



Extractive Reactive Crushing Process (E-RCP) : a break- innovation in biorefineries of oleiferous fruits & seeds

Extraction réactive de composants de graines
oléagineuses et de fruits : valorisation de coproduits
en chimie de spécialités

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1) Valagro carbone renouvelable, 2) Biosynthis, Dissay, 3) Arkema

Coprinov, 11-12 octobre 2016

Current oilseeds biorefinery – State of art



Oilseeds world market



Storage & Shipment



Crude seed oil



Refining

- vitamin E*
- phytosterols*
- squalene*
- beta-carotene*

Refined Seed oil

Food

- Biodiesel*
- glycerin*
- oleochemicals*

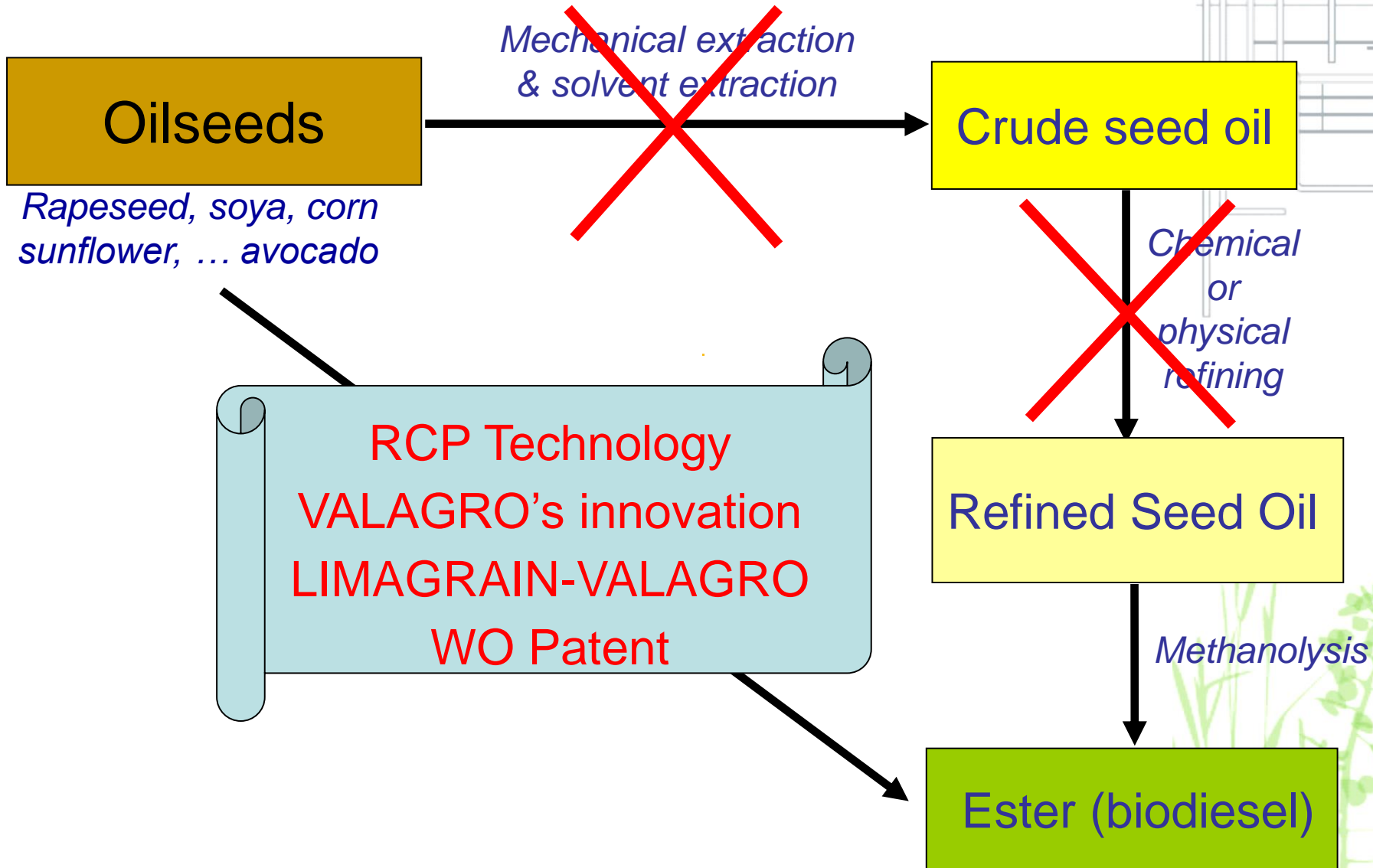
Seeds crushing

Oil cake (for feed/food)

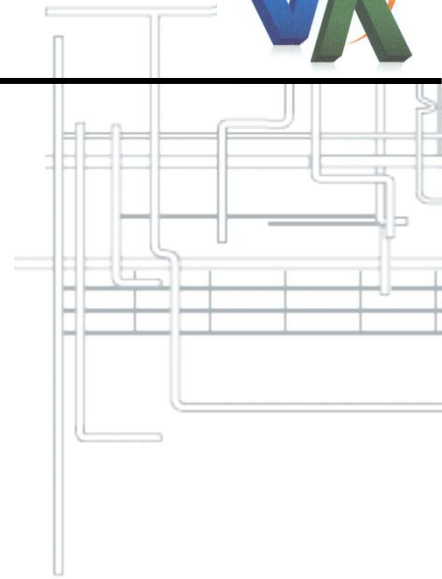
- Molasses*
- Lecithins*
- Isoflavones*

Fibers (for feed)

What is reactive crushing process (RCP) ?

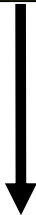


Applications of the RCP Technology



RCP Technology
VALAGRO's innovation
LIMAGRAIN-VALAGRO
WO Patent

Rapeseed



Biodiesel

Castor seed



methyl ricinoleate chemistry

Avocado fruit



Avocadofuran extraction



Pilot demo-plant (La Rochelle, France)



*15 000 T/y
ethyl esters plant
100% biobased
continuous process*

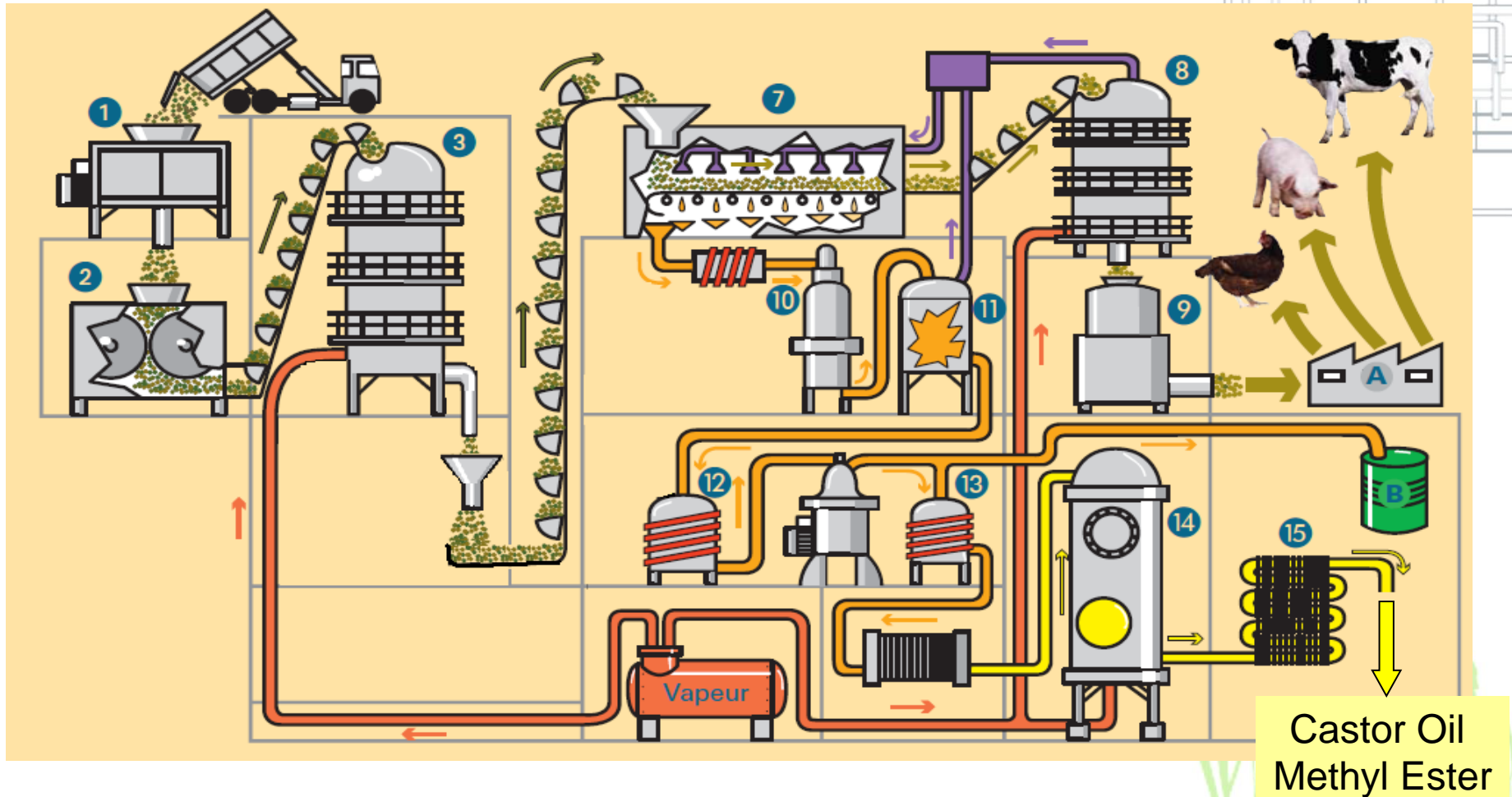


Continuous RCP (demo-plant)



RCP is validated for many oilseeds: rapeseed, sunflower, soya bean

Reactive Crushing Plant w detoxified seed meal



RCP is validated for producing methyl ricinoleate and detoxified castor meal

Detoxification. Ricine and Allergen (CB-1A)

Immunologic Assay + Mass spectrometry test done by CEA (Saclay)

Seed/Seed meal	Drying T°C/(h)	Solvent removal T°C/(h)	Final Drying (T°C, h)	Ricin (%)	Active Ricine reduction (%)
Defatted flakes (60°C, 10h)	-	-	-	1.8	-
Batch process, agitated bed	100°C / 16h	120°C / 4h	-	0.01	94.50%
Continuous fixed bed process	100°C / 16h	120°C / 4h	-	8.6×10^{-4}	99.95%
Continuous fixed bed process	100°C / 16h	120°C / 4h	100°C/4h	2.2×10^{-4}	99.99%

Seed/Seed meal	Final Drying (T°C, h)	Acute toxicity on rats (DL50, mg/kg)	Cutaneous sensitivity test (Local Lymph Node Assay)
Defatted flakes (60°C, 10h)	-	300 < DL50 < 2000* (*mortality 100%)	Allergenic at 10%
Continuous fixed bed process	150°C, 4h	> 2000	non allergenic at 10%
Continuous fixed bed process	120°C, 4h	> 2000	non allergenic at 10%

List of patents developed with ARKEMA



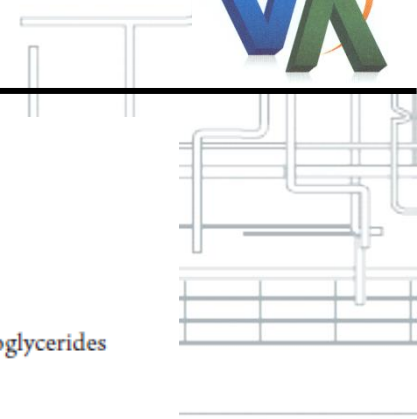
FR 2 940 804 - Procédé de trituration réactive des graines de ricin

FR 2 955 589 - Procédé de trituration réactive des graines de jatropha

FR 2 975 702 - Procédé de trituration réactive directement sur un tourteau gras

FR 2 962 434 - Procédé de purification d'un ester alkylique d'acide gras par extraction liquide / liquide





PATENTS

Encapsulation of oxidatively unstable compounds

Hendrickson, W.A., *et al.*, Aveka, Inc., US8741337, June 3, 2014

An encapsulated material containing an oxidation-sensitive core is covered by at least a dried phospholipid layer, and contains at least one phytosterol in the core, the phospholipid layer or in a further layer or layers. By using microencapsulation, oxidatively unstable materials may be provided with a synthetic protective barrier and rendered less susceptible to oxidative degradation.

Method for stabilizing diesel engine lubricating oil against degradation by biodiesel fuel

Habeeb, J.J., *et al.*, ExxonMobil Research and Engineering Co., US8748357, June 10, 2014

The lubricating oil used to lubricate diesel engines is stabilized against the detrimental degradation effects of biodiesel fuel by the addition to the lubricating oil of an additive concentrate comprising a premix of a first antioxidant, a second antioxidant of a type different from the first and an organometallic compound.

predigested fats include fatty acid-containing monoglycerides and/or a fatty acid component.

Degradable perforation balls and associated methods of use in subterranean applications

Luo, H., and D.D. Fulton, Halliburton Energy Services, Inc., US8757260, June 24, 2014

Methods and compositions that include a method of treating a subterranean formation comprising the steps of providing a carrier fluid comprising degradable balls that comprise a carboxylic acid, a fatty alcohol, a fatty acid salt, a fatty ester, a fatty acid salt, or a combination thereof, and introducing the carrier fluid to the subterranean formation during a treatment.

Method for obtaining a fraction enriched with functionalized fatty acid esters from seeds of oleaginous plants

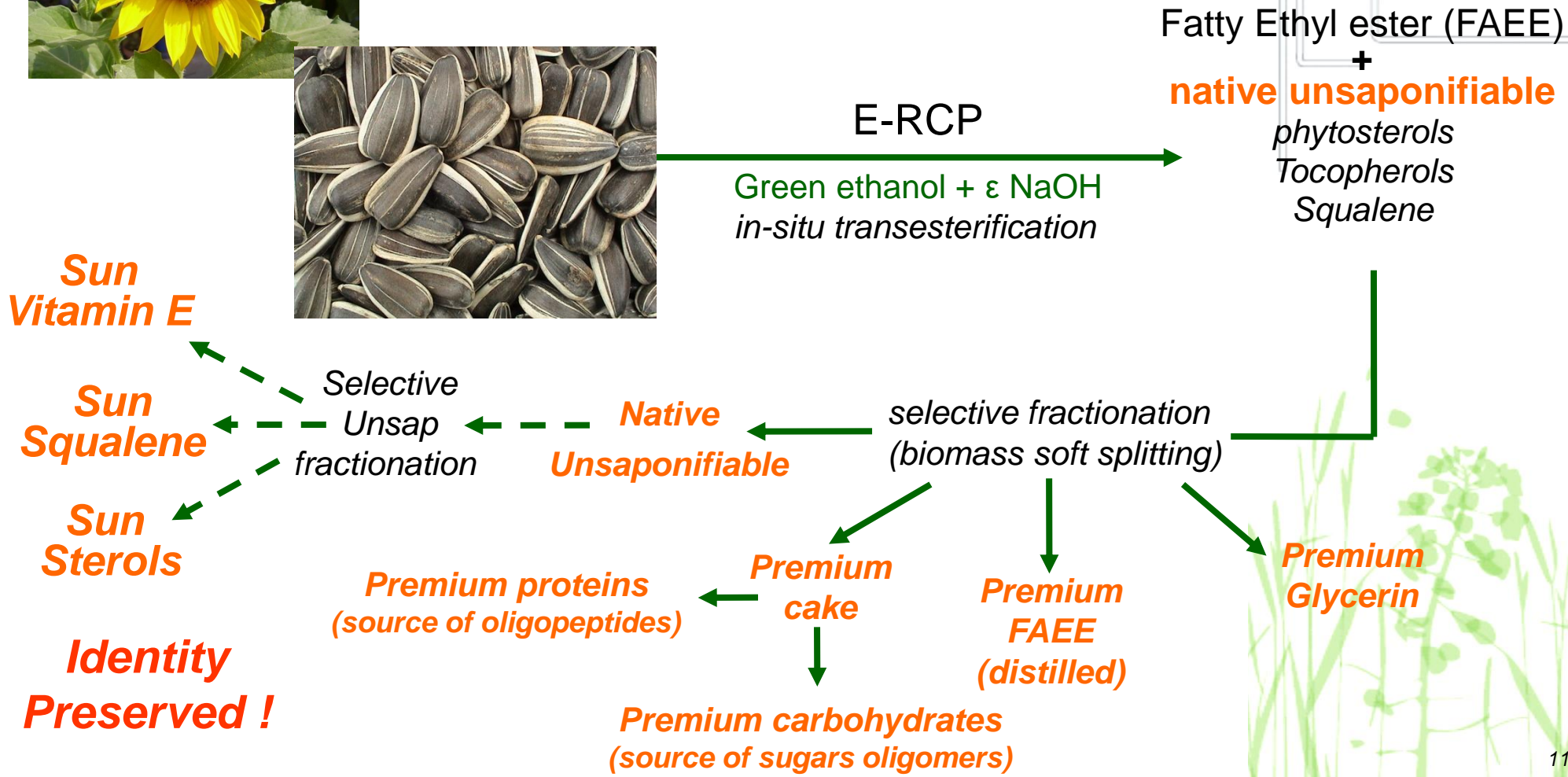
Piccirilli, A., *et al.*, US8759556, June 24, 2014

The invention relates to a method for the selective extraction of functionalized fatty acid esters from seeds of oleaginous plants, wherein said method includes: (i) at least one step of extracting fatty acid esters that comprises simultaneously feeding into a reactor containing said seeds a light anhydrous alcohol a

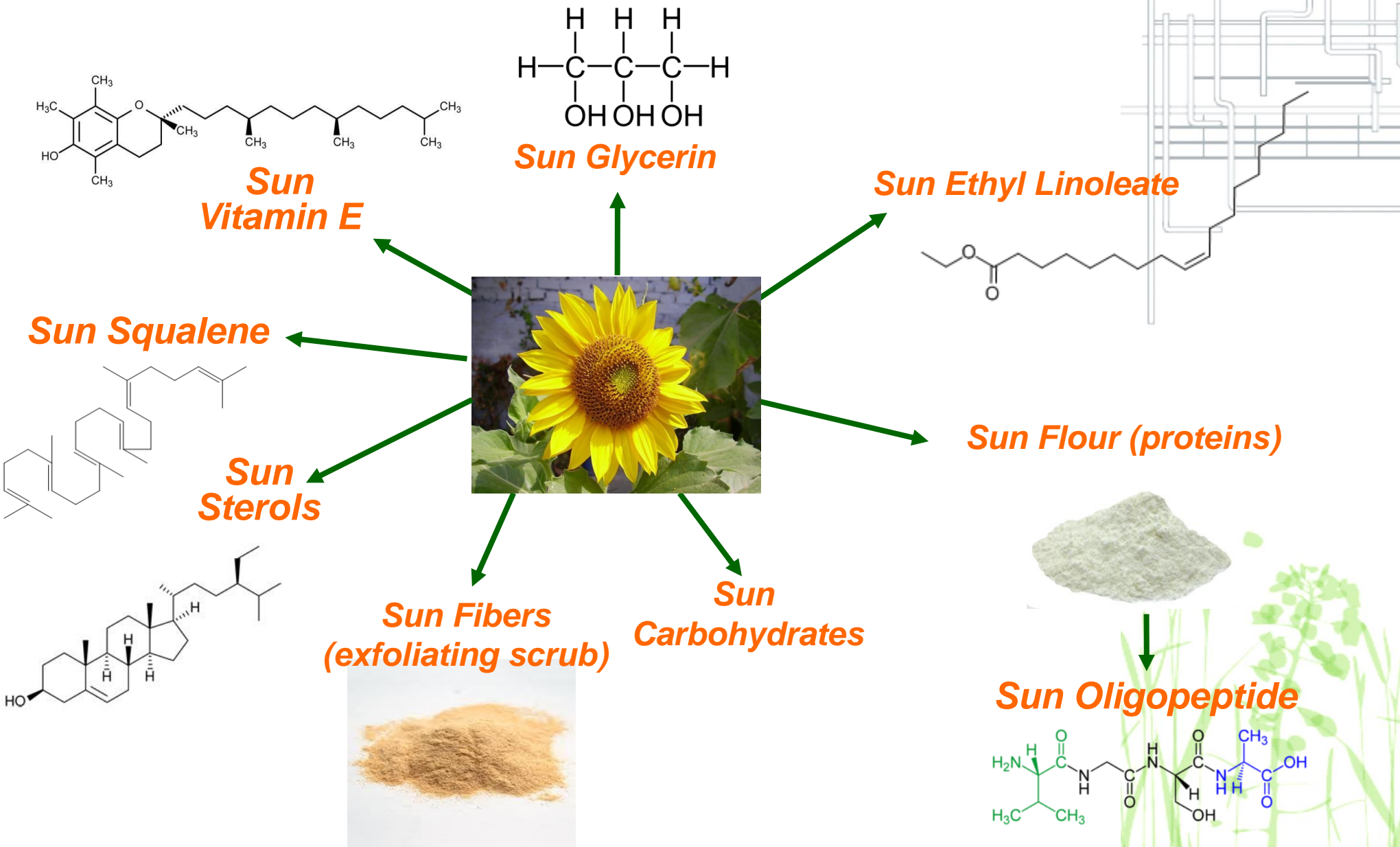
Extractive RCP : a new concept of oilseeds biorefinery



Patent WO 2011/048339
Valagro



Sunflower biorefinery : from the seed to fine phyto-actives



Extractive RCP : a new concept of oleiferous fruits biorefinery



Patent WO 2011/048339
Valagro

Oilseeds & Oleiferous fruits
Organic or conventional

E-RCP

Green ethanol + ϵ NaOH
in-situ transesterification

Fatty Ethyl ester (FAEE)
+
native unsaponifiable
phytosterols
Tocopherols
Squalene
Triterpenic alcohols
phyto-actives

Selective
Unsap
fractionation

**Native
Unsaponifiable**

selective fractionation
(biomass soft splitting)

**Phytochemicals
Identity
Preserved !**

Premium proteins
(source of oligopeptides)

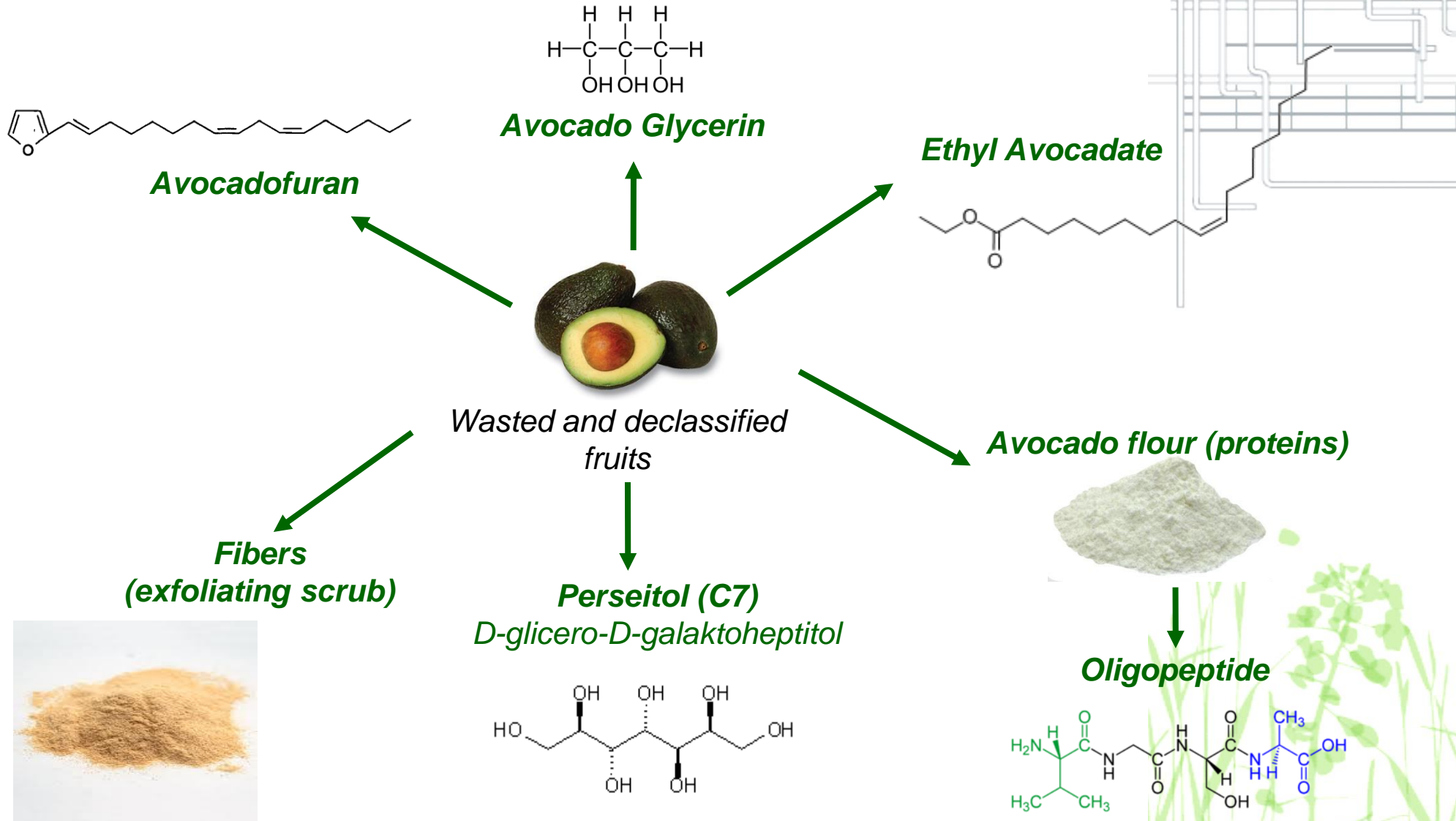
**Premium
cake**

Premium carbohydrates
(source of sugars oligomers)

**Premium
FAEE**
(distilled)

**Premium
Glycerin**

Avocado biorefinery : from the fruit to fine phyto-actives



Extractive-RCP vs Sustainability & market expectations



Sustainable criteria	Extractive-RCP
Environmental footprint	100% biobased raw materials & processing aids Co-products valorization / valorization : + 90% of fruit/seed Biogenic solvent recycling
Energy / atom economy	Very low wastes formation
Impact on biodiversity	No adverse effects / high yield of valorization = energy and atom economy
Impact on water ressource	Ultra low use of water / water treatment unit is not needed
Land use conflict / food vs non food	Atom economy = high product yield /acre = land preservation
Sustainable identity preservation	Traceability (from the seed to the finished product) and identity prevervation (non GMO) can be guaranteed
Safety	Hexan free process / products free of contaminants or anti-nutritional products (cake)
Products naturability	Very high
Profitability ans sustainability	Full-valorization of the fruit/seed improves drastically profitability allowing a better return to the farmers