Enzymatic Oil Refining:
The Solution to Quality and Profitability

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Edible Oil Refining

‘Purpose of refining of oils for edible uses is to remove undesirable substances and components while maintaining the nutritional quality and stability of the refined oil’

**Undesirable components**
- FFA
- Phospholipids
- Traces of metals
- Pigments
- Contaminants
- Colouring components

**Quality requirements**
- Good stability
- Good shelf life
- Bland odor & taste
- Good nutritional quality
- Safe (no contaminants)
- Healthy (vitamins)

Required refining capacity: > 500,000 TPD
Gradual improvement of the process technology

* Processing under low vacuum (for oil quality reasons);
* Evolution from batch to semi- to continuous operation (plant performance);
* Optimized deodorization (low pressure, optimum heat recovery)
* Milder processing, less chemicals (chem > phys)  

USE OF ENZYMES
ENZYMATIC OIL REFINING

1. Mechanical Pressing
2. Solvent extraction
3. Enzymes in Oil Refining
4. Alkali Neutralisation
5. Acid degumming

Crude Oil → Oil Extraction → Deoiled Meal

Soapstock

Alkali Neutralisation → Bleaching

Deodorization → Deodorizer Distillate → Refined Oil

Spent bleaching earth

Acid Gums

Physical deacidification Deodorization

Chemical

Physical
Enzymatic Oil Refining: some proven, some under development and some waiting to be proven industrially

<table>
<thead>
<tr>
<th>Enzymatic Process</th>
<th>Objective</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Miscella Degumming</td>
<td>Max. PL removal + <em>yield increase.</em> On crude oil miscella (crushing plant)</td>
<td>Under development</td>
</tr>
<tr>
<td>(Partial)Water Degumming</td>
<td>Partial PL removal + <em>yield increase.</em> On crude, non-WDG oils (crushing plant)</td>
<td>Industrially applied</td>
</tr>
<tr>
<td>Gums Deoiling</td>
<td>Max. <em>Oil recovery</em> from wet gums On wet gums (crushing plant)</td>
<td>Ready for industrial application</td>
</tr>
<tr>
<td>Full (‘deep’) Degumming</td>
<td>Full PL removal + <em>yield increase</em> On waterdegummed oils (refining plant)</td>
<td>Industrially applied</td>
</tr>
<tr>
<td>Bleaching</td>
<td>Degradation of color pigments On waterdegummed oils (refining plant)</td>
<td>Under development</td>
</tr>
</tbody>
</table>

**Enzymatic Oil Degumming** : industrially proven and well accepted

Efficient degumming and higher oil yield
Enzymatic oil degumming

The degumming process for the 21st century finally come true?

**CURRENT SITUATION**

- Availability of more stable & (cost-) efficient enzymes
- Different enzymes/enzyme suppliers
  - Lecitase Ultra (PL-A1, Novozymes)
  - Rohalase PL-XTRA (PL-A2, AB Enzymes)
  - Lysomax Oil (LAT, PL-A2, Du Pont)
  - Purifine PLC (PL-C, DSM)
  - Purifine 2G/3G (PL-C + PL-A2, DSM)
- Different approach
  - Increased oil yield as main driver
  - (Also) applied on crude oils

**Chemical Structure**

![Chemical structure diagram](image)

- Phospholipase A1
- Phospholipase A2
- Phospholipase B
- Phospholipase C
- Phospholipase D

- $R_1$, $R_2$ can be H, choline, ethanolamine, serine, inositol, etc.

$X = H, \text{choline, ethanolamine, serine, inositol, etc.}$
* Worldwide: > 30 crushing/refining plants applying enzymatic degumming

* Mostly soybean oil processors in Latin America and USA
Enzymatic water degumming

✓ Applied in crushing plants
  * On crude oil
  * With PL-C or PL-C/PL-A cocktails
  * Not for Lecithin producers

✓ Higher oil yield is main driver
  * Max. generation of diglycerides (from PL)
  * Some formation of FFA (also from PL)
  * Less oil entrainment in less gums

✓ Net revenue will depend on:
  * PL-content in crude oil (highest in soybean oil from expandates)
  * Price difference between WDG oil and meal (lecithin!)
  * Enzyme cost (enzyme price x dosing rate)
Enzymatic water degumming: PLC most preferred

Phospholipids

\[
\begin{align*}
\text{CH}_2-\text{O}-\text{C}-\text{R}_1 \\
\text{R}_2\text{-C-O-CH} \\
\text{HO-P-O-}\text{X} \\
\text{CH}_2-\text{O-P-O-}\text{X} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{O} \\
\text{PLC} \\
\text{CH}_2-\text{O-C-}\text{R}_1 \\
\text{R}_2\text{-C-O-CH} \\
\text{HO-P-O-}\text{X} \\
\text{CH}_2-\text{O-P-O-}\text{X} \\
\end{align*}
\]

DIGLYCERIDES

PHOSPHATE-ESTER

Yield increase: 

\[
\text{DAG} + \text{Less entrained Neutral Oil in less gums}
\]

<table>
<thead>
<tr>
<th>Commercial Enzyme</th>
<th>Active enzymes</th>
<th>Selectivity</th>
<th>Conversion products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purifine® - PLC</td>
<td>PLC</td>
<td>Only PC+ PE</td>
<td>Only DAG</td>
</tr>
<tr>
<td>Purifine® - 2G</td>
<td>PLC + PLA2</td>
<td>Mainly PC + PE</td>
<td>Mainly DAG + some FFA</td>
</tr>
<tr>
<td>Purifine® - 3G</td>
<td>PLC + PLA2 + PI-PLC</td>
<td>PC + PE + PI</td>
<td>Mainly DAG + some FFA</td>
</tr>
</tbody>
</table>
Enzymatic water degumming of soybean oil

Crude soybean oil: Phospholipid composition

<table>
<thead>
<tr>
<th></th>
<th>Crude oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total PL (%)</td>
<td>2.06</td>
</tr>
<tr>
<td>PC</td>
<td>0.70</td>
</tr>
<tr>
<td>PE</td>
<td>0.54</td>
</tr>
<tr>
<td>PI</td>
<td>0.36</td>
</tr>
<tr>
<td>PA</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Enzymatic water degumming with Purifine 3G (=PLC + PLA2 + PI-PLC)

<table>
<thead>
<tr>
<th></th>
<th>Crude</th>
<th>Enzymatic degummed</th>
</tr>
</thead>
<tbody>
<tr>
<td>FFA (%)</td>
<td>0.83</td>
<td>1.18</td>
</tr>
<tr>
<td>P</td>
<td>845</td>
<td>52</td>
</tr>
<tr>
<td>Ca</td>
<td>111</td>
<td>27</td>
</tr>
<tr>
<td>Mg</td>
<td>117</td>
<td>17</td>
</tr>
<tr>
<td>DAG (%)</td>
<td>0.87</td>
<td>1.49</td>
</tr>
</tbody>
</table>

Max. theoretical DAG formation:

\[
\text{Max. theoretical DAG formation} = PC \times 0.7717 + PE \times 0.8154 + PI \times 0.7027 \\
= 1.23\%
\]

- Slight FFA increase (from PLA2 action)
- No deep degumming (yet)
- 0.62% extra DAG (PLC action)
  = approx. 50% of theoretical max.
Extra Revenue from Enzymatic Water degumming

Average $\Delta$ (01/2013 – 09/2015) : 400 USD/ton
Average $\Delta$ (01/2010 – 09/2015) : 550 USD/ton

Determining Factors

✓ Price difference oil – meal
✓ Enzyme cost
✓ Achievable oil yield increase

Revenue i.f.o. enzyme cost and $\Delta$ (oil-meal)

1.8% oil yield increase

Oil and Enzyme dependent
Extra Oil Yield Increase from Enzymatic Water degumming

**Enzymatic WDG with Purifine®**

- **Enzymatic WDG of crude soybean oil with 2.5% phospholipids**

**INDUSTRIAL DATA**

<table>
<thead>
<tr>
<th>Enzyme</th>
<th>Oil yield increase (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purifine® - PLC</td>
<td>1.4-1.7</td>
</tr>
<tr>
<td>Purifine® - 2G</td>
<td>1.9</td>
</tr>
<tr>
<td>Purifine® - 3G</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Source: Ventrici, E., Molinos. Data presented at the 2014 AOCS Conference (Orlando, FL)

**Highest Oil Yield increase with Purifine 3G on crude soybean oil from expandates (max. P content)**

Feedstock dependent (ppm P)
Full ‘deep’ enzymatic degumming

✔ Applied in crushing or refining plants
  * On crude or waterdegummed oil
  * With PL-A₁ or PL-A₂
  * Not yet fully proven with Purifine® enzymes

✔ Degumming efficiency vs Yield increase
  * Efficient degumming (P < 10 ppm) required
  * Yield increase from formation of FFA and reduced entrained oil in gums
  * FFA will be stripped during refining and valorized as distillate

✔ Applications
  * Mainly on (crude) soybean oil, but also on other oils (rape, sun,...)
  * As part of the pretreatment process for biodiesel production
  * Missing link for physical refining of soft oils?
Full 'deep' enzymatic degumming

Phospholipids

\[ \text{R}_2\text{-C-O-CH} + \text{H}_2\text{O} \rightarrow \text{R}_2\text{-C-O-CH OH} \]  

Lyso-Phospholipids

\[ \text{CH}_2\text{-O-P-O-}X \]  

\[ \text{O}^{\cdot} \]  

\[ \text{O}^{\cdot} \]  

\[ \text{R}_1 \]  

\[ \text{CH}_2\text{-O-P-O-}X \]  

\[ \text{O}^{\cdot} \]  

\[ \text{O}^{\cdot} \]  

\[ \text{R}_1 \]  

\[ \text{CH}_2\text{-O-C-} \]

\[ \text{O}^{\cdot} \]  

\[ \text{O}^{\cdot} \]  

\[ \text{R}_1 \]  

PLA1

\[ \text{CH}_2\text{-O-P-O-}X \]  

\[ \text{O}^{\cdot} \]  

\[ \text{O}^{\cdot} \]  

\[ \text{R}_1 \]  

+ PLA2

\[ \text{H-O-C-} \]

\[ \text{O}^{\cdot} \]  

\[ \text{O}^{\cdot} \]  

\[ \text{R}_1 \]  

FFA

Yield increase: FFA + Less entrained Neutral Oil in less gums

Valorized as deodorizer distillate

✓ Phospholipase- A1 (Lecitase Ultra, Novozymes) : most industrially applied
✓ Phospholipase-A2 (Rohalase PL-XTRA, AB Enzymes) – splits off FFA at sn-2 position
✓ Conversion of ALL phospholipids in hydratable lyso-phospholipids and FFA
Deep Enzymatic Degumming of Crude Soybean Oil

- After **10 min.**: good degumming (32 ppm P), but almost no yield increase (Δ FFA = 0.1%)
- After **120 min.**: good degumming (7 ppm P), and good yield increase (Δ FFA = 0.5%)

Reaction time required for yield increase
Applications

Crude Oil → DEEP ENZYMATIC DEGUMMING → EDG Oil → Silica treatment or washing

Distillate → FFA stripping → Transesterification → BIODIESEL

Acid Esterification

Additional biodiesel yield

Lyso-Gums

Bleaching → Physical deacidification Deodorization

Distillate → Refined Food Oil

meeting EN/ASTM specs

Light color, bland taste
Good stability
No contaminants,

Extra biodiesel yield
# Deep Enzymatic Degumming of Rapeseed Oil

**Enzyme assisted Acid degumming** ↔ **Acid assisted Enzymatic degumming**

<table>
<thead>
<tr>
<th></th>
<th>Crude Oil</th>
<th>Rohalase PL-XTRA (PLA2)</th>
<th>Lecitase Ultra (PLA1)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oil conditioning</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Citric acid (ppm)</td>
<td>300</td>
<td>650</td>
<td>300</td>
</tr>
<tr>
<td>NaOH (ppm)</td>
<td>65</td>
<td>150</td>
<td>90</td>
</tr>
<tr>
<td><strong>Enzyme reaction</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Enzyme dosing (ppm)</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Reaction time (hr)</td>
<td>1</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td><strong>Oil quality</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FFA</td>
<td>1.42</td>
<td>1.56</td>
<td>1.68</td>
</tr>
<tr>
<td>P</td>
<td>477</td>
<td>83</td>
<td>4.6</td>
</tr>
<tr>
<td>Ca + Mg</td>
<td>231</td>
<td>77</td>
<td>1.1</td>
</tr>
</tbody>
</table>

- Deep enzymatic degumming (P < 5 ppm) is possible with PLA1 & PLA2
- Correct acid conditioning and enzyme dosing is required
Deep Enzymatic Degumming for Biodiesel Production

Crude Rapeseed oil

Enzymatic degumming
(50 ppm Lecitase Ultra – 90 min.-55°C)

Silica treatment
(500 ppm citric acid – 0.3% Silica)

FFA stripping
(235°C - 3mbar – 1.5% steam – 90 min)

Crude RS oil
FFA : 2.40%
P : 552 ppm
Ca : 213 ppm
Mg : 50 ppm

Refined RS oil
FFA : 0.15%
P : 0.9 ppm
Ca/Mg : < 0.5 ppm

BIODIESEL
MAG : 0.43%
DAG : 0.12%
TAG : 0.09%
Free SG : 11 ppm
Brilliant appearance

BIODEILE PRODUCTION

Good quality
Enzymatic degumming: current situation

Most widely applied enzymatic oil process

• Different enzyme (cocktails) are today commercially available
• Enzymatic waterdegumming or deep degumming
• Proven oil yield increase

Conversion of PL in FFA or diglycerides
Less neutral oil entrainment in the lyso-gums phase

Why not applied more?

• Economical reasons (crude oil vs lecithin vs meal price)
• Process reasons (consistent full enzymatic degumming remains a challenge)
• Confusion (when to apply, on which oil, what to do with sidestream, dependency..)

Is enzymatic gums deoiling an alternative?
Enzymatic gums deoiling: potential benefits

Wet Gums → Enzyme reaction → Lyso-Lecithin + Recovered Oil

1. Applied on a side stream (wet gums) with no impact on the degumming process
   * Wet gums: 4-5% of crude oil flow (40-50 TPD vs 1000 TPD enzymatic degumming for SBO)

2. High flexibility
   * Can be applied depending on economics (lecithin vs oil vs meal)

3. Recovered oil (additional yield) is collected as separate stream
   * Can be recycled back to crude/WDG oil or valorized separately (e.g. biodiesel)

4. Potential lower enzyme consumption (compared to oil degumming)
Recovered oil quality (from soy gums)

Soy gums with 41% moisture and 32% NO on DM, 250-400 ppm Lecitase Ultra, 4-6 hr at 55°C

Oil recovery : up to 90% (on NO in gums) = \textbf{0.8-1.0%} on crude soy oil

Recovered oil quality :

- FFA : 30-35%
- P-content : 70-100 ppm
Conclusions

✓ Enzymatic oil processing appeals to the growing demand for milder and more sustainable refining;

✓ Today, enzymatic oil degumming is the only industrially proven enzymatic process in oil refining

✓ Enzymatic water degumming is successfully applied on crude soybean oil, but not yet with same success on other crude oils (too low P-content)

✓ Full enzymatic degumming is mostly applied in the pretreatment of soybean/rapeseed oil for biodiesel production.

✓ Enzymatic lecithin deoiling is an interesting alternative, ready to be tested industrially (PLC/PLA cocktail)
Thank you for your attention!!