Pro / Con Physical / Chemical Refining of Rice Bran Oil

OR

Rice Bran Oil Refining Options

Steen Balchen,
Ling Hua
&
CheeMing Lee

Alfa Laval CPH
&
Alfa Laval Malaysia

Outline

Refining fundamentals

- Common understanding of terms / definitions
- Historical development
- Refining objective
- Unit operations

Process routes - Chem. vs. Phys. refining

- “Standard” Chem and Phys
- Phys combined with alkali wash
- Phys combined with cold degumming

Potential improvements

- Cold enzymatic degumming
- Enzymatic FFA re-esterification
- Dual strip / Deo in integrated equipment

Recap / conclusion

Terms in this presentation

Refining of glyceride oils only – for human consumption only

- Not covering refining of essential oils, fatty acids, alkane esters (Me-ester for biofuel) etc
- Not covering other applications like feed, biofuel…

Physical / Chemical refining

- Chemical: Removing FFA by alkali neutralisation (saponification / phase separation)
- Physical: Removing FFA by vaporization / stripping (typically combined with deodorization)

Modification processes / crystallization

- Only touching a bit the Dewaxing and Winterisation processes
- Not covering glyceride fractionation (Dry Frac / Solvent Frac)
- Not covering hydrogenation, trans- / inter-esterification

History of oils/fats and their refining

Use of fat in human diet

- Butter / Ghee types used since animal domestication 10.000 years ago
- Oil from high-oil content crops refined since 1850ties
- Margarine: Based on PKO ≈ 1870ties; on partially hydrogenated fat ≈ 1920 (after commercialization of hydro process); back to non-trans types since 2010
- Edible soybean oil refining since 1930ties – after developing industrial solvent extraction
- Edible Palm (fruit) Oil: Industrialized refining since 1970ties (until then some use in local house holds and for non-edible purposes)
- Edible RBO: Industrialized refining since 1990ties (until then used as animal feed)

Undesired components in RBO

Present in oil crop, co-extracted

- Phosphatides (of various hydratability)
- Waxes (esters of FA and fatty alcohols, m.p. often 60+C)
- Colorized components (chlorophyll, carotenes, other)
- Natural flavour – related to origin

Derived by reactions (occurring upstream or during refining)

- Hydrolysis – FFA formation
- Oxidation – hydroperoxides
- Odorous break-down components (short chain aldehydes etc)
- Trans-FA, MCPD, …

Contaminants

- Metals: Fe, Cu, Cl, As (mostly from the processing itself)
- Contaminants/POP (Pesticides, PAH, Dioxine/PCB, etc)

Refining unit operations

Industrial refining

- Industrialized extraction and chemical refining of veg. oil since 1850ties
- Physical refining introduced since 1980ties for Palm Oil and other non-gum oils, then followed by high-P seed oils in 1990ties, and RBO around 2000

"Pure" refining (separation) of glyceride oil

- Clarification (solids removal) – located at extraction site
- Aqueous extraction (alkali / acid / neutral) – degumming / neutralisation
- Adsorption (bleaching)
- Crystallisation (dewaxing / winterisation / DryFrac)
- Steam distillation (stripping / deodorisation)

Filtration (+/- filter aid) is part of several unit steps

Modification (reaction)

- Blending of oil types
- Hydrogenation (since 1915)
- Trans- / Inter-esterification (random / selective)

Refining steps history

Degumming

- Until 1960ties almost exclusively degumming with pure (neutral pH) water. Since then optimized degumming utilizing enzymes, chelators, integrated acid treatment - possibly with partial neutralisation, low-temp approaches

Bleaching

- Various powders used for bleaching clothes were in mid 1800 adopted for oil bleaching. Natural clays (Fuller's earth) used since beginning of 1900. During 1920ties acid activated earths were replacing most of the natural clays. Since then only marginal development (fast filtration obtained through sieving etc).

Deodorization

- Until 1970ties gradually increasing temperature and vacuum while reducing holding time:
  - 1900: 180C / 20 mbara / 4 hrs ▌ 1970: 260C / 5 mbara / 30 min
- Since 1970ties: Process conditions diversified according to oil type
  - To control artefact formation temp was reduced (250C max, except palm oil)
  - Deeper vacuum (2 mbara suction is common today)

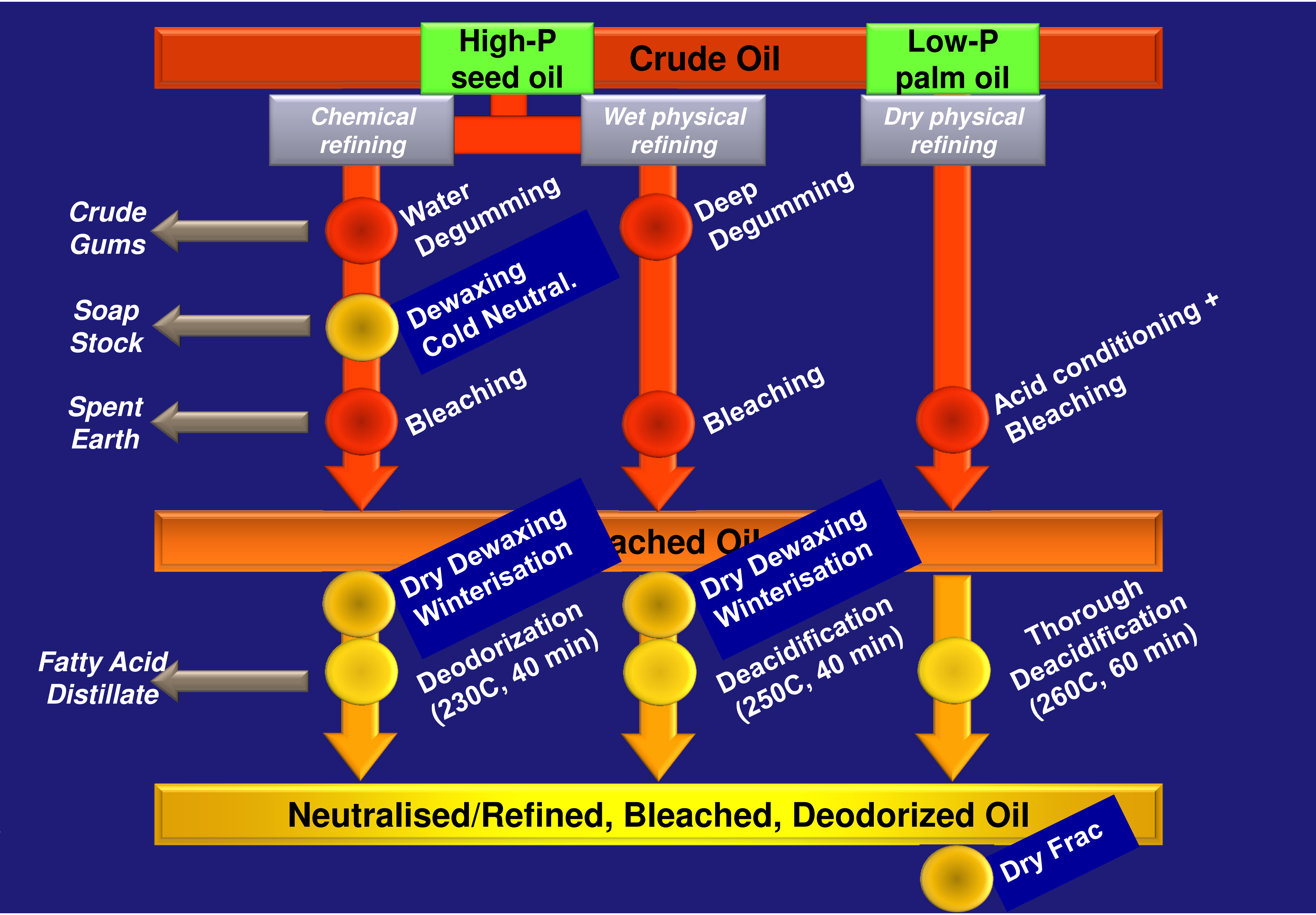
RBO history

Bran and crude oil

- Bran produced in 2000 years (small scale rice polishing due to Hi-So demand)
- “Industrial” milling since 1900 (started as farm machines, later consolidated in mills). Bran used as feed
- Industrial bran extraction since 1950ties. Crude oil mostly used as feed

RBO refining

- Industrialized (chemical) refining slowly began in 1960ties, but edible quality only since 1990ties
- Physical refining introduced from early 2000
- The refining process is complex since the crude oil contains - in high amounts - more or less all undesired components found in other oils (high FFA; gums; waxes; color) Dual processing by same type of unit operation are often applied
  - Dual crystallization (initial Dewaxing and since Winterization)
  - Dual adsorption / bleaching (handling of spent earth amount, remove created color, and reduce overall B.E. consumption)
  - Dual thermal treatment for FFA-stripping and then deodorization



Crude Oil
High-P seed oil
Low-P palm oil
Chemical refining
Wet physical refining
Dry physical refining
Crude Gums
Water Degumming
Deep Degumming
Soap Stock
Dewaxing Cold Neutral.
Spent Earth
Bleaching
Bleaching
Acid conditioning + Bleaching
Dry Dewaxing Winterisation
Dry Dewaxing Winterisation
Fatty Acid Distillate
Deodorization (230C, 40 min)
Deacidification (250C, 40 min)
Thorough Deacidification (260C, 60 min)
Neutralised/Refined, Bleached, Deodorized Oil
Dry Frac

Typical RBO chemical refining route

Overview of the FFA, DG, and Element Contents, the Color Change, and the FA Composition During Chemical Refining of Rice Bran Oil

Parameters	Crude	Neutralized	Bleached	Dewaxed	Deodorized
	Oil sample				
FFA[a] (g/100 g)	7.53	0.12	0.19	0.19	0.04
DG (g/100 g)	3.9	4.0	4.1	3.9	4.0
Color					
1-in.	70Y/13R/6B	70Y/4.3R/2B	12Y/2R	—	—
5.25-in.	—	—	70Y/10R/0.2B	35Y/3.8R	13Y/2.2R
Minerals (ppm)					
P	488.30	3.90	0.10	0.20	0.20
Fe	5.30	0.30	0.30	0.01	ND[b]
Ca	27.40	1.20	0.40	0.10	0.10
Mg	118.10	0.90	0.10	0.01	0.03

Parameters (g/100 g)	Crude	Neutralized	Bleached	Dewaxed	Deodorized
Unsaps[a]	5.4	4.2	3.8	3.6	2.7
Squalene	0.028	0.022	0.021	0.019	0.008
Total sterols	2.94	2.15	1.92	1.91	1.83
Total tocols[b]	0.078	0.080	0.078	0.078	0.062
Rest unsaps[c]	2.3	2.0	1.8	1.6	0.8

	Crude	Neutralized	Bleached	Dewaxed	Deodorized
Oryzanol (g/100 g)	1.8	0.4	0.4	0.3	0.3
Total sterols (g/100 g)	2.94	2.15	1.92	1.91	1.83

Influence of Chemical Refining on the Major and Minor Components of Rice Bran Oil

V. Van Hoed[a,*], G. Depaemelaere[a], J. Vila Ayala[b], P. Santiwattana[c], R. Verhé[a], and W. De Greyt[b]

To comply with Cold Stability / Cloud Point bottled oil specs a Winterisation step is often added to above route.

Double bleach would normally not be applied (Neutral. ensures sufficient color reduction); enhanced stripping (to remove FFA) is not needed.

RBO "standard" phys. refining

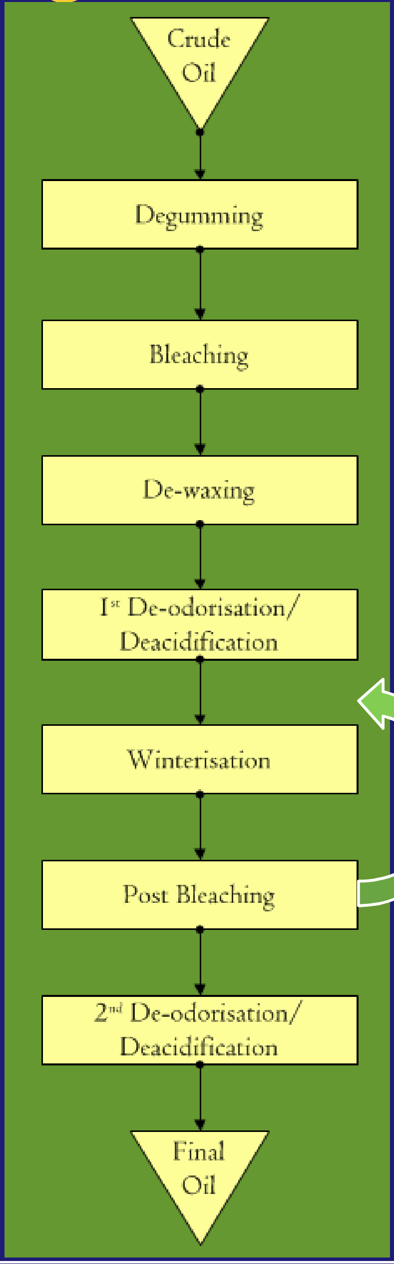
Concept: Remove FFA by stripping and avoid alkali neutralisation (which also reduces Oryzanol content).

The shown process is probably the most widely used route. It contains separate Dewax and Wint steps (which for some applications could be combined).

Omitting the alkali extraction step increases color in end product; the amount as well as fixation depends especially of 1) metal removal during degumming; 2) air leaks present in the high temp steps.

Intensified bleaching can – in some situations / to some extent – compensate.

(Pre-)bleach is required to remove residual gums prior entering a hi-temp step; phys. refining thus normally always comprise 2 bleach steps to obtain sufficient color reduction.



AP REFINERY

www.riceactive.com

2018

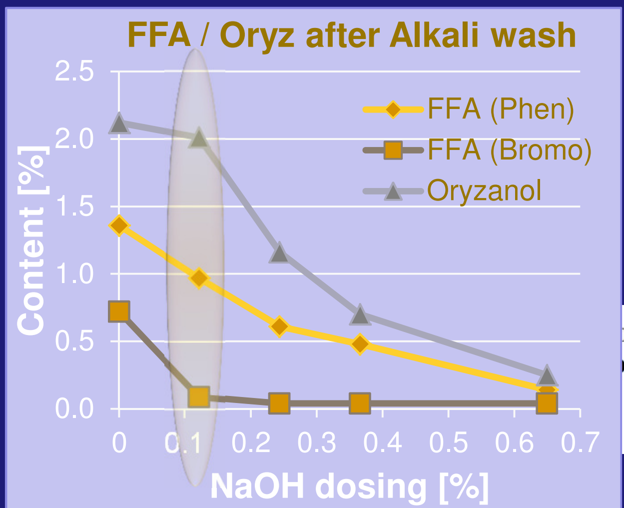
www.alfalaval.com

RBO phys. refining w. Alkali Wash (1)

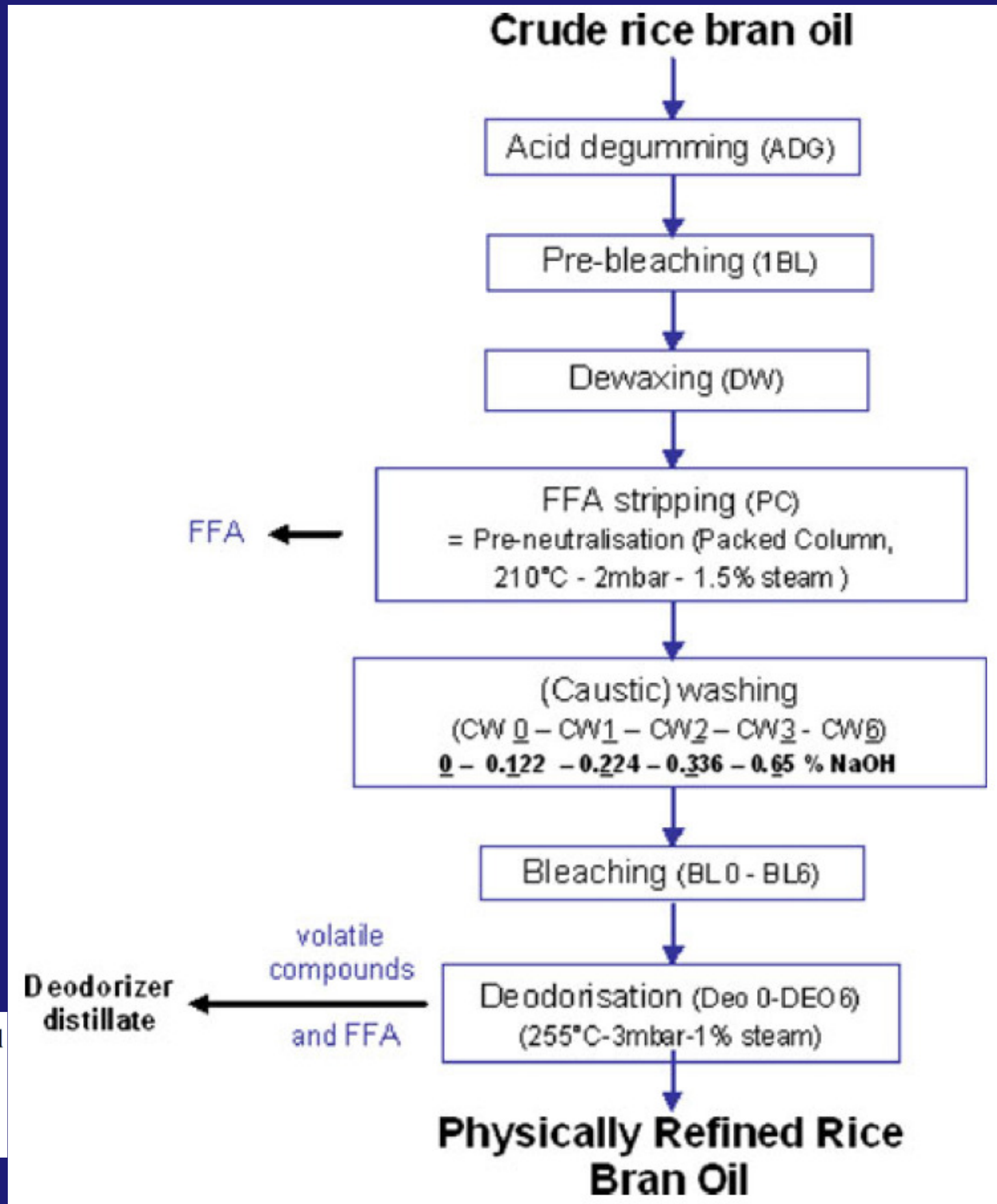
Concept: Remove most of FFA by stripping, in order to reduce oil loss during a subsequent alkali wash step, added for improving color reduction.

Pre-bleaching is required in order to remove residual gum prior dewaxing.

The partial caustic hot wash is reducing FFA, but also Oryzanol. The trade-off ?? Bad if believing in the Phen titration, but OK with Bromo indicator. FFA assessment to be improved.



›duce Rice Bran Oil
›ntent

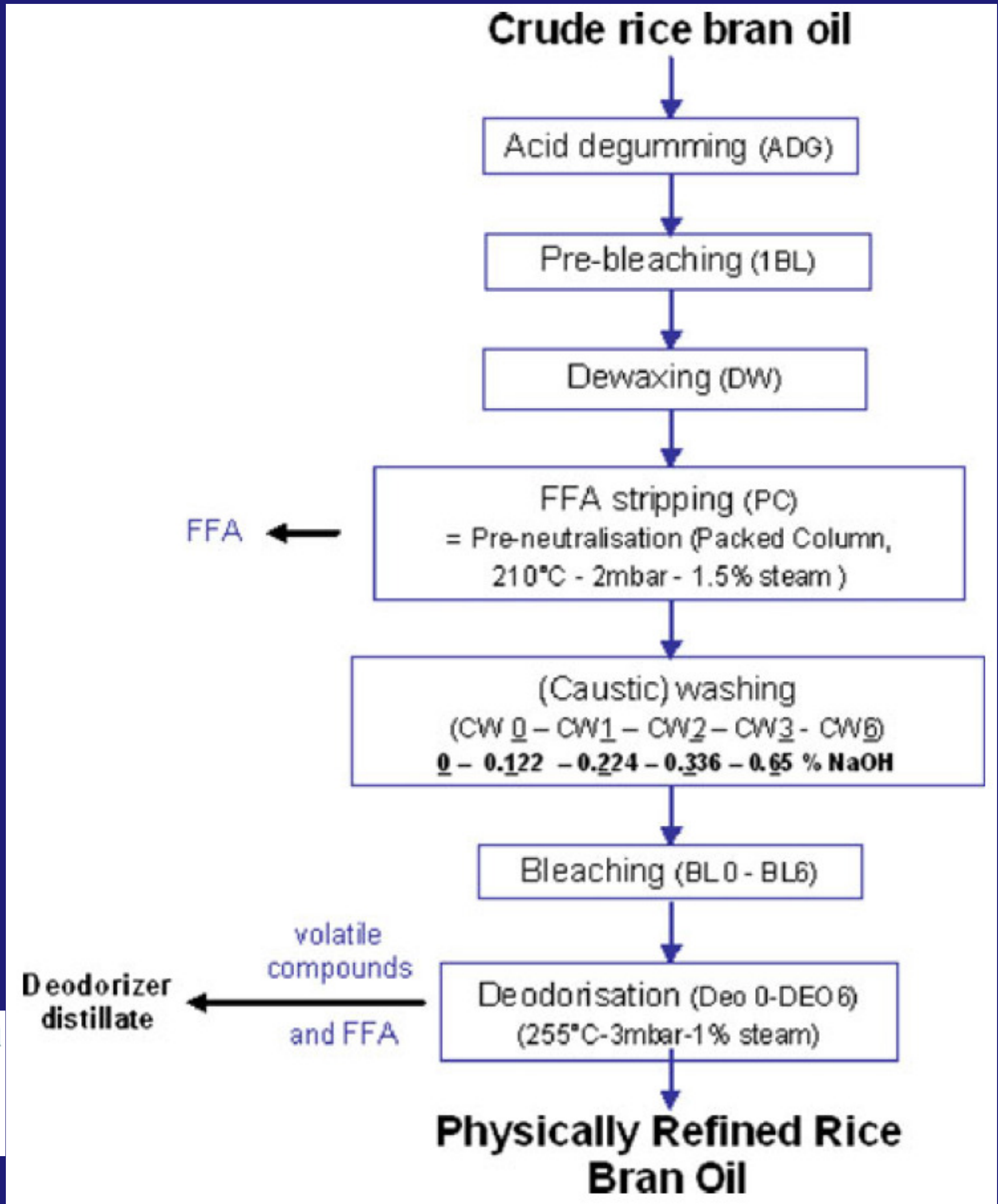


RBO phys. refining w. Alkali Wash (2)

Oil is twice subjected to high temp (initial strip and since deo). Very high deo temp.

Dewaxing **c**ould probably (optionally) be conducted post stripping - while pre-bleach is required prior.

Claimed a cold stability 0C / 5.5 hrs, which IMO is questionable (where are the hi-melting TAGs removed?)

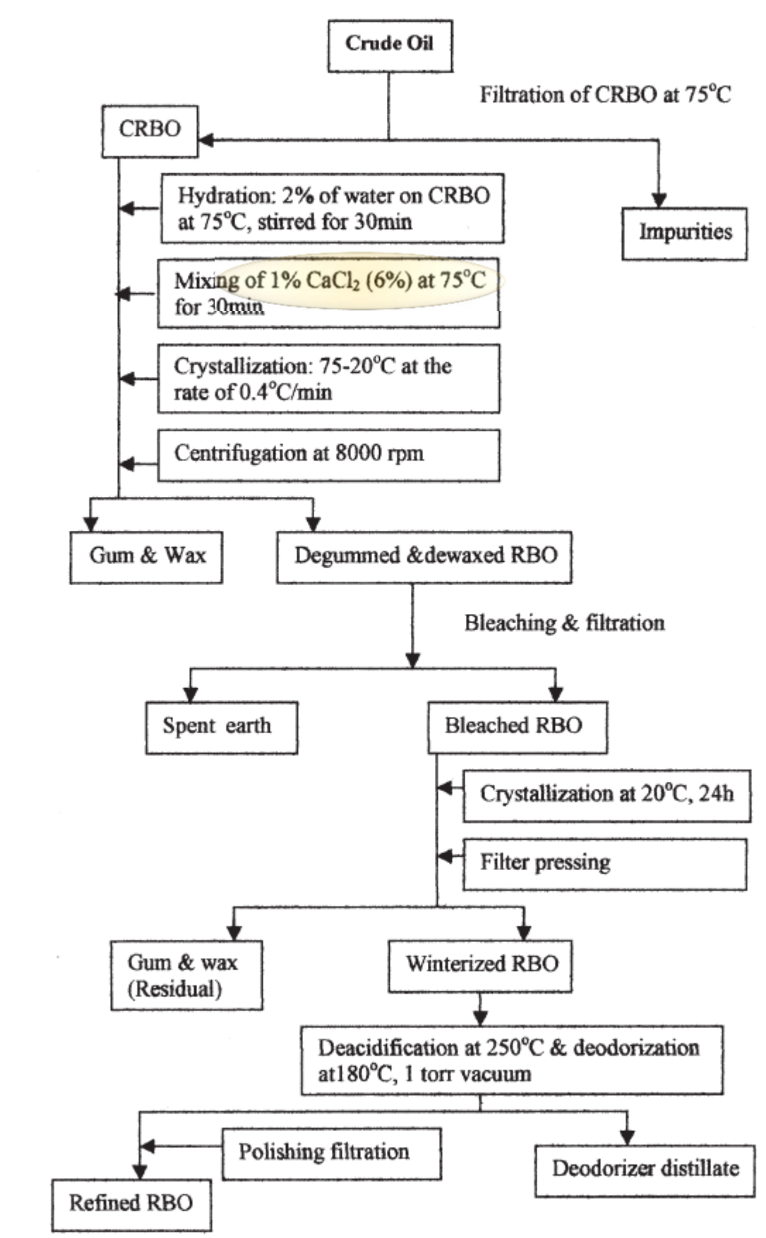


Optimization of Physical Refining to Produce Rice Bran Oil with Light Color and High Oryzanol Content

Vera Van Hoed · Jose Vila Ayala · Marta Czarnowska · Wim De Greyt · Roland Verhé

JAOCS, 2010

RBO phys. refining w. Cold Degumming



Combining degum / dewax at cold conditions can solidify and remove most of the wax together with the gum fraction in a HSS. Increased viscosity and thus higher oil loss (if pH neutral water degumming). pH-neutral cold degumming (a la the Unilever seed oil Unidegumming) might provide sufficiently low gum levels (5 ppm P). The effect of added $CaCl_2$ is not explained (could be emulsion breaking electrolyte).

A subsequent Winterisation step removes the residual wax together with high-melting glycerides; thus only one crystallization step is applied (stearin composition thus altered).

Only **one** bleaching step (using 2-4% B.E. + 10% Activated Carbon). Color unit was Lovibond 1”, presented as one (total?) value. Fully refined oil was around 12 units = high?

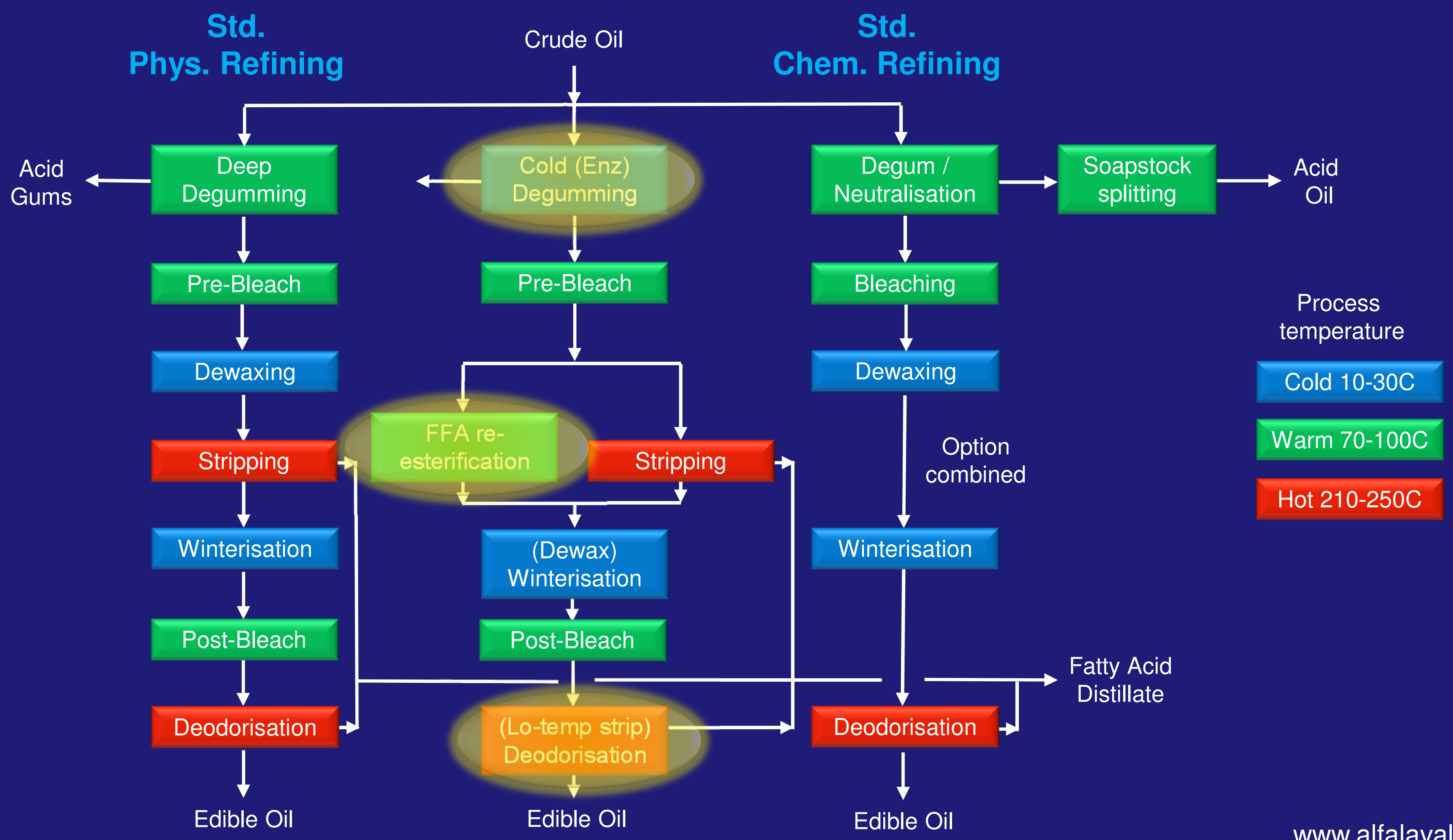
A Novel Process for Physically Refining Rice Bran Oil Through Simultaneous Degumming and Dewaxing

L. Rajam, D.R. Soban Kumar, A. Sundaresan, and C. Arumughan*

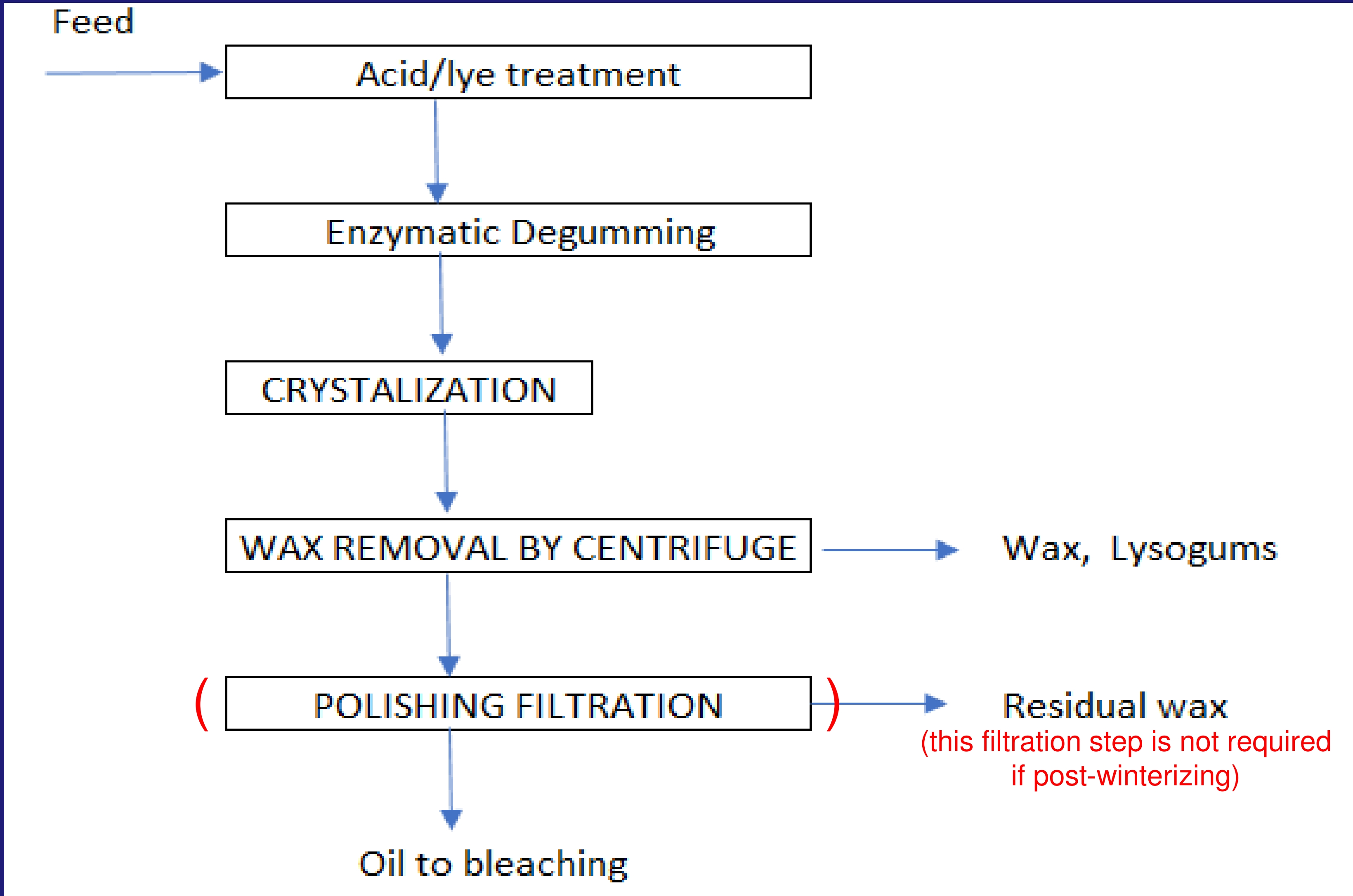
JAOCS, 2005

Refining alternatives for bottled RBO

Go for only 1 cold step and 1 hot step in process route...



Cold Enzymatic Degumming (CED)*

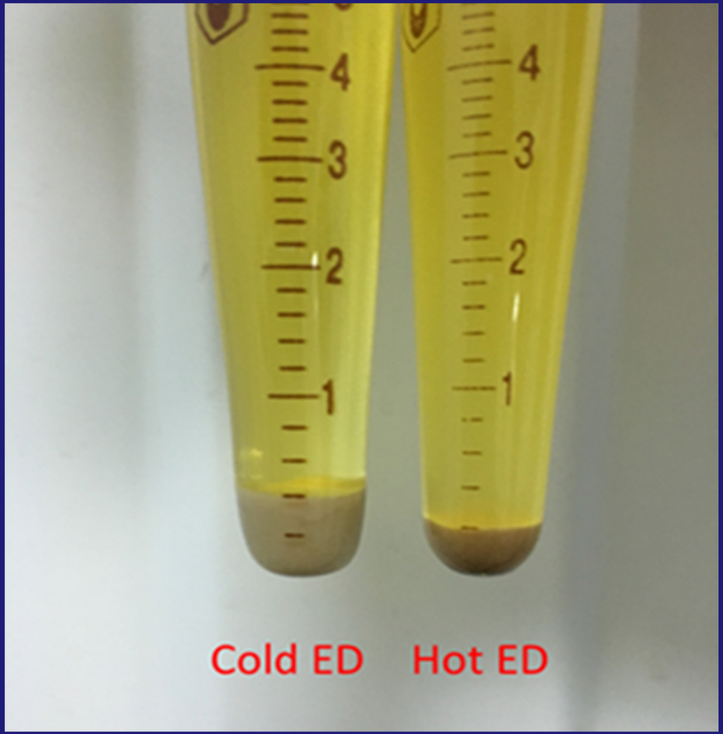


* Patented Alfa Laval EP2592133B1 and others pending

CED results on Sunflower oil

Plant scale retrofit

		Crude SFO	Hot ED	Cold ED
FFA /oleic acid	%	0,90	1,0	1,1
Fe / ICP	ppm	0,85	0,11	0,06
Phosphorus / ICP	ppm	148	7,0	2,2
Calcium / ICP	ppm	36,0	0,4	0,2
Magnesium / ICP	ppm	31,4	0,8	<0,1
Wax	ppm	413		62



CED conclusions (on SFO)

- Cold Enzymatic Degumming brings significant cost savings in physical refining of wax containing oils
- Wide range of wax content in feed can be processed
- Up to 85% of initial wax content removed
- Reduction of effluents is achieved
- The process was stable and robust

Removing FFA from high-FFA oils

1) Alkali neutralization (saponification / aqueous extraction)

- Robust and proven process
- High losses ~ 2+*FFA content – due to partial glycerides (especially MAG) emulsify the TAG with aqueous soapy phase

2) De-acidification by stripping (separation by vaporization)

- Limited loss ~ 1.1*FFA content
- High thermal exposure – formation of contaminants (transFA)
- Color fixation

3) Re-esterification with partial glycerides / glycerol

- Net reaction conversion of FFA into TAG, thus yield >100% (no oil loss)
- Optional A) enzymatic or B) non-catalytic, high-temperature route
- Required feed pretreatment
- Current concerns about edible applications (GRAS status)

FFA reduction by re-esterification

Enzymatically catalyzed esterification with glycerol / partial glycerides into triglycerides

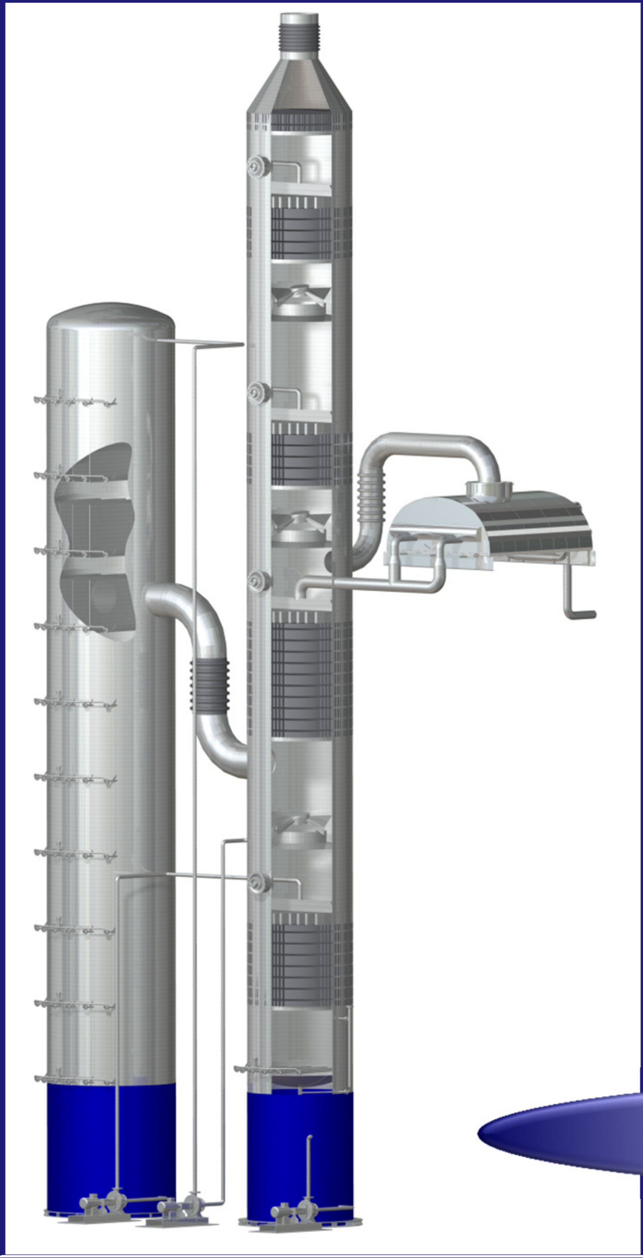
Under-utilized process as part of refining ?

Tendencies

- Glycerolysis using "excess" glycerol is growing for pre-treatment for biodiesel (only little emphasis on resulting MAG/DAG content)
- Non-catalytic route requires high temp / long time reaction, so only for non-food (significant artefact formation)
- Enzymatic concept has been developed*: 75C / 20 hrs reaction can reduce FFA in 15% RBO to <3% at moderate enzyme costs.

* Presented at ICRBO 2017 Bangkok by Alfa Laval

Dual Strip Deodoriser



Features

- Dual oil strip - **prestrip** for removing reactive volatiles before entering holding section, - **poststrip** for effectively removing formed volatiles.
- Can deacidify and deodorize at lower than normal temp. Optional dual temperature process by adding intermediate cooling in top tray.
- Double scrubbing of vapours.
- In case of high capacity the Strip and Holding functions can be split up into separate vessels as shown (ease of vessel fabrication / installation).

Continuous deodorizer of tomorrow?

Process recommendations

Mildest possible refining, of best possible crude oil quality - using the most appropriate technology

- Milder processing will prevail in the future, especially for hi-end products like RBO. Latent risk of discovery of other artifacts (transFA, MCPD, GE, intra-polymers, …)
- Make an effort to prevent hydrolysis prior oil extraction. Enzyme inactivation has been solved for other oil crops - transfer/modify that technology
- If high FFA in CRBO cannot be avoided then consider reducing by (enz) re-esterification instead of separation (stripping or saponification)
- Consider implementing Cold (Enzymatic) degumming. “Cold” in order to partially remove waxes, allowing to combine the traditional Dewax and Wint step into one single step. “Enzymatic” to alter the emulsification properties of the gum, thereby reducing viscosity and oil loss (which however still will be quite high). Otherwise consider Cold, Acid-degumming. The business case needs investigation…
- Avoid two high temperature steps in the process route, since the oil is sensitive/reactive at elevated temp (and heat and cool phases consume energy).
- Consider implementing milder deodorization temperature by selecting a design that utilizes packed column technology for improved stripping.

Conclusive remarks

- Not yet broad consensus about how to best refine RBO… Reason??
- "Go with the flow" and consider milder and less processing
- Improve the CRBO quality (less FFA) to reduce the refining task
- Avoid alkali conditions to preserve oryzanol – deal with the color by other means. Traditional chemical refining (FFA removal by saponification) is thus out as option.
- Current phys refining often comprises 2 **cold** steps and 2 **hot** steps – indicating over-processing that ought to be eliminated
- A single cold step is probably not feasible for bottled oil, but 1 step could be integrated with the degumming step.
- A single hot step, which is important to keep artefact formation low, requires stripping-deacidification to be integrated with deodorisation (like for other oil types), or implementing another FFA reduction technology (re-esterification is a possibility). But best if solving the FFA problem upstream by prevention ☺

Thank you for your attention !

www.alfalaval.com