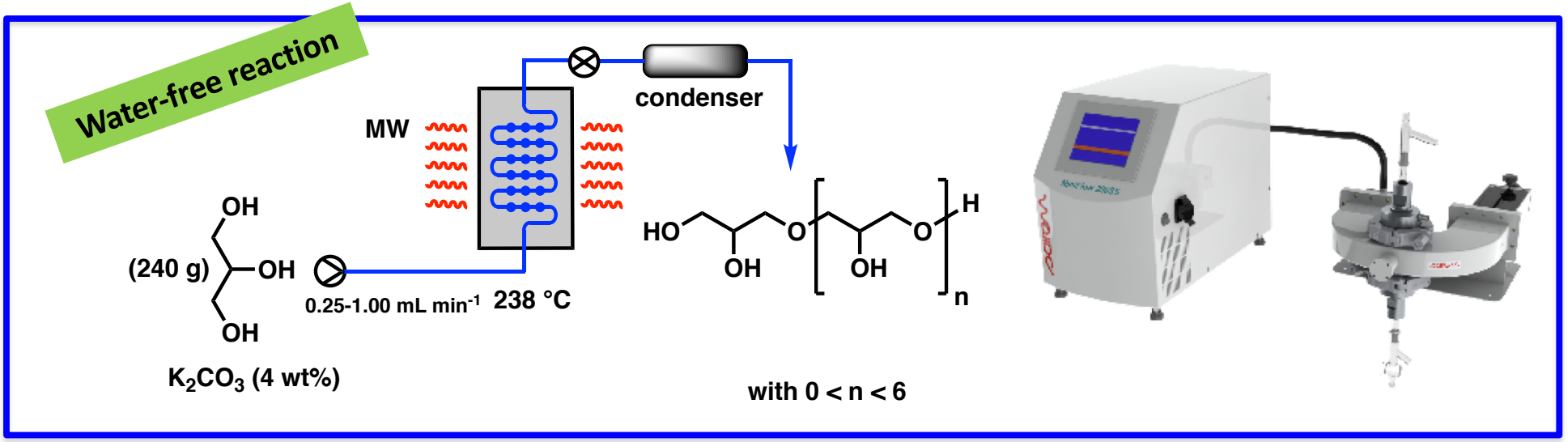
MW-ASSISTED CONT. GLYCEROL OLIGOMERIZATION





GLYCEROL 240 g

oleon
a natural chemistry

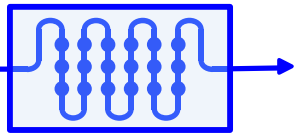
Company's specifications

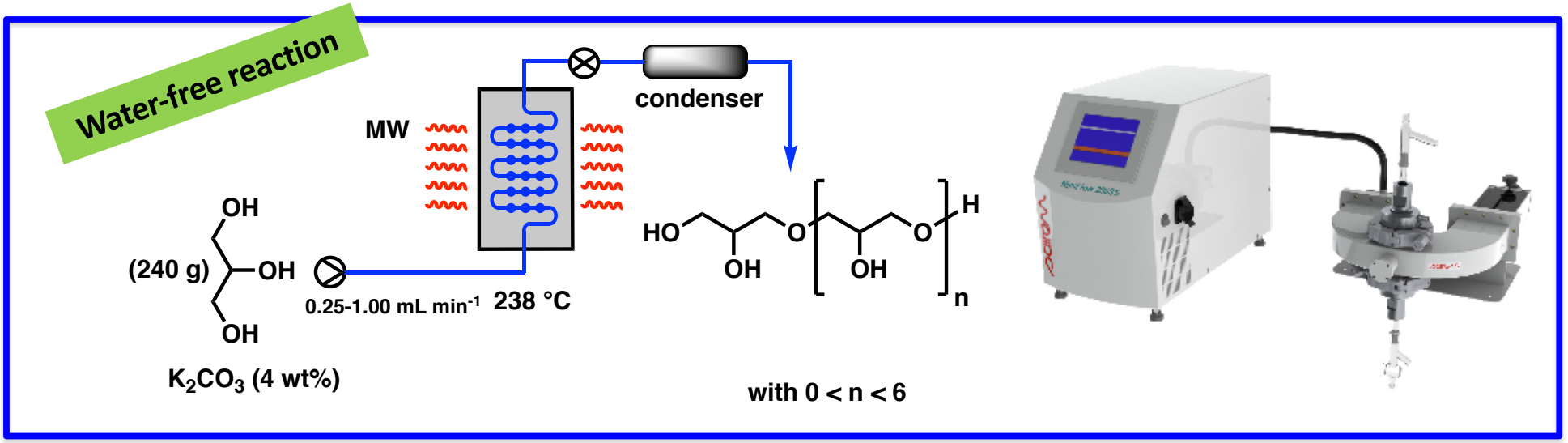
Cheapest possible catalyst that gives the best possible result.

Not working on 1 mg of glycerol but on more than 200 g of glycerol.

Molecules **2016**, *21*, 1038; *J. Ind. Eng. Chem.* **2017**, *51*, 312; *Catalysts* **2017**, *7*, 123; *J. Ind. Eng. Chem.* **2017**, *51*, 312; *Catalysts.* **2017**, *7*, 123.

MW-ASSISTED CONT. GLYCEROL OLIGOMERIZATION

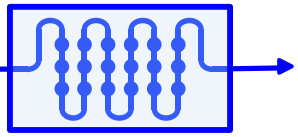




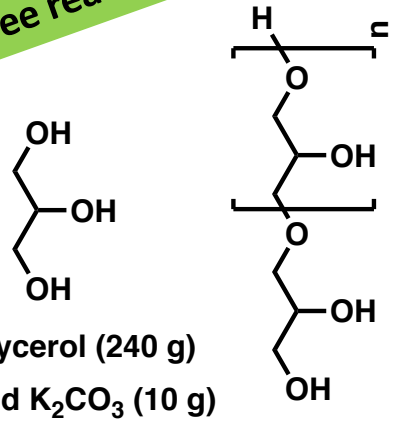
Entry	Flow (mL min^{-1})	Res. Time (min)	Composition (wt%) of the product by GC				
			PG1	PG2	PG3	PG4	other
1	1.0	20	84.0	12.1	2.4	0.2	0.4
2	0.5	40	70.3	19.5	6.3	1.0	2.0
3	0.25	80	59.1	22.1	9.3	4.4	5.0

Reaction conditions: glycerol (240 g, 2.61 mol), K_2CO_3 (10.0 g, 72.4 mmol), 238 °C.

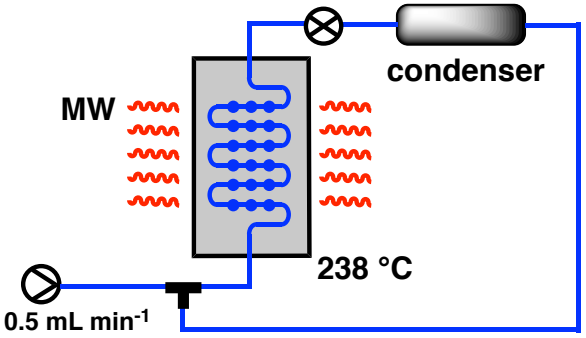
MW-ASSISTED CONT. GLYCEROL OLIGOMERIZATION



Water-free reaction



at t_0, glycerol (240 g)
and K_2CO_3 (10 g)

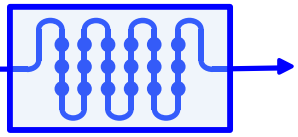


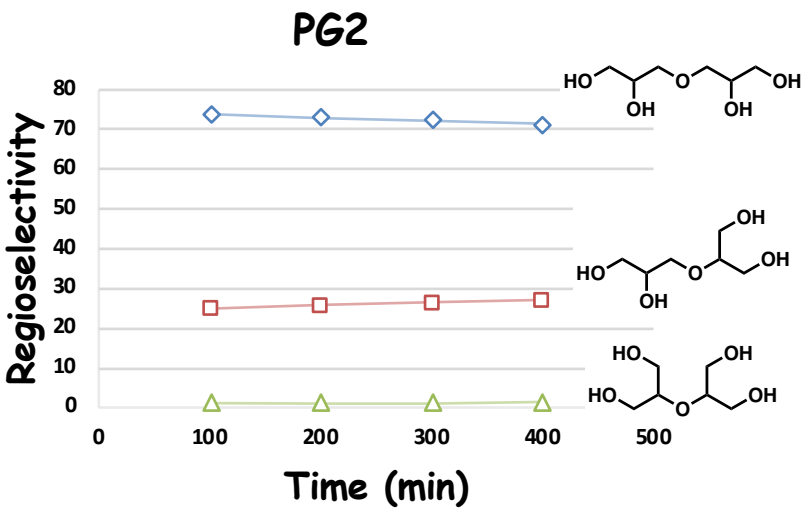
To achieve higher conversion, our system has been transformed to work in cycle by continuously reinjecting the output in the reactor

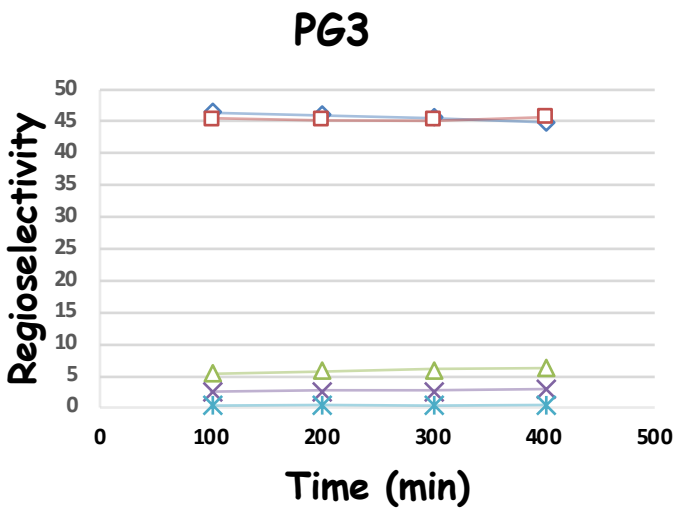
Entry	Time (min)	Composition (wt%) of the product by GC				
		PG1	PG2	PG3	PG4	other
1	50	85.9	12.3	1.5	0.2	0.1
2	100	71.8	20.6	5.2	1.2	1.2
3	150	62.1	25.5	7.9	2.3	2.2
4	250	55.1	26.4	10.0	3.7	4.8
5	250	55.2	24.2	9.2	3.4	7.4

Reaction conditions: glycerol (240 g, 2.61 mol), K_2CO_3 (10.0 g, 72.4 mmol), 238 °C, 0.5 mL min^{-1}.

MW-ASSISTED CONT. GLYCEROL OLIGOMERIZATION





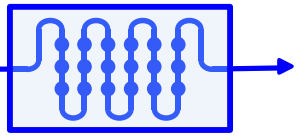


α,α-diglycerol selectivity **72-74%**
α,β-diglycerol selectivity **25-27%**
β,β-diglycerol selectivity **1%**

α,α-α,α-triglycerol selectivity **45%**
α,α-α,β-triglycerol selectivity } **45%**
α,α-β,α-triglycerol selectivity }
Others less than **6%**

Reaction conditions: glycerol (240 g, 2.61 mol), K_2CO_3 (10.0 g, 72.4 mmol), 238 ° C, 250 min, 0.5 mL min^{-1}.

MW-ASSISTED CONT. GLYCEROL OLIGOMERIZATION



In order to obtain a sample of oligomers with no glycerol or less amount of glycerol, short path evaporation has been explored.

Entry	Fraction	Composition (wt%) of the product by GC								
		PG1	cPG2	PG2	cPG3	PG3	PG4	PG5	PG6	other
1	Crude	55.2	1.6	24.2	0.7	9.2	3.4	1.5	0.6	3.0
2 [a]	Distillat	90	2.2	6.3	0.2	0.5	-	-	-	0.8
3 [a]	Residue	-	-	50.2	2.0	22.1	9.5	4.3	2.0	7.4

[a] Short path evaporation: 0.1 mbar and 150° C.

Reaction conditions: glycerol (240 g, 2.61 mol), K_2CO_3 (10.0 g, 72.4 mmol), 238 ° C, 250 min, 0.5 mL min^{-1}.

Furthermore the purification removed PG1, cPG2, a more lipophylic byproduct and PG2
and a 50% enriched dimer mixture is obtained.

CONCLUSION AND PERSPECTIVES

GLYCERIN

Energy consuming process !

GLYCEROL

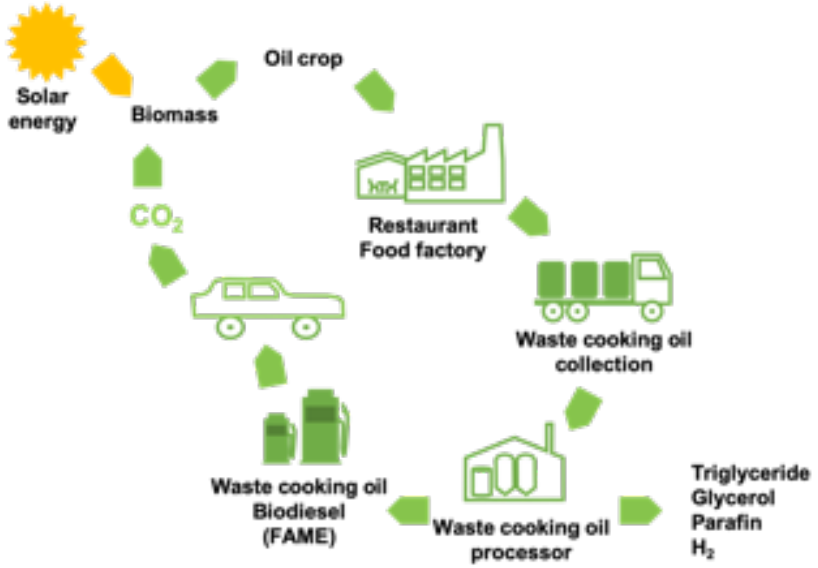
(1.2 Ton)
Price: 270 €/Ton (2017)

(1 Ton)
Price: 550 €/Ton (2017)
Price: 1324 €/Ton (<2000)

Due to a substantial decrease in the price of purified glycerol between 2000 and today, the purification of glycerin is getting less attractive.

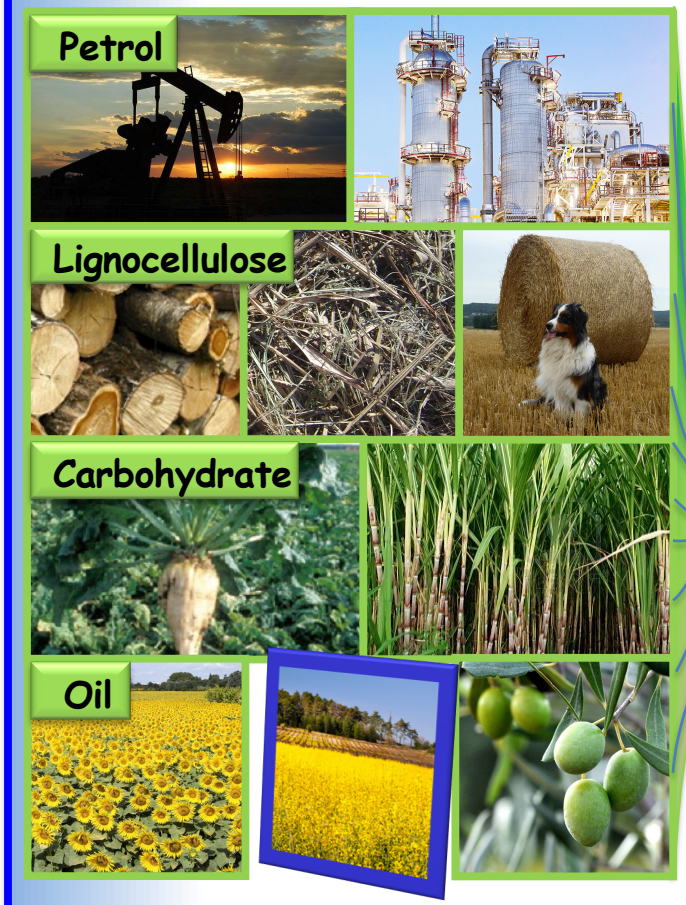
Therefore, direct use of crude glycerol (or glycerin) is becoming promising as well as the transformation of Used Cooking Oil

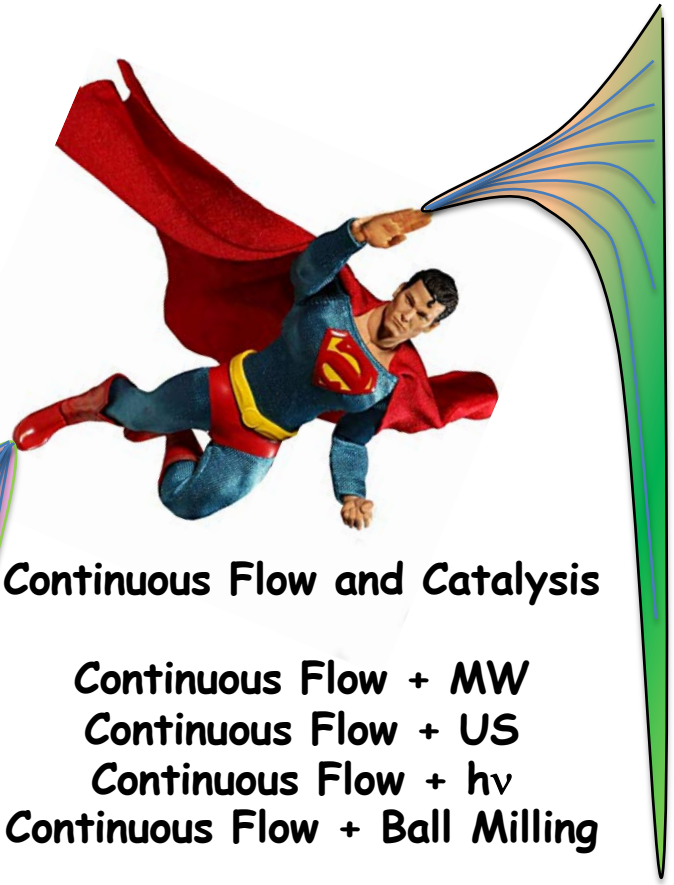
Starting from Used Cooking Oil and Glycerin, chemical production can be manufactured with low price and sustainable supply.



Mol. Catal. **2020**, *494*, 111128.

CONCLUSION AND PERSPECTIVES





Continuous Flow and Catalysis

Continuous Flow + MW
Continuous Flow + US
Continuous Flow + hν
Continuous Flow + Ball Milling




MICROWAVE-ASSISTED CONTINUOUS FLOW FOR THE SELECTIVE OLIGOMERIZATION OF GLYCEROL

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