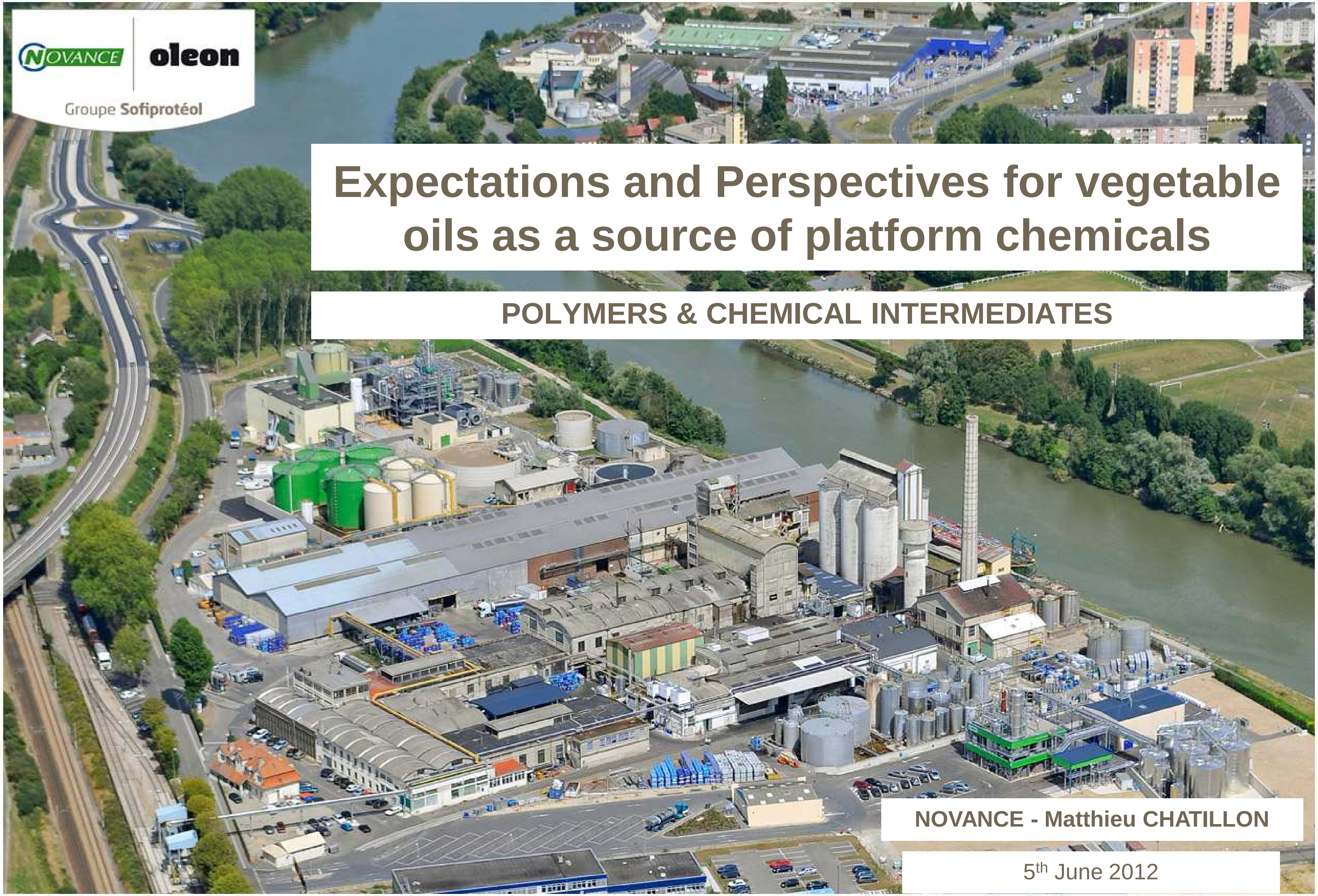

Expectations and Perspectives for vegetable oils as a source of platform chemicals

POLYMERS & CHEMICAL INTERMEDIATES

NOVANCE - Matthieu CHATILLON

5th June 2012

Agenda

1. **Availability, composition and prices as first criterias for new molecule development**

2. **Value chain of Oleochemistry : Towards a new innovation complexity & more added value platform molecules**

   a. **The first generation platform molecules : Fatty acid, fatty alcohol & fatty esters**

   b. **The second generation platform molecules :**

      i. **New development routes**

      ii. **More added value products based on fatty acid & glycerol**

      iii. **The 2nd generation molecule : a industrial reality**

3. **The Markets drivers**

4. **The Other factors of those platform molecules developments**

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Availability, composition and prices of vegetable oils : The first criterias

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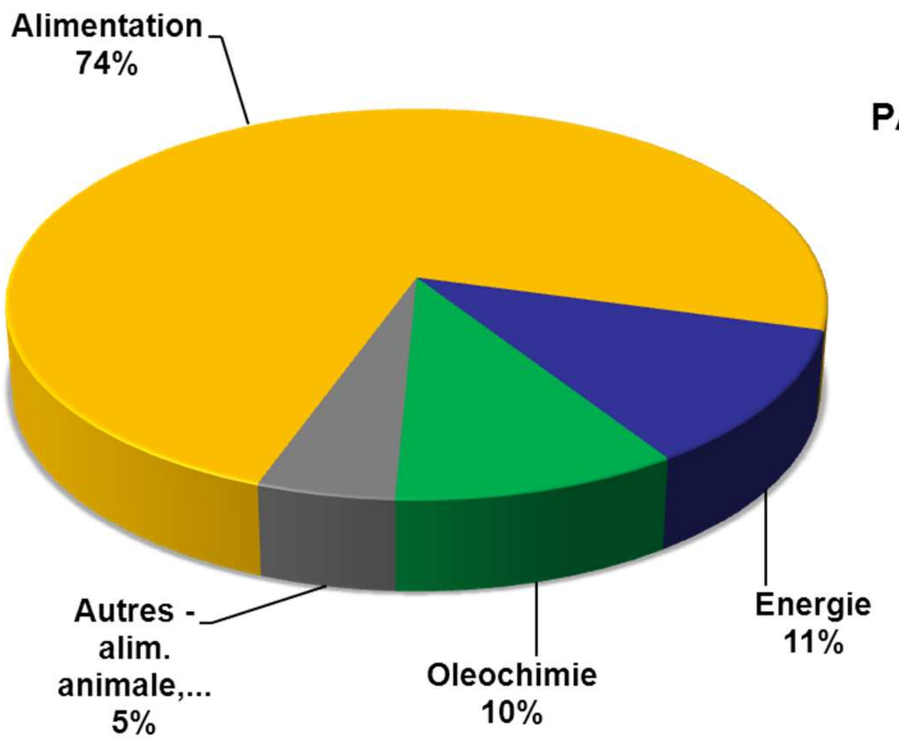
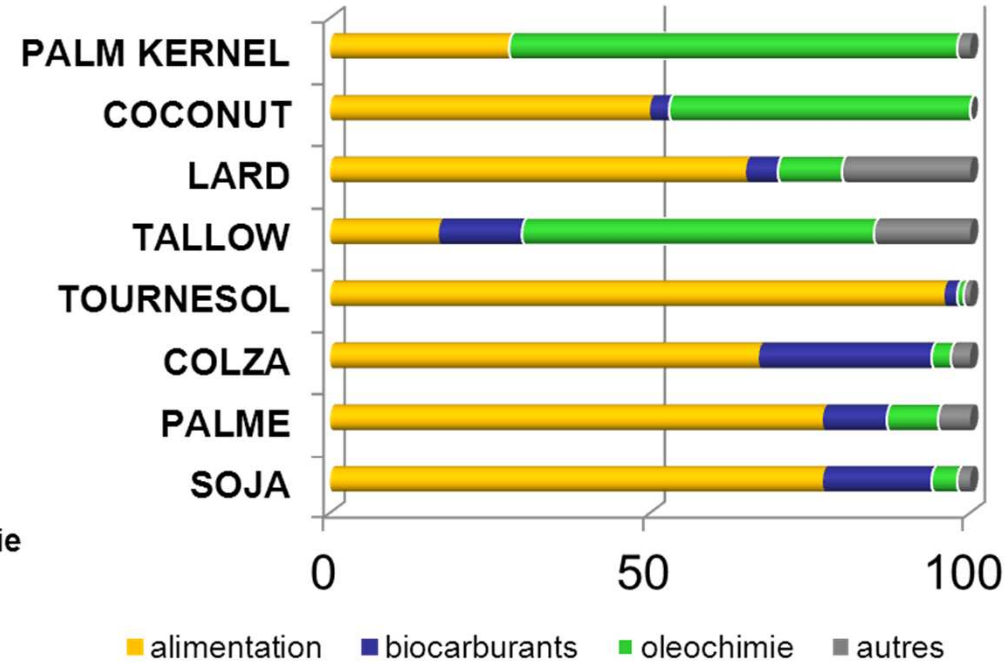
Availability of vegetable oil and fats

The worldwide production is approximately 180 millions of tonnes

Worlwide consumption



Application uses splitting



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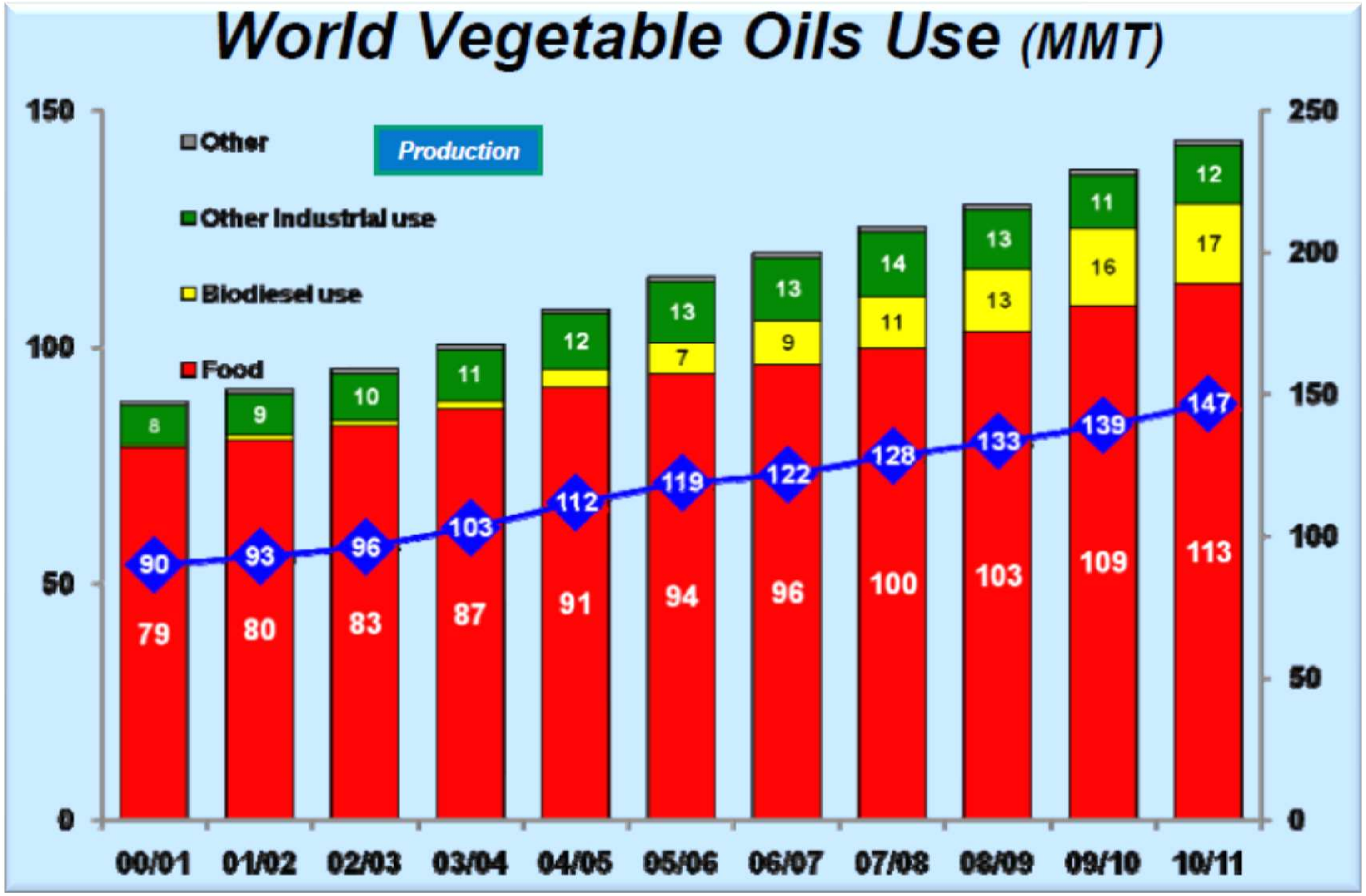
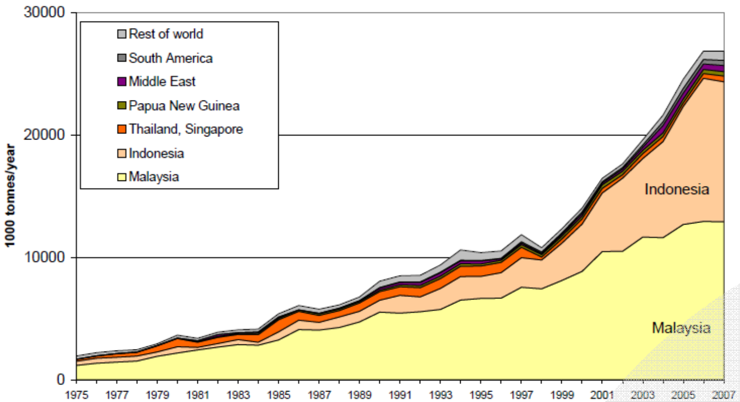
« Only » 10% for chemical applications



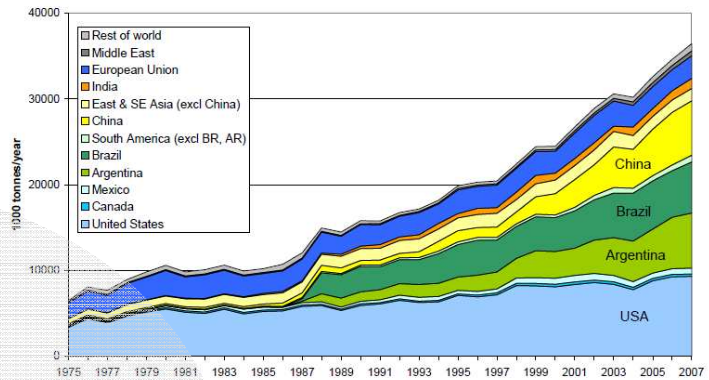
Adapted from: Klaus Schumaker, Developments on the markets for grains, oilseeds and feedstuffs

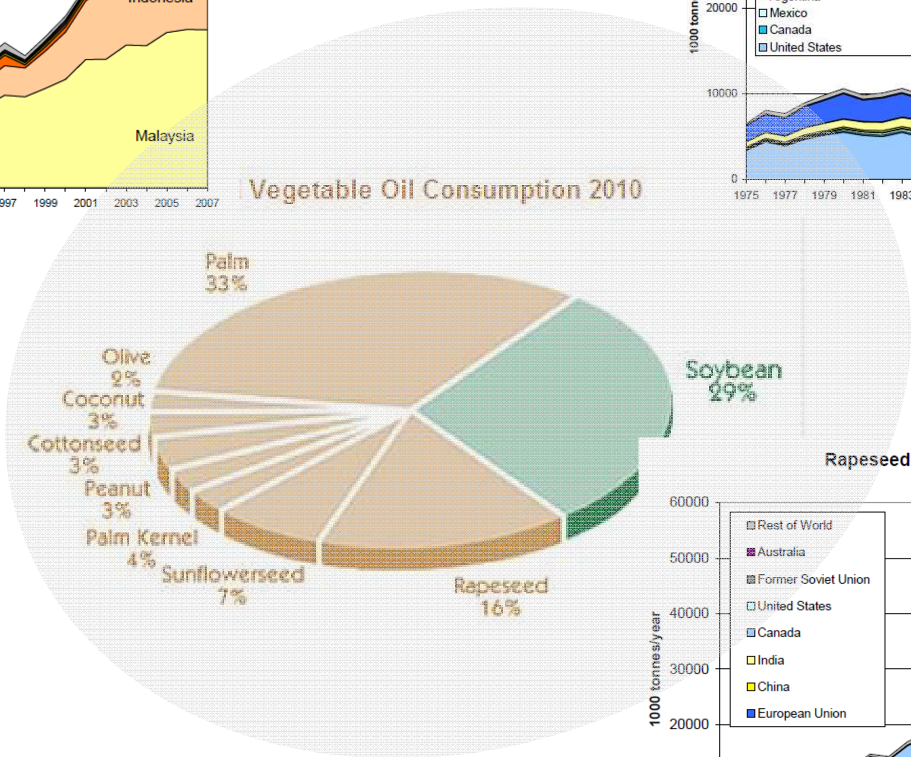
Vegetable oils, available raw material all around the world

Palm oil export by country / region

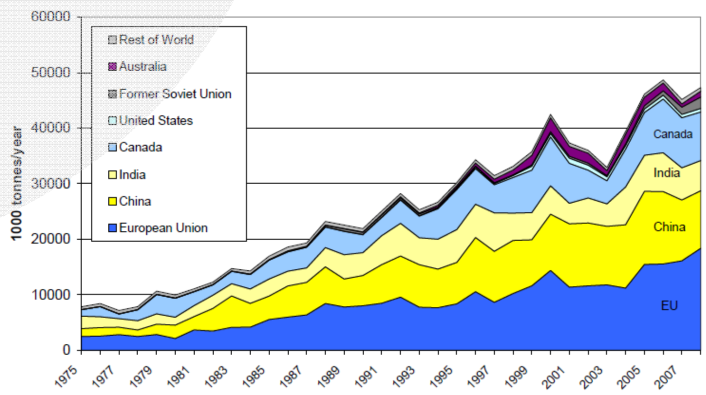


Soya oil production by country / region

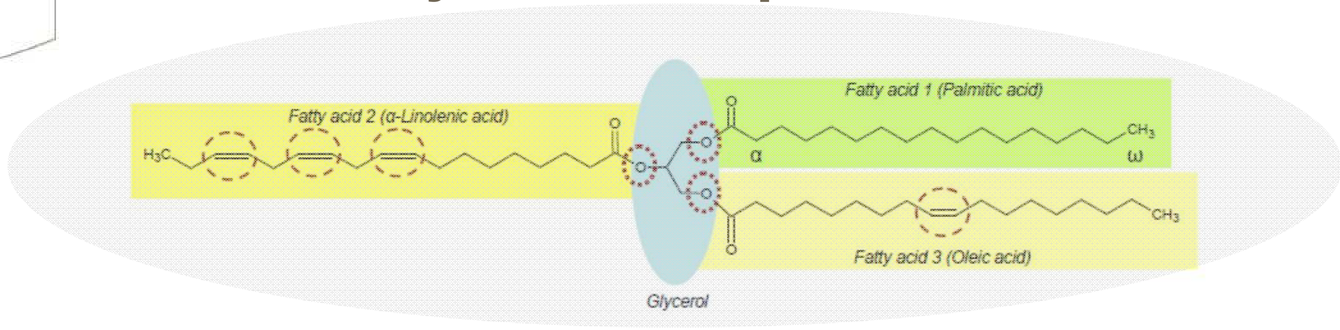




Rapeseed production by country / region



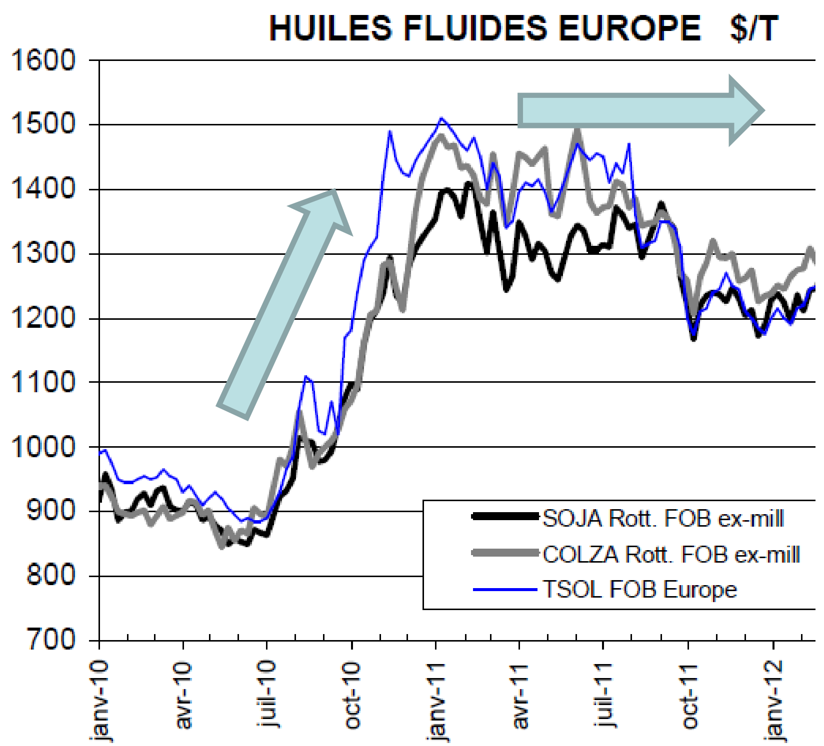
The fatty acid composition, the first step

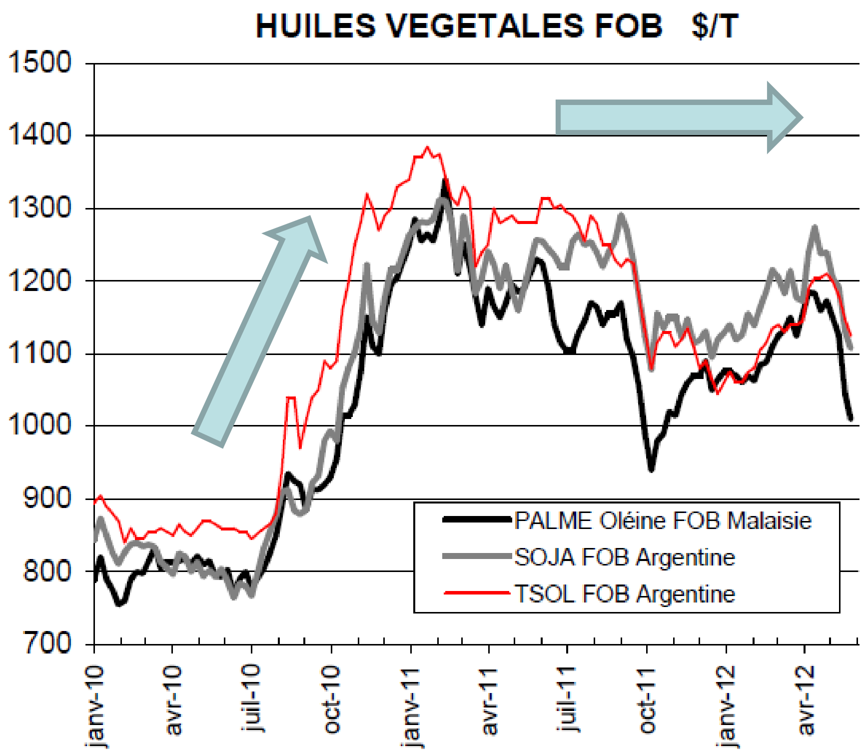


Acides gras	Type	Colza		Tournesol		Soja	Coco	Palme		Ricin
		0:0	érucique	classique	oléique		coprah	palmiste	palme	
caprylique	C8:0	-	-	-	-	-	6 – 10	2-5	-	-
caprique	C10:0	-	-	-	-	-	6 – 10	3-5	-	-
laurique	C12:0	-	-	-	-	-	**39- 54**	**44-51**	traces	-
myristique	C14:0	0 - 1	-	-	-	traces	15- 23	15-17	1 – 2	-
palmitique	C16:0	1 - 5	3	5 – 7	4	8 – 13	6 – 11	7-10	**43– 46**	0.5-1
stéarique	C18:0	0.5 – 2	1	4 – 6	5	2 – 5	1 – 4	2-3	4 – 6	0.5-1
oléique	C18:1	**50– 65**	16	15 - 25	**>(75) 80**	17- 26	4 – 11	11-18	37- 41	2-6
ricinoléique	C18:1	-	-	-	-	-	-	-	-	**85-95**
linoléique	C18:2	15- 30	14	**62 - 70**	8 (< 10)	**50- 62**	1 – 2	1-4	9 – 12	1-5
linolénique	C18:3	6 – 13	10	< 0.2	< 1	4 – 10	traces	traces	traces	0.5-1
eicosénoïque	C20:1	1 – 3	6	< 0.5	-	< 0.4	-	-	-	-
bethénique	C22:0	0.5	-	< 1	-	< 0.5	-	-	-	-
érucique	C22:1	0 – 5	**> 45 (50)**	-	-	-	-	-	-	-

Source : Karleskind 1992, F. Gunstone, The chemistry of oils and fats, 2004.

Price, a key for futur development

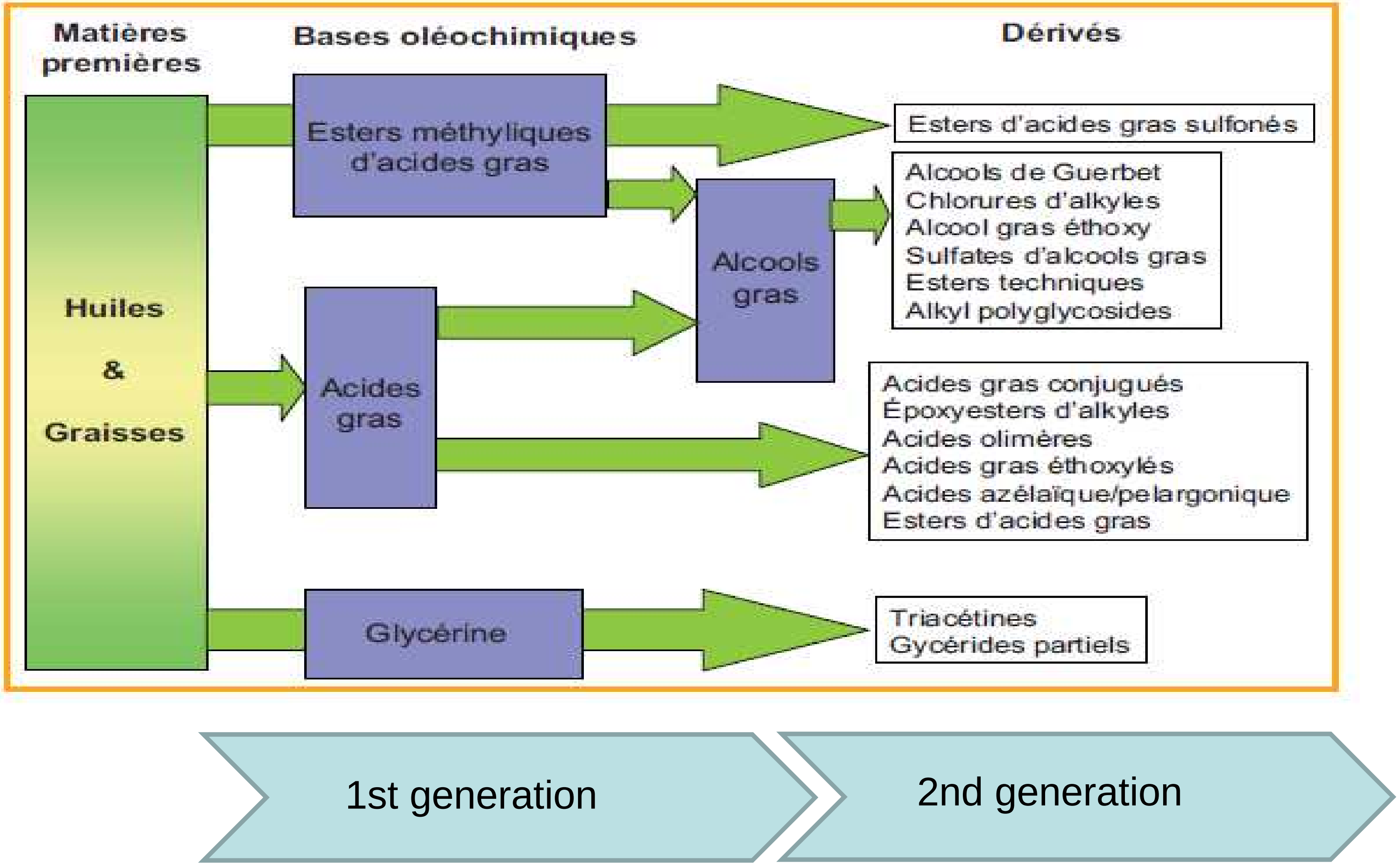




Prices are coming to be more stable to better select the main adapted outlet for new development

Value chain of Oleochemistry : Towards a new innovation complexity & more added value platform molecules

Value chain of the Oleochemistry



Oleochemistry aspiration

Innovation of substitution : different molecule structure compared to petrochemical ones but with same activities

Innovation of substitution (2) : Same molecule substitution

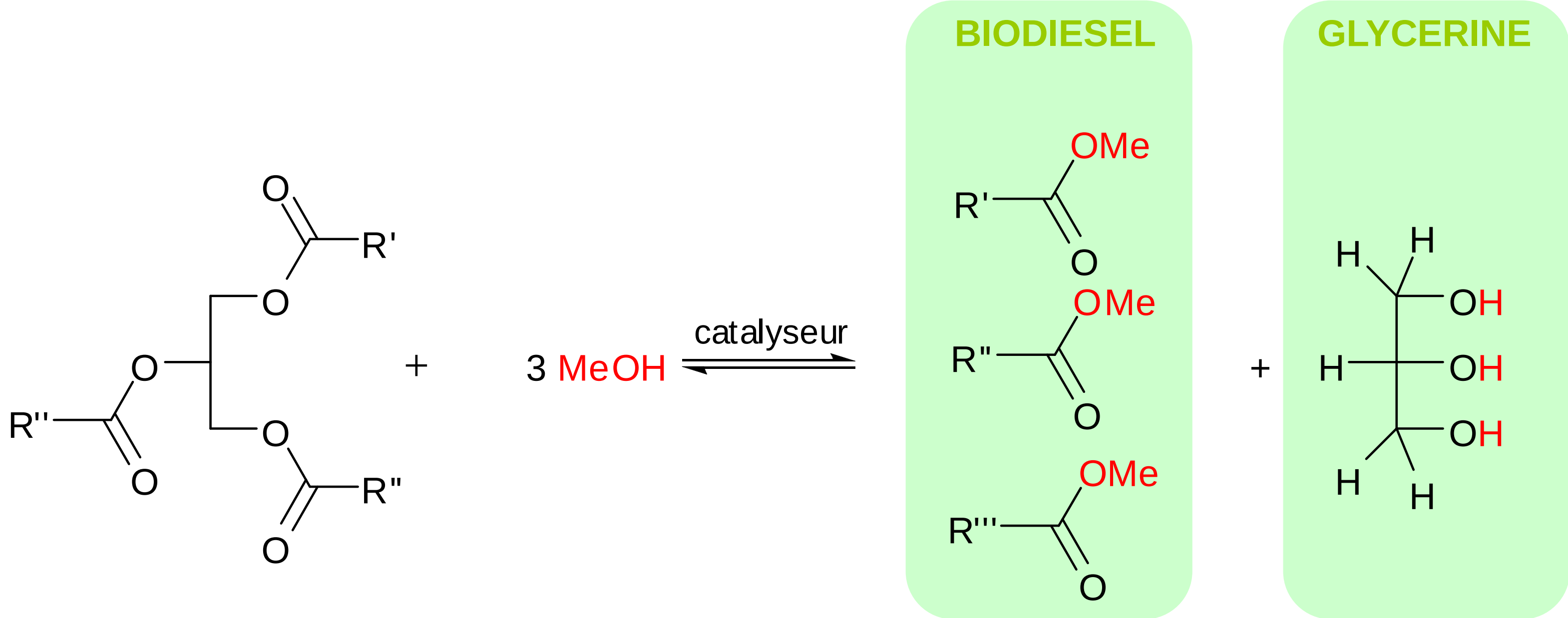
Rupture of technologies : New molecules and new activities

The 1st oleochemistry generation is lead to innovation of substitution whereas the 2nd generation will lead to a more traditional innovation

BUT all innovation will continue to exist simultaneously

1st generation oleochemistry (1/3)

Trans-esterification (exemple : Biodiesel)

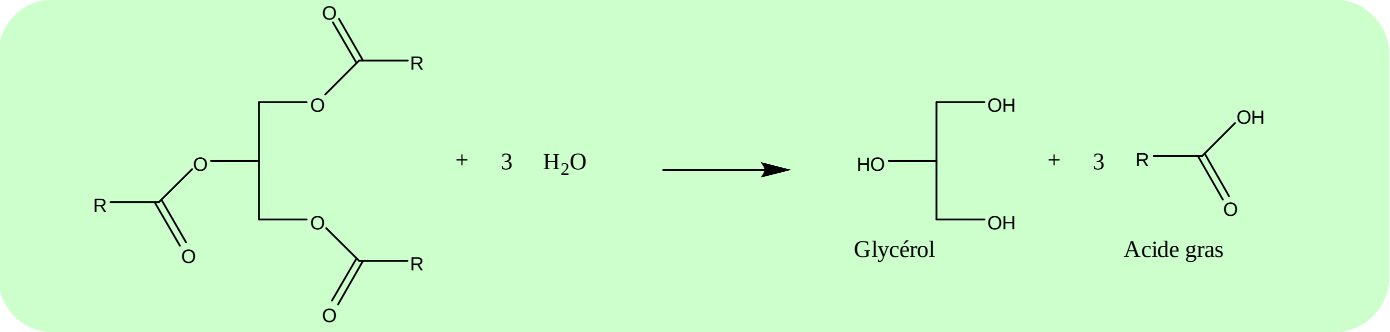


Triglycéride		Alcool (méthanol)		Mélange d'Esters de méthyle		Glycérol
1000 kg	**+**	**100 kg**	→	**1000 kg**	**+**	**100 kg**

1st generation oleochemistry (2/3)

Hydrolysis : Production of fatty acid and glycerine

- **Description**
  Basic reaction mixture (NaOH, KOH) at 100℃ ⇨ Saponif ication



- **Contineous process**
  Oil + water at 250℃ under 20 to 60 Bars

- **Production and market estimation**
  - Production 2010 : nearly 6.8 Mn T
  - Main raw material source : Palm oil
  - Main Chain length fatty acids : C12, C14, C16

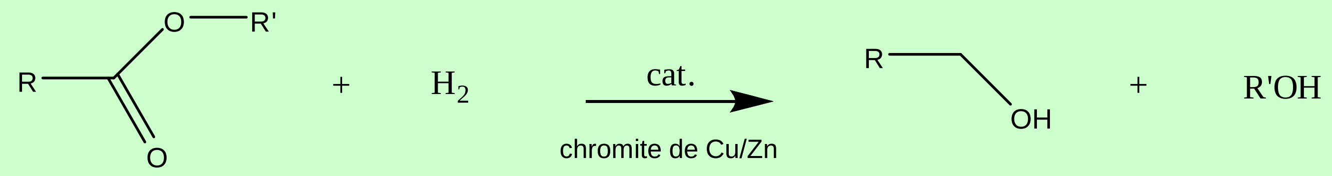
1st generation oleochemistry (3/3)

Hydrogenation : Production of saturated fatty acid and fatty alcohol

- **Transformation**

  Hydrogenation at 250-300℃ under 200-300 bars

  Possible reduction of unsaturation with speicla catalyst



- **Products**
  - Fractions **C8-11, C12-14, C12-15, C16-18** (from coco, palmist, palm)
  - Price **x 2** en 2010 (**$3/kg**, Jan 2011 ICIS)
    - └ High demand in renewable fatty alcohol
    - └ Raw materials price increase

- **Main outlet = Detergency**

	2004	2010[1]
Worldwide production (10^6 t)	2.2	3.1
Petrochemical based	40%	27%
Vegetable based	**60%**	**73%**

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2nd generation oleochemistry : a richer chemistry

TAG

ESTERS → **BIODIESEL**

ESTERS / FATTY ACID:

- Esterification, Amidation, Hydrogenolysis → Fonctionnalised derivatives **Esters, amides, alcohols,…**
- Dimerisation, Ozonolyse → Nex building blocks **Diacides, diols,…**
- Metathesis → New building blocks **Diacides, acides gras, ω-insaturés**
- Hydroformylation → Fonctionnalised derivatives **Polyaldehydes, polyacides,…**

Polymers
Intermediates
Lubricants
Surfactants
Adjuvants
Solvents
…

GLYCEROL:

- Oxydation → Building blocks **Dihydroxyacétone, acide glycérique**
- Hydrogenolysis, Transcarbonatation → Solvents, additives & building blocks **1,2- Propanediol, Glycerol carbonate**
- Polymerisation, Glycérolyse, Esterification → Surfactants and polymers **Polyglycerol esters , Partial glycerides**

- The 2nd generation oleochemistry is reacting on unsaturation and produce new reactive functions
- Biotechnology, thermal and chemical technologies are existing simultaneously

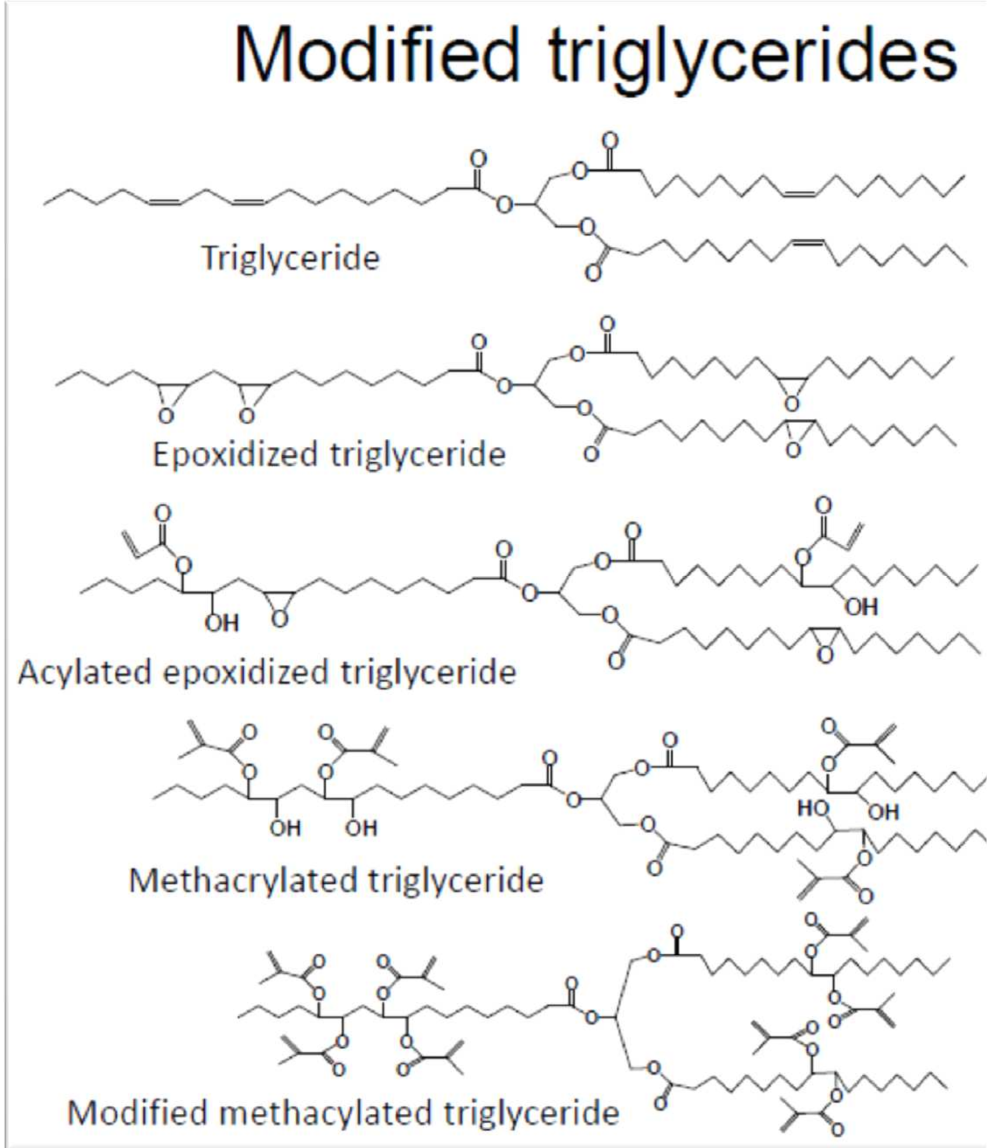
The 2nd generation Fatty acid chemistry (1/3)

Epoxydation as a source of new reactive oleochemicals

- **Transformation**
  - Organic catalyst : formic or acetic acid
  - H_2O_2
  - Temperature : 60 to 80℃
  - Atmospheric pressure

- **Products**
  - Epoxidized vegetable oil
  - Epoxidized esters
  - Hydroxylated esters & vegetable oils

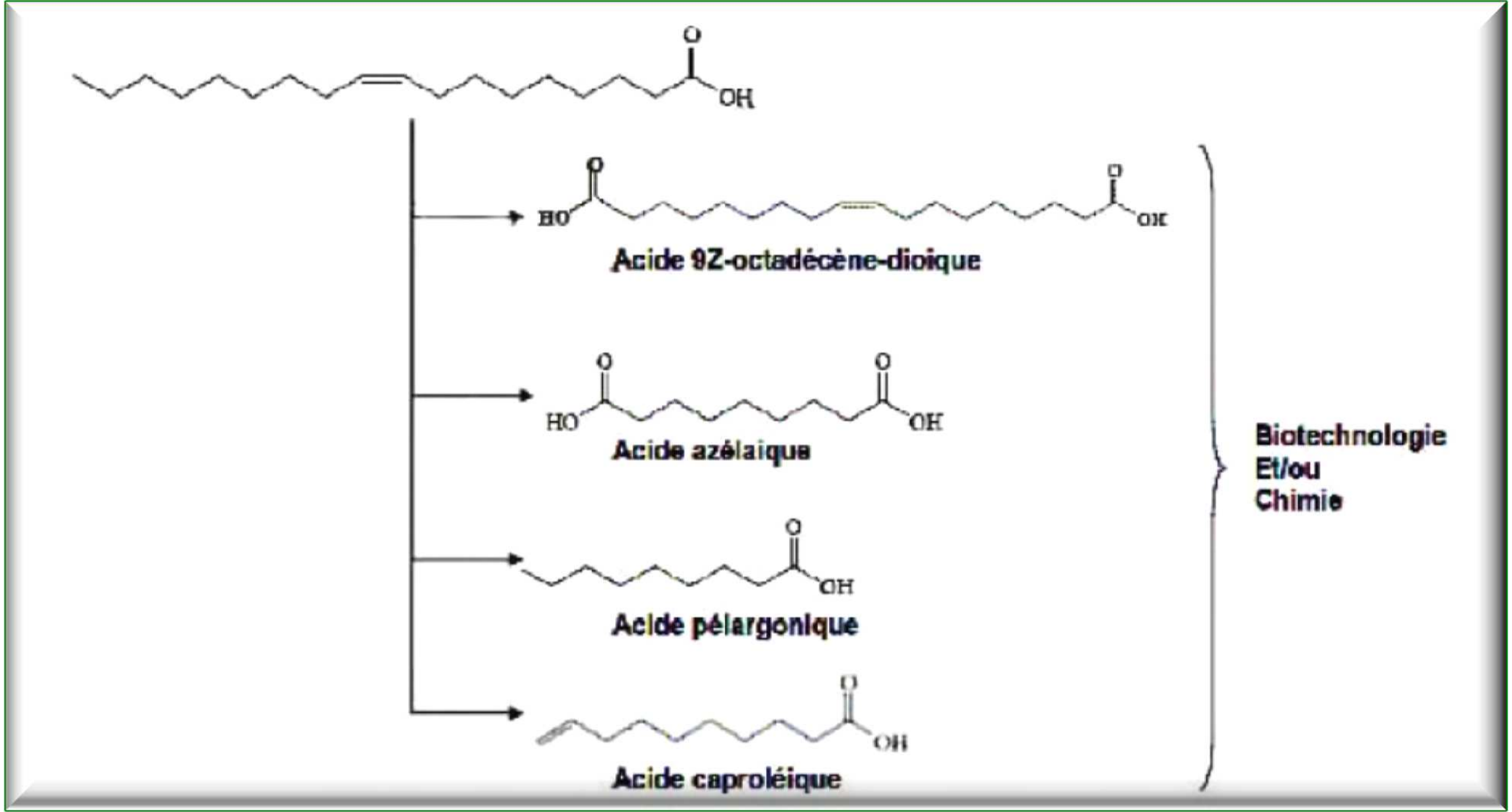
- **Main outlet = Plasticizers**



The 2nd generation fatty acid chemistry (2/3)

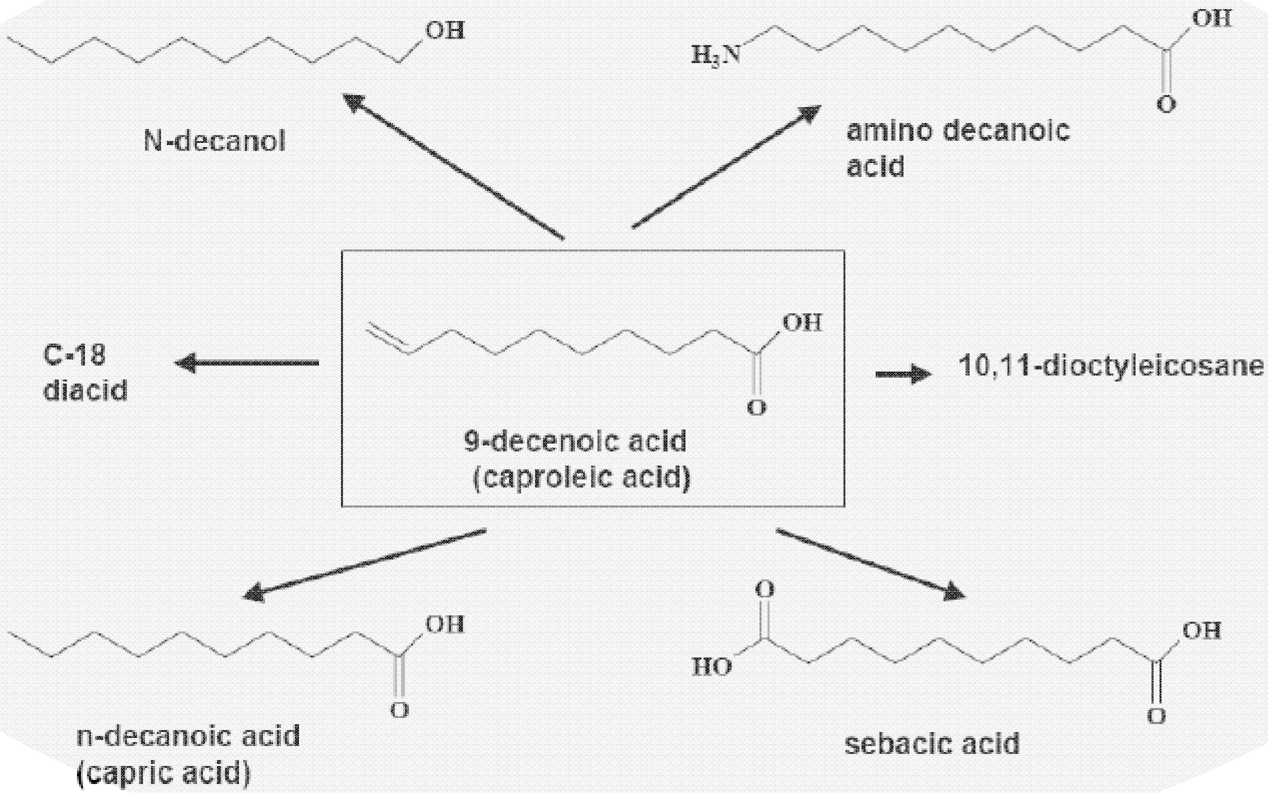
Fatty acid, a platform molecule

An access to new buidling blocks (few exemples below)



The 2nd generation fatty acid chemistry (3/3)

A high added value chain products

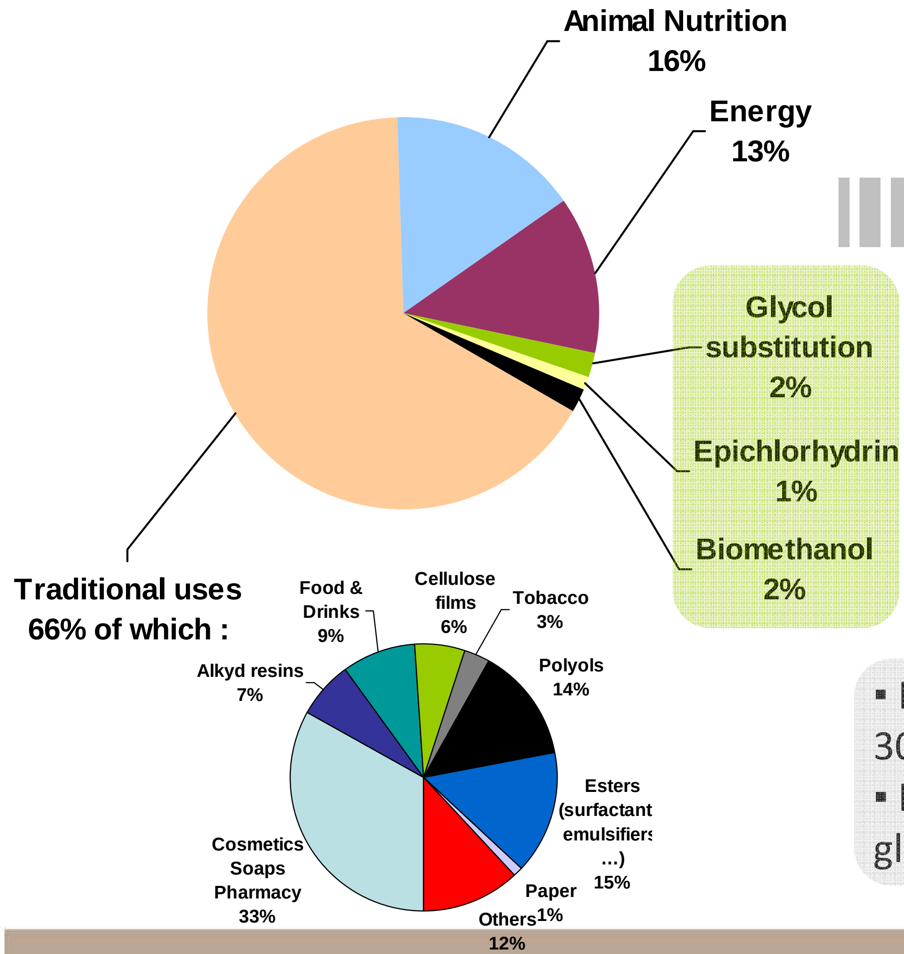


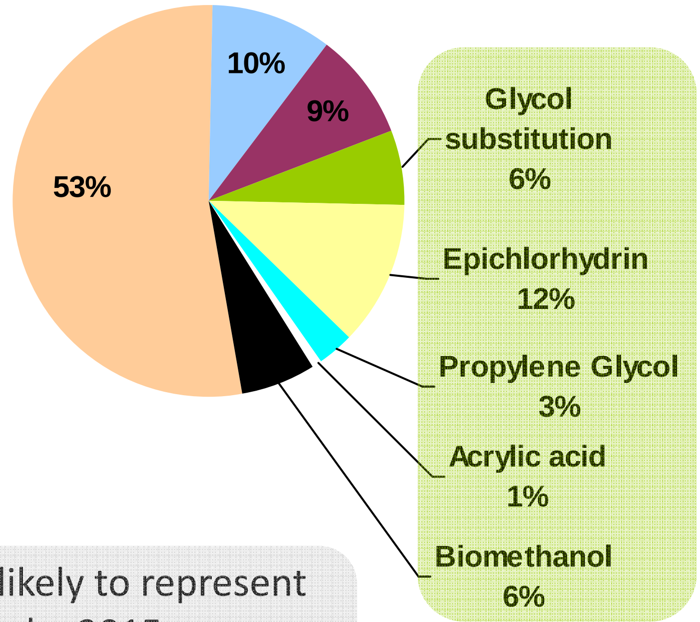
Source : DC Cameron, Cargill

The 2nd generation glycerol chemistry (1/3)

2009
2.2 million tons

2015 (est.)
3.5 million tons



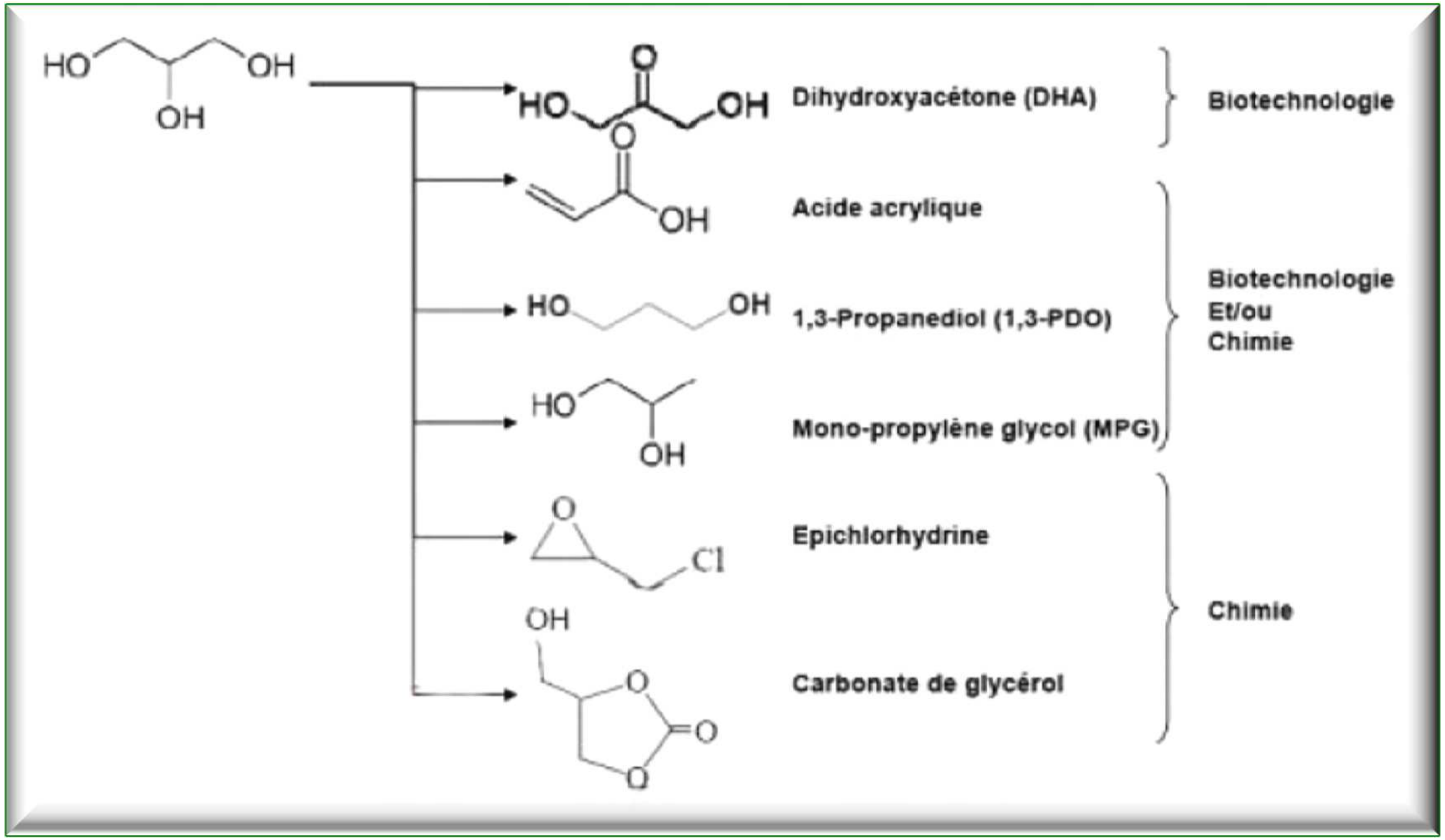


- New applications likely to represent 30% of glycerin uses by 2015
- Higher requirement in refined glycerin for these applications

The 2nd generation glycerol chemistry (2/3)

Glycerol, a platform molecule

An access to new buidling blocks through different routes



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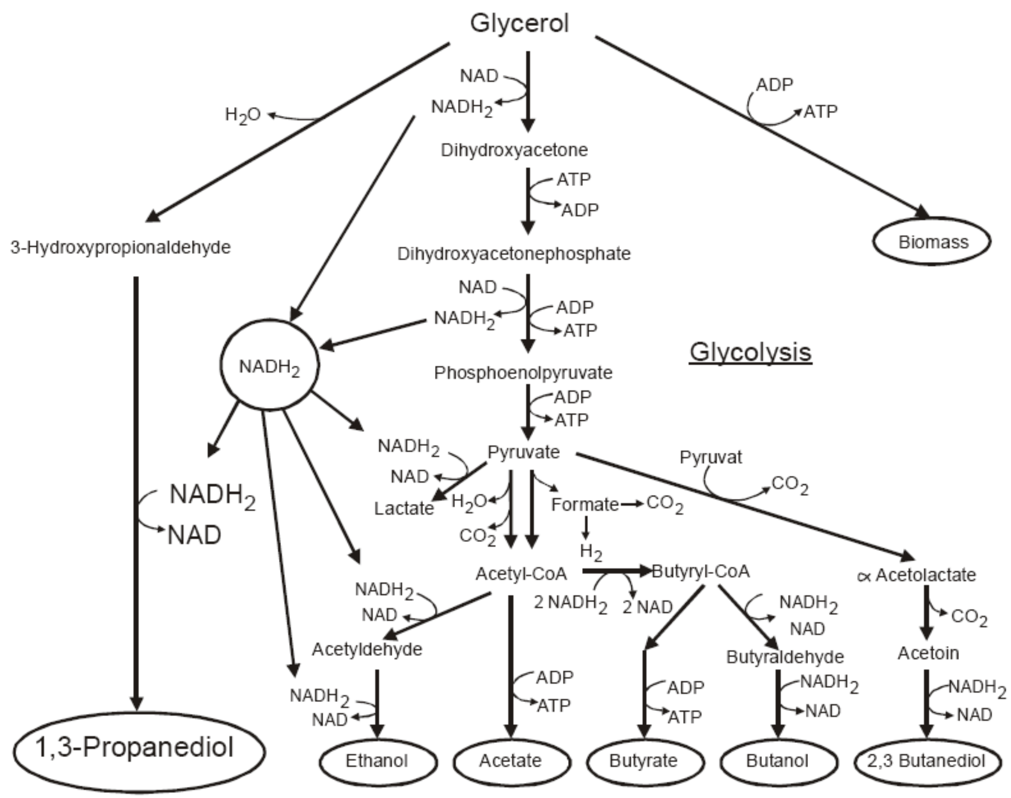
The 2nd generation glycerol chemistry (3/3)

An exceptional feed for micro-organisms

A source for easy way access to multi-step chemistry

Figure 8.5
METABOLIC PATHWAYS OF GLYCEROL METABOLISM



Source: 257225

The 2nd generation oleochemistry as a industrial and market reality (1/2)

Réaction	Produit principal	Applications	Commentaires
Reformation	Gaz de synthèse CO, H_2	Dérivés d'une réaction de Fischer-Tropsch	Bon ratio CO/H_2 pour obtenir du méthanol.
Déshydratation	Acroléine Acide acrylique Acrylonitrile	Nombreux dérivés polymères (peintures et résines acryliques, fibres textiles, résines ABS), détergents, etc. Importants marchés.	Travaux d'**Arkema** de production d'acide acrylique via l'acroléine. Des procédés émergents d'obtention directe d'acide acrylique et d'acrylonitrile à partir du glycérol. *L'acide acrylique peut être obtenu également par fermentation du glucose (**OPX** aux USA). **Cargill** et **Novozymes** mènent un projet où le 3-HPA est un intermédiaire.*
Oxydation sélective ou **fermentation**	Acide glycérique	Polymères, etc.	Encore au stade de recherche.
	Dihydroxyacétone	Cosmétique : agent autobronzant.	Petits marchés. Produit par **ARD** par fermentation du glycérol.

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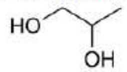
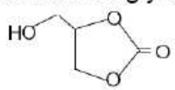
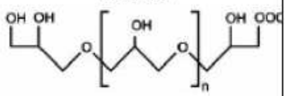
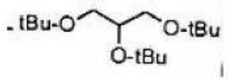
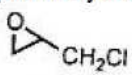
The 2nd generation oleochemistry as a industrial and market reality (1/2)

Hydrogénolyse ou **fermentation**	Propylène glycol MPG, 1,2 propanediol 	Emulsifiant alimentaire, solvant, humectant. Dégivrant, liquides de refroidissement, fibres polyesters. Importants marchés.	Productions à partir de glycérol par **ADM** (unité de 100 Kt), + *projets Cargill, Virent, Dow, Huntsman ??* Projets par fermentation ? **Met Ex** développe un procédé par fermentation. De glucose ou de glycérol ?
	1,3 propanediol (1,3 PDO) 	Composant de polyesters pour fibres, films et revêtements. Important marché.	**Met Ex** dispose d'un procédé au stade pilote de production du 1,3 PDO à partir de glycérol. ***DuPont / Tate & Lyle** produisent du 1,3 PDO à partir de glucose.*
Carboxylation	Carbonate de glycérol 	Emollient (cosmétique). Potentiel pour produire des polycarbonates.	Deux procédés au point mais coûts de revient encore élevés. Acteurs : **Novance** et **Huntsman**.
	↳ Glycidol 	Polyglicidol, utilisable dans les résines époxy ou les polyuréthanes.	Le glycidol peut être produit à partir du carbonate de glycérol ou de l'épichlorhydrine.
Estérification, transestérification	Polyglycérols et leurs esters 	Emulsifiants cosmétiques et agroalimentaires.	Nombreuses autres applications potentielles : nouveaux polymères.
Ethérification	Tertiobutyl éther 	Additifs de carburants concurrents du MTBE et de l'ETBE.	Pas encore de développement industriel.
Chlorination	Epichlorhydrine 	Résines époxy, etc.	Unité de 10 000 t de **Solvay** opérationnelle en France. Construction d'une unité de 100 Kt en Thaïlande.

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The Markets Drivers

High markets needs as a good perspective

(kT)	2005	2015	2030
Organic intermediates	~0	4 500	11 250
Surfactants	110	184	205
Biolubricants	1	95	145
Biosolvents	9	46	84
Pigments, inks and coating	29	109	198
Biopolymers	10	2 334	4 623

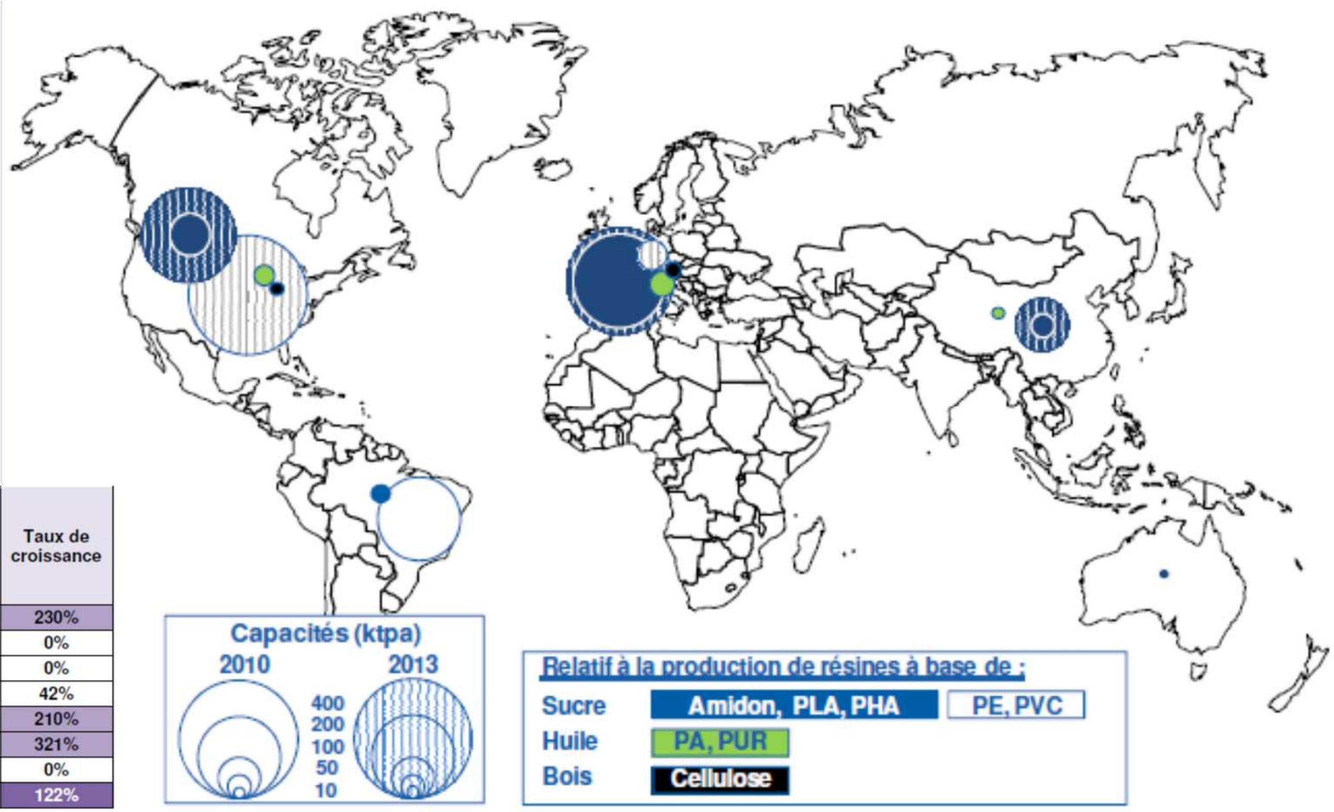
- Source: Marché actuel des bioproduits énergétiques et industriels & évolutions prévisibles à échéance 2015/2030. ALCIMED 2007
- Données basées sur un scénario qui parie sur un fort développement des bioproduits reposant sur une forte augmentation du prix du baril de pétrole, une pression sociétale s'exprimant pour les bioproduits et une mobilisation forte de la recherche en faveur des bioproduits.

Polymers, the largest outlet for renewable building blocks (1/3)

What are the expectation for oleochemistry ?

Plastic worldwide production	245 Mn T (2010)
└Bioplastics capacity	0.72 Mn T (0.3%)

Study ADEME/ALCIMED January 2011



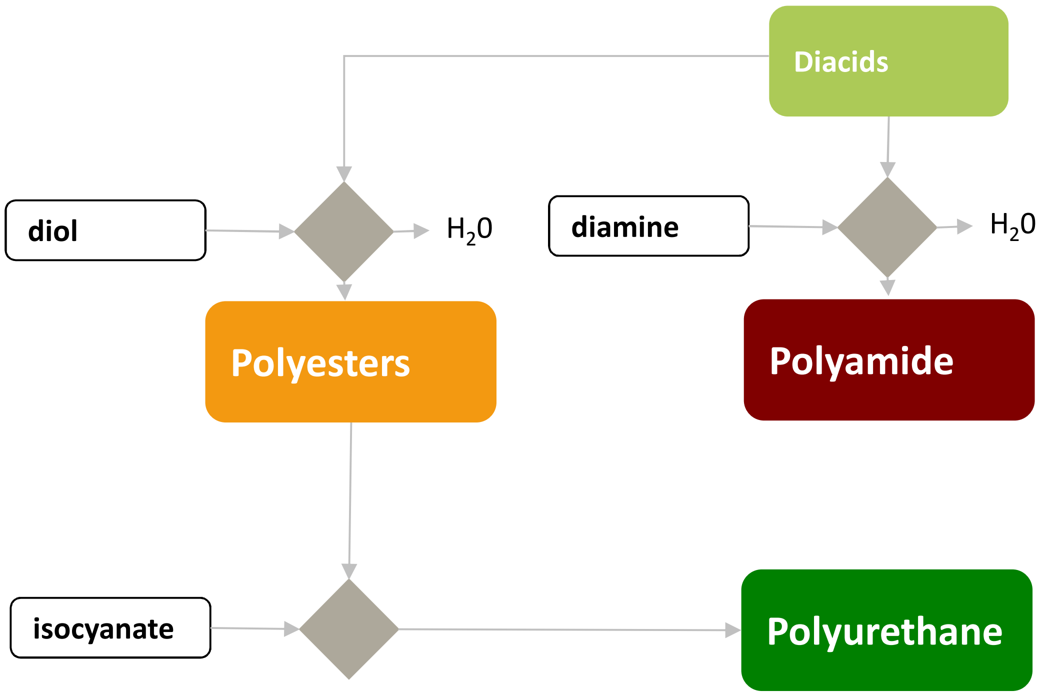
Résines	Capacités 2010 (ktpa)	Pourcentage de la capacité totale	Capacités 2013 (ktpa)	Pourcentage de la capacité totale	Taux de croissance
PE/PVC	200	28%	660	42%	230%
Cellulose	25	3%	25	2%	0%
PA	62	9%	62	4%	0%
Amidon	298	41%	423	26%	42%
PLA	75	10%	232,5	14%	210%
PHA	43	6%	181	11%	321%
PUR	20	3%	20	1%	0%
SOMME	723	100%	1603,5	100%	122%

Polymers, the largest outlet for renewable building blocks (2/3)

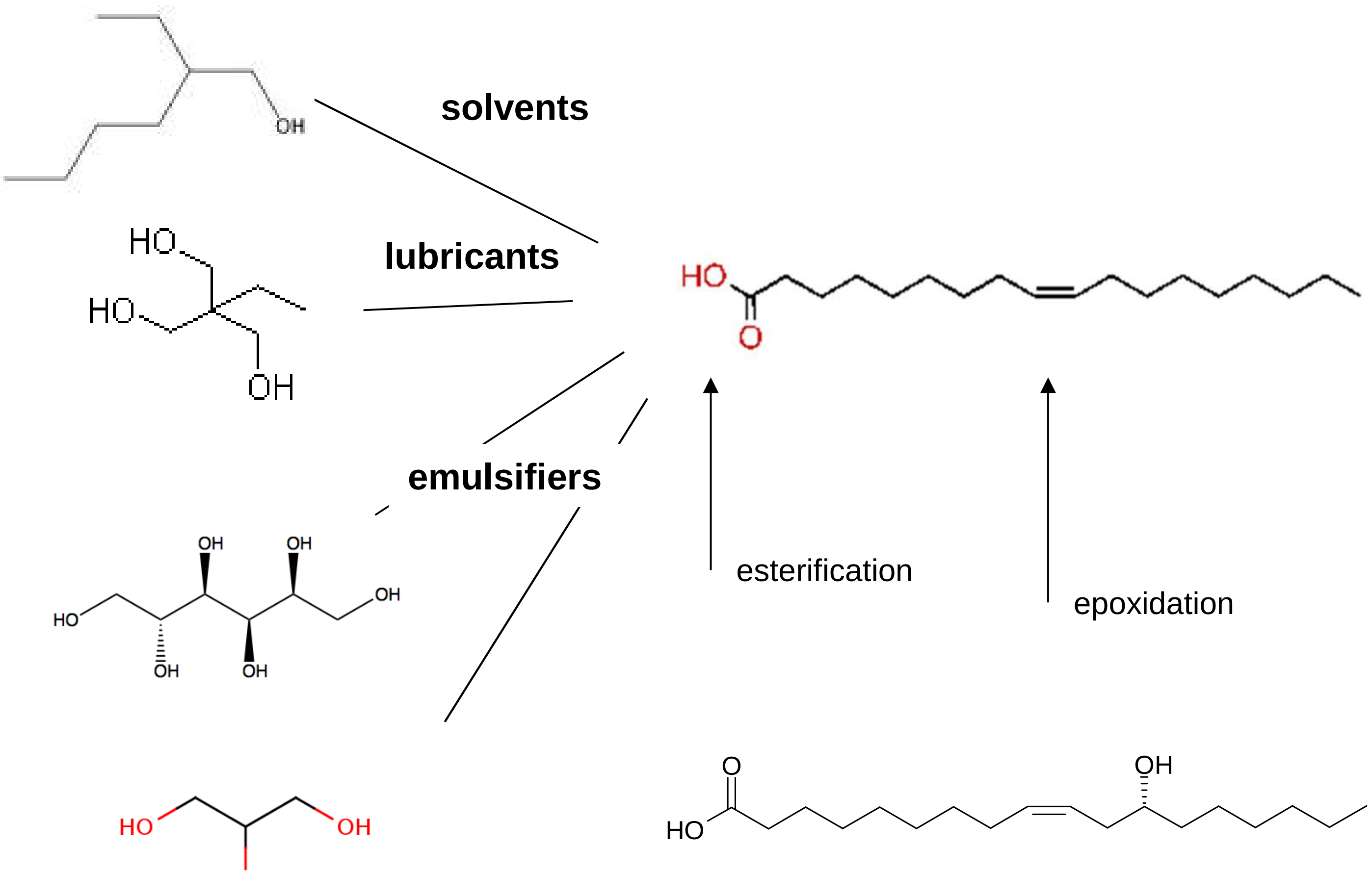
- Biobased building blocks for PA, PU from castor, rapeseed and sunflow oil
- Glycerol and derivatives for renewable polyols

	APPLICATION		SOURCE
Polymers - Polymerized soyabean or castor oil - Linseed oil	Siccative oil Linoleum	**>50 ktpa**	Soja, castor and linseed oil
Polymers additives - Epoxidized oil - Soap (Ba/Cd, Ca/Zn)	Stabilizers, Plasticizers Lubricants	**100 ktpa**	Soja and rapeseed oil Stearic acid
Intermediates fors polymers - Diacids - Polyol esters & ethers	Polyamides, polyesters, Alkyds, Polyurethanes	**100 ktpa**	Soja, castor, rapeseed oil Oleic acid

Polymers, the largest outlet for renewable building blocks (3/3)



Esters derivatives, a good answer to the other markets



(+)-*R*-12-Hydroxy-octadec-9*c*-enic acid

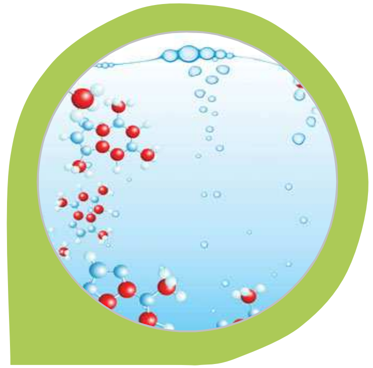
Ester solvents can be excellent alternatives for petrochemical distillates

- methanol
- isopropanol
- butanol
- isobutanol
- 2-ethylhexanol
- isotridecanol

Monoalcohol

230℃, catalyst

Ester Solvent

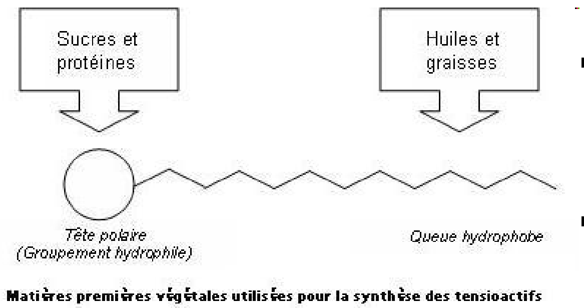


Fatty acid

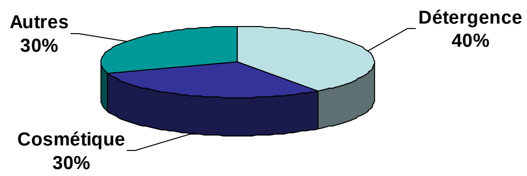
H_20

- caprylic / capric acid
- lauric acid
- myristic acid
- palmitic acid
- stearic acid
- oleic acid
- coconut fatty acid
- …

Biosurfactants



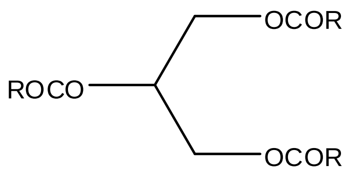
- **Amphiphilic molecules : divided into**
  - an hydrophilic part (sugar, polyols, …)
  - a lipophilic part (fatty acid)
- **Application properties are linked to the chain length**
  - wetter (C8-C10)
  - Solvent
  - Detergency properties (C12-C16)
  - Emsulifier an softer (C18-C22)=
- **Key factors for the biobased surfactant development :**
  - ➔ Less toxicity for human and environment
  - ➔ Higher biodegradability
  - ➔ Special technical performance
    - polyfonctionnal (e.g. emuslifier + wetting + softing agent)
    - Elimination of odour from petrochemical oils



- **European market** ~2.5 10^6 t , With nearly **625 000 t of biobased surfactant (25%)**
- 90% of surfactants on the market price : **€1 to €1.5 /kg**

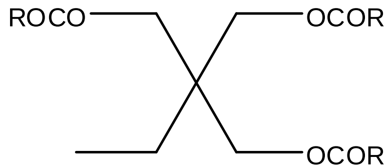
Biolubricants

- **Performance**
  - ➢ Oleic acid is the main fatty acid used in lubricants application (under esters structure) due to its best compromise between oxidation stability and behaviour at low temperature
  - ➢ **Triglyceride structure**
    - The vegetable oil used without transformation
      - Uses for applications under 70°C
      - Sensitive to oxidation and thermal degradation



Triglycerides

  - ➢ **Ester structure**
    - Monoalcohol esters
      - Use to adapt viscosity of lubricant (to be chosen according use temperature)
    - Polyols esters :
      - Uses for high performance lubricants (till more than 120°C in operation)
      - Very stable to oxidation and thermal degradation
- **Biodegaradability and environmental issues**



Esters de triméthylolpropane

The Other factors of those platform molecules developments

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The regulation, as an other opportunity of oleochemistry development

- **REACH Regulation**

- **Solvent regulation : limits of exposition to organic volatile solvents**
  - **Directive 2004/42/CE for coating applications**
  - **Directive 1999/13/EC on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations**

- **Construction regulation : ISO 15804 about sustainability of construction works and environmental product declarations**

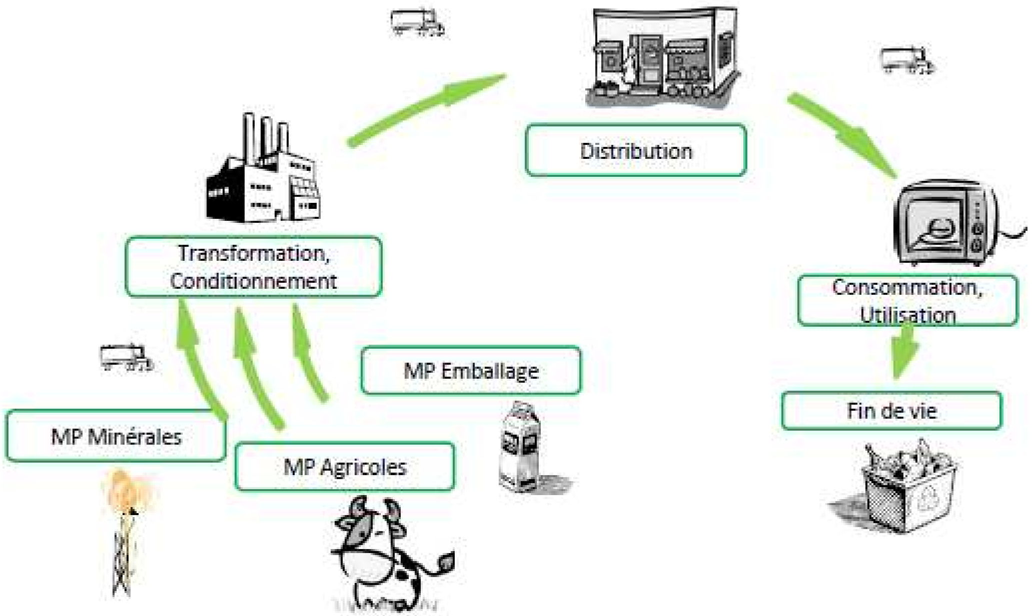
- **National and european labellization : blue angel, NF Environment, White swan, Ecolabel**

- **Labelling : Renewable content based on C14 (ASTM D 6866) and complete atomic origin study**

- **Environment, chemical industry and distribution pressure**

The Life cycle analysis, as the judge for a solid and sustainable development

All products have environmental impacts



The main objective is to reduce the impact (carbone footprint and all other environmental impacts according ISO 14040 & 14044).

This issues is a key driver of oleochemistry development in parallel to petrochemical one

Main Conclusions

- **The main key drivers for new platform molecules :**
  - **Cost**
  - **The link between the raw material availability and the market potential**
  - **Quality of the molecule**
  - **Sustainability**
  - **Regulation**

- **Markets needs :**
  - **Polymers**
  - **Intermediates**
  - **Solvents and coating**
  - **Biolubricants**

- **Platform molecules :**
  - **The traditional ones will stay the starters : fatty acid and glycerine**
  - **New ones will be developped with new routes (fermentation, catalyst development)**
    - **Diacid**
    - **Monoacids or amino or hydroacids**

Groupe Sofiprotéol

Thank you for your attention

Questions and Answers ?

Matthieu CHATILLON
m.chatillon@novance.com