ENZYME ASSISTED CHEMICAL REFINING OF VEGETABLE OILS

- DR. SAMBASIVARAO JAVVADI
- SHIRDI SAI NUTRACEUTICALS PVT LTD
  BENGALAURU

REFINING TECHNIQUES
CHEMICAL VS PHYSICAL

CHEMICAL REFINING	PHYSICAL REFINING
MORE TOLERANT TO QUALITY OF CRUDE OIL	SENSITIVE TO QUALITY OF CRUDE OIL-SOLUTIONS IN PLACE
VERY GOOD SHELF STABILITY	VERY GOOD SHELF STABILITY-EXTRA CARE NEEDED
VERY LOW COLOR	EXTRA COST TO PRODUCE LOW COLOR
	TRANS FAT COULD BE AN ISSUE
HIGHER PRICE OF FATTY ACID DISTILLATE	LOWER PRICE OF FATTY ACID DISTILLATE

REFINING TECHNIQUES
CHEMICAL VS PHYSICAL

CHEMICAL REFINING	PHYSICAL REFINING
LOSS OF NEUTRAL OIL	HIGHER YIELD OF NEUTRAL OIL
LOSS OF FATTY ACIDS TO LOW QUALITY ACID OIL	RECOVERY OF HIGH QUALITY FATTY ACIDS – HIGHER PRICE THAN ACID OIL
HIGH EFFLUENT GENERATION	MINIMUM EFFLUENT & POLLUTION
ENVIRONMENTAL POLLUTION	CLEANER ENVIRONMENT
HIGH PHOSPHOROUS IN NEUTRAL OIL	
HIGH SOAP IN NEUTRAL OIL	

REFINING TECHNIQUES
CHEMICAL VS PHYSICAL

WE PROPOSE AN ***ENZYMATIC SOLUTION***

THAT REDUCES IMPACT OF

NEGATIVE FACTORS OF REFINING

REFINING TECHNIQUES
CHEMICAL VS PHYSICAL

CHEMICAL REFINING

- LOSS OF NEUTRAL OIL ↓
- LOSS OF FATTY ACIDS TO LOW QUALITY ACID OIL ↑
- HIGH EFFLUENT GENERATION ↓
- ENVIRONMENTAL POLLUTION →
- HIGH PHOSPHOROUS IN NEUTRAL OIL ↓
- HIGH SOAP IN NEUTRAL OIL ↓

HIGHER PROFITABILITY

PHYSICAL REFINING

HIGHER YIELD OF NEUTRAL OIL

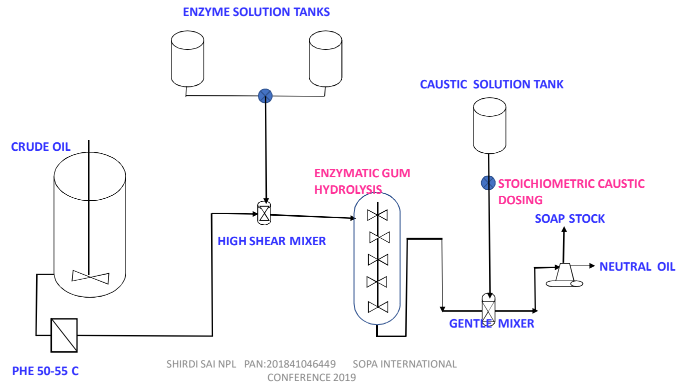
RECOVERY OF HIGH QUALITY FATTY ACIDS

MINIMUM EFFLUENT & POLLUTION

CLEANER ENVIRONMENT

BETTER QUALITY & STABILITY

ENZYME ASSISTED CHEMCIAL REFINING
PROCESS DIAGRAM



ENZYME ASSISTED CHEMICAL REFINING
DELIVERABLES

- **NEUTRAL OIL PARAMETERS:**
  - PHOSPHOROUS: 3-4 ppm
  - SOAP CONTENT: ~250 ppm
  - FFA: 0.08 %
  - SOAP STOCK: ALMOST FREE FROM GUMS- CAN BE SPLIT AT 80° C ADJUSTING pH to 4.5.

RESULTS OBTAINED ON WATER DEGUMMED SOY OIL WITH
ROHALASE PLXTRA & ROHALASE F – PHOSPHOLIPID HYDROLYSING ENZYMES OF AB ENZYMES GmbH

ENZYME ASSISTED CHEMICAL REFINING
BENEFITS

- INCREASED YIELD OF NEUTRAL OIL UP TO 0. 4 %
- LOWER NEUTRALIZATION LOSS
- NO SAPONIFICATION LOSS
- REDUCED OR NIL EMULSIFICATION LOSS
- NO SOAP ADSORBANT
- LOWER CONSUMPTION OF BLEACHING EARTH
- HIGH QUALITY OIL RECOVERED FROM SOAP
- REDUCED EFFLUENT GENERATION

- HIGHER PROFITABILITY

ENZYME ASSISTED WATER DEGUMMING

THANK YOU FOR YOUR ATTENTION
&
LET'S JOIN HANDS

- Introduction DSM
- Enzymes in General
- Enzymes in Degumming
- Potential benefits of EDG gums
- Tech Lessons Learned

Enzymatic Degumming in vegetable Oil Processing

Remco Muntendam
Ghent
22-09-2016

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DSM Life Sciences and Material Sciences company

active in: nutrition | health | materials

We create solutions to bring healthier, better performing and more sustainable products to the lives of people today and for generations to come.

Net sales	about € 10,000m
Workforce	25,000

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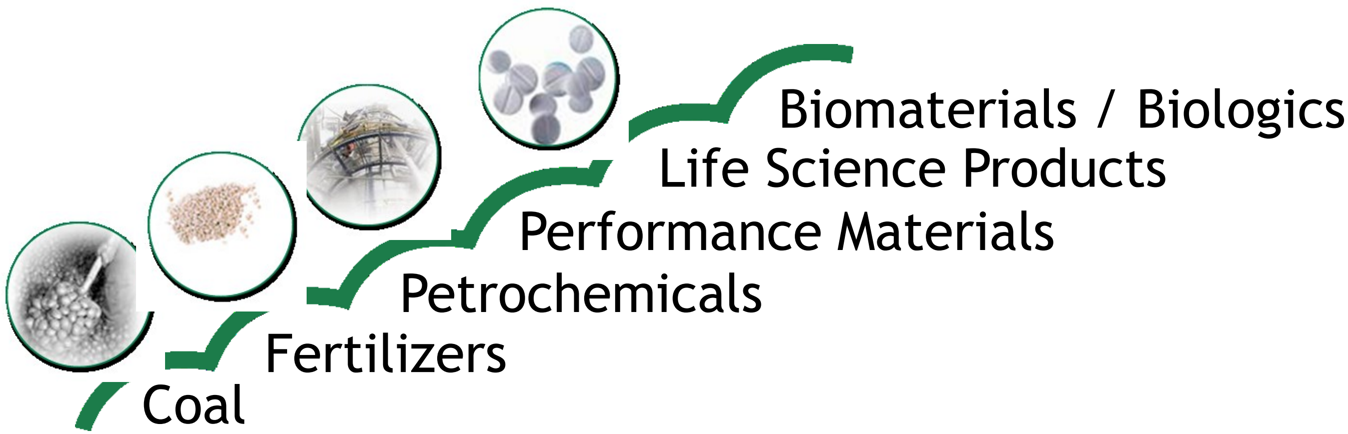
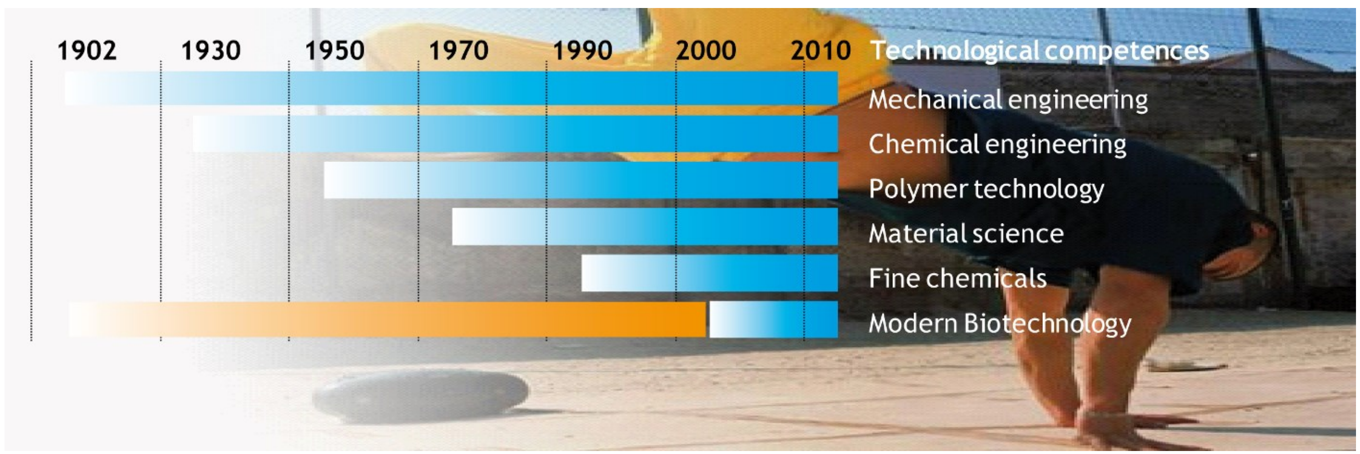
100 years of successful transformation





#1 position in the Dow Jones Sustainability World Index
material industry sector; see www.sustainability-index.com

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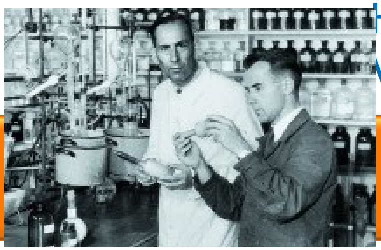
Building on an impressive history



Hoffman La Roche's
Vitamins (1930s)

Chemical synthesis &
biotechnology

Life Sciences

Gist-Brocades (1869)

Biotechnology

Materials Sciences

DSM (1902)

Energy, chemistry &
polymer technology

Vitamins
Omega's
Carotenoids
Premixes for food & feed
Enzymes
Minerals
Cultures & Yeasts
Nutraceuticals
Pharmaceuticals
Cellulosic bioethanol
Biomedical materials
Bio-plastics
High Performance Plastics
Coating Resins
Functional Materials
Solar – advanced surfaces

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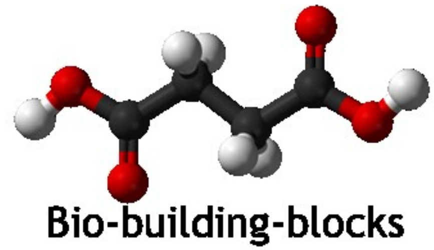
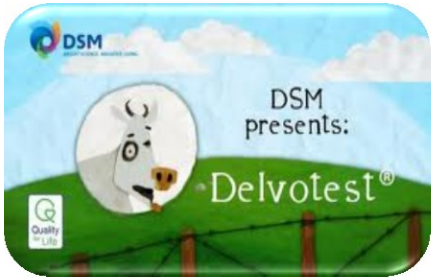
Biotechnology is everywhere…





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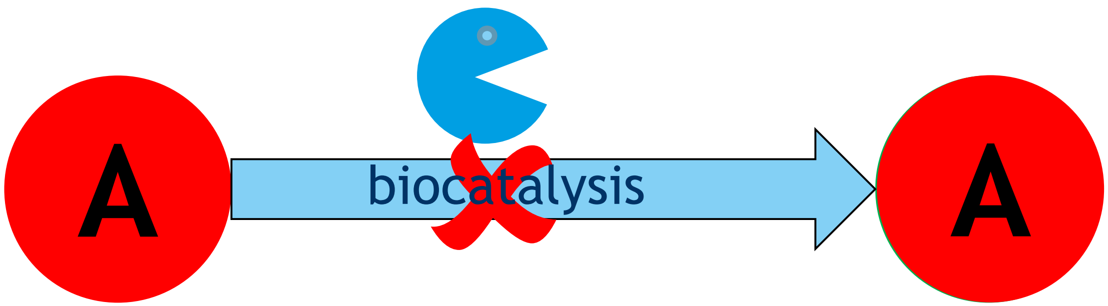
Enzymes are biocatalysts



Accelerate reaction rate by lowering energy threshold:

- Specific, resulting in desired conversion
- Lower temperatures, natural environment and less chemicals

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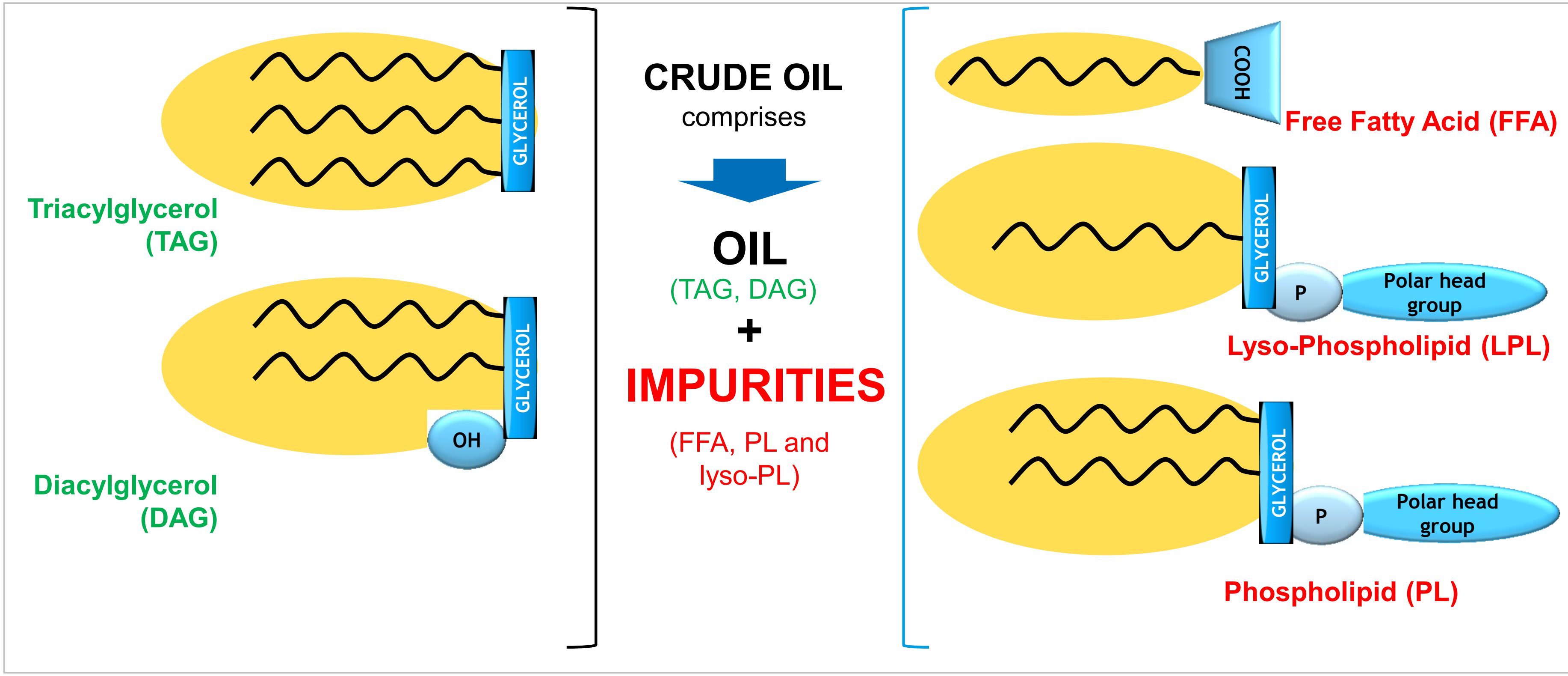
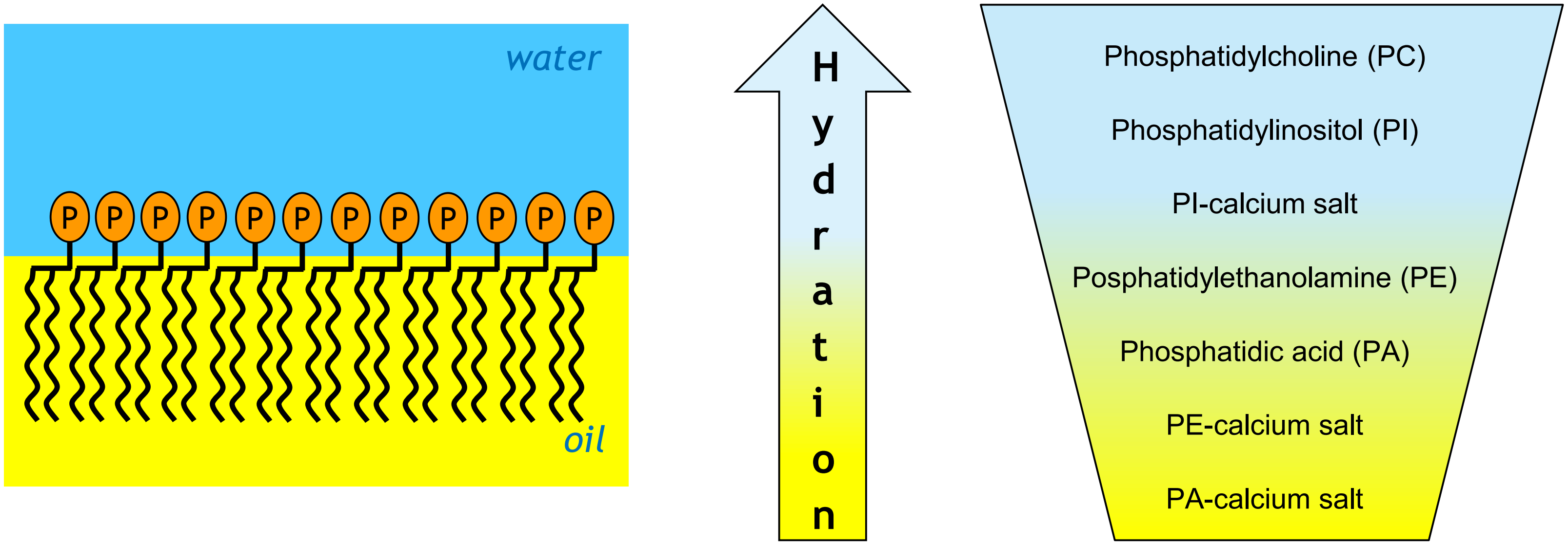
Main constituents of crude vegetable oil?



Amounts & types of impurities in crude oil are determined by:

- Growing conditions
- Seed storage & handling
- Oil extraction method
- Other impurities (metals, tocopherols, carotenoids, chlorophylls)

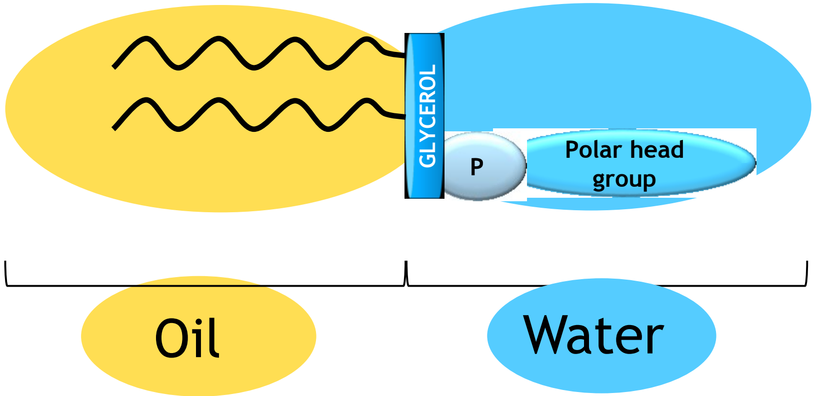
Phospholipid Impurities Make A Difference

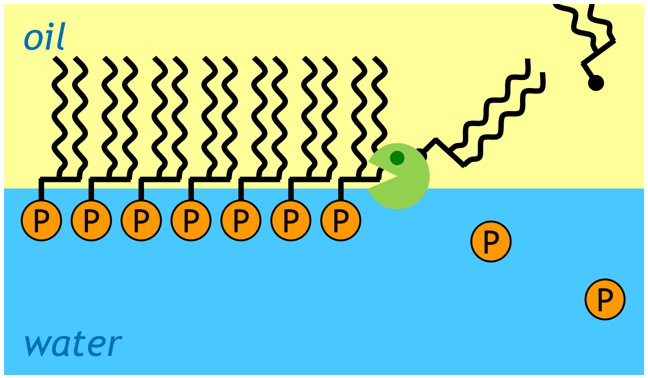


- Hydration increases with polarity and correlates with emulsifying strength
- Formation of metal salts reduces polarity and results in “non-hydratable” phospholipids

1. Sen Gupta, A.K., Fette Seifen Anstrichmittel V.88 pages 79-86 (1986) *in* Segers, J.C., et al., “Degumming – Theory and Practice” published by American Oil Chemists’s Society in “Edible fats and Oils processing: basic principals and modern practices: World conference proceedings”, edited by David Erickson, (1990) pages 88-93.

Emulsion Causes Yield Loss: Phospholipids





Oil losses are caused by intact phospholipids:

- Phospholipids (PLs) are emulsifiers
- PLs reduce surface tension between water and oil
- Oil is emulsified (& trapped) in the gum fraction
- Different PLs have different properties – Hydratable or Non-hydratable

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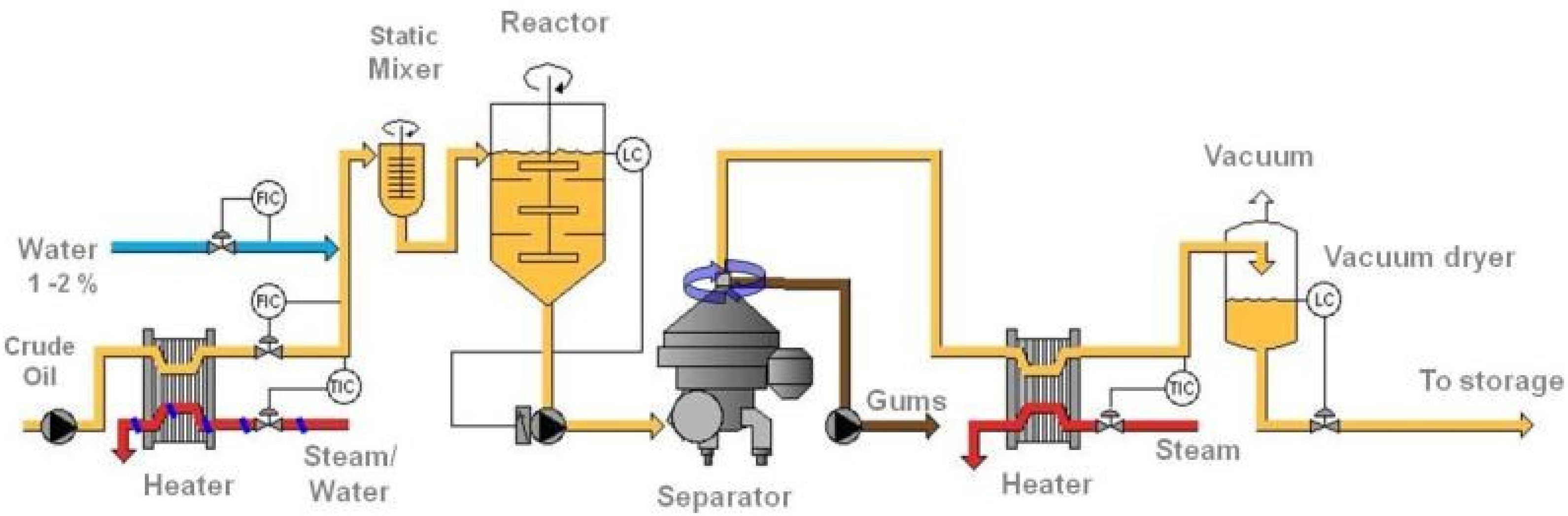
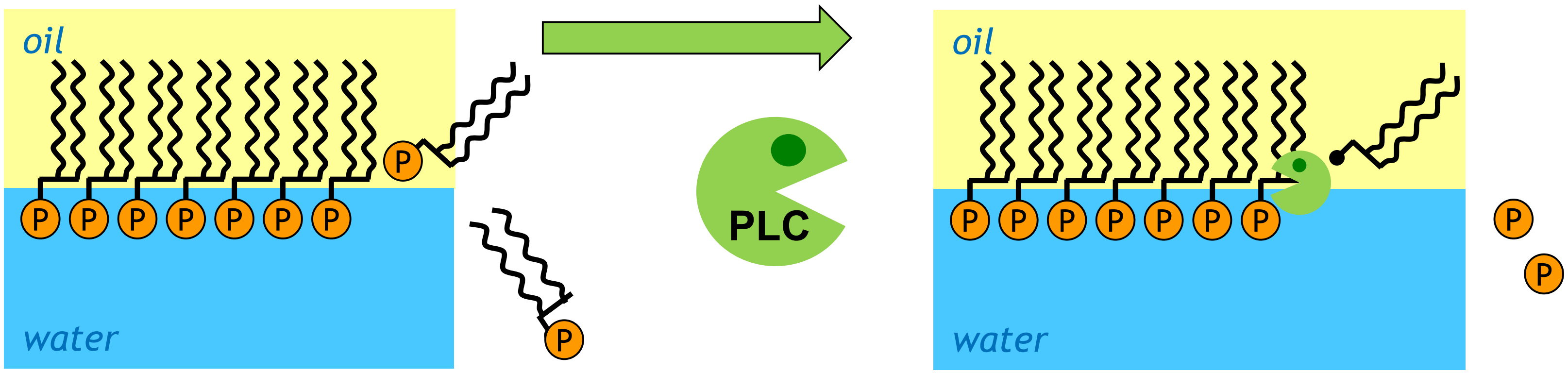
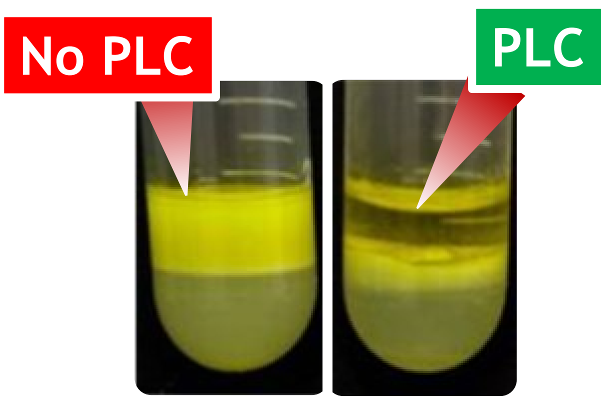
Water Degumming: Separation of Phospholipids



- Basic process to remove phospholipids falls between extraction & refining
- Process designed to minimize emulsion
- Target water wash degummed oil specification of < 200 ppm residual P
- Basic measurement of step yield AND little control of process
- Attention to “quality” only if coupled with caustic refining

Phospholipase Enzymes Break Emulsion





Disclaimer: more water added in favor of demonstrated effect

- Phospholipase enzymes uncouple oil & water-soluble parts of phospholipids
- Reaction requires contact between enzyme and phospholipid (*i.e.* emulsion)
- Enzyme action on phospholipids breaks down emulsion and releases entrained oil
- Reaction products create additional value

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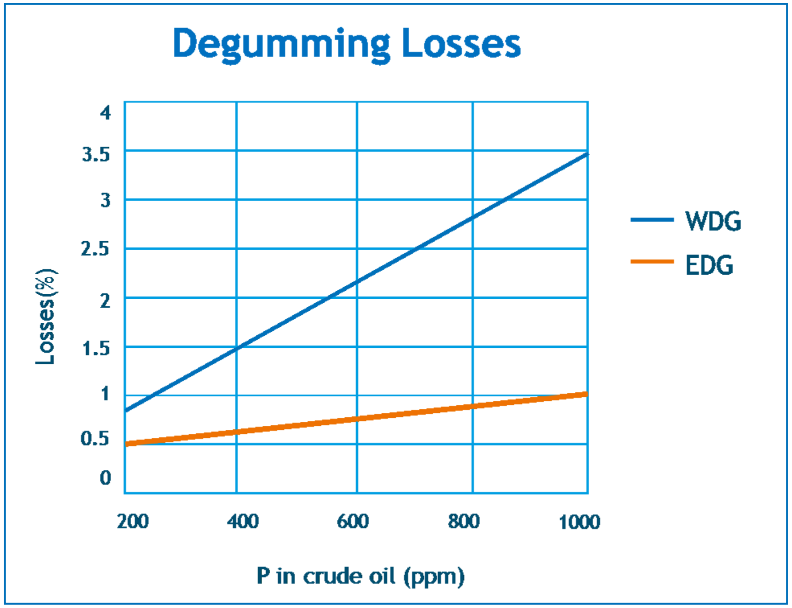
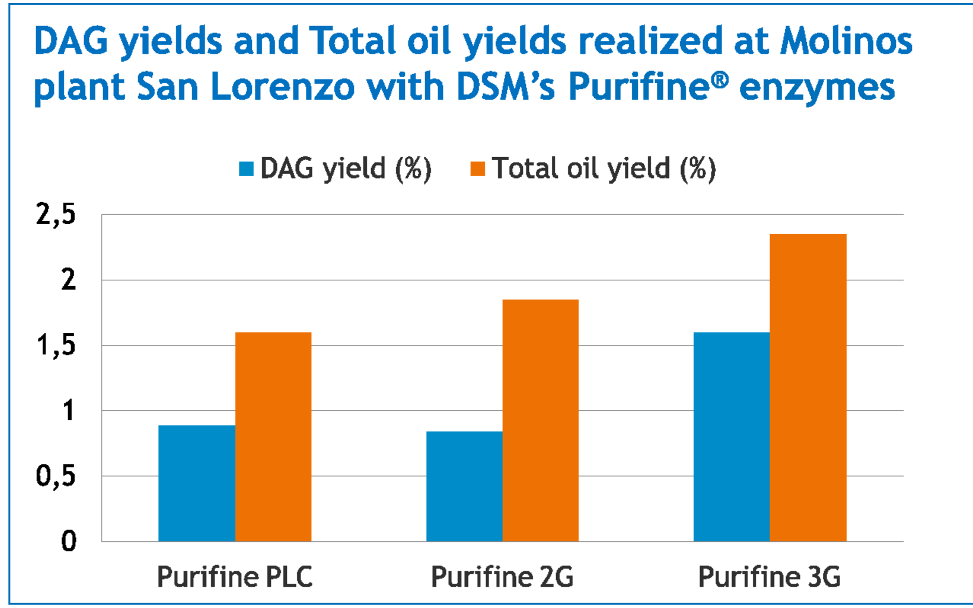
High Industrial potential for Purifine based enzymatic degumming





- Enzymatic degumming provides extra oil
- Less oil entrapment after enzymatic degumming

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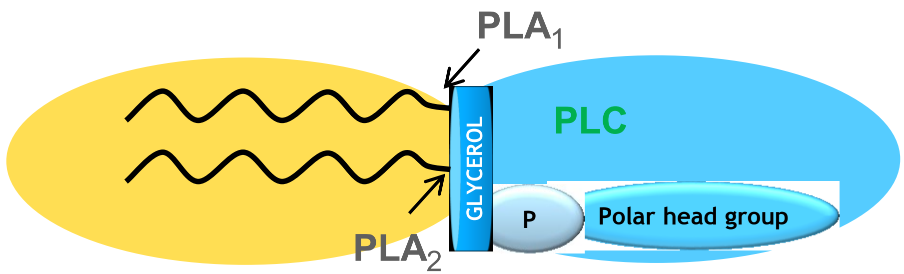
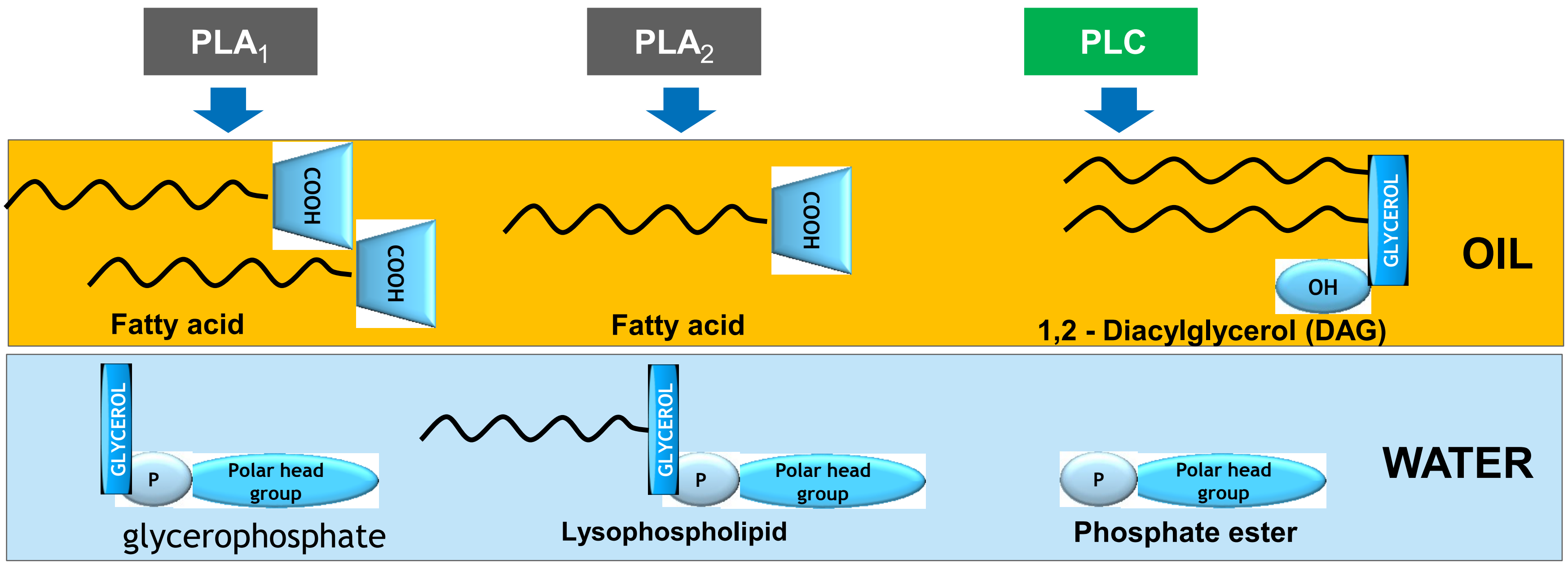
Commercial Degumming Enzymes





Lecitase® Ultra
(Novozymes)

Rohalase® MPL (AB Enzymes)
LysoMax® Oil (Danisco)
Purifine PLA2 (DSM)

Purifine® PLC and Purifine ® 3G (DSM)

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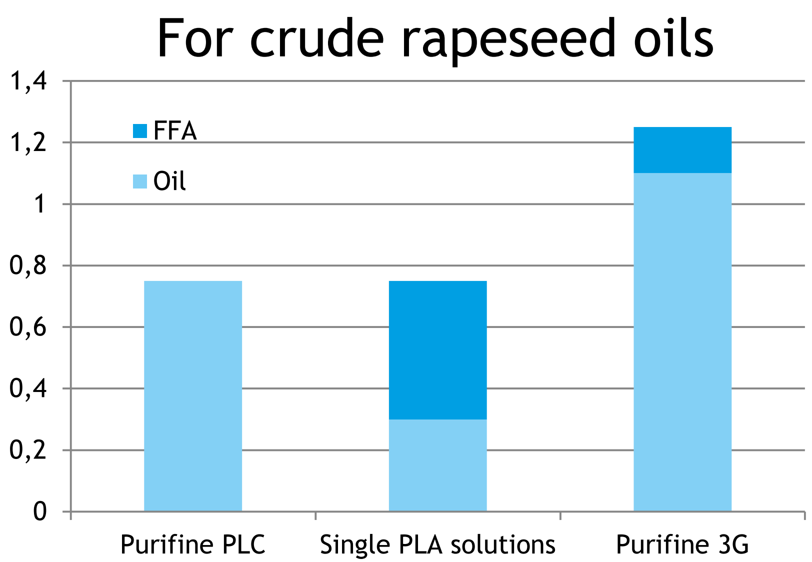
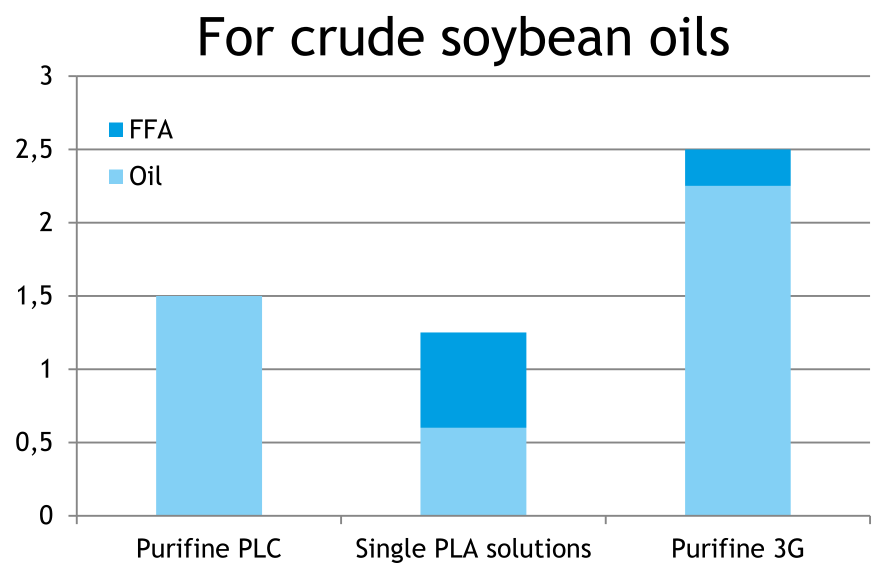
(1) Gramatikova, S., US Patent 7,226,771

Purifine vs. PLA compared





600 ppm P rapeseed oil			
	Purifine PLC	Single PLA	Purifine 3G
Oil	0,75	0,3	1,1
FFA	0	0,45	0,15

1200 ppm P soybean oil			
	Purifine PLC	Single PLA	Purifine 3G
Oil	1,5	0,6	2,25
FFA	0	0,65	0,25

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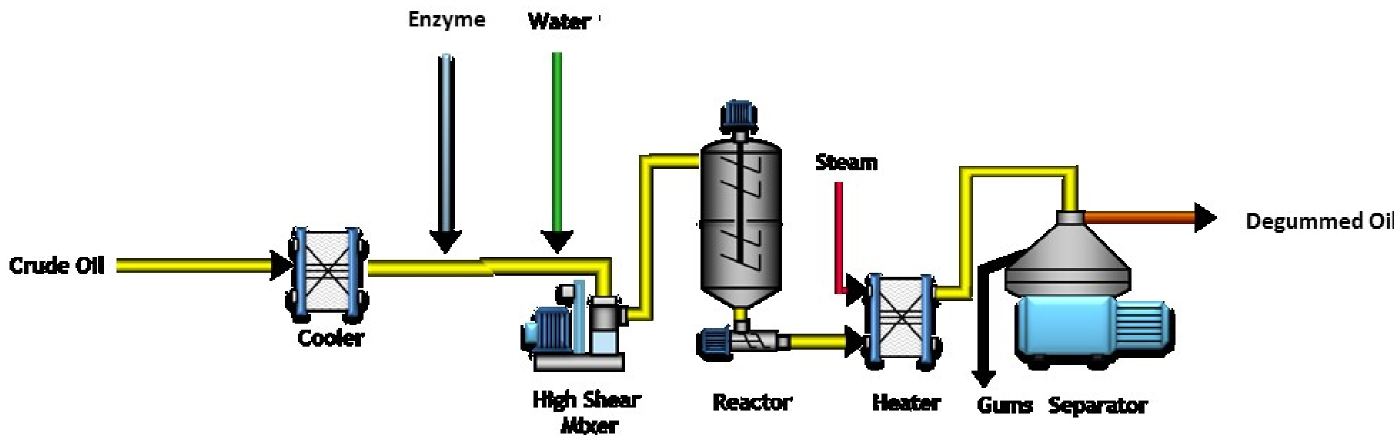
Basic principles of Enzymatic Degumming



Simple modification of standard degumming

Variable	Implementation
Crude Oil Temperature	Cooled for Emulsion stability + Enzyme activity
Process Control	Enzyme & water dosing, steady process flow
Reaction Interface	High-shear emulsion maintained by agitation
Reaction Time	Plug-flow reactor of sufficient size
Effective Separation	Heat to break emulsion & optimized stack-disk centrifuge
Maximize Reaction - Minimize Losses	

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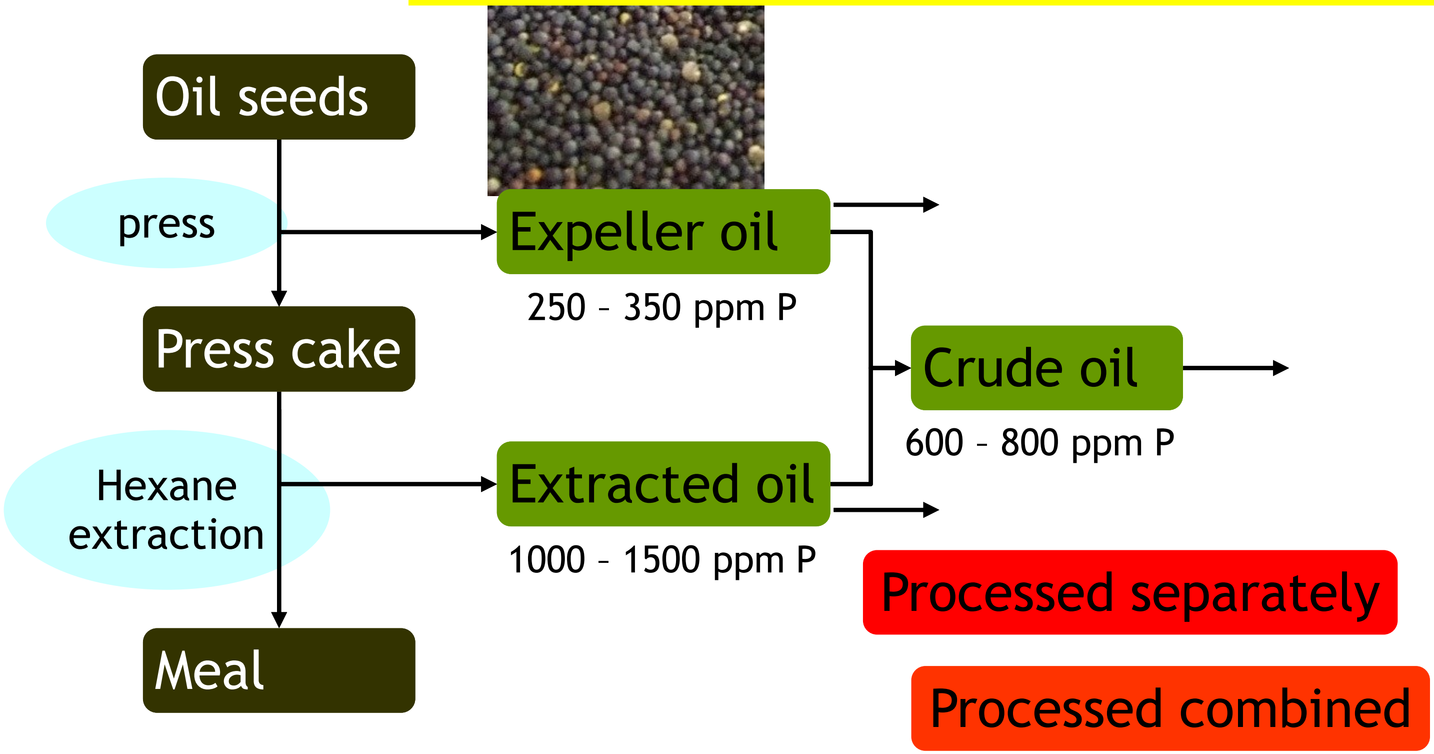
Rapeseed oil processes:

multiple or flexible processing options



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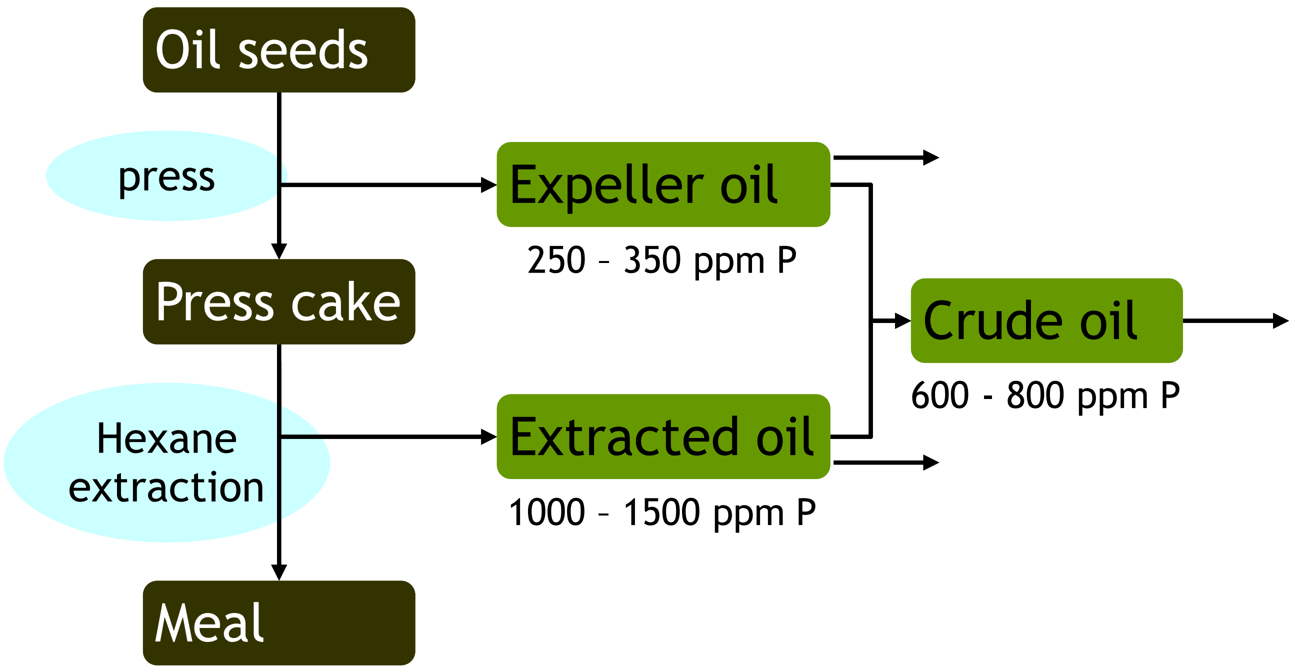

Rapeseed oil processes:
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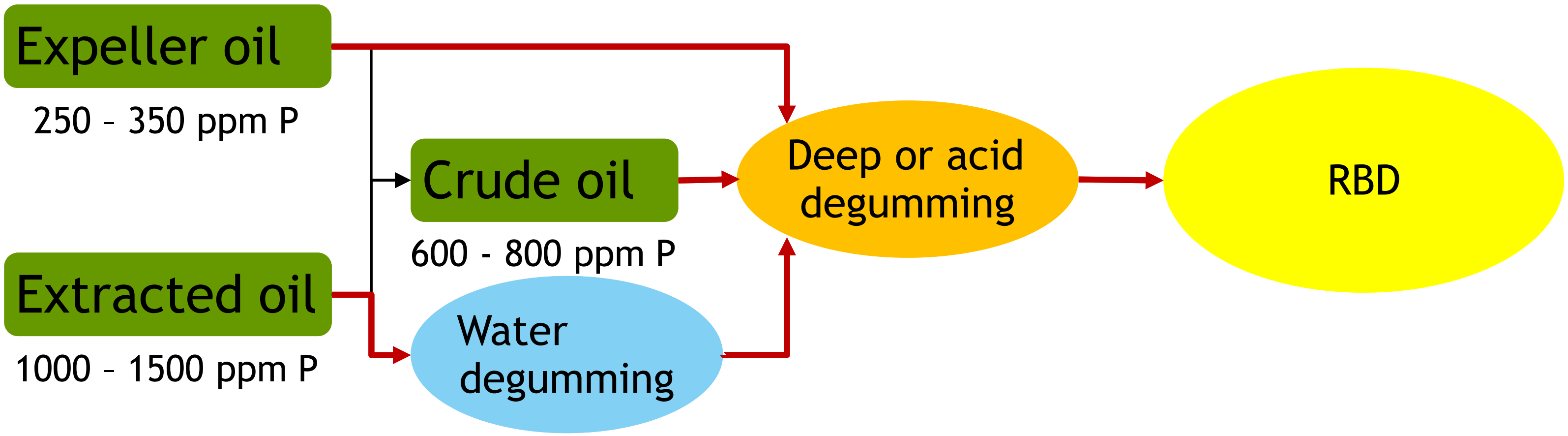
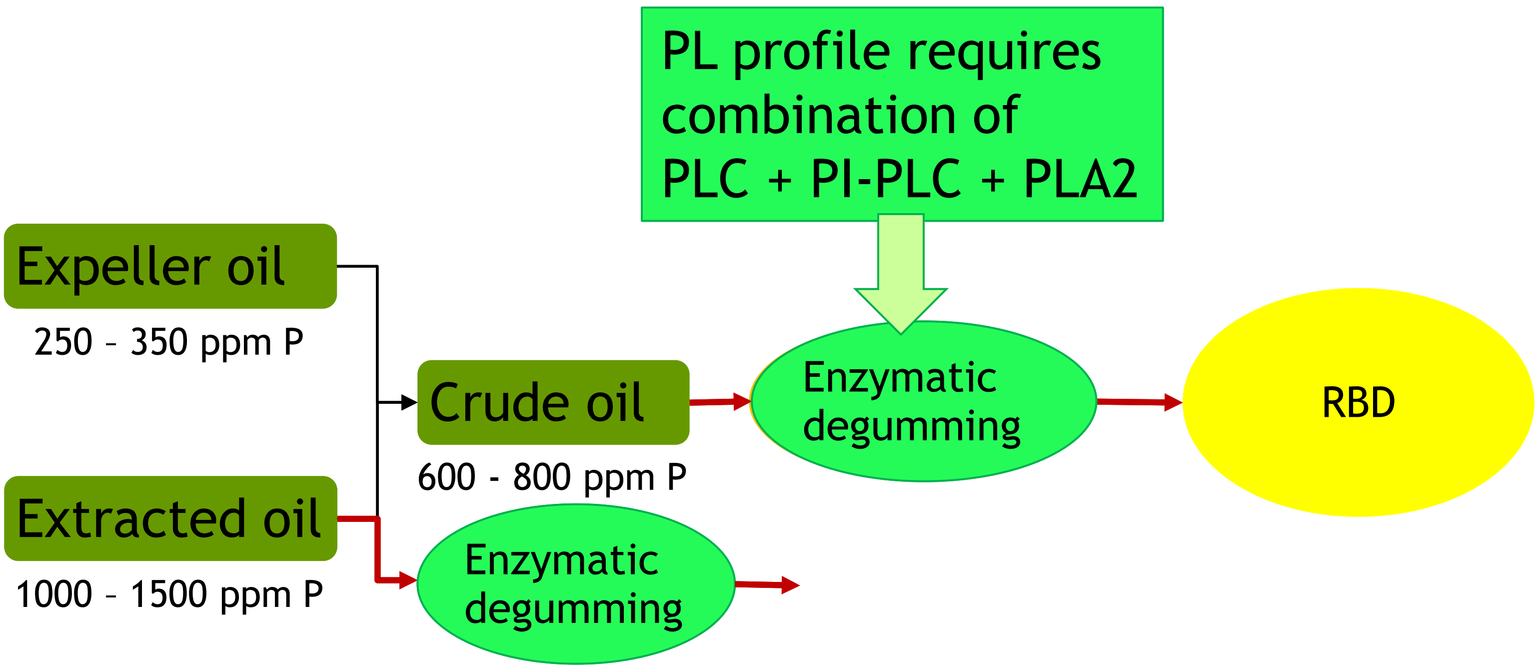


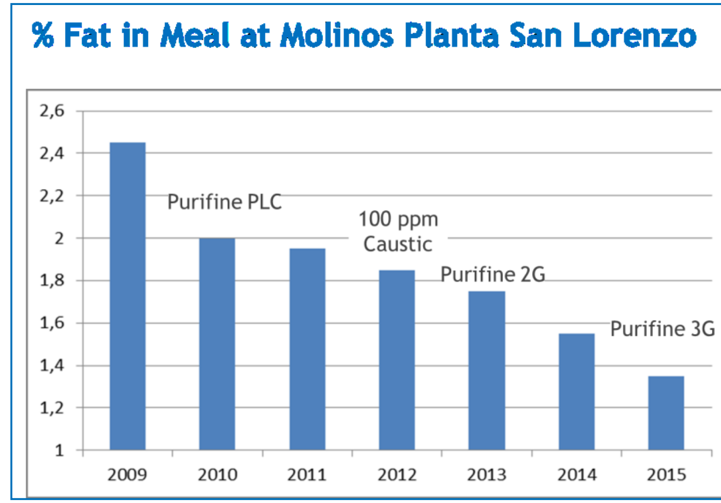
Introducing phospholipase-assisted degumming



More Oil Means Higher Protein

Soy meal is the premier protein source, but:

- Soy protein levels are declining due to new varieties of seeds & farmers focus on yield
- Increased competition coming from DDGS, canola meal, synthetic amino acids & other ingredients



➢ Soy producers need to maintain leadership position by
  - Keeping protein levels high in meal products
  - Running plants efficiently and at capacity

✓ Purifine 3G EDG can help!

Sources:
Thomas A. Hammer, NOPA http://unitedsoybean.org/wp-content/uploads/meal-supply-hammer.pdf
Park Waldroup, U. Arkansas http://www.soymeal.org/FactSheets/soymealdemand.pdf

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Special Gum Product Creates Opportunities

Traditional outlets for gums are:
- Lecithin, meal additive, acid oil feedstock, fuel

Enzymatic degumming Gums have different chemical, nutritional and energy profile:
- P content 3X higher
- Energy content 25% lower
- Reaction products from PLC action on phospholipids are present at high levels and could be "natural" source of high-value ingredients

Nutrient	Unit	WDG gums	3G gums
Energy	*% of oil*	84%	62%
Phosphorus	*g/kg*	19	62
Choline	*g/kg*	20	72
Inositol	*g/kg*	21	63
Lyso-PL	*g/kg*	None	13

Table: WDG vs. 3G gums content compared

[1]Indepedent research on behalf of DSM. Research under leadership of Willem Smink of Feed Innovation Services (The Netherlands)
[2]Cowieson et al., 2013; Zyla et al

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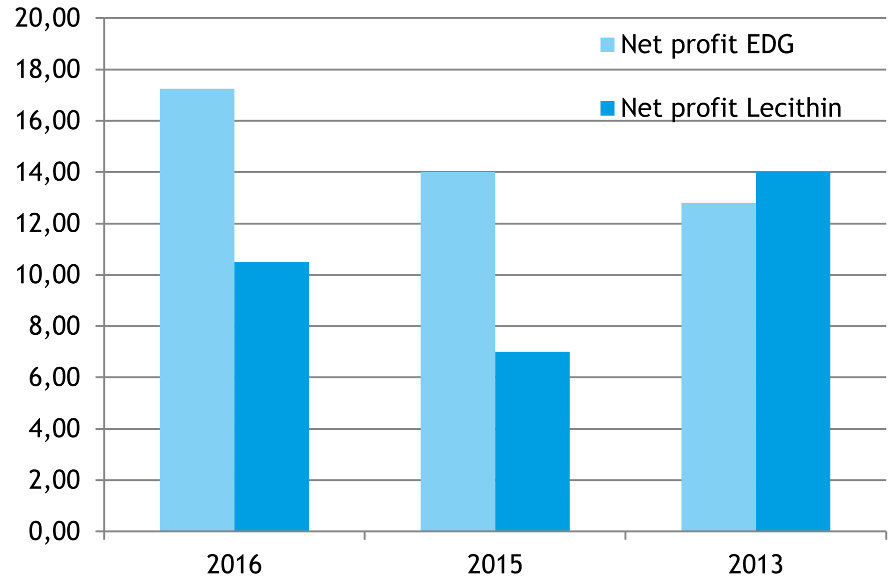
Enzymatic degumming vs. Lecithin Drying for Soy Crushing Installations

- Maximizing profitability calls for flexible set-up?
- Lecithin plants that are EDG capable do exist
- Future value of GM soy lecithin in EU market?
- Enzyme degumming for a soy crushing plant is an off-the-shelf option!



Driver	Unit	2016	2015	2013
Refined Soybean Oil Price	€/MT	750	600	800
GM Crude Soy Lecithin Price	€/MT	300	200	400
GM Soy Meal Price	€/MT	300	350	450
Enzyme Dosing	ppm	200	200	200
Purifine 3G Price	€/MT	22,5	22,5	22,5
Total Yield	in %	2,50%	2,50%	1,60%
Lecithin Yield	in %	3,50%	3,50%	3,50%
Net profit EDG	€/MT	17,25	14,00	12,80
Net profit Lecithin	€/MT	10,50	7,00	14,00

2016 prices correspond with global average levels in April '16

Lessons From the Field: Optimizing Reaction Yields

- Enough reaction time is critical:
  - 2 Hr for simple degumming; 4-6 Hr for deep degumming
- Temperature control is critical:
  - Enzymatic degumming activities optimal between 55-60°C = (131-140°F)
- Emulsion is important:
  - Silverson or IKA high shear mixer for emulsification of the oil
  - Water dosage (1.5-3%) impacts emulsification
- Low caustic dose enhances emulsion & degumming robustness:
  - 50-200 ppm dosed in crude oil before enzyme addition
  - Dilute (15-20%) solution for accurate & safe dosing
  - Mix thoroughly in oil before enzyme addition
  - Optional: acid injection before separator for increase separation robustness.

DSM provides on site support for maximizing reaction conditions

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Lessons From the Field: Driving for Low P

- Ensure availability & removal of NHP:
  - Citric is preferred to phosphoric acid (30-60 min)
  - Make sure oil is at 85-90ºC during acid treatment

- Maximize reaction:
  - 4-6 h reaction time needed.
  - Bottom feed tanks, & ensure effective agitation to maintain emulsion
  - IKA-type HS mixer

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Lessons From the Field: Visual Clues

- Visual observations can provide clues that a reaction is occurring

Emulsion after HS mixer

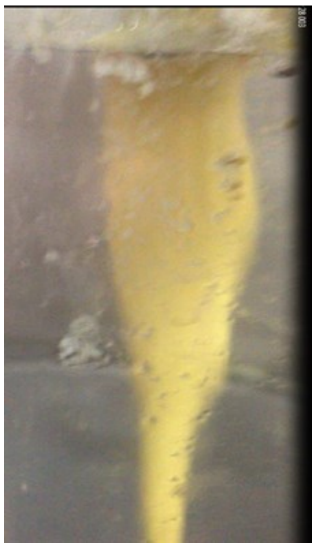
VS

Particles agglomerate, Cloudlike appearance

To stabile, bad separation

Gums exiting centrifuge

VS



Liquid, flowing EDG

Lumps of gums WDG

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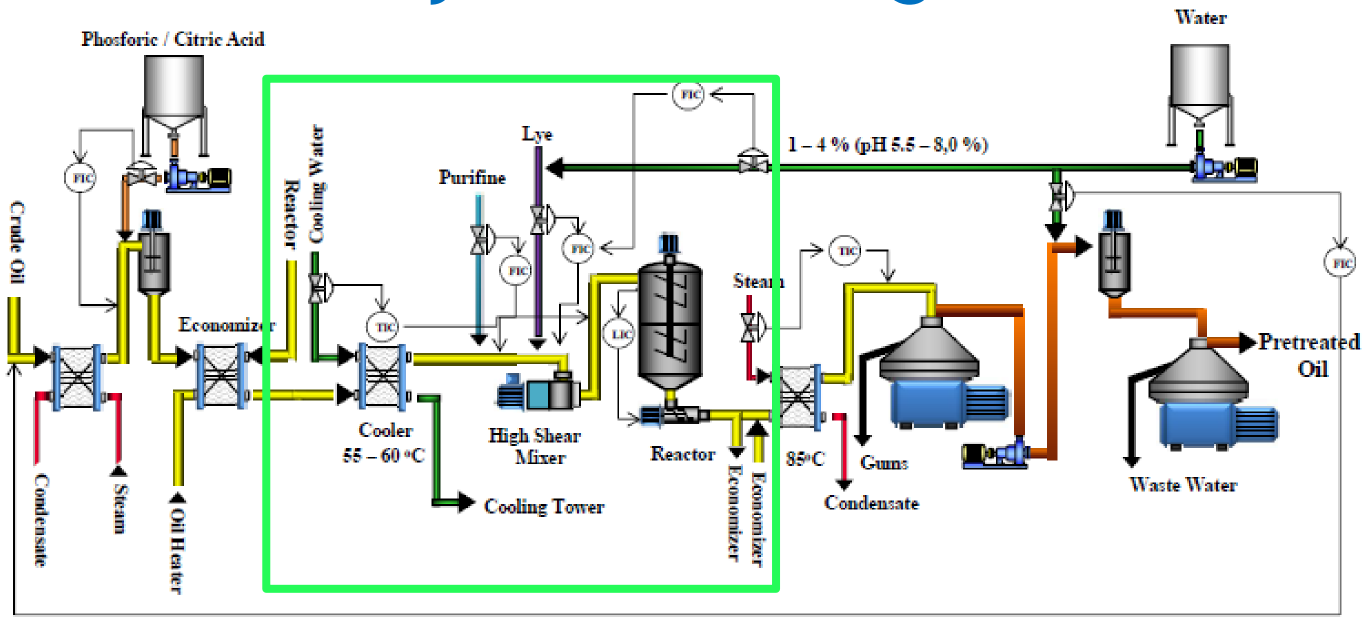
Purifine 3G: Enabler of Deep Degumming & Physical Refining?



- Prevent high losses in acid degumming or physical refining
- Enzymatic degumming is <u>the</u> enabling technology for physical refining on soy oil
- Other innovations (eg double scrubber) potentially increases overall value

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Deep EDG: Comparison of Process Options

	PLA1	PLC+PLA1 (sequential)	Purifine 3G*
1 Separator P	< 20 ppm	< 20 ppm	< 30 ppm
2 Separator P	< 5 ppm	< 5 ppm	< 10 ppm
Est. Oil Yield Gain†	1.2%	2%	2.5%
Status	• Validated on industrial scale • 10-15 Plants running	• Validated on industrial scale • 3 Plants running	• Industrial trialing in progress
Specific Process Requirements	• 4-8 h reaction time • Acidic conditions • Acid to prevent salts in separator	• 4-8 h reaction time • Acid to prevent salts in separator	• 2-6 h reaction time
Comments	• Low enzyme dose in good oils • Much higher dose in poor oils • Significant increase in FFA • Lowest yield potential	• Low PLA1 dose in good oils, may need higher in poor oils • Complicated engineering • 2 Enzyme suppliers required • Mid yield potential	• Highest yield potential • Drop in for PLA1 plants

*Based on preliminary industrial trials
†Compared with caustic refining assuming 4.5% losses & excluding FFA recovery

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Take home message

- Purifine® solutions in enzymatic degumming provides higher yield due to less entrapment of oil and release of diacylglycerol with marginal fatty acid increase.
- Low P solution possible with minor process adaptation.
- Deliver technical field support from industrial experts to get process up and running efficiently.
- Purifine®: More oil more profit!

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Need More information?

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