VALUE ADDED BYPRODUCTS FROM OILSEED CAKES

Dr. R.B.N. PRASAD
Deputy Director & Head
Lipid Science & Technology Division
Indian Institute of Chemical Technology
Hyderabad – 500 007

February 7, 2008
### GLOBAL MAJOR EDIBLE OILSEED / MEAL SCENARIO (2006-07)

<table>
<thead>
<tr>
<th></th>
<th>Oilseed (million MT)</th>
<th>Meal (million MT)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Soyabean</strong></td>
<td>220.35</td>
<td>161.45</td>
</tr>
<tr>
<td><strong>Rapeseed</strong></td>
<td>48.29</td>
<td>27.59</td>
</tr>
<tr>
<td><strong>Cottonseed</strong></td>
<td>44.99</td>
<td>15.39</td>
</tr>
<tr>
<td><strong>Groundnut</strong></td>
<td>32.51</td>
<td>5.73</td>
</tr>
<tr>
<td><strong>Sunflower</strong></td>
<td>27.29</td>
<td>10.85</td>
</tr>
<tr>
<td><strong>Palm kernel</strong></td>
<td>10.95</td>
<td>5.69</td>
</tr>
<tr>
<td><strong>Copra</strong></td>
<td>5.37</td>
<td>1.71</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td>389.75</td>
<td>228.1</td>
</tr>
</tbody>
</table>

**SOURCE:** USDA, January 2008
### GLOBAL VEGETABLE OIL (MAJOR) SCENARIO

<table>
<thead>
<tr>
<th>OIL</th>
<th>PRODUCTION Million MT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palm</td>
<td>40.20</td>
</tr>
<tr>
<td>Soybean</td>
<td>38.04</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>18.27</td>
</tr>
<tr>
<td>Sunflower</td>
<td>10.05</td>
</tr>
<tr>
<td>Cottonseed</td>
<td>4.92</td>
</tr>
<tr>
<td>Peanut</td>
<td>4.86</td>
</tr>
<tr>
<td>Palm Kernel</td>
<td>4.79</td>
</tr>
<tr>
<td>Coconut</td>
<td>3.32</td>
</tr>
<tr>
<td>Olive</td>
<td>3.02</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>127.47</strong></td>
</tr>
</tbody>
</table>

**Source:** USDA, Jan. 2008
## DISTRIBUTION OF VEGETABLE OIL PRODUCTION IN INDIA

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Rape / Mustard</td>
<td>1.09</td>
<td>2.31</td>
<td>2.13</td>
<td>2.27</td>
</tr>
<tr>
<td>Soya</td>
<td>0.63</td>
<td>1.04</td>
<td>0.87</td>
<td>1.07</td>
</tr>
<tr>
<td>Groundnut</td>
<td>0.73</td>
<td>1.32</td>
<td>1.00</td>
<td>0.99</td>
</tr>
<tr>
<td>Rice Bran</td>
<td>0.60</td>
<td>0.65</td>
<td>0.68</td>
<td>0.73</td>
</tr>
<tr>
<td>Cottonseed</td>
<td>0.39</td>
<td>0.48</td>
<td>0.72</td>
<td>0.77</td>
</tr>
<tr>
<td>Sunflower</td>
<td>0.37</td>
<td>0.41</td>
<td>0.55</td>
<td>0.56</td>
</tr>
<tr>
<td>Coconut</td>
<td>0.42</td>
<td>0.42</td>
<td>0.42</td>
<td>0.42</td>
</tr>
<tr>
<td>Castor</td>
<td>0.19</td>
<td>0.28</td>
<td>0.34</td>
<td>0.38</td>
</tr>
<tr>
<td>Sesame</td>
<td>0.17</td>
<td>0.19</td>
<td>0.19</td>
<td>0.13</td>
</tr>
<tr>
<td>Niger</td>
<td>0.02</td>
<td>0.02</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>Safflower</td>
<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>Linseed</td>
<td>0.09</td>
<td>0.10</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>Palm oil</td>
<td>0.05</td>
<td>0.05</td>
<td>0.04</td>
<td>0.05</td>
</tr>
<tr>
<td>Oils from expelled cakes</td>
<td>0.26</td>
<td>0.37</td>
<td>0.38</td>
<td>0.41</td>
</tr>
<tr>
<td>Minor oilseeds</td>
<td>0.05</td>
<td>0.05</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>TOTAL</td>
<td>5.12</td>
<td>7.78</td>
<td>7.59</td>
<td>8.03</td>
</tr>
</tbody>
</table>
## INDIAN VEGETABLE OIL PRODUCTION AND IMPORT STATUS

<table>
<thead>
<tr>
<th>Year</th>
<th>Domestic Edible Oil Production (million tones)</th>
<th>Import of Edible Oils (million tones)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2006-07</td>
<td>7.72</td>
<td>4.71</td>
</tr>
<tr>
<td>2005-06</td>
<td>8.03</td>
<td>4.42</td>
</tr>
<tr>
<td>2004-05</td>
<td>7.59</td>
<td>5.04</td>
</tr>
<tr>
<td>2003-04</td>
<td>7.78</td>
<td>4.28</td>
</tr>
<tr>
<td>2002-03</td>
<td>5.12</td>
<td>5.38</td>
</tr>
<tr>
<td>2001-02</td>
<td>6.67</td>
<td>4.42</td>
</tr>
<tr>
<td>2000-01</td>
<td>5.81</td>
<td>4.83</td>
</tr>
</tbody>
</table>
PRESENT INDIAN SCENARIO OF OILSEED CAKES

- Producing about 34 million metric tones of oilseeds
- Annual Production of Oil is about 7.7 million metric tones
- Annual Production of Oilseed Cakes is about 18 million metric tones and Exporting about 5.2 million metric tones of Oilseed Cakes
- Quantity of Non-edible Oilseed Cakes – Presently Insignificant
## PRESENT INDIAN SCENARIO OF TREE-BORNE OILS

<table>
<thead>
<tr>
<th>SEED</th>
<th>POTENTIAL (in lakh tones)</th>
<th>PRESENT COLLECTION* (in lakhs tones)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAL</td>
<td>15.0</td>
<td>2.0</td>
</tr>
<tr>
<td>NEEM</td>
<td>5.0</td>
<td>1.0</td>
</tr>
<tr>
<td>MAHUA</td>
<td>5.0</td>
<td>1.0</td>
</tr>
<tr>
<td>MANGO</td>
<td>4.0</td>
<td>0.25</td>
</tr>
<tr>
<td>KARANJA</td>
<td>2.0</td>
<td>0.30</td>
</tr>
<tr>
<td>KUSUM</td>
<td>1.0</td>
<td>0.10</td>
</tr>
<tr>
<td>OTHER OILSEEDS</td>
<td>3.0</td>
<td>0.35</td>
</tr>
<tr>
<td>TOTAL</td>
<td>35.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Present production of oil: 1.25 lakh tones
FEEDSTOCK FOR INDIAN BIODIESEL

• Difficult to Divert Edible Oils

• Indian Government identified Jatropha and Karanja Plants for exploitation to Produce the Respective Seeds for Biodiesel Production

• May take Another Couple of Years to talk about the Quantities of these Seeds Available for Biodiesel Production

• 2 tonnes of Oilseed Cake will be Produced for Every tonne of Biodiesel Produced

• Huge Quantities of Oilseed Cakes will be available if both Jatropha and Karanja Plantations Succeed…

• We should Look for Optimum Utilization of Oilseed Cakes
JATROPHA PLANT WITH SEEDS

February 7, 2008
KARANJA FLOWERS SEEDS

[Image of karanja flowers on the left and seeds on the right]

February 7, 2008
HOW TO MAKE BIODIESEL CHEAPER?

- Efficient Process for Biodiesel Production
- Alternate Applications for Oilseed Cake (rich in Starch and Protein)
- Newer Application for Glycerol
- Phytochemicals & Nutraceuticals of Oil & Other Parts of the Tree (Leaves, Flowers, Bark etc.)

THIS PRESENTATION RESTRICTS TO OILSEED CAKES

- Purpose of this Presentation is to Project Potential Applications for the Optimum Utilization of Oilseed Cakes
- Difficult to Comment on any Pathways at this Stage...
- Lot of Exploratory work has to be carried out to Prove these Concepts

February 3, 2007
HOW DO WE PRODUCE CAKES?

- High Oil-bearing Seeds - Expelling

- Expelled Oilseed Cake contains 8-12% Oil depending on the Efficiency of Expeller

- Low Oil-bearing Seeds / Expelled Cake – Solvent Extraction

- Hexane as Extracting Solvent ‘Deoiled Meal’ contains 1% Oil
MAJOR APPLICATIONS OF OILSEED CAKES-
PRESENT STATUS

➢ Edible Oilseed Cakes
  • Source of Protein in Case of Clean Cakes like Groundnut, Soybean, etc.
  • Animal Feed Formulations

➢ Non-edible Oilseed Cakes
  • Manure
  • To Explore for Variety of Applications
JATROPHA / KARANJA CAKES

• Huge Quantities of Jatropha / Karanja Cakes if these Plantations Succeed...

• Every Tonne of Biodiesel Results in about 2 tonnes of Oilseed Cake

• Oilseed Cakes – Real Asset for the Nation as they are Biodegradable

• Potential Feedstock – To Make Biodiesel Industry More Attractive

• To Develop variety of Products from these Cakes
## COMPOSITION OF JATROPHA AND KARANJA OILSEED CAKES

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Jatropha</th>
<th>Karanja</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen/Protein (wt %)</td>
<td>4-6/25-40</td>
<td>4-7/25-40</td>
</tr>
<tr>
<td>Carbohydrate (wt %)</td>
<td>15-20</td>
<td>15-20</td>
</tr>
<tr>
<td>Fibre (wt %)</td>
<td>15-20</td>
<td>15-20</td>
</tr>
<tr>
<td>Ash (wt %)</td>
<td>3-5</td>
<td>3-5</td>
</tr>
<tr>
<td>Phosphorus (wt %)</td>
<td>1.5-3</td>
<td>1-2</td>
</tr>
<tr>
<td>Potassium (wt %)</td>
<td>1-2</td>
<td>0.5-1.5</td>
</tr>
<tr>
<td>Calcium (wt %)</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Magnesium (wt %)</td>
<td>&lt;1</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Zinc, Copper, Magnesium, Boron (ppm)</td>
<td>&lt;100</td>
<td>&lt;100</td>
</tr>
<tr>
<td>Sulphur (ppm)</td>
<td>&lt;3000</td>
<td>&lt;4000</td>
</tr>
</tbody>
</table>

* Compositions may not be authentic as all the results are isolated / very old reports
OILSEED CAKE (BIOMASS)

- Oil
  - Deoiled Cake
    - Protein
      - Protein Hydrolysate
      - Surfactants
    - Carbohydrates
      - Bioactive Constituents
      - Composite Materials, Surfactants
    - Bioactive Constituents
      - Fermentation
        - Bioethanol
      - Biogas (Methane-rich)
        - Syngas
          - Fuel, Chemicals
    - Carbon Source for Microbial Lipids / Enzymes

- Fertilizer
  - Surfactants
  - Lubricants, Surfactants, Polymers
BIO-ACTIVE CONSTITUENTS OF KARANJA

- Uses of Karanja Plant in Ayurveda – Well Documented
- To Look More Closely at Different Parts of Plant – Stem, Bark, Seed, Flower, Leaf, etc.
- Seed / Oil – Potential Source for Biopesticides & Other Important Chemicals
  - Karanja, Pongamol, Karanjin, Pongamol, Pongapin, Kanjone, Pongaglabrone, Isolonchocarpin, Pongachalkone Glabone, Pongacoumestan, Karanchromene, etc.
- Most of the Components Distribute Both in Oil & Cake
- Only Polar Solvents Extract Completely
- No Report on Karanja Cake
- IICT is very Actively Working on the Isolation of Different Bioactive Constituents from Cake
BASIC MOIETIES REPORTED IN DIFFERENT PARTS OF KARANJA TREE

- **Flavonoids**
- **Chromenochalkones**
- **Furanoflavonoids**
- **Furanodiketones**
- **Chromenoflavones**
- **Rotenoids**

February 7, 2008
REPORTED ACTIVITIES FOR SELECTED COMPOUNDS...

Pongaglabol Methylether
Antifungal agent

Synergist to insectide

Pongamol
Sedative and Depressant and
Quinone reductase activity
Synergist to insectide

Pongapinone A
Interleukin I production and/or secretion inhibitors
useful for the treatment of anti immuno
and inflammatory diseases

Chalcone
Quinone reductase inducing activity
IICT’s Integrated Project for Development of Processes/Technologies for Value-added Products from Karanja Oil and Cake

Sponsored by DST (2006-08) Rs. 1.88 Crores

KARANJA SEEDS

Bioactive Constituents

Cake

Protein, Starch, Oil

Fatty Acid Alkyl Esters

Lubricant Base Oils & Additives

Crude Glycerol

Minor Constituents

Bioactive Constituents

Varieties of Products like Surfactants, Fertilizer etc.

Lubricant Base Oils & Additives

Different Grades of Glycerol

Variety of Value added Products

KARANJA BIOREFINERY

February 7, 2008
BIOACTIVE CONSTITUENTS OF JATROPHA

• All Parts of the Plant – Traditional Medicine & Veterinary Applications

• Seeds contain Several Toxic Constituents like Phytates, Saponins and Trypsine Inhibitor, Curcanoleic acid, Curcin, Phorbol Esters, Lectin and Protease Inhibitors

• During Extraction – Distribute in Cake and Oil

• CURCIN – Toxic Protein - Inhibits denovo Protein Synthesis

• Phorbol Esters (Mixed Esters of Tetracyclic Diterpene-Phorbol) - Irritation, Purgative, Co-carcinogen

• Extracts of Seeds & Leaves – Molluscicidal, Insecticidal and Fungicidal Activity

• Antinutritional Components in the kernels & Press Cake- Jatropha Nut Poisoning in Humans – Accidental Consumption - Giddiness, Vomiting, Diarhoea; Extreme Conditions – Death
PHORBOL AND ITS ESTERS PRESENT IN JATROPHA CAKE

Tigliane

12-Deoxy-16-hydroxyphorbol-4'-[12',14'-butadienyl]-6'-[16',18',20'-nonatrienyl]-bicyclo[3.1.0]hexane-(13-O)-2'-[carboxylate]-(16-O)-3'-[8'-butenoic-10']ate (DHPB)
OILSEED CAKES AS MANURE

- Rich in Protein, Carbohydrate & Fibre
- Unpalatable & Toxic to Cattle even at Lower Levels
- Good NPK Ratio
  - Usefull Organic Manure for Sugarcane, Coffee, Oranges, Paddy and Several Other Crops (Jatropha)
  - One Tonne of Jatropha Cake = 200 kg Mineral Fertilizer having NPK Ratio of 12:24:12 – Several Advantages over Synthetic Fertilizers or Pesticides can Offer
- Controlled Release of Urea during the Infield Studies to Save the Urea effectively using Jatropha Cake
- Oilseed cakes provide slow and steady Nourishment, Stimulation, Protection from Soil Nematodes and Insects
- Retard Nitrification of the soil/urea and thereby increase N uptake by the plants
- Several Reports on Karanja Cake as an Effective Manure and Pesticide

February 7, 2008
# NPK Ratio in Oilseed Cakes

<table>
<thead>
<tr>
<th>Cake</th>
<th>Nitrogen</th>
<th>Phosphorus</th>
<th>Potassium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Karanja</td>
<td>4.0</td>
<td>0.9</td>
<td>1.3</td>
</tr>
<tr>
<td>Neem</td>
<td>5.2</td>
<td>1.1</td>
<td>1.5</td>
</tr>
<tr>
<td>Castor</td>
<td>4.3</td>
<td>1.9</td>
<td>1.4</td>
</tr>
<tr>
<td>Mahua</td>
<td>2.5</td>
<td>0.8</td>
<td>1.9</td>
</tr>
<tr>
<td>Mustard</td>
<td>5.4</td>
<td>1.9</td>
<td>1.2</td>
</tr>
<tr>
<td>Cottonseed</td>
<td>6.6</td>
<td>3.0</td>
<td>1.6</td>
</tr>
<tr>
<td>Peanut</td>
<td>7.4</td>
<td>1.5</td>
<td>1.3</td>
</tr>
<tr>
<td>Til</td>
<td>6.2</td>
<td>2.1</td>
<td>1.3</td>
</tr>
<tr>
<td>Safflower</td>
<td>7.8</td>
<td>2.2</td>
<td>1.9</td>
</tr>
</tbody>
</table>

J Sci Club, HBTI, 1952
Studies Carried out at IICT using Karanja Cake as Fertilizer in Tomato Plants

Control Plant and Plant having Expelled Cake as Fertilizer after one Month

February 7, 2008
Pest Attack in Control Plant

Healthy leaves and Fruits in Karanja Cake Treated Plant

February 7, 2008
Pest Infestation in Control Plant
... Karanja Cake as Fertilizer
PROTEIN-BASED SURFACTANTS

- Only as Manure eventhough Cakes contain 25-40% Protein
- Environmental Concerns & Statutory Regulations force to replace petrochemical-based Surfactants Partly with those based on Naturally occurring Renewable Sources
- Growing Interest in the Synthesis & Formulation Applications of Surfactants from Natural Biopolymers
- Biodegradable & Biocompatible
- Very Limited Information in this Area
- Oilseed Cakes are Extra-ordinary Feed Stock for the Preparation of Protein-based Surfactants
PROTEIN-BASED SURFACANTs

Protein Alkaline Hydrolysis:

ALKANOLAMIDES OF SHORTER PEPTIDES

N-ACYL AMINO ACIDS / PEPTIDES
CARBOHYDRATE-BASED PRODUCTS

• Oilseed Cakes are good source for Carbohydrates

• Mono-, Oligo- and Polysaccharides Present in Carbohydrates may be exploited for the Preparation of Several Classes of Compounds like Surfactants, Lubricants, Composite Materials, Adhesives, Plastics etc.,

• Starch is an Abundant, Cheap, Versatile Biopolymer being used as Bioplastic

• Starch has a number of Unfavorable Properties – Can be Addressed by Chemical Modification, Blending and Thermal and Physical Treatments
VALUE ADDITION TO CARBOHYDRATES

St-OH Starch

Hydroxypropyl Derivative
Ethyl Derivative
Hydroxyethyl Derivative

Dialdehyde Oxidized product (dicarboxylic acid)
Phosphate diester
Xanthate

Esterification
Etherification
Cross-linking
Polyacrylonitrile copolymer

Carboxymethyl Product
Acetate
Phosphate
Cross-linked citrate

Oxidized Product
Dialdehyde (Oxidized product (dicarboxylic acid))
Cyanamide starch

February 7, 2008
BIOETHANOL FROM CAKES

• Currently, Ethanol is made from Corn Grain Starch / Sugarcane Molasses

• Newer Feedstocks Required to Meet the Future Demands

• Oilseed Cakes / Hulls – Potential Feedstock as they are Made up of Cellulosic Materials

• Efficiency of the Pre-treatment and Fermentation Process has to be Optimized based on the Yield of Free Sugars and Ethanol
CARBON SOURCE FOR MICOBIAL GROWTH

• For the Production of Microbial Lipids / Non-lipids or Enzymes – Carbon Source Required

• Microbial Degradation of Solid Agricultural Waste (Carbon Source) is a Natural Process

• Known / Specific Microbial Strains may Produce Desired Products / Enzymes in Presence of a Carbon Source

• Oilseed Cakes can be Directly Used as Carbon and Energy Source for Microbial Growth / Production of Desired Products for Many Potential Applications

• To Produce Extra Cellular Enzymes such as Proteases, Lipases, Xylanase and Cellulase by Solid-state Fermentation [Bioresource Tech. Vol. 99 (2008), 1729-35]
BIOMETHANATION OF OILSEED CAKES

• Several Biogas Plants not in Use for Want of Feedstock

• Oilseed Cakes – Excellent Feedstock

• 0.25 to 0.35 cubic meters of Biogas can be Produced from 1 kg of Jatropha Cake with ≈ 70-80% Methane Content [Satish Lele (www.Svlele.com)]

• Area of Plot, 300m² ; Manpower, Two unskilled; Power Supply, 1 kw; Cost, Rs. 5 Lakhs

• Methane gas – For Generating Electricity – To Promote On-farm Energy Self-sufficiency

• Left out Slurry from the Bioreactor – Serves as Organic Manure

February 7, 2008
BIOMASS

- Biomass – Most Important Energy Source for Humans Since the Discovery of Fire
- Agricultural Waste – Gaining Interest as Biomass
- Inexpensive and Abundant Resource
- Renewable Energy Source for Electricity, Gaseous and Liquid Biofuels, Hydrogen etc., and also for Variety of Chemicals
- Energy Content Less in Biomass compared to Petroleum Products – Several Advantages to Outplay Fossil Fuel
- Provides Biofuel in the form of solids, liquids or gases
- Three Main Pathways of Conversion
  - Thermo-chemical (Carbonization, Gasification, Pyrolysis)
  - Physical-chemical Conversion (Pressing, Extraction, Transesterification)
  - Biochemical Conversion (Alcoholic and Aerobic Fermentation; Composting)
GASIFICATION OF OILSEED CAKES

- Since Ancient Times Direct Combustion of Biomass for Cooking & Heating
- Several Difficulties – Transportation, Storage and Usage due to its High Moisture Content & Low Density
- Seed Cake Biomass can be Efficiently Converted to Fuel Products / Feedstocks by Thermal Conversion Methods like Pyrolysis, Gasification and Carbonization
- Biomass to Synthetic Gas (H₂, CO and CO₂) and to Biofuels / Several Chemicals
- Syngas Production Conditions (H₂, CO Ratio) have to be Fine Tuned for Efficient Conversions
- To remove Pollutants from the syngas
- Complex and High Capital Expenditure Technology
- Solid Char after Pyrolysis can be Used as Fuel Either as Briquette, Activated Carbon or as Char Oil or Charcoal – Water Slurries
BIOREFINERY OF OILSEED CAKES – POTENTIAL PATHWAYS

OILSEED CAKE (BIOMASS)

- Oil
  - Deoiled Cake
    - Fertilizer
    - Protein
    - Protein Hydrolysate
      - Surfactants
    - Carbohydrates
      - Lubricants, Surfactants, Polymers
    - Bioactive Constituents
    - Composite Materials, Surfactants
      - Fermentation
        - Bioethanol
      - Biogas (Methane-rich)
      - Syngas
        - Fuel, Chemicals
        - Carbon Source for Microbial Lipids / Enzymes
Thank you...