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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Coprinov, 11-12 octobre 2016
Current oilseeds biorefinery – State of art

Storage & Shipment

Oilseeds world market

Oilseeds crushing

Crude seed oil

Re宁ing

Refined Seed oil

Food

Refined seed oil

Oil cake (for feed/food)

Seeds crushing

Molasses

Lecithins

Isoflavones

Fibers (for feed)

Refined seed oil

vitamin E

phytosterols

squalene

beta-carotene

Biodiesel

glycerin

oleochemicals
What is reactive crushing process (RCP) ?

Oilseeds
- Rapeseed, soya, corn
- sunflower, ... avocado

Mechanical extraction & solvent extraction

Crude seed oil

Chemical or physical refining

Refined Seed Oil

RCP Technology
- VALAGRO’s innovation
- LIMAGRAIN-VALAGRO
- WO Patent

Methanolysis

Ester (biodiesel)
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
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

February 4th 2010 / Jean-Luc Dubois - CONFIDENTIAL
### Detoxification. Ricine and Allergen (CB-1A)

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

<table>
<thead>
<tr>
<th>Seed/Seed meal</th>
<th>Drying T°C/(h)</th>
<th>Solvent removal T°C/(h)</th>
<th>Final Drying (T°C, h)</th>
<th>Ricin (%)</th>
<th>Active Ricine reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Defatted flakes (60°C, 10h)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.8</td>
<td>-</td>
</tr>
<tr>
<td>Batch process, agitated bed</td>
<td>100°C / 16h</td>
<td>120°C / 4h</td>
<td>-</td>
<td>0.01</td>
<td>94.50%</td>
</tr>
<tr>
<td>Continuous fixed bed process</td>
<td>100°C / 16h</td>
<td>120°C / 4h</td>
<td>-</td>
<td>8.6 × 10⁻⁴</td>
<td>99.95%</td>
</tr>
<tr>
<td>Continuous fixed bed process</td>
<td>100°C / 16h</td>
<td>120°C / 4h</td>
<td>100°C/4h</td>
<td>2.2 × 10⁻⁴</td>
<td>99.99%</td>
</tr>
</tbody>
</table>

#### Acute toxicity on rats (DL50, mg/kg) and Cutaneous sensitivity test (Local Lymph Node Assay)

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<th>Seed/Seed meal</th>
<th>Final Drying (T°C, h)</th>
<th>Acute toxicity on rats (DL50, mg/kg)</th>
<th>Cutaneous sensitivity test (Local Lymph Node Assay)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Defatted flakes (60°C, 10h)</td>
<td>-</td>
<td>300&lt; DL50 &lt; 2000* (*mortality 100%)</td>
<td>Allergenic at 10%</td>
</tr>
<tr>
<td>Continuous fixed bed process</td>
<td>150°C, 4h</td>
<td>&gt; 2000</td>
<td>non allergenic at 10%</td>
</tr>
<tr>
<td>Continuous fixed bed process</td>
<td>120°C, 4h</td>
<td>&gt; 2000</td>
<td>non allergenic at 10%</td>
</tr>
</tbody>
</table>
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
Encapsulation of oxidatively unstable compounds


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


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.

Degradable perforation balls and associated methods of use in subterranean applications


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


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 acid under a light halogenated hydrocarbo
Extractive RCP: a new concept of oilseeds biorefinery

E-RCP

Green ethanol + ε NaOH
in-situ transesterification

E-RCPPremium

Fatty Ethyl ester (FAEE) +
native unsaponifiable
phytosterols
Tocopherols
Squalene

Valagro

Patent WO 2011/048339

Identity Preserved!

selective fractionation
(biomass soft splitting)

Premium proteins
(source of oligopeptides)

Premium cake

Premium FAEE
(distilled)

Premium carbohydrates
(source of sugars oligomers)

Premium Glycerin

Selective Unsaponifiable

Native Unsaponifiable

Selective Unsaponifiable

Lot

Sun Sterols

Sun Squalene

Sun Vitamin E

Identity Preserved!
Sunflower biorefinery: from the seed to fine phyto-actives

- Sun Glycerin
- Sun Ethyl Linoleate
- Sun Squalene
- Sun Flour (proteins)
- Sun Sterols
- Sun Carbohydrates
- Sun Fibers (exfoliating scrub)
- Sun Oligopeptide
- Sun Vitamin E
- Sun Squalene
- Sun Oligopeptide
Extractive RCP: a new concept of oleiferous fruits biorefinery

**Oilseeds & Oleiferous fruits**
Organic or conventional

**E-RCP**
Green ethanol + \( \varepsilon \) NaOH
in-situ transesterification

**Selective Unsap fractionation**

**Native Unsaponifiable**

**selective fractionation** (biomass soft splitting)

**Fatty Ethyl ester (FAEE)** +

**native unsaponifiable**
- Phytosterols
- Tocopherols
- Squalene
- Triterpenic alcohols
- Phyto-actives

**Premium cake**

**Premium FAEE** (distilled)

**Premium carboxhydrates**
(source of sugars oligomers)

**Premium proteins**
(source of oligopeptides)

**Native Unsap fractionation**

**Premium Glycerin**

**Phytochemicals Identity Preserved!**

Patent WO 2011/048339
Valagro
Avocado biorefinery: from the fruit to fine phyto-actives

- **Avocado Glycerin**
- **Ethyl Avocadate**
- **Wasted and declassified fruits**
- **Avocadofuran**
- **Fibers (exfoliating scrub)**
- **Perseitol (C7)**
  - D-glicerol-D-galaktoheptitol
- **Avocado flour (proteins)**
- **Oligopeptide**
### Extractive-RCP vs Sustainability & market expectations

<table>
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<th>Sustainable criteria</th>
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| 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 resource                    | 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 preservation (non GMO) can be guaranted                                                  |
| 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                                                  |