A whole crop biorefinery process based on cereals

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Few things are certain but...

- One day finite resources will be exhausted
The need for renewable replacements is therefore ABSOLUTE.
Despite increasing costs of production and processing, renewable resources will eventually be cheaper than finite resources.
Environmental impact

Atmospheric CO₂
Environmental impact

Finite Renewable
Raw Materials, Agriculture and Chemistry

“Petrochemical processes have provided low cost production routes for fuels, plastics and chemicals for well over 50 years but the escalating impact on the environment and the inevitable future depletion of fossil feedstocks make it essential that benign, sustainable, alternatives be developed commercially in the very near future.”

RSC, 2003
Sustainable raw materials

- Photosynthetic biomass
  - Starchy crops
  - Sugar crops
  - Oil seeds
  - Lignocellulosics
- Water
- Atmospheric gases (e.g. CO$_2$, methane)
New products or new processes?

- Sustainable Raw Material → New Process → Conventional Product Replacement
- Sustainable Raw Material → Conventional Process → Alternative Products
- Sustainable Raw Material → New Process → Alternative Products
Bioprocessing

- Bioprocessing will lead to more *natural* and cost-effective means of converting natural feedstocks into *platform* chemicals.

- Platform chemicals that can be produced in large quantities by microorganisms include acetic acid, ethanol, glycerol, succinic acid, pyruvic acid, 2,3-butanediol and 1,3-propanediol.

- They are different from current petrochemical building blocks (e.g. ethylene, propylene and butadiene) and therefore require significant technological research.

- Benefit will come from collaboration of chemists, biotechnologists and bio-engineers.
Key areas being explored

- Identification of the full range of platform chemicals obtainable from agricultural raw materials.
  - bio-related research directed downstream from the raw material
  - retro-synthetic chemical analysis, starting from the other end.
- Development of new synthetic protocols and methodologies, to produce both traditional and new products
- Development of fermentation and associated biotechnology, including tools such as metabolic engineering
- Research into process technology for appropriate scales of production
- Life cycle analysis
Whole crop biorefinery from cereals - the raw material:

- For every tonne of grain most cereals produce approximately one tonne of straw and other residues
- Ligno-cellulosic material is much more difficult to process than starchy material
- Straw has a bulk density 1/15th of that of grain
- Biorefinery processing of straw is currently not feasible
- Like petroleum refining we should start simple (glucose cf. gasoline; lignocellulose cf. bitumen)
The raw material:
World annual cereal grain production
Current usage of cereals
Potential for non-food use

- Developing nations waste large amounts of cereal grain through poor post-harvest techniques
- Developed nations produce and stockpile surplus cereal grain
- Grain processing for human consumption leaves approximately 15% of the grain as waste product
- and...yields are still increasing
Cereal productivity increases (world)
Most types of chemical produced from petroleum can be produced from cereals

Many of these can be produced through bioprocessing (fermentation) of the grain.

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Ethanol</th>
<th>Bio-deisel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>Butanol</td>
<td>Furfural</td>
</tr>
<tr>
<td>Organic acids</td>
<td>Sugars</td>
<td></td>
</tr>
<tr>
<td>PHB</td>
<td>PLLA</td>
<td>Cellulose</td>
</tr>
<tr>
<td>Wide range</td>
<td>Corn oil</td>
<td>Germ oil</td>
</tr>
</tbody>
</table>
CHEMICALS FROM GLUCOSE:

GLUCOSE → SCPS → 2,3-BUTANEDIOL → BUTANEDIOL ACETATE → BUTADIENE

GLUCOSE → LACTIC ACID → ACRYLATE RESINS

GLUCOSE → ACETONE → BISPHENOL A → POLYCARBONATE RESINS

GLUCOSE → ACETONE → METHYL METHACRYLATE

GLUCOSE → ACETONE → METHYL iso-BUTYL KETONE

GLUCOSE → ACETONE → METHYL ETHYL KETONE

GLUCOSE → ACETONE → METHYL VINYL KETONE

GLUCOSE → ACETONE → POLYBUTADIENE

GLUCOSE → ACETONE → DIBUTYL PHTHHALATE → PVC RESINS

GLUCOSE → ACETIC ACID → DIMETHYL TEREPTHALATE

GLUCOSE → ACETIC ACID → ACETIC RESINS

GLUCOSE → ETHANOL → ETHYLENE

GLUCOSE → ETHANOL → ETHYLAMINES

GLUCOSE → ETHANOL → BUTADIENE

GLUCOSE → ETHANOL → POLYETHYLENE

GLUCOSE → ETHANOL → VINYL ACETATE

GLUCOSE → ETHANOL → STYRENE

GLUCOSE → ETHANOL → ACETALDEHYDE

GLUCOSE → ETHANOL → ETHYLENE GLYCOL

GLUCOSE → SORBITOL → DRUGS

GLUCOSE → SORBITOL → POLYURETHANES

GLUCOSE → SORBITOL → SURFACTANTS

GLUCOSE → HYDROXYMETHYL FURFURAL → POLYURETHANES

GLUCOSE → HYDROXYMETHYL FURFURAL → SURFACTANTS

GLUCOSE → HYDROXYMETHYL FURFURAL → TEREPTHHALIC ACID
Nutrient requirement for a fermentation medium

- Carbon source
- Nitrogen source
- Minerals:
  - Macronutrients: P, S, Mg, Fe, K, Ca;
  - Micronutrients: Mo, Zn, Mn, Co, Ni, Cu, I, Br, V
- Growth factors (vitamins, amino acids, purines, pyrimidines)
Cereal grains contain all the nutrients for a generic fermentation medium

<table>
<thead>
<tr>
<th>Macronutrients (µg g(^{-1}), db)</th>
<th>Micronutrients (µg g(^{-1}), db)</th>
<th>Vitamins (µg g(^{-1}), db)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starch 620000 - 750000</td>
<td>Na 30</td>
<td>B1 5.4</td>
</tr>
<tr>
<td>N 2006</td>
<td>Cu 4.5</td>
<td>B2 1.1</td>
</tr>
<tr>
<td>P 3400</td>
<td>Cd 0.1</td>
<td>B3 110</td>
</tr>
<tr>
<td>S 912 - 1995</td>
<td>Cr 0.4</td>
<td>B6 3.3</td>
</tr>
<tr>
<td>Mg 1589</td>
<td>Pb 1</td>
<td>E 54</td>
</tr>
<tr>
<td>Fe 37</td>
<td>Ni 0.3</td>
<td></td>
</tr>
<tr>
<td>K 4180</td>
<td>Mn 35</td>
<td></td>
</tr>
<tr>
<td>Ca 390</td>
<td>Sn 7.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zn 5</td>
<td></td>
</tr>
</tbody>
</table>

Macronutrients: Starch, N, P, S, Mg, Fe, K, Ca

Micronutrients: Na, Cu, Cd, Cr, Pb, Ni, Mn, Sn, Zn

Vitamins: B1, B2, B3, B6, E
Cereals as a universal fermentation feed stock

- Unfortunately, the carbon source is mostly in the form of starch
  - most fermentations require simpler sugars
  - some pre-processing is therefore required
- Likewise most of the Nitrogen is not directly accessible
Conventional process for converting cereals to fermentation products

Grain
Conventional process for converting cereals to fermentation products

- Grain
- Starch processor
- Gluten
- Feed
Conventional process for converting cereals to fermentation products

Grain → Starch processor → Enzyme producers → Nutrients

Grain → Gluten

Grain → Feed
Conventional process for converting cereals to fermentation products

- **Grain** → **Starch processor** → **Enzyme producers** → **Nutrients**
  - Amylase: Starch → Hydrolysate (glucose rich)
  - Gluten → Feed
Conventional process for converting cereals to fermentation products

- Grain
- Starch processor
  - Enzyme producers
  - Amylases
  - Hydrolysate (glucose rich)
- Nutrients
- Fermentation industry
  - Corn steep liquor (nitrogen rich)
- Products
  - Feed
  - Gluten
  - Products
Conventional process for converting cereals to fermentation products

**Grain** → **Starch processor** → **Enzyme producers** → **Nutrients**

- Amylases
- Hydrolysate (glucose rich)
- Corn steep liquor (nitrogen rich)

**Fermentation industry** → **Products**

- Feed
- Gluten
Proposed process for converting cereals to fermentation products

Grain → Starch processor → Enzyme producers → Nutrients

- Amylases
- Hydrolysate (glucose rich)
- Corn steep liquor (nitrogen rich)

Grain → Gluten → Feed → Fermentation industry → Products

- Nutrients
Proposed process for converting cereals to fermentation products

Grain → Bioprocessing to glucose rich and nitrogen rich streams → Fermentation industry → Products
Bioprocessing of cereals

- Use an organism with amylolytic activity to hydrolyse starch to glucose (*Aspergillus awamori*)
- Filter off cells and allow to autolyse (to release free amino nitrogen (FAN))
- Retain ALL other nutrients in broth
- Use broth to enhance glucose production...
Full proposed process for bioconversion of whole grain
Full proposed process for bioconversion of whole grain

Whole wheat flour 
Dough mixing
Water

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Full proposed process for bioconversion of whole grain

Whole wheat flour → Dough mixing → Washing → Drying → Gluten
Full proposed process for bioconversion of whole grain

- Whole wheat flour
- Dough mixing
- Washing
- Centrifugation
- Supernatant
- Water
- Drying
- Gluten
Full proposed process for bioconversion of whole grain
Full proposed process for bioconversion of whole grain

1. Whole wheat flour
2. Water
3. Dough mixing
4. Washing
5. Centrifugation
6. Drying
7. Continuous bioconversion
8. Filtration
9. Filtrate
10. Solids
11. Gluten
12. Supernatant
Full proposed process for bioconversion of whole grain

- Whole wheat flour
- Water
- Dough mixing
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- Glucose enhancement (hydrolysis)
- Supernatant
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- Filtrate
- C-rich Hydolysate
- Solids
Full proposed process for bioconversion of whole grain

Whole wheat flour → Dough mixing → Washing → Centrifugation → Glucose enhancement (hydrolysis) → C-rich Hydolysate

Water → Washing → Supernatant

Drying → Continuous bioconversion → Filtration

Gluten → Filtration

Continuous bioconversion → Filtration

Filtrate → Nitrogen enhancement (autolysis)

Solids
Full proposed process for bioconversion of whole grain:

1. Whole wheat flour
2. Water
3. Dough mixing
4. Washing
5. Centrifugation
6. Glucose enhancement (hydrolysis)
7. Filtration
8. Filtrate
9. C-rich Hydolysate
10. Drying
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12. Filtration
13. N-rich Autolysate
14. Gluten
15. Nitrogen enhancement (autolysis)
16. Filtration
17. Solids
Full proposed process for bioconversion of whole grain

- Whole wheat flour
  - Dough mixing
  - Washing
  - Centrifugation
  - Glucose enhancement (hydrolysis)
    - Filtration
    - Filtrate
    - C-rich Hydolysate
  - Drying
  - Continuous bioconversion
  - Filtration
  - Solids
    - Nitrogen enhancement (autolysis)
      - Filtration
      - N-rich Autolysate
  - Gluten
  - Supernatant

- Water

- Fermentation feedstock
  - N-rich Autolysate
  - Solids
Full proposed process for bioconversion of whole grain

- Whole wheat flour
- Water
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- Washing
- Centrifugation
- Glucose enhancement (hydrolysis)
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- N-rich Autolysate
- Products
- Gluten
- Solids

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Full proposed process for bioconversion of whole grain

- Whole wheat flour
- Water
- Dough mixing
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- Glucose enhancement (hydrolysis)
- C-rich Hydrolysate
- Supernatant
- Glutens
- Continuous bioconversion
- Filtration
- Solids
- Nitrogen enhancement (autolysis)
- Filtration
- N-rich Autolysate
- Fermentation feedstock
- Fermentation
- Products

- Filtrate
- Solids
Comparison of costs

![Comparison of costs](chart.png)

- Glucose
- Glucose syrup
- Starch
- Molasses
- Generic Feedstock

**Raw material cost per kg glucose**

**Plant capacity (m$^3$/day)**
Research focus

- Develop viable cereal-based biorefineries for the production of fuels, chemicals and plastics
- Integrate chemical, biochemical and physical processing
- Reduce environmental burdens (CO$_2$ sequestration, waste minimisation/utilisation)
- Create interdisciplinary research
- Reduce process economics
- Create food and non-food outlets
Selected bioproducts for developing novel cereal-based biorefineries

- **Biofuels**
  - Bioethanol
- **Platform chemicals**
  - Succinic acid
  - Lactic acid
- **Biodegradable plastics**
  - Polyhydroxybutyrate (PHB)
Advantages of succinic acid ($C_4H_6O_4$) bioproduction

- Unique properties mainly because of the reactivity of the methyl groups
- Important intermediate in the manufacture of:
  - pharmaceuticals, elastomers, protective coatings, electrical insulations, foods, detergents, surfactants, corrosion inhibitors and cosmetics
  - with a total market size of more than $400,000,000 per year.
- Bioproduction could decrease production cost from $7/kg to $0.6/kg
- Its mass production requires CO$_2$ fixation creating a novel CO$_2$ sequestration process
Indirect CO$_2$ sequestration
Proposed biorefinery based on the traditional wheat flour milling process

- Wheat cleaning (Wheat) → Conditioning → Breaking (Coarser material sent to later breaks)
- Succinic acid bioproduction
  - Generic feedstock production
    - Enzymes
    - Solid state fungal bioconversion
    - Fungal autolysis
    - Animal feed
  - Starch-rich suspension
- Washing (Washing)
  - Screening (Screening)
  - Bran-rich solids
  - Gasification
    - Unhydrolysed solids
    - Energy
    - Biodegradable plastics
    - Acetic acid as platform chemical
- Wheat flour milling by-products (20-30%)
  - Wheat flour (70-80%)
  - Shorts, bran, germ
  - Bran
- Green chemical conversion of succinic acid
- CO₂ sequestration
- Commodity chemicals
- Green solvents
- Biodegradable plastics
- Lubricants
- Hydraulic fluids
- Nutrient supplements
- Green chemical conversion of succinic acid
Debranning (Pearling)
Proposed biorefinery based on debranning of wheat

- **Wheat**
- Debranning → Debranned wheat → One stage milling → Cooking → Fungal fermentation → Nutrient enhancement
- Gluten processing → Gluten- and bran free flour
- Dashed lines: Arabinoxylan, Proteins, Lipids, Gluten, Biodegradable plastics, Biofuels, Platform chemicals
- Microbial bioconversion → Microbial feedstock → Solids
Pearling studies at SCGPE

- Refinement of pearling conditions
  - Optimisation of conditioning prior to pearling
  - Speed
  - Pressure of abrasion rolls
  - Feeding rate of wheat

- Recovery of aleurone section via pearling
  - Production of streams rich in pericarp, seed coat, nucellus, aleurone

- Separation of germ and subaleurone rich streams from milling flour via Buhler Laboratory Mill and Satake Test Purifier
  - Production of germ, crease bran and endosperm streams
  - Compositional mapping of the various sections
  - Use of air classification and flotation to fractionate subaleurone materials
Proposed oat-based biorefinery

Oat → Debranning

Pearlings (oat bran) 1-15% w/w → Polar solvent extraction → Non-Polar solvent extraction → Antioxidant solution 1

Non-Polar solvent extraction → β-glucan rich fraction 1 → Yellow light oat oil

Non-Polar solvent extraction → Dark oat oil

Aqueous extraction 85°C, 1 h → Drying → Starch hydrolysis by α-amylase → Ethanol extraction → Ethanol extraction → β-glucan rich fraction 1

Enzymatic hydrolysis of pearled oat flour → One step dry milling → Optional

Amylolytic, proteolytic enzymes

Aqueous steeping → Maceration and screening (ethanol) → Bran rich fraction

Alkali extraction → Centrifugation → Anti-irritant solution 2

Downstream processing → Product

Lipase → β-glucan rich fraction 2

Drying → Dark oat oil

Polar solvent extraction

Non-Polar solvent extraction

Proposed oat-based biorefinery
Research challenges

- Ex. extraction of valuable end products
- Cracking and reforming intermediates (platform chemicals)
- Develop chemistry to synthesise familiar molecules
- Develop new set of chemistry based on the chemicals that are readily available
- Optimise crops to produce specific end products
- Develop end uses for by-product materials.

Wheat Grain

- Milled Bran
  - Pentosans: 25%
  - Cellulose: 21%
  - Crude fiber: 10%
  - Protein: 13%
  - Phytate: 4%
  - Starch: 8%
  - Total sugar: 5%
  - Reducing sugars: 4%
  - Lipid: 4%
  - Vitamins: Choline, Inositol, Niacin, Tocopherols, Pantothenic acid, p-Aminobenzoic acid, Thiamine, Riboflavin, Folic acid, Biotin

- Milled Endosperm
  - Starch: 70%
  - Protein: 10%
  - Phytate: 0.5%
  - Vitamins: Inositol, Niacin, Tocopherols, Pantothenic acid, Pyridoxine, Thiamine, Riboflavin, p-Aminobenzoic acid, Folic acid, Biotin

- Germ
  - Protein: 25%
  - Total sugar: 17%
  - Raffinose: 7%
  - Lipid: 12%
  - Phytate: 2%
  - Vitamins: Inositol, Niacin, Pyridoxine, Pantothenic acid, Thiamine, Riboflavin, p-Aminobenzoic, Folic acid, Biotin

- Aleurone layer
  - Protein: 18%
  - Vitamins: Niacin, Pantothenic acid, Pyridoxine, Thiamine, Riboflavin, Betaine
Studies on the feasibility of platform chemicals production from cereal raw materials

Dr. Chenyu Du

Biodegradable bacterial plastics from cereals

Dr. Apostolis Koutinas

Succinic acid production from wheat milling by-products

Miss Carol Lin

Economic and process engineering aspects of PHB production from cereals

Miss Yunji Xu

Studies in particulate bioprocessing

Miss Carolina Botella

Production of value added products from waste bread

Mr. Mehmet Melikoglu

Thank you!