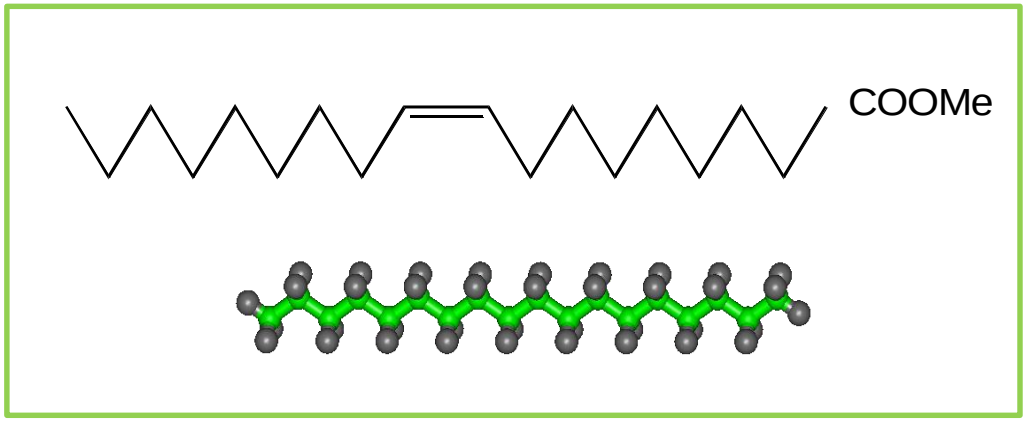
The role of oils and fats in the future of Biorefineries

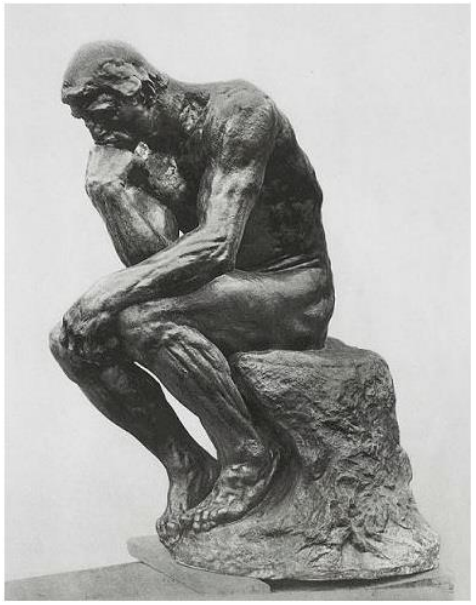
Nicoletta Ravasio
CNR ISTM, Milano

Gela, 25-27 May 2017

Rethink our raw material pool



Food /Feed



A. Rodin, The thinker

- Non food oils from dedicated crops (flax, camelina)
- Food Supply Chain Wastes

Linear economy

Oils and fats from food wastes

- animal fats
- Tall Oil
- acidic oils from refining of food grade oils
- Used cooking oils
- Grape pomace
- Tomato pomace
- Pumpkin seeds
- Rice bran
- Spent coffee ground
- Brewer spent grain

Transesterification with MeOH → Biodiesel

Hydrolysis + esterification
Transesterification → Lubricants
Hydraulic fluids

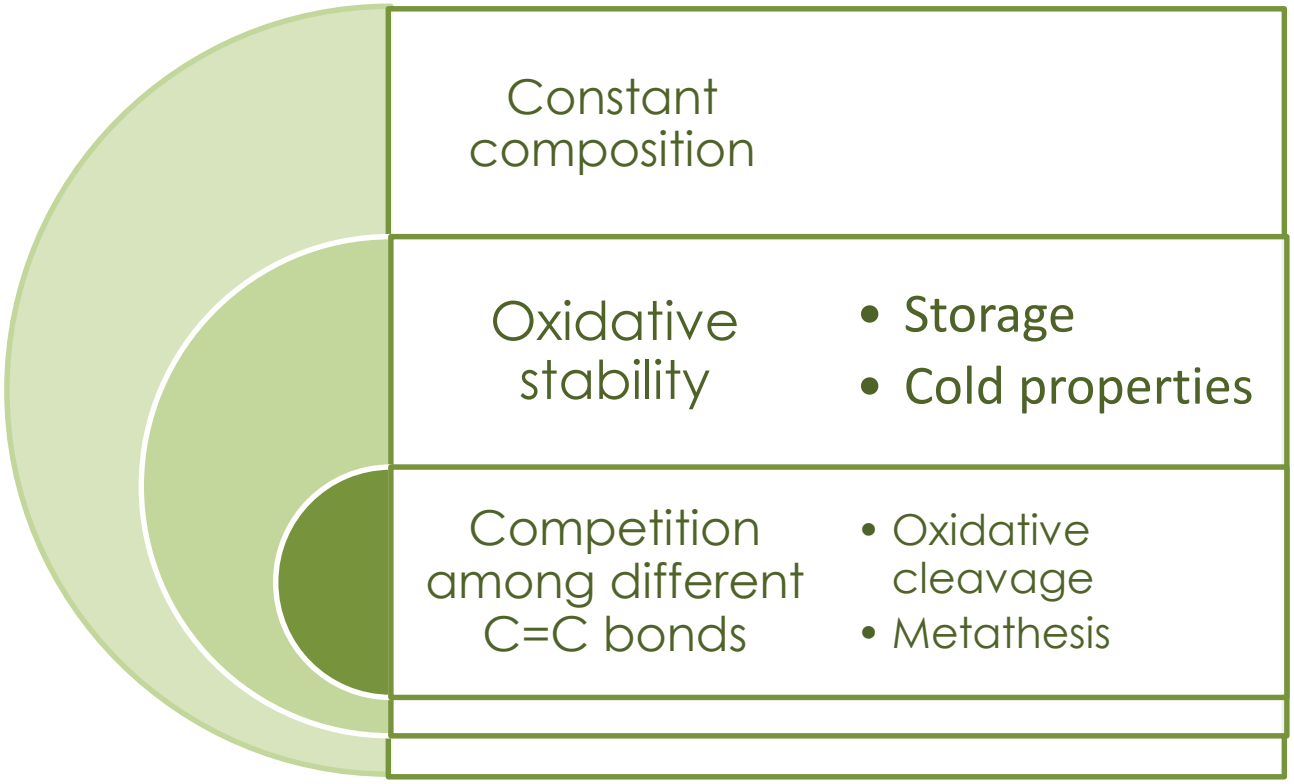
Epoxidation
Ring opening → Polyols → Polyurethanes

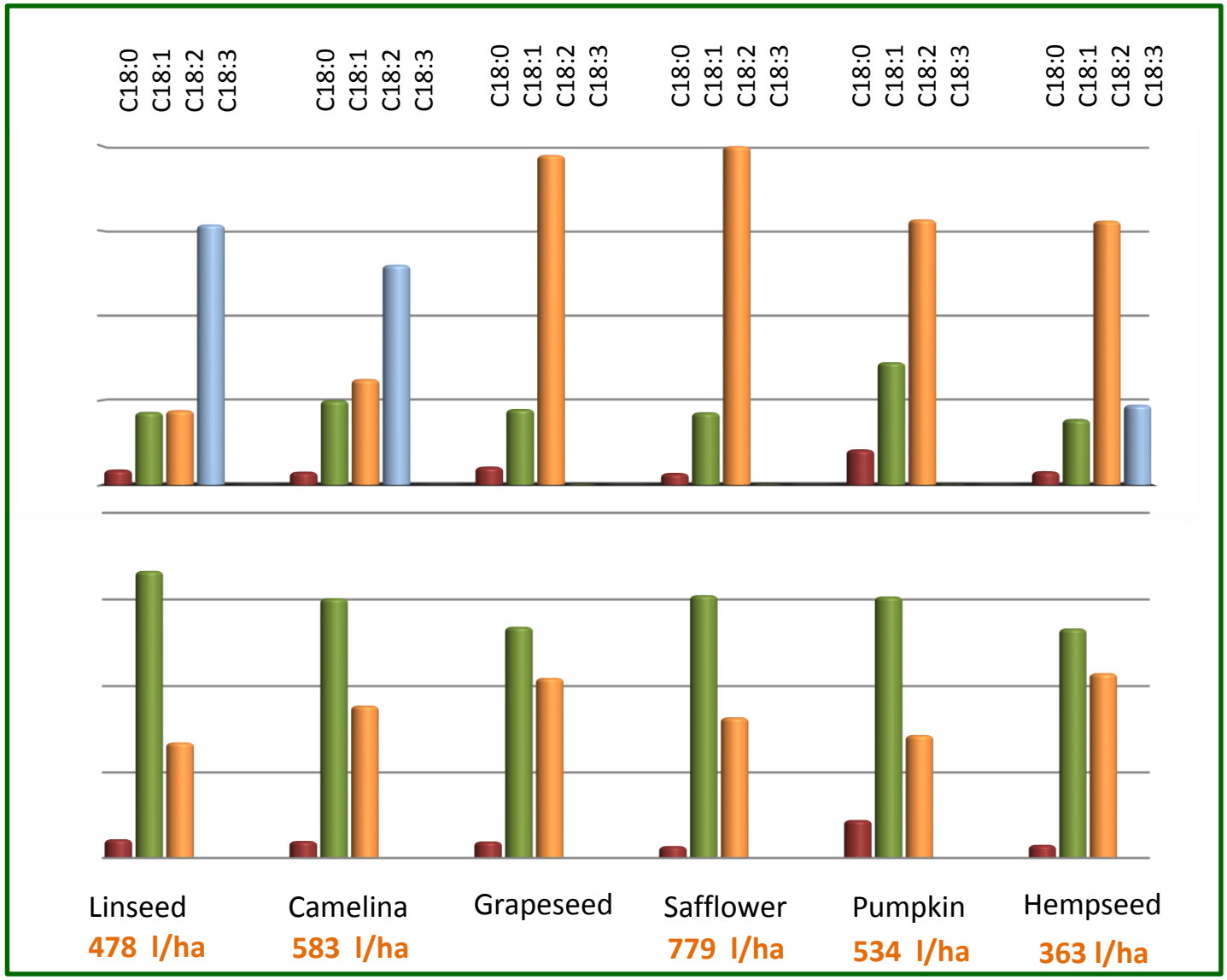
Cross metathesis
Self methatesis → Polymers
oleochemicals

Oxidative cleavage → Monomers

Oil		C16:0	C18:0	C18:1	C18:2	C18:3
Flax	*Linus usitatissimus*	5	3	16	17	58
Hemp	*Cannabis sativa*	6	3	14	57	17
Camelina	*Camelina sativa*	6	2	16	21	37
Tobacco	*Nicotiana tabacum*	11	3	15	69	1
Brassica	*Brassica carinata*	5	-	43	36	16
Cardoon	*Cynara cardunculus*	14	3	25	56	
Safflower	*Carthamus tintorius*	7	2	14	77	
Cottonseed	*Gossypium spp*	28	1	13	57	
Jatropha	*Jatropha Curcas*	15	6	46	32	
Sacha Inchi	*Plukenetia volubilis*		3	9	34	50
Grapeseed	*Vitis vinifera*	7	4	17	72	
Rubberseed	*Hevea brasiliensis*	10	9	25	40	16

The issue of polyunsaturation





IV = 202

IV = 104

IV = 117

IV = 95

- **PCT/IT2006/000258** WO2006/111997 A1; **EP Appl**. 06745284.7 (12 november 2007)

The ideal raw material: oleic acid

Global oleic acid market is growing at a CAGR 4,6%

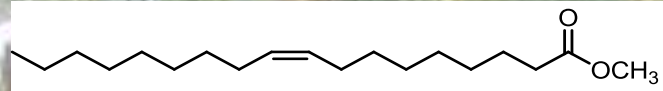
C18:1 Δ^9

Cold properties vs oxidative stability

Mars pledges to use 100% high oleic peanuts in M&M, Munch bars by the end of 2017

ISTM

Deloitte Greenhouse™

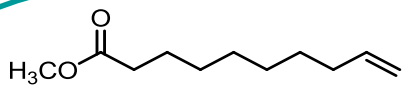


Oleic acid, methyl ester

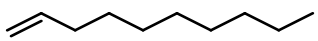
+

$H_2C{=}CH_2$

ethene



9-decenoic acid, Me ester

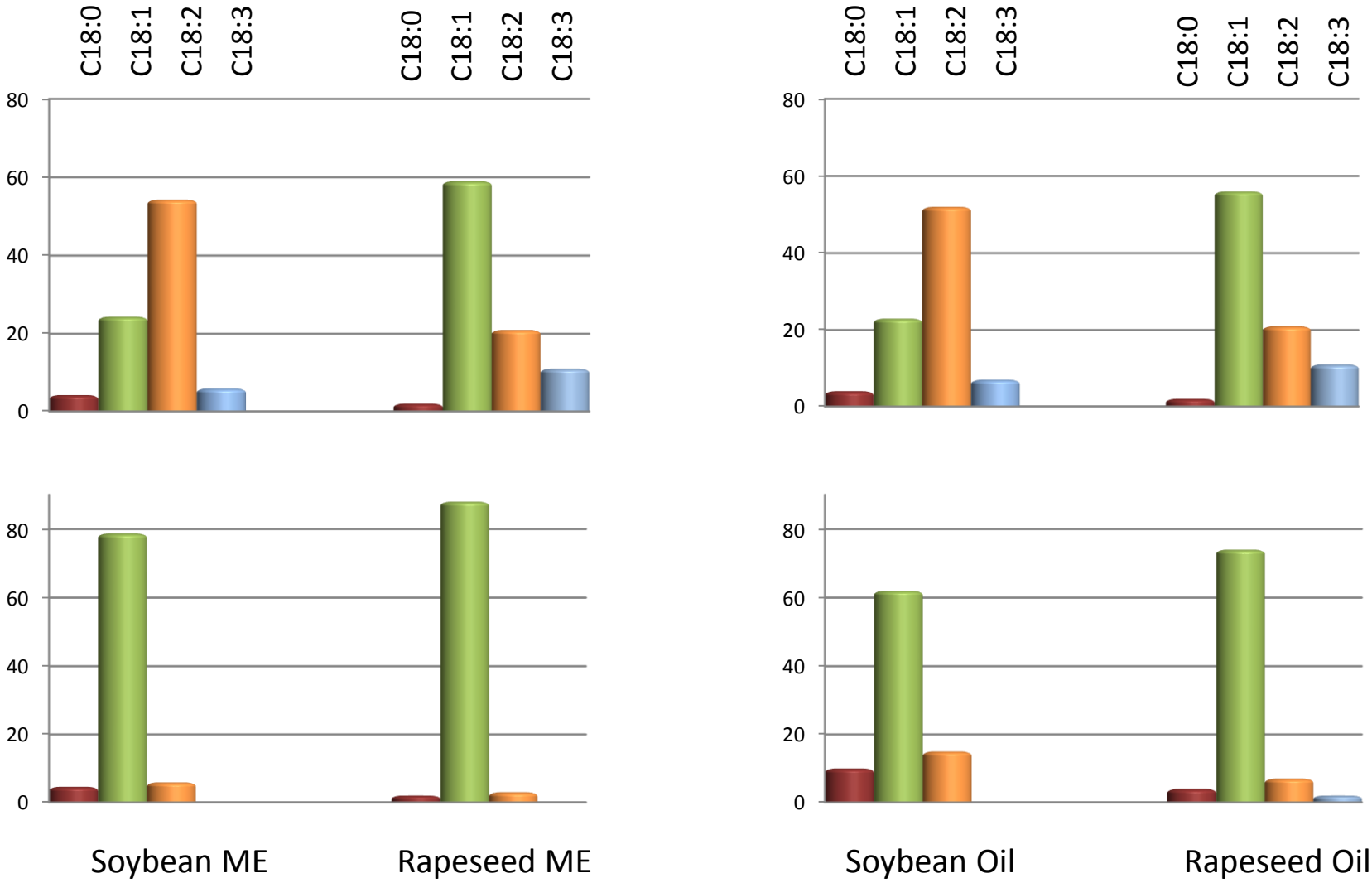


1-decene

Elevance RENEWABLE SCIENCES

wilmar

We Invest • You Harvest

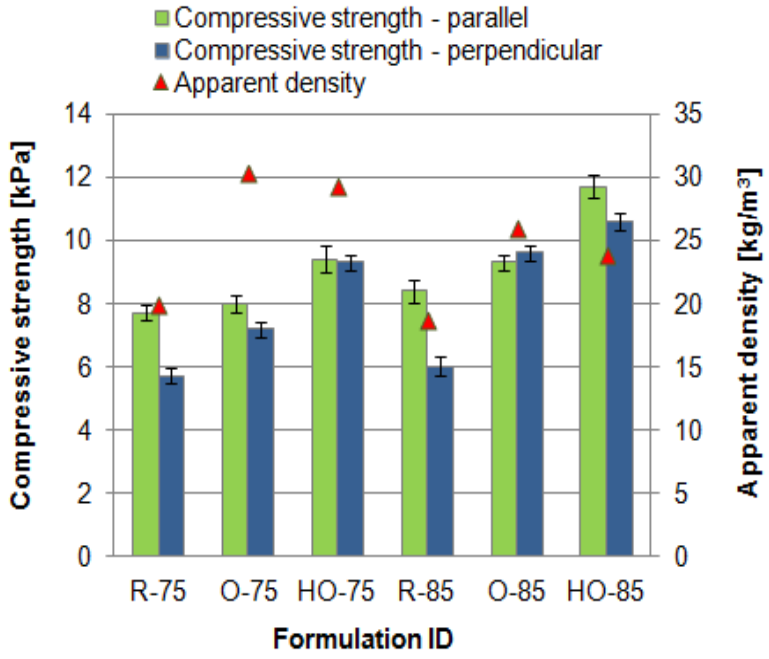

C18:0
C18:1
C18:2
C18:3
80
60
40
20
0
Soybean ME
Rapeseed ME
Soybean Oil
Rapeseed Oil

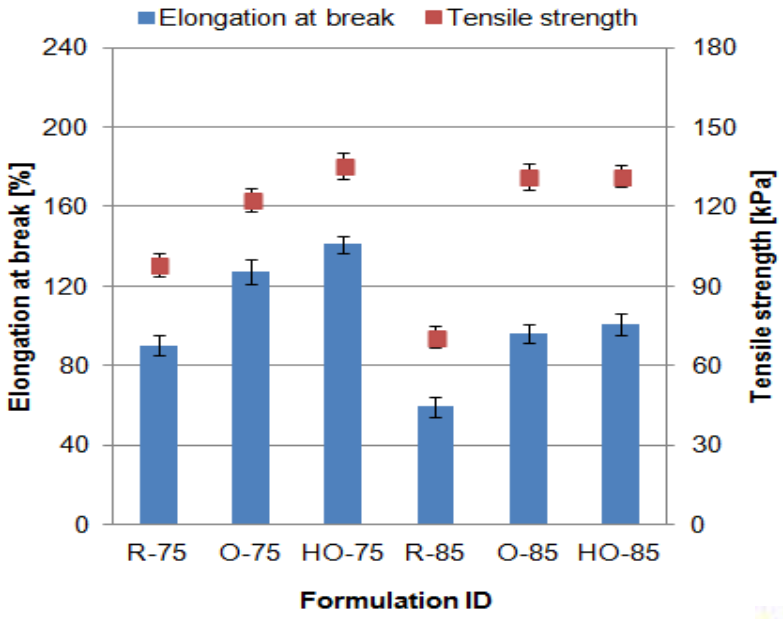
Improved physical properties

✓Polyurethane foams

The higher CS and AD the better the product

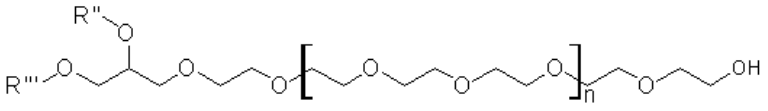
R = reference foam
O = foam modified with rapeseed oil
HO = foam modified with hydrogenated rapeseed oil



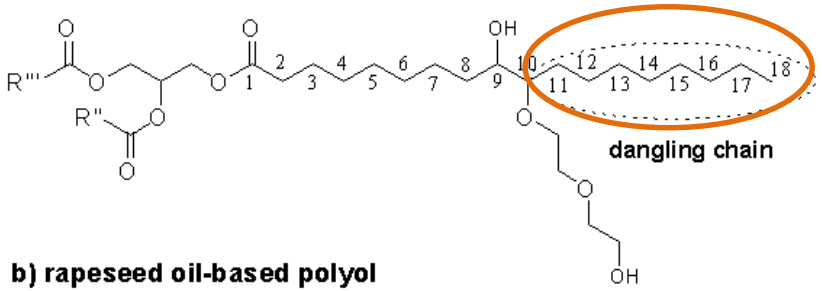


Catalysis Today, **2014**, 223, 148– 156

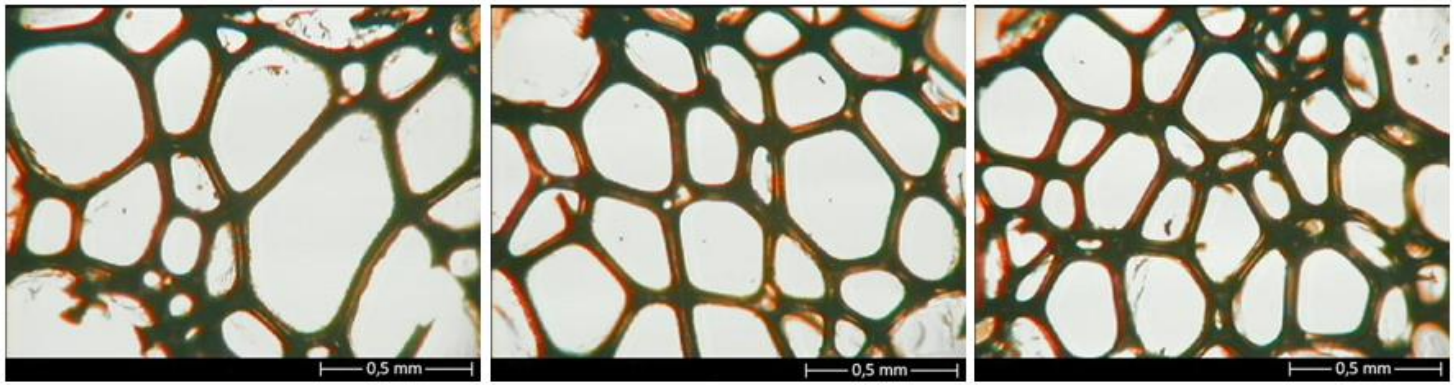
✓ Increase in flexibility when the foam is under loading strongly depends on the presence of longer dangling chains acting as plasticizer in the polyol structure



a) petrochemical polyol

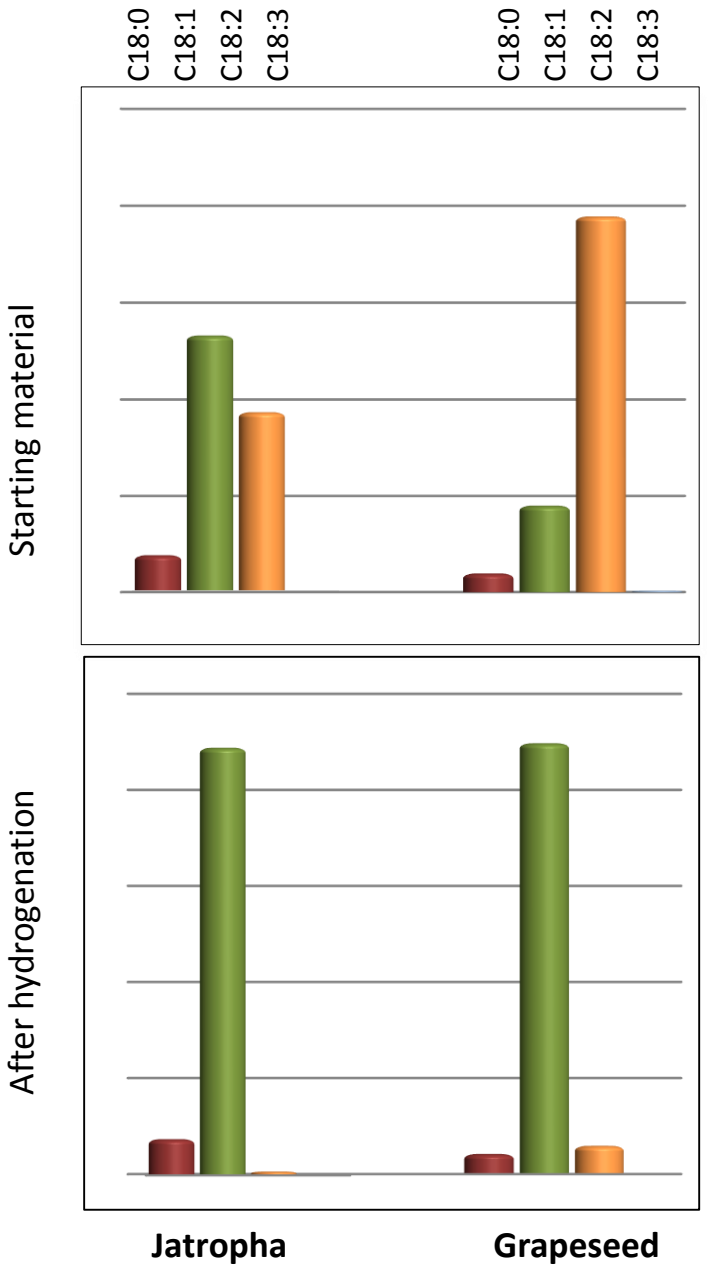


b) rapeseed oil-based polyol



R-85 O-85 HO-85

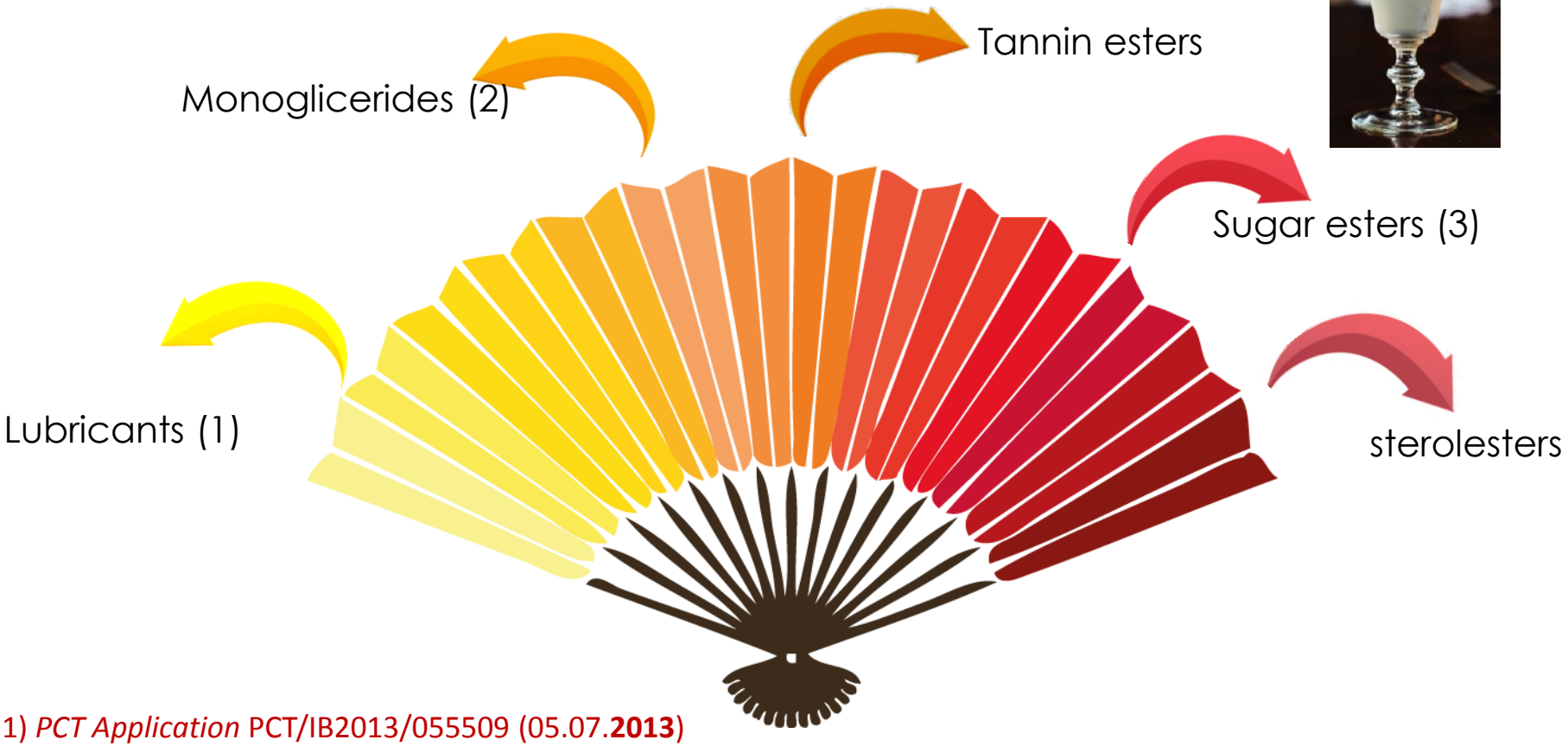
7,8 Mtonn → **1. 9 Mtonn/year**



IV 120

High Oleic

Esterification reactions



(1) *PCT Application* PCT/IB2013/055509 (05.07.**2013**)

(2) *Chem. Biol. Technol. Agric*. (2015) **2**, 23-30; *ChemistrySelect* **2016**, 1, 2999 – 3004

(3) *Molecular Catal.* **2017**, 433C, 383-390

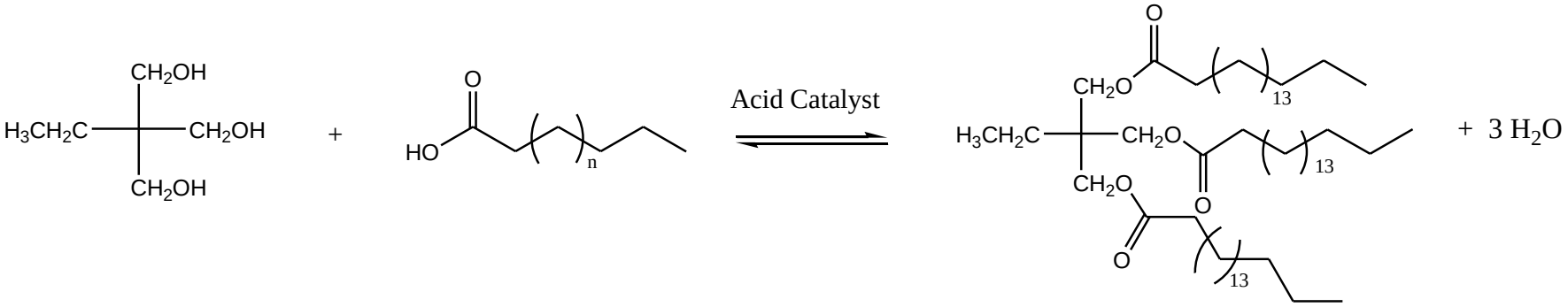
Lubricants

- Renewables ✓
- High lubricity ✓
- High viscosity Index ✓
- High flash point ✓
- Absence of PAH ✓
- Low aquatic toxicity ✓
- Poor oxidative stability ✗
- Poor thermal/hydrolytic stability ✗

40 M tonn in 2012

44 M tonn in 2017

50% into the environment

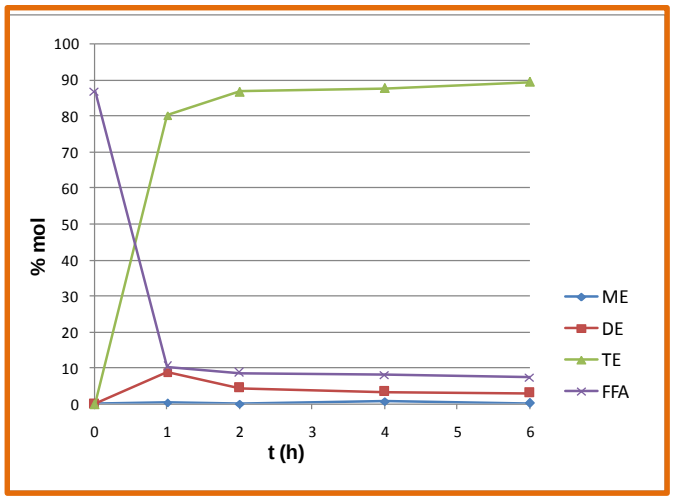


catalyst	Starting material	Conv (%)
SiO_2-ZrO_2 (5 %)	Oleic acid	**99.3**
SiO_2-ZrO_2 (3 %)	Oleic acid	**90.2**
SiO_2-TiO_2	Oleic acid	**96.8**
SiO_2-Al_2O_3	Oleic acid	**85.5**
SiO_2-ZrO_2	PFAD	**94.5**
SiO_2-ZrO_2	RBO	**94.8**

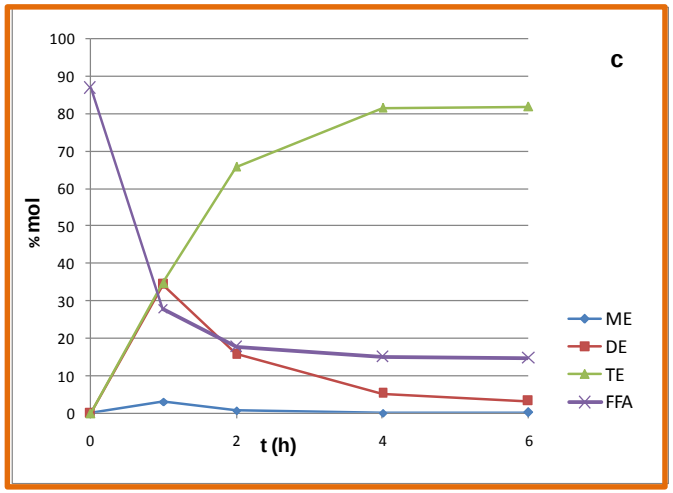
Sel. to triesters up to 95 %

It.Pat.Appl. MI**2012**A001189 ; *PCT Application* PCT/IB**2013**/055509 WO**2014**006595 A1

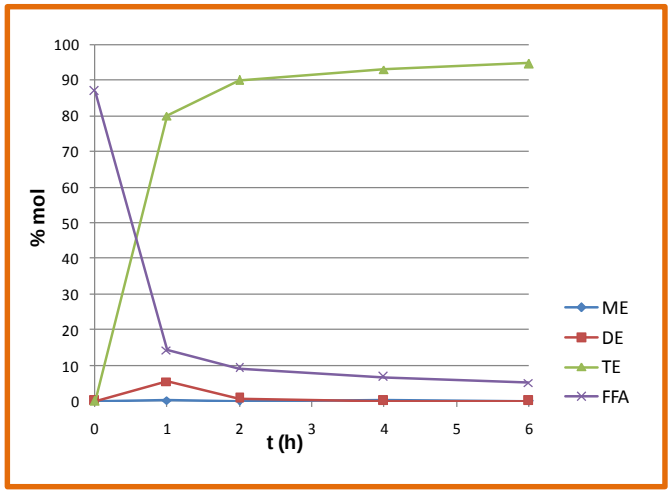
Selectivity to triesters



SnO



SiO_2-ZrO_2 3%



SiO_2-ZrO_2 5%

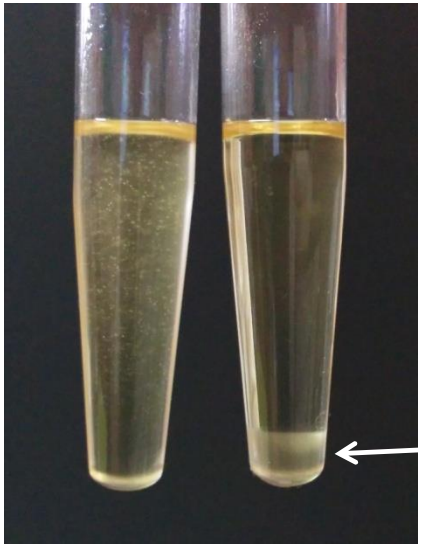
Appl. Catal. B : Environm. 2016, 181, 581–586

Reaction work-up

- ✓ No neutralization
- ✓ No washing

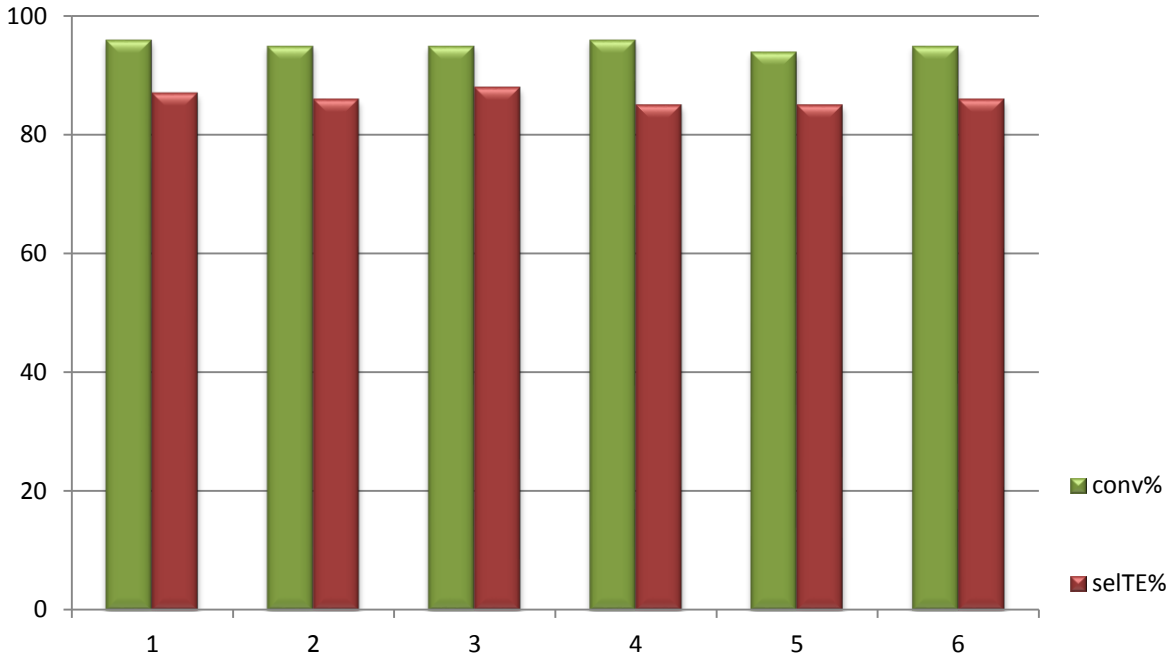
Before centrifugation

After centrifugation



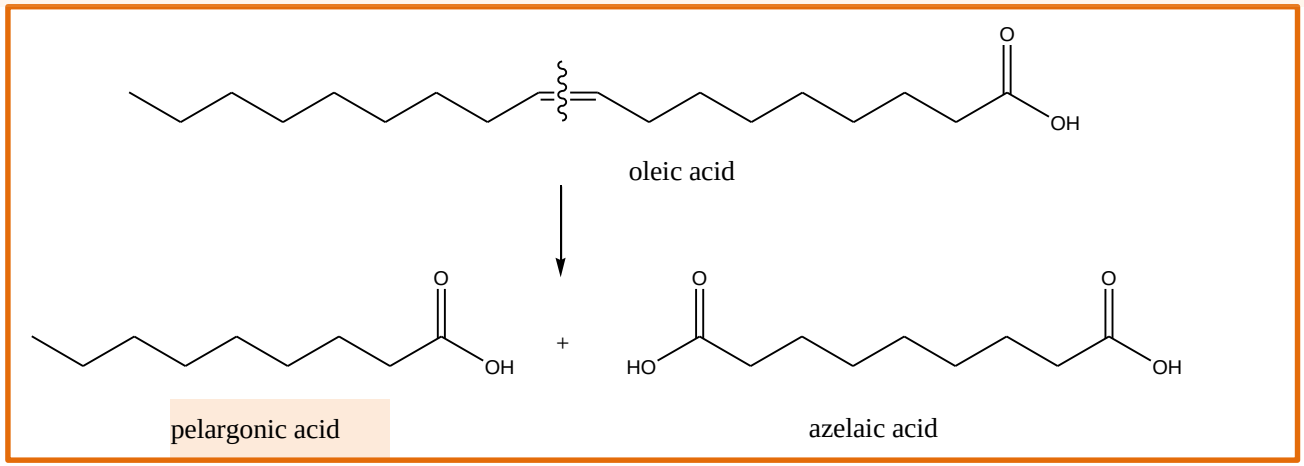
Catalyst

The catalyst is recyclable



The catalyst, after hot filtration, was washed with acetone and dried.
No activation (or re-activation) is required

Physical properties of C_9 TMP esters



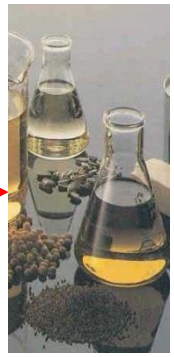
Viscosity 40°C (cSt)	Viscosity 100°C (cSt)	Viscosity Index	PP (°C)
22,3	4,5	118	

Catalyst	T (°C)	t (h)	Conv %	Color
SiO_2-ZrO_2 5%	200	6	>98	
SiO_2-Al_2O_3 135	200	6	94	
SiO_2-TiO_2 2.3%	200	6	94	

Protein hydrolisates

Pressing

Oil



ω-3, ω-6

Biofuels

Lubricants

Polyols

scrutching

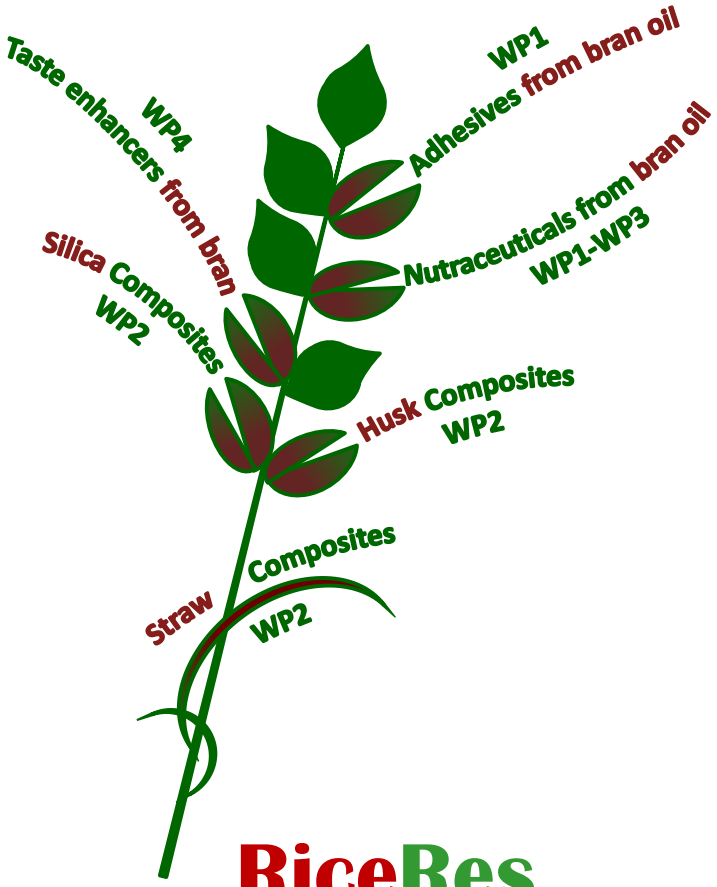
Fiber

Biomass

Oligomers and sugars

Green building materials

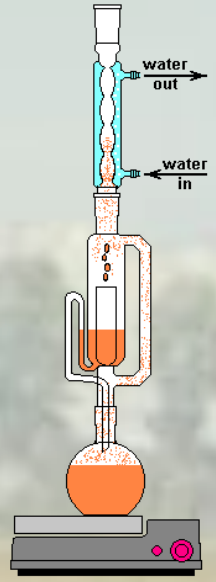
www.velica.org



RiceRes

ISTM

fondazione cariplo



Defatted Bran

Proteins

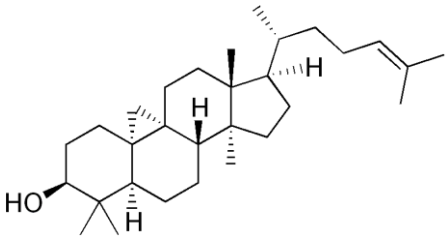
polysaccharides

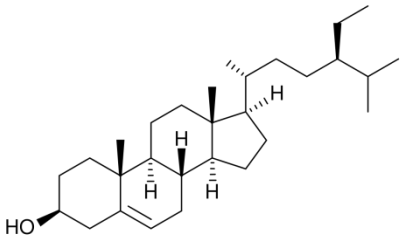
Rice Bran Oil

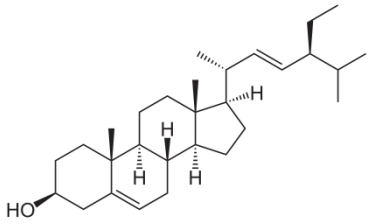
Waxes

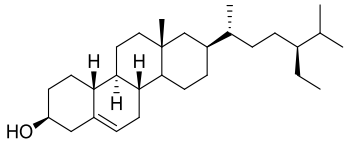
γ - orizanol

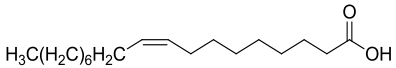
Sterols from gamma orizanol





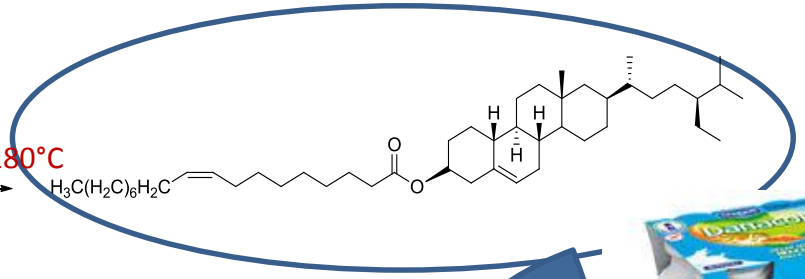






SiZr 5, 180°C

12 h



Conv 93%

Sel 100 %

Federica Zaccheria

Nicola Scotti Matteo Mariani

Valeria Pappalardo

KT
Kinetics Technology

intercos
GROUP

bellini S.p.A.
TECNOLOGIA DELLA LUBRIFICAZIONE

GRACE Davison

LINNAEUS
PLANT SCIENCES INC.

Eni Corporate

Arizona
CHEMICAL

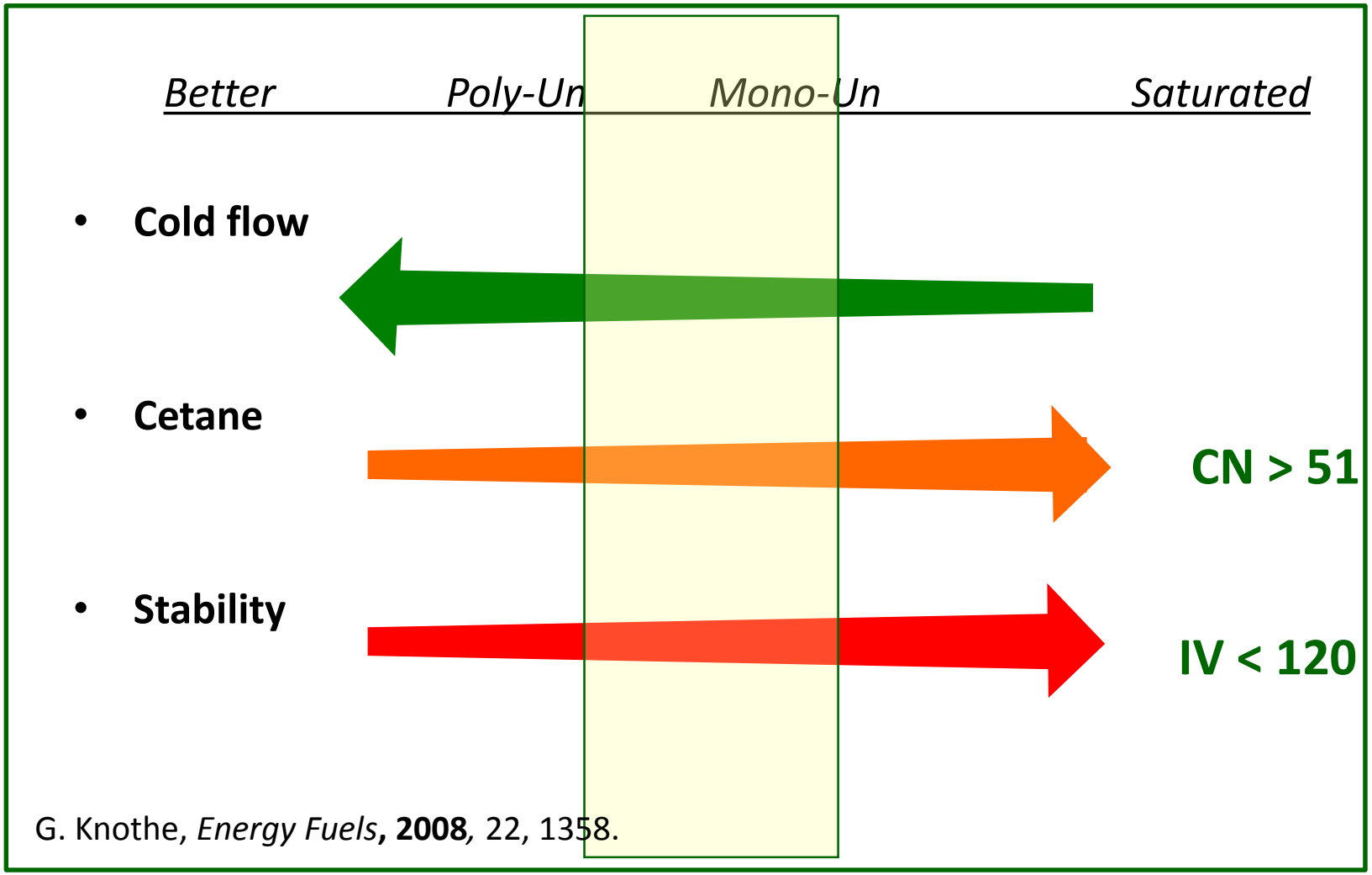
domus S.p.A.
CHEMICALS

FRI-ELGREENPOWER
THE CLEAN ENERGY COMPANY

t (min)	C18:0	*trans* (% mol)	posit. (% mol)	IV	Pour p. (°C)
Flaxseed oil methyl esters					
0	3.4	-	-	186	-23
30	4.2	19.8	15	112	-11
Plukenetia volubilis oil methyl esters					
0	2.7	-	-	202	-25
30	3.0	26.0	24.0	115	-13
Safflower oil methyl esters					
0	2.5	-	-	140	-22
30	2.6	36.0	4.5	95	-10
Grapeseed oil methyl esters					
0	3.9	-	-	145	-18
60	3.6	35.0	5.6	108	-12
Pumpkin oil methyl esters					
0	6.7	-	-	107	-8
120	7.1	26.0	2.0	96	-2

Biodiesel quality

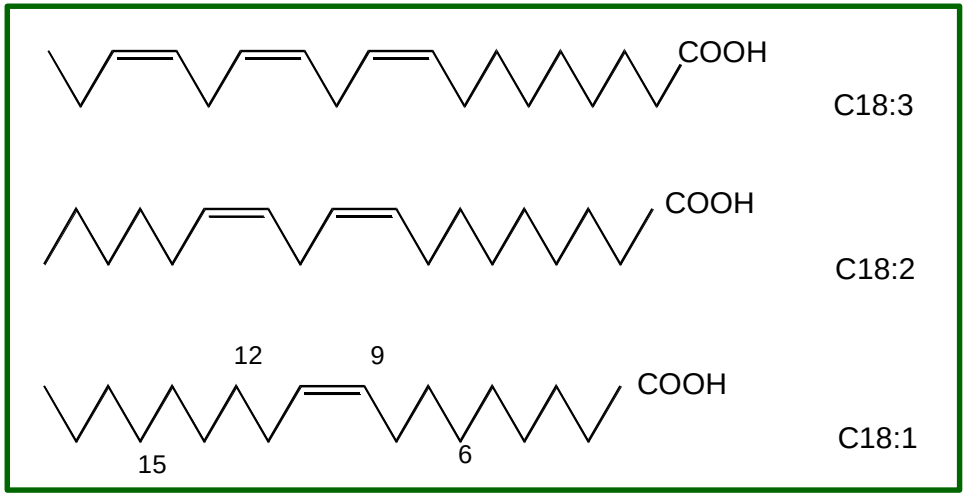
EN



G. Knothe, *Energy Fuels*, **2008**, 22, 1358.

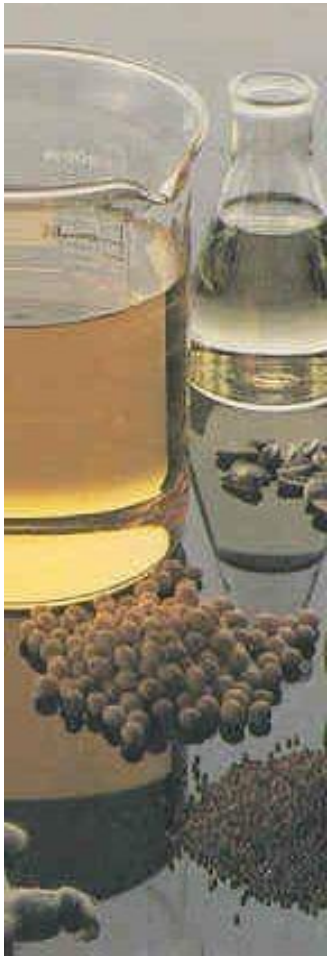
PLANET GREEN CHEM

Relazione struttura-stabilità ossidativa- proprietà a freddo



	V_{ox}	mp (°C)
C18:3	100	-13
C18:2	40	-7
C18:1	10	+16
C18:0	1	+30

	mp Z	mp E
6(7)	28	53
9(10)	16	45
12(13)	27	52
15(16)	40	58



PLANET GREEN CHEM

Polioli da olio vegetale

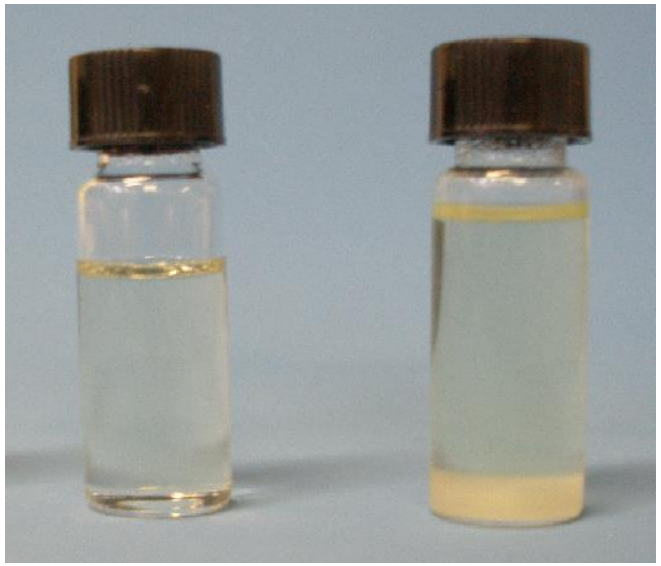
POLIURETANI

US 2002/0161161 A1 to Cognis:

- almeno 85% acido oleico
- alto oleico, basso stearico(85-95%, 0.5-2.5%)

PLANET GREEN CHEM

Metilesteri di lino idogenati



Cu catalyst **Ni catalyst** **Cu catalyst** **Ni catalyst**

Stabilità ossidativa(Rancimat) da < 1h → 5.3 h

PLANET GREEN CHEM