RICE BRAN OIL PROCESSING AND VALUE ADDED PRODUCTS

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World Production of Rice ≈ 500 MMT

World Production of Rice Bran ≈ 50 MMT

Estimated Annual Global Potential of RBO 9 to 10 MMT (Actual Production ~ 1.2 million tons)

India produces 103 MMT of rice

- 10 MMT of bran
- 1.5 to 2.0 MMT of Oil (Potential)
- 0.95 MMT of oil (Actual)
  - 0.90 MMT – Edible
  - 0.05 MMT – Non-edible
VALUE ADDED PRODUCTS FROM PADDY

**PADDY**

- Husk
- White Rice
  - Fufural
  - Silicon
- Rice Bran
  - Deodorizer
  - Distillate
  - Cooking oil
  - Salad oil
  - Crude Oil
  - Defatted Rice Meal
  - Polysaccharide
  - Dietary Fiber
  - Hydrogenated Oil
  - Phytic Acid
  - Fine Rice Meal
  - Inositol Triphosphate
- Rice Germ
- Ground Rice
- White Rice
  - Silicon
- Silicon
- Silicon
  - Crude Oil
  - Defatted Rice Meal
  - Dietary Fiber
  - Polysaccharide
- Crude Oil
  - Hydrogenated Oil
- Phytic Acid
- Fine Rice Meal
- Hydroxy-apatite

- Fatty Acid
- Triglycerides
- Tocopherol
- Tocotrienol
- Squalene
- Sterol
- Tocopherol
- Tocotrienol

- Hemicellulose
- Polysaccharide
- Dietary Fiber
- Tocopherol
- Inositol
- Inositol Triphosphate
- Calcium Phosphate Di-Basic
- Hydroxy-apatite

- Bleached Wax
- Fatty Acid
- Glycerine
- γ-Oryzanol
- Ferulic Acid

- Soap
- Alkyd Resin
- Polyglycerol
- Polyglycerol Esters
- Ferulic Acid

- Dimer Acid
- Polyglycerol
- Titerpene Alcohol
- Phytosterol

- Long Chain Fatty Acid
- Fatty Acid Ester
- Polyglycerol
- Titerpene Alcohol
- Phytosterol

- Modified lecithins
- Triacontanol / Octacosanol
- Calcium Phosphate Di-Basic

- Lecithin
- Glycolipid

- Hydroxy-apatite

- Ferulic Acid
  - Caffeic Acid
  - Vanillin
  - Ferulic Ester
WHAT IS RICE BRAN OIL?

- Oil produced from the layer around the endosperm of rice obtained from paddy, which is removed during the process of rice milling and is generally known as rice bran.

- Nutritional quality of Brown rice is due to BRAN present on the grain...
DIFFERENT OIL!!

- ‘RBO’ is not a seed oil
- Contains <90% triglyceride
- Excellent oil for frying, pleasant flavor to the foods etc., - Well suited for many applications
- Good Natural antioxidant source
- How to retain natural integration of rice bran oil?
- CHEMICAL REFINING: Removes most of the nutrients of the oil
- PHYSICAL REFINING - Retains all the nutritional constituents and losses are less – Requires an efficient pre-treatment and phosphorus should be less than 5 ppm for deacidification step – which is challenging task
GOLDEN HEALTH OIL

- Popularly Known as Heart Oil / Health Food in Western Countries
- A Balanced fatty Acid Profile … Closer to the Recommended Levels of Health Organizations
- Contains 1-2% of Alpha Linolenic Acid - Meets the Requirement of n-3 Fatty Acids.
- Lower Retention in Foods
- Presence of a Host of Biologically and Nutritionally Active Constituents – Three Natural Antioxidants
  - Oryzanol
  - Tocopherols
  - Tocotrienols
  - Steryl Esters
  - Squalene
  - Diglyceride
## COMPOSITION OF CRUDE RICE BRAN OIL

<table>
<thead>
<tr>
<th>LIPID CLASS</th>
<th>Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triglyceride</td>
<td>80-90</td>
</tr>
<tr>
<td>Diglyceride</td>
<td>1-5</td>
</tr>
<tr>
<td>Monoglyceride</td>
<td>1-2</td>
</tr>
<tr>
<td>Wax</td>
<td>1-6</td>
</tr>
<tr>
<td>Phospholipids</td>
<td>1-2</td>
</tr>
<tr>
<td>Glycolipid</td>
<td>1-3</td>
</tr>
<tr>
<td>Steryl Esters</td>
<td>2-3</td>
</tr>
<tr>
<td>Oryzanol</td>
<td>1-2</td>
</tr>
<tr>
<td>Unsaponifiables</td>
<td></td>
</tr>
<tr>
<td>Sterols (Major), Tocopherols, Tocotrienols, Triterpenols, Hydrocarbons</td>
<td>3-8</td>
</tr>
</tbody>
</table>

**FFA – Varies from 3 to 40%**

A Different Oil Compared to Seed Oils...
# Fatty Acid Ratios of Common Edible Oils of India

<table>
<thead>
<tr>
<th>Edible Oil</th>
<th>Saturated (S)</th>
<th>Mono Unsaturated (MU)</th>
<th>Polyunsaturated (PUFA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundnut</td>
<td>20</td>
<td>50</td>
<td>30</td>
</tr>
<tr>
<td>Sunflower</td>
<td>10</td>
<td>25</td>
<td>65</td>
</tr>
<tr>
<td>Mustard</td>
<td>5</td>
<td>65</td>
<td>25</td>
</tr>
<tr>
<td>Safflower</td>
<td>10</td>
<td>15</td>
<td>75</td>
</tr>
<tr>
<td>Soybean</td>
<td>15</td>
<td>20</td>
<td>65</td>
</tr>
<tr>
<td>Sesame</td>
<td>10</td>
<td>50</td>
<td>40</td>
</tr>
<tr>
<td>Cottonseed</td>
<td>30</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>Coconut</td>
<td>92</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>Palm</td>
<td>50</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>Rice bran</td>
<td>20</td>
<td>45</td>
<td>35</td>
</tr>
</tbody>
</table>

\[ \frac{S}{MU} \quad PUFA \]

<table>
<thead>
<tr>
<th></th>
<th>1 : 1</th>
<th>33.3 : 33.3 : 33.3</th>
<th>(American Heart Association)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 : 1.5 : 1</td>
<td>28.5 : 43 : 28.5</td>
<td>(Japan’s Ministry of Health &amp; Welfare)</td>
<td></td>
</tr>
<tr>
<td>1 : 1.5 : 0.7</td>
<td>31 : 48 : 21</td>
<td>(WHO)</td>
<td></td>
</tr>
</tbody>
</table>

April 12, 2016
RICH IN NUTRACEUTICALS

RICE BRAN OIL IS RICH IN SEVERAL NUTRACEUTICALS AND MAKES THIS OIL HIGHLY NUTRITIOUS

- ORYZANOL
- TOCOPHEROLS
- TOCOTRIENOLS
- SQUALENE
- PHYTOSTEROLS
- PHYTOSTERYL ESTERS
WHY SO DIFFICULT TO PROCESS?!

- LOOKS LIKE A WONDERFUL OIL…
- MOST COMPLEX OIL TO HANDLE
- VERY TOUGH TO PROCESS…
- WHY SO!?...
- LIPASE IN THE BRAN IS THE CULPRIT…
RICE BRAN LIPASE

• Rice Bran Contains 1,3-Specific Lipase
• Starts Hydrolyzing TG Immediately after Removal of Bran from the Grain
• FFA Raises 4 to 40% within 15 Days

\[
\text{CH}_2\text{O-}\text{C-R}_1 + \text{CH}_2\text{O-}\text{C-R}_2 + \text{CH}_2\text{O-}\text{C-R}_3 \xrightarrow{\text{Lipase}} \text{CH}_2\text{OH} + \text{CH}_2\text{O-C-R}_2 + \text{R-COOH}
\]

Triglyceride   Monoglyceride   Free fatty acid
Efforts were made to develop technologies for stabilizing the raw rice bran to restrict the FFA in crude rice bran oil and to reduce chemical refining losses.

Various technologies of stabilization such as steam stabilization, chemical stabilization & extrusion technology were tried for this purpose.

None of the technologies became popular because of various techno-commercial reasons.

Ultimately the search started for some alternative refining technologies which could economically refine crude rice bran oil with higher levels of free fatty acids.

**ANSWER FOR THIS WAS PHYSICAL REFINING**
MAJOR PROBLEMS IN RICE BRAN OIL REFINING

- High Content of Free Fatty Acids
- Presence of Mono- and Diglycerides
- Unusually High Content of Waxes
- Presence of Polar Lipids like non-hydratable Phospholipids and Glycolipids
- High Content of Unsaponifiables like Hydrocarbons, Sterols, Tocopherols and Tocotrienols etc.,
- High Content of Steryl Esters and Oryzanol
- Dark Color Due to Pigments and Oxidized Lipids
## QUALITY OF INDIAN RICE BRAN OIL

<table>
<thead>
<tr>
<th>Crude Rice Bran (Quantity in tons)</th>
<th>FFA Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>200,000</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>500,000</td>
<td>&lt;20%</td>
</tr>
<tr>
<td>150,000</td>
<td>20-30%</td>
</tr>
<tr>
<td>50,000</td>
<td>30-40%</td>
</tr>
</tbody>
</table>
WHY PHYSICAL REFINING FOR RICE BRAN OIL?

- To Retain Most of the Nutritional Components like Oryzanol in the Refined oil
- Physical Refining Losses (Only 1.1 times of FFA) are Less Compared to Chemical Refining (2.5 to 3 times of FFA)
- More Profitability and Less Environment Pollution
- Important Pre-requisite for Successful Physical Refining - Phosphorus Content in the Oil < 5 ppm
- Industry Struggled Due to Non-availability of Appropriate Degumming Process
WHY ENZYMATIC DEGUMMING?

- Water Degumming - Simplest Method for Removing Phospholipids from Vegetable Oils
- Water Degumming Removes Only Hydratable Phospholipids - Residual Phosphorus in Water Degummed Oil - 80-150 ppm
- Non-hydratable Phospholipids (Ca and Mg salts of PE and PA) Retains in Water Degummed Oil
- Existing Degumming Methods like Phosphoric Acid Degumming may not Reduce the P levels to < 5 ppm
- Enzymatic Degumming Hydrolyses the Phospholipids including Non-hydratable Phospholipids into Water-soluble Lyso-lecithin - Separates from Oil Phase by Centrifugation
Enzymatic Degumming First Reported by Lurgi Using Phospholipase A₂ Isolated from Porcine Pancrease (Lecitase 10 L)

Lecitase Novo – A Microbial-based phospholipase A₁ - Introduced in the Market in 2002.

Enzymatic degumming using these enzymes were reported for soybean, rape seed and sunflower oils only

IlCT Came out with an Improved Process with Both the Enzymes for the Degumming of Vegetable Oils including Rice Bran Oil [India, US, Indonesia, China, Japan and Vietnam Patents granted / pending]
WHAT IS NEW IN IICT ENZYMATIC PROCESS?

- New Protocol – Simpler than the Existing Enzymatic Degumming Processes
- No Complex Processing Step
- Can be Implemented with Minor Modifications in the Existing Refineries
- Can be Converted into a Continuous Process Very Easily
ADVANTAGES OF IICT PROCESS

“P” Levels in the Pre-treated RBO Brought Down to 0-5 ppm

1 to 1.5% Gums with an Oil Content of 15-25% in Enzymatic Degumming; 2-4% Gums with 50-60% Oil in Conventional Degumming

No Alteration of Fatty Acid Composition in RBO

Water wash not Necessary after Enzymatic Degumming - Oil Loss and Effluent can be Avoided

Oryzanol of Crude RBO Remains Almost Intact
IMPACT OF ENZYMATIC DEGUMMING PROCESS

- **LESS WATER CONSUMPTION**
  7% against 14 to 20% used for other degumming methods

- **No effluent**
  Phosphoric acid degumming requires water wash

- **MORE OIL RECOVERY**
  0.6 to 1.5% in case of physical refinery
  2 to 3 folds more recovery in case of chemical refinery

- **MORE FATTY ACID**
  0.3 to 0.6% additional fatty acid production due to the hydrolysis of lecithin

- **BETTER QUALITY OIL**

- **MORE PROFITS**

- **VALUE ADDITION TO BY-PRODUCTS**
  High value lyso lecithin
  Better quality wax

April 12, 2016
ENZYMATIC DEGUMMING OF RICE BRAN OIL

M/s. Ganpati Solvex Pvt. Ltd., Rajnandgaon

- Rice Bran Oil (RBO) – Known as Healthy Heart Oil
- Most of the Nutraceuticals Get Destroyed During Alkali Refining of RBO
- Physical Refining – The Preferred Process for RBO
- Degumming – The Key Pre-treatment Step for Physical Refining of any Oil
- No Methodology was available for Efficient Degumming of Crude RBO
- IICT’s Enzymatic Degumming Process Succeeded in Removing Both Hydratable and Non-hydratable Phospholipids using Phospholipase A1 Hydrolysis
- Enzymatically Degummed RBO Retains all the Nutrients and Contains < 5ppm Phosphorus and Ensures Efficient Physical Refining


- IICT Process Requires Less Water and Releases No Effluent
- Technology Developed and Demonstrated at Commercial Scale (50 TPD)
- Investment Required for Switching Over to Enzymatic Degumming from Conventional Degumming in the Existing 50 TPD Refinery : Rs 15 Lakhs

IMPACT ON INDIAN RICE BRAN OIL INDUSTRY

Total Annual Production of RBO in India : 9.5 lakh tons
Production of RBO using IICT Process : ~4 to 5 lakh tons

If Total Production of RBO Routes through IICT Process...
- Extra Oil Recovery @ 1 to 1.5 % : 9500 to 14,250 tons (Rs.48 to 70Crore)
- Extra Fatty Acid Recovery @ 0.3 to 0.6 % : 2,850 to 5700 tons (Rs. 8 to 15 Crores)
- Minimum Water Saving @ 10 % of Crude oil : 95,000 KL

New Industries Established Employing IICT’s Enzymatic Degumming Process Annually Producing about 2 Lakh Tons of RBO (Worth of > Rs. 1000 crores ) – Helping the Nation in Saving Foreign Exchange to Import Edible Oils

SEA Golden Jubilee Award-2013
First Industrial Green Chemistry Award – 2009
CSIR Technology Prize-2005
TDB National Award 2009

27 Clients so far Covering 9 states
ENZYMATIC DEGUMMING OF RICE BRAN OIL

CSIR TECHNOLOGY PRIZE
2005

INDUSTRIAL GREEN CHEMISTRY AWARD
2009

TDB NATIONAL AWARD
2009
<table>
<thead>
<tr>
<th>Processing step</th>
<th>Color</th>
<th>A.V.</th>
<th>Phosphorus (ppm)</th>
<th>Oryzanol (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude oil</td>
<td>35-50*</td>
<td>7-15</td>
<td>350-650</td>
<td>1.4-1.6</td>
</tr>
<tr>
<td>Enzymatic degumming</td>
<td>40-55**</td>
<td>7.5-15.5</td>
<td>20-50</td>
<td>-</td>
</tr>
<tr>
<td>Bleaching</td>
<td>25-32**</td>
<td>7.5-15.5</td>
<td>5-15</td>
<td>-</td>
</tr>
<tr>
<td>Dewaxing</td>
<td>20-27**</td>
<td>7.5-15.5</td>
<td>0-5</td>
<td>-</td>
</tr>
<tr>
<td>Physical Refining</td>
<td>8-20**</td>
<td>0.1-0.25</td>
<td>0-5</td>
<td>1.3-1.5</td>
</tr>
</tbody>
</table>
RICE BRAN OIL TRIGLYCERIDE COMPOSITION

<table>
<thead>
<tr>
<th>Triglyceride</th>
<th>Content, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSS</td>
<td>0</td>
</tr>
<tr>
<td>SSU</td>
<td>20.5</td>
</tr>
<tr>
<td>SUU</td>
<td>49.7</td>
</tr>
<tr>
<td>UUU</td>
<td>29.8</td>
</tr>
</tbody>
</table>

Due to higher content of SSU molecular species Rice bran oil is hazy at lower temperatures and winterization is necessary in addition to dewaxing to get transparent oil.
WINTERIZATION

- To remove traces of wax and stearin
- To remain clear even at 0°C for good export market
- RBO tends to form $\beta'$ prime crystals - Slow cooling cycle is recommended
- A high filter surface-to-oil ratio is needed to accommodate the separation of fine crystals
- Filter aids may be used to increase flow rates and to extend filter cycle time
- RBO stearins may be added to shortening, fry oil, or margarine oil formulations
CASE STUDY ON REFINING OF RICE BRAN OIL
- Presented By Sri A.R. Sharma At 1st National Seminar On Rice Bran Oil – Sea, April 25, 1998, Hyderabad

• Basic requirement of physical deacidification is that the phosphorus content in the feed oil should be less than 5 ppm
• So far no commercially viable technology is available to achieve the desired level of phosphorus
• The only way by which ‘P’ content can be reduced to the minimum possible level is continuous degumming followed by bleaching with heavy dose of neutral earth ranging between 7 to 8% with 0.5 to 1% activated carbon to get better color reduction
• RBO color after deacidification – 25 to 40 units in 1” cell

SEPTEMBER 2005

• A P Solvex / A P Organics could able to achieve ‘Zero’ Phosphorus in the Feed Oil of Deacidification with just 2.5% Bleaching Earth (Without Carbon) by employing Enzymatic Degumming Process!!
• Color after Deacidification – 12 to 14 Units in 1” Cell
• Sri A R Sharma implemented Enzymatic Degumming Process in May 2002 for the First Time in The Country using IICT Technology
SOME INDIAN BRANDS OF RICE BRAN OIL
VALUE ADDED PRODUCTS FROM THE PROCESSING BY-PRODUCTS OF RICE BRAN OIL (IICT’S TECHNOLOGIES)
EXPLOITATION OF BY-PRODUCTS

• Overall capacity utilization of bran production, solvent extraction and oil refining remains low due to large capacities installed

• Only way to balance the economics of bran extraction and oil processing is to exploit the by-products obtained during processing for value addition

• IICT motivated several Industries to go for Value addition to the by-products of the processing industry

• Developed a Number of Products and Processes using the By-products of Rice Bran Oil Processing Industry

• Transferred Many Products to Industries
Integrated Technology Management of Value added By-products from Rice Bran and RBO

- The moment rice bran milled from rice grain, the lipase present in rice bran gets activated and hydrolyzes the oil present in it.

- Need to extract the oil at the earliest possible to arrest the increase in FFA.

- Bran contains large amounts of silica and silica has to be removed for edible applications.

- Bran particles should not enter into oil which may create lot of problems to the quality of oil and by-products.

- Integrated technology management is highly essential for the production of value added products with high quality from rice bran or rice bran oil...
PHYTIC ACID

- Hexa phosphoric acid ester of myoinositol (5% of Rice Bran)

- Anti cancer activity, Inhibitory effect on tumors, prevents the formation of calcium oxalate crystals in the kidney, Dentifrice formulations (mouth wash), Descaling and washing of printing plates
  - Source of Inositol - another biological active product
SUPER CRITICAL CARBON DIOXIDE EXTRACTION

- Attractive Alternative for Traditional Solvent Extraction Process
- Green Process – IICT initiated work at 12 litre capacity Pilot Plant
- 100% Extractability – Good Quality Oil
- Low Phosphorus Content (<20 ppm) in the oil
- Expensive Compared to Traditional Solvent Extraction
- Deoiled cake may be a very attractive source for good quality protein
VALUE ADDITION TO BY-PRODUCTS

- Foodgrade Lecithin Glycolipids
- Oryzanol
- Triacontanol Octacosanol
- Activation of Spent Earth
- Tocopherols Tocotrienols

GUMS

- Modified Lecithins
- Soapstock Acid Oil
- Crude Wax
- Spent Bleaching Earth
- Deodorizer Distillate

- Fatty Acid Methyl Esters
- Bleached Wax
- Fatty Acid Methyl Ester
- Sterols
γ-oryzanol is a naturally occurring component in rice bran and rice germ, consisting of a mixture five major ferulic acid ester of sterols and triterpene alcohols.
Crude rice bran oil contains 1-2% of Oryzanol

Rice bran oil soap-stock, a byproduct in RBO chemical refinery contains 3-4% of Oryzanol

Soap-stock contains gums, waxes, pigments etc. – difficult to handle

CSIR-IICT Developed Technology to isolate oryzanol in enriched form from such complex matrix Employing Solvent Fractionation/Soap Noodles
CSIR-IICT developed Synthetic oryzanol (>95% Purity: a mixture of campesterol, stigmasterol and β-Sitosterol ferulates)- Prepared from Phytosterols Isolated from Soya DOD (Lab Scale)

- Campesterol
- Stigmasterol
- β-Sitosterol

**METABOLIC STUDY**
- Syrian hamsters: Lipid profile (TC, TAG, HDL-C and LDL-C) and Body weights assessed on weekly interval basis.
- Both Natural & Synthetic Oryzanol Exhibited Similar Hypocholesteremic activity

**APPLICATIONS**
- **FOOD** (98% pure)– Soft Capsules, tablets, fortification with vegetable oil and other food products.
- **COSMETICS** (5% in emulsified form) – Soap, Facial Wash, Shampoo, Lotion, lip balm, lipsticks etc.
RICE BRAN WAX

- 3-6% In crude oil
- By-product obtained during dewaxing

CRUDE WAX

- Oil: 20-70%
- Free fatty acids: 0-20%
- Wax: 25-65%
- Resinous matter: 5-12%
RICE BRAN WAX

- **Crude rice bran wax**
  - Organic solvent
  - Resinous Matter
  - Upgraded Wax
    - Bleaching agent
    - Oil
  - BLEACHED WAX

Indian and Japanese Patents

- **Applications:**
  - Paper coating, Polish (floor, furniture, shoe), Fruit & Vegetable coatings, Adhesives, Greases, Electric insulation, Water proofing, Lubricants, Carbon paper, Printing inks, Type writer ribbons, Textile & Leather sizing, Candles, Cosmetics, Chewing gums, Pharmaceuticals

**PHYSICAL AND CHEMICAL CHARACTERISTICS**

<table>
<thead>
<tr>
<th></th>
<th>M.P. (°C)</th>
<th>A.V.</th>
<th>S.V.</th>
<th>I.V.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bleached rice bran wax (IICT-H)</td>
<td>79-80</td>
<td>0-5</td>
<td>75-90</td>
<td>8-15</td>
</tr>
<tr>
<td>Rice bran wax (FDA specifications)</td>
<td>75-80</td>
<td>20 (max)</td>
<td>75-120</td>
<td>20 (max)</td>
</tr>
<tr>
<td>Carnauba wax</td>
<td>83-86</td>
<td>3-8</td>
<td>72-85</td>
<td>8-12</td>
</tr>
</tbody>
</table>

April 12, 2016
HYDROGENATED WAX

Crude Rice Bran Wax

\( \text{H}_2 / \text{Catalyst} \)

Hydrogenated wax

- Applications: Shoe and Floor Polishes, Candles, Additive in Tyre Manufacture, Pharmaceuticals, Cosmetics etc.

- Product Specifications: Melting Point, 78 - 80°C; A.V: Depends on the A.V. of Crude Wax; Iodine Value, 10-15
PROCESS FOR TRIACONTANOL / OCTACOSANOL (POLICOSANOL) FROM RICE BRAN WAX

- Triacontanol is useful for stimulating growth in a wide variety of plants, including agricultural crops such as corn, soybean, wheat, rice and tomatoes.

- Oral preparations containing 0.5-5% of a mixture of higher fatty alcohol formulations were reported to be useful for the treatment of hypercholesterolemia and hyperlipoproteinemia.

- Octacosanol can block the formation of cholesterol in the liver.

- In addition to preventing the formation of cholesterol, octacosanol can also help to clear the blood of "bad" cholesterol that is already present.
## COMPOSITION OF POLYCOSANOL / OCTACOSANOL

<table>
<thead>
<tr>
<th></th>
<th>Sugar Cane Wax</th>
<th>Rice Bran Wax</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Octacosanol</td>
<td>60-70</td>
<td>15-20</td>
</tr>
<tr>
<td>1-Triacontanol</td>
<td>10-15</td>
<td>25-30</td>
</tr>
<tr>
<td>1-Dotriacontanol</td>
<td>5-10</td>
<td>15-20</td>
</tr>
</tbody>
</table>
PHOSPHOLIPID: A NEGLECTED MOLECULE IN INDIA

- India producing about 9.5 lakh tones of rice bran oil
- About 20,000 tons potential for rice bran lecithin
- No industry is producing rice bran lecithin in the country
- Lecithin (not even soya lecithin) Not yet introduced as a NUTRACEUTICAL in the country
- As on today Phospholipid is a neglected molecule in the country
India producing about 9.5 lakh tones of rice bran oil

About 20,000 tons potential for rice bran lecithin

No industry is producing food grade rice bran lecithin in the country

Lecithin (not even soya lecithin) Not yet introduced as NUTRACEUTICAL in the country

As on today Phospholipid is a neglected molecule in the country

Extra-ordinary potential to exploit rice bran lecithin globally as it is superior to soybean lecithin
Composition of lecithin varies depending on the source of crude oil and processing conditions of degumming.
PHOSPHOLIPID CONTENT & COMPOSITION OF SOME SELECTED VEGETABLE OILS

<table>
<thead>
<tr>
<th>Source</th>
<th>% in oil</th>
<th>PC (%)</th>
<th>PE (%)</th>
<th>PI (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soybean</td>
<td>2-4</td>
<td>20-22</td>
<td>21-23</td>
<td>18-20</td>
</tr>
<tr>
<td>Rice Bran</td>
<td>1-2</td>
<td>20-23</td>
<td>18-20</td>
<td>6-7</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>1-2</td>
<td>20-25</td>
<td>15-22</td>
<td>15-18</td>
</tr>
<tr>
<td>Sunflower</td>
<td>0.5-1.0</td>
<td>42-65</td>
<td>30-46</td>
<td>21-37</td>
</tr>
<tr>
<td>Groundnut</td>
<td>0.4-0.5</td>
<td>45-50</td>
<td>14-18</td>
<td>20-22</td>
</tr>
<tr>
<td>Cottonseed</td>
<td>1-1.5</td>
<td>34-36</td>
<td>20-24</td>
<td>20-22</td>
</tr>
<tr>
<td>Palm</td>
<td>0.5-0.7</td>
<td>25.30</td>
<td>30-35</td>
<td>20-25</td>
</tr>
</tbody>
</table>
APPLICATIONS OF LECITHIN

• FOOD

• BAKING

• NUTRACEUTICAL & PHARMACEUTICALS

• COSMETICS

• AQUACULTURE

• ANTIOXIDANT
GLOBAL SCENARIO LECITHIN USAGES

- Commercial lecithin is currently available in more than 40 formulations.

<table>
<thead>
<tr>
<th>Product</th>
<th>Usage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Margarine</td>
<td>25-30%</td>
</tr>
<tr>
<td>Baking/Chocolate &amp; Ice cream</td>
<td>25-30%</td>
</tr>
<tr>
<td>Technical Products</td>
<td>10-20%</td>
</tr>
<tr>
<td>Cosmetics</td>
<td>3-5%</td>
</tr>
<tr>
<td>Pharmaceuticals</td>
<td>10-12%</td>
</tr>
</tbody>
</table>

Major Uses as:

- Emulsifying
- Dispersing
- Wetting
- Penetrating
- Modifying
- Crystal Formation
- Anti-dusting
- Anti-oxidizing agent
MAJOR PHOSPHOLIPIDS PRESENT IN LECITHIN

\[
\begin{align*}
\text{Phosphatidylcholine} & : \\
\text{Phosphatidylethanolamine} & : \\
\text{Phosphatidylinositol} & :
\end{align*}
\]

R₁ and R₂ = C₁₅ = C₁₇
Hydrocarbon chains
WHY RICE BRAN LECITHIN IS UNIQUE?

<table>
<thead>
<tr>
<th>Lecithin</th>
<th>Fatty acid (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>16:0</td>
</tr>
<tr>
<td>Soybean Lecithin</td>
<td>20.5</td>
</tr>
<tr>
<td>Rice bran Lecithin</td>
<td>22.1</td>
</tr>
<tr>
<td>Rice bran Lyso lecithin</td>
<td>18.2</td>
</tr>
</tbody>
</table>

- **Rice bran lecithin** – More Oxidative Stability due to Less PUFA

- **Rich in Nutraceuticals:** Contains Oryzanol, Tocopherol, Tocotrienol, Steryl Esters etc.
CONSTRAINS FOR MAKING GOOD QUALITY RICE BRAN LECITHIN

- Considerable amounts of fines and metallic impurities are present in the crude rice bran oil.

- Gums contaminated with fines if degumming is done without proper filtration of oil.

- Fines effect the purity and functional properties of lecithin.

- Chemical Refining: Only gum conditioning and the gums are separated along with soap stock – No Lecithn!!

- Physical Refining: If Phosphoric acid degumming is practiced, lecithin is contaminated with phosphoric acid; Gums cannot be used as a source of lecithin due to the presence of acidic/basic contaminants.
HOW TO PRODUCE GOOD QUALITY LECITHIN?

- To remove fines and metallic impurities by adopting suitable methodologies in the solvent extraction plant.

- To use proper filtration methods using efficient micronic filters to remove the fines and unwanted impurities from crude oil before degumming as the lecithin produced is used for food applications.

- To adopt water degumming method to remove hydratable phospholipids.

- Water degummed oil to subject to enzymatic degumming to remove remaining hydratable and non-hydratable gums – Consumption of low amounts of enzyme.

JOIN HANDS WITH CSIR-IICT FOR THE PRODUCTION OF HIGH QUALITY FOOD GRADE RICE BRAN LECITHIN.
LECITHIN AND LYSO LECITHIN

CRUDE OIL

Water Degumming

Wet Gums
- Removal of water
  - Lecithin (contains 35-50% oil)

Degummed Oil
- Phospholipase A1
  - Wet Lyso Gums
  - Degummed Oil (with low ‘P’)
    - Removal of water
      - Lyso Lecithin (Contains 25-30% oil)
RICE BRAN LYSOLECITHIN

- By-product of Rice Bran Oil Enzymatic Degumming Process
- 100 TPD Plant produces around 1 to 1.5 Tons of Lysolecithin
- Contains Less Oil (15-25%) – Difficult to Convert into Soap
- Potential Applications – Surfactant, Poultry feed
# PHYSICO-CHEMICAL PROPERTIES OF RICE BRAN AND SOYA LECITHIN

<table>
<thead>
<tr>
<th>Property</th>
<th>Rice Bran</th>
<th>Soya</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone Insoluble (%)</td>
<td>50-65</td>
<td>50-65</td>
</tr>
<tr>
<td>Hexane Insoluble (%)</td>
<td>1-3</td>
<td>0.1-0.4</td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>0.2-0.8</td>
<td>0.2-0.8</td>
</tr>
<tr>
<td>Acid Value (mg KOH/g)</td>
<td>25-35</td>
<td>25-30</td>
</tr>
<tr>
<td>Color (Gardner Scale)</td>
<td>18+</td>
<td>18+</td>
</tr>
<tr>
<td>Peroxide Value (ppm)</td>
<td>15-20</td>
<td>20-25</td>
</tr>
<tr>
<td>Oryzanol and other nutritional components (%)</td>
<td>1.0-2.0</td>
<td>0.5</td>
</tr>
</tbody>
</table>
RB Lyso-lecithin as a Source of Energy in Broiler Chicken Diet

- Collaborative Studies with Project Directorate on Poultry (ICAR)
- Proved as Good Energy Supplement in Broiler Chicken Diet

<table>
<thead>
<tr>
<th>Trt. No</th>
<th>Gum % in diet</th>
<th>Body weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0-21 days</td>
<td>22-35 days</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>2.5</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>2.5</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>6</td>
<td>2.5</td>
<td>5</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>5</td>
<td>2.5</td>
</tr>
<tr>
<td>9</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

British Poultry Science, 52 (2011) 769-774
VALUE-ADDED PRODUCTS FROM LECITHIN

CRUDE LECITHIN

- Solvent fractionation
- PLA₁/PLA₂
- Lyso Lecithin
- Lecithin Enriched with Phospholipids
- Acetylated Lecithins
- Hydroxylation
- Microwave-irradiated
- H₂ / Catalyst
- Hydroxylated Lecithin

Phospholipids with Specific Compositions

Individual Phospholipid eg. PE, PC
GLYCOLIPIDS FROM RICE BRAN AND SOYBEAN OIL GUMS

- Glycolipids – Potent & Biologically Active Molecules – Emerging area of research
- Vegetable Oil based Glycolipids – Information are too sparse
- Polar lipid fraction enriched with glycolipids isolated using chromatographic techniques at laboratory scale
- IICT Developed a Process for the Isolation of Novel Phosphoglyceroglycolipid from Crude Rice Bran Oil Gums [US Patent Number 6,953,849 (2005)]

IICT developed a formulation of gene carrying lipids in which glycolipids of rice bran showed its efficacy in delivering genes selectively to cancer cells.
DEODORIZER DISTILLATES

• Soybean DOD is a good source for fatty acids, tocopherols, tocotrienols and phytosterols [DOD contains triglycerides (35-40%), free fatty acids (40-45%), tocopherols (1-8%) and sterols (2-10%)] – Exploited for Value Addition

• Rice bran oil distillate – Not a very good source for tocopherols, tocotrienols and phytosterols and not yet exploited for value addition
TOCOPHEROLS

alpha Tocopherol (R1, R2, R3 = Methyl)  gamma Tocopherol (R1 = H; R2, R3 =Methyl)
beta Tocopherol (R1, R3 = Methyl, R2 = H)    delta Tocopherol (R1, R2 = H; R3 = Methyl)

TOCOTRIENOLS

alpha Tocotrienol (R1, R2, R3 = Methyl)  gamma Tocotrienol (R1 = H; R2, R3 =Methyl)
beta Tocotrienol (R1, R3 = Methyl, R2 = H)    delta Tocotrienol (R1, R2 = H; R3 = Methyl)
### COMPOSITION OF TOCOPHEROLS AND TOCOTRIENOLS (PPM) OF SELECTED VEGETABLE OILS

<table>
<thead>
<tr>
<th>Oil</th>
<th>Tocopherols (ppm)</th>
<th>Tocotrienols (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>α</td>
<td>β</td>
</tr>
<tr>
<td>Palm</td>
<td>256</td>
<td>-</td>
</tr>
<tr>
<td>Soybean</td>
<td>101</td>
<td>-</td>
</tr>
<tr>
<td>Sunflower</td>
<td>487</td>
<td>-</td>
</tr>
<tr>
<td>Groundnut</td>
<td>130</td>
<td>-</td>
</tr>
<tr>
<td>Corn</td>
<td>112</td>
<td>50</td>
</tr>
<tr>
<td>Safflower</td>
<td>387</td>
<td>-</td>
</tr>
<tr>
<td>Rice bran</td>
<td>104</td>
<td>-</td>
</tr>
<tr>
<td>Wheat germ</td>
<td>1100</td>
<td>440</td>
</tr>
</tbody>
</table>
STEROLS

Cholesterol

β-Sitosterol

Campesterol

Stigmasterol
### Sterol Content (mg / 100 g) and Composition (%) in Selected Oils

<table>
<thead>
<tr>
<th>Oil</th>
<th>Sterols</th>
<th>Brassicasterol</th>
<th>Campesterol</th>
<th>Stigmasterol</th>
<th>β-Sitosterol</th>
<th>Δ5-Avenasterol</th>
<th>Δ7-Stigmasterol</th>
<th>Δ7-Avenasterol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canola / rapeseed</td>
<td>350-840</td>
<td>5-19</td>
<td>22-37</td>
<td>Trace</td>
<td>52-62</td>
<td>2-6</td>
<td>Trace-6</td>
<td>-</td>
</tr>
<tr>
<td>Coconut</td>
<td>60-220</td>
<td>Trace-2</td>
<td>6-9</td>
<td>13-19</td>
<td>58-75</td>
<td>4-14</td>
<td>2-6</td>
<td>-</td>
</tr>
<tr>
<td>Corn</td>
<td>580-1,500</td>
<td>Trace</td>
<td>10-23</td>
<td>Trace-6</td>
<td>61-89</td>
<td>4</td>
<td>1</td>
<td>Trace</td>
</tr>
<tr>
<td>Olive</td>
<td>160-600</td>
<td>1-4</td>
<td>1-2</td>
<td>1-3</td>
<td>80-97</td>
<td>9-12</td>
<td>Trace-4</td>
<td>Trace</td>
</tr>
<tr>
<td>Palm</td>
<td>30-260</td>
<td>Trace</td>
<td>14-22</td>
<td>8-13</td>
<td>81-74</td>
<td>2</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Peanut</td>
<td>190-470</td>
<td>Trace-1</td>
<td>10-19</td>
<td>6-12</td>
<td>64-76</td>
<td>Trace-8</td>
<td>2-3</td>
<td>1</td>
</tr>
<tr>
<td>Ricebran</td>
<td>350-1,800</td>
<td>Traces</td>
<td>14-33</td>
<td>3-15</td>
<td>49-63</td>
<td>5</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Sesame</td>
<td>190-610</td>
<td>-</td>
<td>8-19</td>
<td>6-31</td>
<td>50-62</td>
<td>3-7</td>
<td>1-2</td>
<td>22</td>
</tr>
<tr>
<td>Soybean</td>
<td>150-420</td>
<td>Trace</td>
<td>15-21</td>
<td>10-24</td>
<td>53-72</td>
<td>2-3</td>
<td>2-3</td>
<td>1</td>
</tr>
<tr>
<td>Wheat germ</td>
<td>1,300-2,600</td>
<td>Trace</td>
<td>22</td>
<td>Trace</td>
<td>67</td>
<td>6</td>
<td>3</td>
<td>2</td>
</tr>
</tbody>
</table>
STERYL ESTERS
(Rice Bran Oil Contains ~2-3% Steryl Esters)

![Steryl Esters Structure]

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Wt (%)</th>
<th>Sterol</th>
<th>Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>14:0</td>
<td>0.4</td>
<td>Campesterol</td>
<td>19.8</td>
</tr>
<tr>
<td>16:0</td>
<td>14.3</td>
<td>Stigmasterol</td>
<td>11.2</td>
</tr>
<tr>
<td>18:0</td>
<td>1.3</td>
<td>β-Sitosterol</td>
<td>54.3</td>
</tr>
<tr>
<td>18:1</td>
<td>46.2</td>
<td>Other sterols and Triterpenols</td>
<td>14.7</td>
</tr>
<tr>
<td>18:2</td>
<td>35.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20:0</td>
<td>1.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22:0</td>
<td>Tr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24:0</td>
<td>1.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Cholesterol Lowering Property

April 12, 2016
SQUALENE

COSMETICS
- Skin Protection creams

PHARMACEUTICALS
- Reduction of Cholesterol & Triglyceride levels
- Cancer Therapy
CONCLUSIONS

- India has taken lot of initiatives for the exploitation of value-added products from rice bran and rice bran oil.

- Some products have already been in the market… but long way to go…

- Rice bran oil R&D is full of challenges and opportunities.

- Integrated technology management is essential for the production of high quality rice bran oil and value added by-products from rice bran and rice bran oil.
List of Patents of Centre for Lipid Research, CSIR-IICT, On Refining of Rice Bran Oil and Value added Processing By-products of Rice Bran Oil

<table>
<thead>
<tr>
<th>Category</th>
<th>Description</th>
<th>Patents</th>
</tr>
</thead>
<tbody>
<tr>
<td>RICE BRAN OIL PHYSICAL REFINING</td>
<td>Enzymatic Degumming of Rice Bran Oil using Phospholipase A1</td>
<td>India, US, Japan, China, Indonesia, Vietnam</td>
</tr>
<tr>
<td>SOAPSTOCK / ACID OIL</td>
<td>Isolation of Gamma oryzanol from Rice Bran Oil Soap-stock</td>
<td>US, Japan, India, Indonesia</td>
</tr>
<tr>
<td>RICE BRAN WAX</td>
<td>Upgradation &amp; Bleaching of Crude Rice Bran Wax</td>
<td>India, Japan</td>
</tr>
<tr>
<td>RICE BRAN WAX</td>
<td>1-Triacontanol from Defatted Rice Bran Wax</td>
<td>India</td>
</tr>
<tr>
<td>SYNTHETIC ORYZANOL</td>
<td>Preparation of Phytosteryl Ferulate (Equivalent to Natural Oryzanol)</td>
<td>Japan, India, China, US</td>
</tr>
<tr>
<td>LECITHIN</td>
<td>Acetylated Lecithin</td>
<td>US, India</td>
</tr>
<tr>
<td>LECITHIN</td>
<td>Hydroxylated Lecithin</td>
<td>US, India</td>
</tr>
<tr>
<td>Category</td>
<td>Description</td>
<td>Patents/Registration Numbers</td>
</tr>
<tr>
<td>---------------------------------------</td>
<td>------------------------------------------------------------------------------</td>
<td>-------------------------------------------------------------------</td>
</tr>
</tbody>
</table>
US Pat: 7494676 (2009)  
Jap. Pat: Application pending  
China Pat: ZL03826393.9-356076  
Indonesia Pat: IDP0033123  
Vietnam Pat: 1-0008605 |
| **SOAPSTOCK / ACID OIL**              | Isolation of Gamma oryzanol from Rice Bran Oil Soap-stock                       | US Pat: 6,410,762 (2002)  
Ind. Pat: 231670 (2009) |
| **RIC BRAN WAX**                      | Upgradation & Bleaching of Crude Rice Bran Wax                                 | Ind. Pat: 228674 (2009)  
|                                       | 1-Triacontanol from Defatted Rice Bran Wax                                     | Ind. Pat: 184307 (2001) |
| **SYNTHETIC ORYZANOL**                | Preparation of Phytosteryl Ferulate (Equivalent to Natural Oryzanol)          | Japan Pat: 5730789 (2015)  
Ind. Pat: Application pending (2009)  
China Pat: Application pending (2011)  
US Pat: Application pending (2013) |
| **LECITHIN**                          | Acetylated Lecithin                                                           | US Pat. No.: 6,403,344 (2002)  
Ind. Pat.: 227530 (2009) |
Ind. Pat.: 199806 (2006) |
| **GLYCOLIPID**                        | Isolation of Glycolipids from Rice Bran Oil Gums                              | Indian Patent 230570 (2009)  
Gums GGG |
|                                       | Specific Rice Bran Glycolipid and Phospholipids associated with Cationic Lipid Formulations | Indian Pat: Application pending (2012) |

List of Patents of Centre for Lipid Research, CSIR-IICT, Hyderabad, India
On Refining of Rice Bran Oil and Value added Products from Processing By-products of Rice Bran Oil

April 12, 2016
THANK YOU...