Biorefinery in China

Tianwei Tan
College of life science and technology
Beijing University of Chemical Technology
Outline

1. Background
2. Bioenergy
3. Biobased Chemicals
4. Biomaterials
Beijing University of Chemical Technology is one of 211 Universities in China

• (1) Biocatalysts
• (2) Bioseparation
• (3) Bioenergy and Bioresources
• (4) Biomaterials
Return to the Future: Time Cycle of Chemical Engineering
Energy Consumption

China’s booming economy has been driving the total energy and oil consumption very rapidly.
More than half of petrol in China depends on import

The largest emitter of greenhouse gases
Oil Import Dependence

The oil import has been rapidly increasing as well, posing serious threat to energy security.

China’s Petroleum Balance in Selected Years
Fuel Demand and Air Pollution

The number of cars is increasing rapidly, causing rising demand for transportation fuel and serious urban air pollution.

Source: China Statistic Yearbook 2006

Source: SETA
Potential Issues and General Ideas of Biomass Economical Industry

Problems exist in Biomass Economical Industry

**Feedstock issues** ---- Competition for food with human?  
Competition for land with food?  
Achievements of Scale Production?  
Convenient to collect ?

**Technological economy issues**---- Competition with current petrochemical resources?  
Friendly to environment  
Breakthrough in costs  

--- **Clean production**--- Liquid fermentation  
Chemical means
Feed stock for biorefinery
Utilization of crop residues (biomass)

- Corn for biorefinery is impossible

- From 1995 to 2005, China produces some 620 million tons of crop residues per year.
- Crop residues of corn, wheat and rice were 239, 137 and 116 million tons, respectively, accounting for nearly 80% of the total crop residues.
- About 33–45% of energy consumption for livelihood in rural areas.
Tonnage of straw by crop categories in China in 2002 (Unit: 10^6 ton)

<table>
<thead>
<tr>
<th>Crops</th>
<th>Yield of Crops</th>
<th>Coefficient</th>
<th>Yield of straw</th>
<th>Percent (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice</td>
<td>174.54</td>
<td>0.623</td>
<td>108.74</td>
<td>17.53</td>
</tr>
<tr>
<td>Wheat</td>
<td>90.29</td>
<td>1.336</td>
<td>120.63</td>
<td>19.45</td>
</tr>
<tr>
<td>Corn</td>
<td>121.31</td>
<td>2</td>
<td>242.62</td>
<td>39.12</td>
</tr>
<tr>
<td>Beans</td>
<td>22.412</td>
<td>1.5</td>
<td>33.62</td>
<td>5.42</td>
</tr>
<tr>
<td>Tubers</td>
<td>36.659</td>
<td>0.5</td>
<td>18.33</td>
<td>2.96</td>
</tr>
<tr>
<td>Oil-bearing crops</td>
<td>28.972</td>
<td>2</td>
<td>57.95</td>
<td>9.34</td>
</tr>
<tr>
<td>Cotton</td>
<td>4.916</td>
<td>3</td>
<td>14.75</td>
<td>2.38</td>
</tr>
<tr>
<td>Hemp</td>
<td>0.964</td>
<td>2.5</td>
<td>2.40</td>
<td>0.38</td>
</tr>
<tr>
<td>Sugar crops</td>
<td>102.927</td>
<td>0.1</td>
<td>10.29</td>
<td>1.66</td>
</tr>
<tr>
<td>Other crops</td>
<td>10.941</td>
<td>1</td>
<td>10.94</td>
<td>1.76</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>620.27</strong></td>
<td></td>
<td></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>
Utilization of crop residues

- Forage: 23.0%
- Direct combustion: 37.0%
- Lost during collection: 15.0%
- Discarded: 20.5%
- Industry materials: 4.0%
- Biogas: 0.5%
2. Bioenergy

- Biodiesel
- Ethanol
- Hydrogen

Biomass
(1) Bioenergy—Biodiesel

- There will be great potential progress about biodiesel in China theoretically.
- Raw materials
  - (1) The oil plants such as *Jatropha* and *Chinese pistache* could produce 5,000,000t biodiesel every year.
  - (2) Waste oil and fats are feat for 2,000,000t biodiesel production annually.
- Recently lots of biodiesel factories with output more than ten thousand tons have been established in China. It is expected that the requirement of biodiesel in China would be more than 20,000,000t till 2010.
Biodiesel in China

• 10 factories, total capacity: 200,000 ton/y
• Raw materials: waste oils,
• acid oil, animal fat
• other oils
• Production Methods:
• (1) Chemical conversion
• (2) Enzymatic conversion
• (3) High pressure method
Bioenergy—Biodiesel

• More than 10 factories use chemical conversion
• 100,000t/a factory employed the traditional alkali as catalyst.
Production of biodiesel by enzymatic conversion

- Chemical method: alkaline catalyst
  - (1) waste water problems
  - (2) high energy consumption (100-200 C°)

- Enzymatic method
  - (1) low pollution and environmental friendly
  - (2) can be used to any oils and fats
Immobilized lipase in reactor

Immobilized lipase on a fabric membrane

Reactor column packed with immobilized lipase membranes
• In October 2007, another factory with lipase catalysis have been set up in Shanghai.

• Lipase of *Candida* sp. 99-125 was used as catalyst in the factory. Waste oil from Shanghai were used as raw materials.
Production of lipid from wastewater for biodiesel

Raw materials (oil) of biodiesel is limited

US: soy bean oil
EU: rape seed oil
China: waste oil

- MSG wastewater: ≥ 25 million tons / year
- Starch wastewater: ≥ 24 million tons / year
- Citric acid wastewater: ≥ 20 million tons / year
- Papermaking wastewater: ≥ 3.67 billion tons / year
1. Reutilization of Waste Resource

--- Microbial Oil Production Using Waste Water

We produce biodiesel from starch waste water

starch waste water

Reutilization
A new idea was firstly proposed by converting sugar-abundant starch waste water into lipids microbial fermentation.

### Composition Analysis of Ruixing Starch Waste Water

<table>
<thead>
<tr>
<th>Components</th>
<th>Type</th>
<th>Gluten Wastewater</th>
<th>Immersion wastewater</th>
<th>Original sugar wastewater</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.73</td>
<td>4.10</td>
<td>2.84</td>
<td></td>
</tr>
<tr>
<td>Glucose content (g/l)</td>
<td>1.5</td>
<td>1.4</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>Protein content (mg/l)</td>
<td>138</td>
<td>4041</td>
<td>32.6</td>
<td></td>
</tr>
<tr>
<td>$\text{PO}_4^{+}$ content (mg/l)</td>
<td>1784</td>
<td>687</td>
<td>630</td>
<td></td>
</tr>
<tr>
<td>COD (mg/l)</td>
<td>14617</td>
<td>144247</td>
<td>729189</td>
<td></td>
</tr>
<tr>
<td>Function</td>
<td>Nitrogen source and water</td>
<td>Nitrogen source</td>
<td>Carbon source</td>
<td></td>
</tr>
</tbody>
</table>
Production of microbial oils from starch wastewater was completed using a 300L pilot fermenter.

Lipid content by *Rhodotorula glutinis* can reach 35—60% without exogenous carbon source and sterilization.
lipid fermentation from monosodium glutamate wastewater

The wastewater did not need dilution

After 156 hours’ fermentation, biomass, lipid content and COD degradation rates were 43.18g/L, 46.67% and 53.04% respectively.
## Prospect

<table>
<thead>
<tr>
<th>Wastewater type</th>
<th>Emission (10000 tons/year)</th>
<th>COD (10000 tons)</th>
<th>Feed yeast (10000 tons/year)</th>
<th>Lipid (10000 tons/year)</th>
<th>Reduction of sewage (10000 tons/year)</th>
<th>Benefit ($10^8$ RMB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starch wastewater</td>
<td>2500</td>
<td>100</td>
<td>62.5</td>
<td>33.33</td>
<td>2250</td>
<td>2.96</td>
</tr>
<tr>
<td>Monosodium glutamate wastewater</td>
<td>2400</td>
<td>80</td>
<td>50.0</td>
<td>26.67</td>
<td>2160</td>
<td>2.15</td>
</tr>
<tr>
<td>Alcohol wastewater</td>
<td>2100</td>
<td>84</td>
<td>52.5</td>
<td>28.00</td>
<td>1890</td>
<td>2.23</td>
</tr>
<tr>
<td>Citric acid wastewater</td>
<td>2000</td>
<td>50</td>
<td>31.3</td>
<td>16.67</td>
<td>1800</td>
<td>1.38</td>
</tr>
<tr>
<td>Sugar wastewater</td>
<td>1000</td>
<td>21</td>
<td>13.1</td>
<td>6.93</td>
<td>900</td>
<td>0.59</td>
</tr>
<tr>
<td>Pharmaceutical wastewater</td>
<td>20000</td>
<td>15</td>
<td>9.4</td>
<td>5.00</td>
<td>18000</td>
<td>1.64</td>
</tr>
<tr>
<td>Papermaking wastewater</td>
<td>400000</td>
<td>180</td>
<td>112.5</td>
<td>60.00</td>
<td>360000</td>
<td>29.70</td>
</tr>
<tr>
<td>total account</td>
<td>430000</td>
<td>530</td>
<td>331.3</td>
<td>176.60</td>
<td>387000</td>
<td>40.65</td>
</tr>
</tbody>
</table>
China has launched a national program and is committed to expand fuel ethanol program since 2000, aiming at more than 100 million tone/year by 2020.
Fuel Ethanol Program Pilot Phase: 2000-2005

- State council decided to launch fuel ethanol program in 2001
- Four plants were built to produce fuel ethanol from corn, with total capacity of 1.02 million tone per year
- PetroChina and Sinopec are responsible for blending fuel with gasoline, distributing and selling gasohol (E10) as fuels for road transport in 9 provinces
- Fuel ethanol producers enjoy favorable policies, including free income tax, VAT refunding, fiscal subsidies
- By 2005, gasohol consumption accounts for nearly 20% of national gasoline consumption
Main Fuel Ethanol Plants in China, 2006

- **Huaren Group in Heilongjiang Province**: Corn 400,000 t/y
- **Jilin Province in North-east China**: Corn 400,000 t/y
- **Tianguan Group in Henan Province**: Corn 400,000 t/y
- **Fengyuan Group in Anhui Province**: Corn 440,000 t/y
- **Zhongliang Group in Guangxi Province**: Cassava 1,000,000 t/y
Nonfood-based biofuel

Cassava

Cellulose

Sweet sorghum
Typical Sweet Sorghum complex

- S.Sorghum Planting
- Harvesting
- Cane crushing
- Trashes
- Baggase
- Juice
- Cell immobilized fermentation
- Distillation
- Dehydratation
- Pelletisation
- Agro-pellets
- Paper making
- Ethanol
- Residue
- SSF
- DDGS Feed
- Food
Ethanol production from concentrated sweet sorghum juice was carried out under very high gravity (VHG) fermentation conditions, the maximum ethanol concentration can keep steadily at 150 g/L.
1. COFCO Introduction

— Status of biomass energy resource and chemical industry

<table>
<thead>
<tr>
<th>Corn processing capacity</th>
<th>Fuel ethanol</th>
<th>Starch</th>
<th>Starch sugar</th>
<th>citric acid</th>
<th>ethylene oxide</th>
<th>L-lactic acid</th>
<th>Lysine</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.95 million tons</td>
<td>0.84 million tons</td>
<td>1.2 million tons</td>
<td>0.4 million tons</td>
<td>0.16 million tons</td>
<td>0.02 million tons</td>
<td>0.03 million tons</td>
<td>0.054 million tons</td>
</tr>
</tbody>
</table>

- **Huang long65**
- **Gong zhu ling60**
- **Yu shu60**
- **Zhao dong120**
- **Feng yuan160**
- **Cerestar 30**

- **Zhao dong18**
- **Guang xi20**
- **Feng yuan38**
- **Ji lin42**

- **Cerestar 20**
- **Huang long40**
- **Gong zhu ling20**
- **Yu shu40**

- **Huang long10**
- **Gong zhu ling20**
- **Cerestar 0**

- **Feng yuan**
- **Feng yuan**
- **Feng yuan**
- **Feng yuan**

- The First
- The First
- The Third
- The Fifth
- The Second
- The First
- The First
- The Forth
1. COFCO Introduction

Biomass energy development strategy

Stabilization of grain 、 Development of non-grain 、 three-step strategy

- COFCO (Zhaodong) Biochemical Energy Co., Ltd.
- Guangxi COFCO Biomass Energy Co., Ltd.
- Anhui BBCA Biochemical Co., Ltd.

Three-step

- Fuel ethanol from corn
- Fuel ethanol from cassava
- Fuel ethanol from cellulose

Two-phase

- Ethanol from grain
- Ethanol from non-grain

2007 2008 2012
2.1 Fuel ethanol

———from cassava

Technical indicators producing Cassava ethanol in Guangxi COFCO

<table>
<thead>
<tr>
<th>Item</th>
<th>Indicator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry cassava consumption(t)</td>
<td>2.95</td>
</tr>
<tr>
<td>Mature mash ethanol concentration（v/v%）</td>
<td>14.0</td>
</tr>
<tr>
<td>Water consumption(t/t EtOH )</td>
<td>6.2</td>
</tr>
<tr>
<td>Steam consumption(t/t EtOH )</td>
<td>2.6</td>
</tr>
<tr>
<td>Comprehensive energy consumption (kgCoal/t EtOH)</td>
<td>396</td>
</tr>
</tbody>
</table>
2.1 Fuel ethanol

— from cellulose (pilot)
Pilot plant of cellulose ethanol in China Resources (Heilongjiang) Co. Ltd.
Situation of Bio-energy Industry in Tianguan – Industry chain in Tianguan

- **Wheat (小麥)**: Bran, Gluten
- **Corn (玉米)**: Feed, Corn Oil
- **Molasses (糖蜜)**: Degradable Plastics
- **Potato & Cassava (薯類)**: Enzymolysis
- **Starch Milk (葡萄糖乳)**: Glucose, Glycerol, 1, 3-PDO, Biobutanol, Biodiesel
- **Glucose**: Ethylene, Polyethylene
- **Other Agricultural Products**: Biofuel, Biobutanol
- **Ethanol Production (酒精生產)**: Methane, Fuel Ethanol
- **CO2 (二氧化碳)**: For Cooking and Electricity Generation
- **Fuel Ethanol**: PTT
- **Enzymolysis (酶解)**: PTT

Additional products include:
- **Dietary Fiber**: Wheat Bran
- **Protein**: Wheat Protein
- **Feed**: Corn Oil
- **Methylcellulose**: Glucose, Glycerol
- **Biobutanol**: 1, 3-PDO
- **Biodiesel**: PTT
Guided by the concept of recycling economy, Tianguan accomplishes resource comprehensive utilization and clean production to make the released matters reused, decreased and harmless, to increase the value of products and environment benefit.
1、Develop fuel ethanol guided by ‘Green Idea’

Tianguan insists on clean process and multiple feedstock for fuel ethanol production. And now Tianguan is on the innovation route of nonfood feedstock and clean technology for ethanol production.
2、秉承绿色理念，开发纤维乙醇  Develop cellulosic ethanol guided by ‘Green Idea’

- 天冠纤维乙醇产业化攻关研究取得重大进展，不仅三大主粮的秸秆原料预处理工艺基本成熟，还有效地降低了纤维素酶的生产成本，正全力进行秸秆乙醇经济性的最后攻关；
  Tianguan has made much progress in cellulosic ethanol production. It owned the mature pretreatment technology for straw materials from three main food plant. And it has lowered effectively the cost of cellulase. It is trying all efforts to reach a profitable cellulosic ethanol production.

- 完全依靠自主知识产权新建的1万吨纤维乙醇一期产业化示范项目已完成建设。A new cellulosic ethanol demonstration facility with a capacity of 10,000 tons per year and owned property right was built in Tianguan.
3、秉承绿色理念，开发二氧化碳全降解塑料

Develop CO₂ degradable plastics guided by ‘Green Idea’

天冠集团历经10余年攻关研究，成功开发生产全降解塑料（PPC），取得了聚合分子量10万以上完全可控的巨大技术突破，现已初步实现产业化生产。After 10 years' research, Tianguan group has successfully developed the production process of degradable plastics (PPC). Huge technological breakthroughs have been made to synthesize polymer with molecular weight over 100,000 completely under control. This process has realized industrial production primarily.
Pilot plant for 3000 tons ethanol from lignocellulosics per year in Dongping
7. Eco-industrial chain Straw Demonstration Project Development

Straw ecological industrial chain development road map

High-value Straw Resource Eco-System
8. Straw straw hemicellulose fermentation of butanol and high-value eco-industrial chain

**Problem:** high cellulase consumption, high energy consumption in production of butanol, low concentration of total solvent fermentation

**Strategy:** breed butanol-fermenting strains that can use xylose effectively

Integrate and optimize efficient methods of lignin and cellulose utilization

**Achievement:** no cost of raw materials in butanol fermentation

completion of pilot (3,000 tons/year)

completion of ton-scale production by the end of July
Cellulose Biorefinery

Corn cob → Xylooligosaccharides → Xylitol → Functional sugar derivatives

Hemicellulose → Xylose residue

Cellulose → Charcoal back to field

Cellulosic ethanol or other chemical

Lignin → Power generation, steam or lignin products

Corn Cob Bio-refining technology
• Cellulosic ethanol pilot (3,000 tons/year) completed in 2007,
• The cost-effectiveness of cellulosic ethanol was improved through co-production of xylose products
(3) Hydrogen Production

- A Two-step Technology for Hydrogen Production by Organic Waste

Maximum Generation yield of Hydrogen: $17 \text{m}^3 \text{H}_2/(\text{d. m}^3)$
Industrial Demonstration for Hydrogen Bio-production

Including:

- hydrogen production by bio-fermentation
- purification
- strain production
- secondary Wastewater Treatment

Hydrogen production yield: 40x10^4 m^3/year
Hydrogen purity: over 99.9%.

Joint Practice Research: cooperated with fuel cell development group of Tsinghua University
(4) Biogas in China

- Straw
- Dejecta
- Garbage

Anaerobic digestion

- Organic Fertilizer
- Household
- Fuel
- Biogas
Anaerobic digestion (biogas technology) is a bioconversion technology widely adopted in China, especially in rural areas.

(5) Bioenergy—Pyrolysis

- Chinese scientists have made several achievements for agricultural residues pyrolysis. Some new kind of reactor, the Hot Ceramic Ball Heated Down-flow Tuber Reactor, for example, was developed.

- On the other hand, some basic research on biomass devolatilization characteristics at flash heating rates was conducted.

- Liquid fuel
- Gasification for electricity
Bioenergy—Pyrolysis

- Biomass Energy Engineering Center of Northeast Forestry University developed a new type of rotary core reactor with the capacity of 200kg/hr.
University of Science and Technology of China built a large scale of fluidized bed biomass liquefaction system in 2006. The capacity is about 600kg/h and bio-oil obtained is 50% to the feeding biomass.
### Major types of gasifier applied for straw in China

<table>
<thead>
<tr>
<th>Gasifier type</th>
<th>Fuel types</th>
<th>Output (kWe)</th>
<th>Low CV of gas (kJ/m³)</th>
<th>Temperature (°C)</th>
<th>Efficiency (%)</th>
<th>Application fields</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFB</td>
<td>Straw, husk, sawdust</td>
<td>400–2000</td>
<td>4600–6300</td>
<td>650–850</td>
<td>65–75</td>
<td>Boiler fuel, electricity generation</td>
</tr>
<tr>
<td>Down-draft</td>
<td>Straw</td>
<td>60–200</td>
<td>3800–4600</td>
<td>~1000</td>
<td>75</td>
<td>Domestic cooking</td>
</tr>
</tbody>
</table>

**CFB:** circulating fluidized-bed  **CV:** calorific values

### Typical straw gasification demonstration projects in China

<table>
<thead>
<tr>
<th>Project</th>
<th>Material</th>
<th>Purpose</th>
<th>Capacity</th>
<th>Gasifier</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Huantai integrate gas-supply system</td>
<td>Crop residues</td>
<td>Cooking</td>
<td>300 kWt</td>
<td>Down draft</td>
<td>Shangdong</td>
</tr>
<tr>
<td>Dalian integrate gas-supply system</td>
<td>Crop residues</td>
<td>Cooking</td>
<td>300 kWt</td>
<td>Down draft</td>
<td>Hunan</td>
</tr>
<tr>
<td>Handan steel works</td>
<td>Straw</td>
<td>Electricity</td>
<td>600 kWe</td>
<td>CFB</td>
<td>Hebei</td>
</tr>
</tbody>
</table>
2. Based Chemicals

Biomass-originated Pathway to Chemicals

- **Renewable Resources**
- **Microorganisms**
- **Reaction conditions**
- **Reactor**
- **Ethanol**
- **Lactic acid**
- **Catalysts**
- **Ethylene**
- **Acrylic Acid**
- **Alternatives**
Biobased $C_2- C_6$ Monomers and Polymers

Starch, Cellulose, Hemicellulose

Bio/Chem Process

Polym Process

Bio Polymer
The production technology of the feedstock Bio-ethanol is very mature presently.

The dehydration process has advantages, such as low energy cost and less byproducts.
Present process design for Bio-ethylene large-scale production

BBCA GROUP’s 17 kt/year bio-ethylene production equipment imported from Petroleo Brasileiro S.A., Brazil in 1980s. (Start using in 2004)
Tandem adiabatic reactor

SINOPEC’s 9 kt/year bio-ethylene production equipment designed by SINOPEC Shanghai Engineering Company (SSEC) in 1980s.
Isothermal bed-fixed tubular reactor
Production of acrylamide in China

200,000 ton / a in China

25000 t/year acrylamide in Beijing
## Table. Comparison of Chemical method and Biotransformations for acrylamide(AM)

<table>
<thead>
<tr>
<th></th>
<th>Chemical method</th>
<th>Biotransformate</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Catalyst</strong></td>
<td>Cu catalyst</td>
<td>Japan immobilized cells</td>
</tr>
<tr>
<td></td>
<td></td>
<td>China free cells</td>
</tr>
<tr>
<td><strong>Acrylonitrile</strong></td>
<td>0.76 t/t AM</td>
<td>0.76 t/t AM</td>
</tr>
<tr>
<td><strong>consumed</strong></td>
<td></td>
<td>0.72 t/t AM</td>
</tr>
<tr>
<td><strong>Conversion(%)</strong></td>
<td>80%</td>
<td>99.9%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>99.9%</td>
</tr>
<tr>
<td><strong>Capacity of reactor</strong></td>
<td>96.15t AM/m³</td>
<td>120t AM/m³</td>
</tr>
<tr>
<td><strong>Steam consumed</strong></td>
<td>1 t/t AM</td>
<td>4 t/t AM</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5 t/t AM</td>
</tr>
<tr>
<td><strong>Electrical energy</strong></td>
<td>315 kw.h</td>
<td>600 kw.h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200 kw.h</td>
</tr>
<tr>
<td><strong>Cost of Catalyst</strong></td>
<td>100U$/t AM</td>
<td>300Yuan/t AM</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50-80Yuan/t AM</td>
</tr>
</tbody>
</table>
## 4. Biomaterials

L-lactic acid production in China (2007)

<table>
<thead>
<tr>
<th>Factory</th>
<th>Product</th>
<th>Output (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Henan Jindan Lactic Acid Co., Ltd.</td>
<td>DL-lactic acid</td>
<td>40,000.00</td>
</tr>
<tr>
<td>Anhui BBCA &amp; GALACTIC Lactic Acid Co., Ltd.</td>
<td>L-lactic acid</td>
<td>25,000.00</td>
</tr>
<tr>
<td>Jiangsu Daosen Biochemical Co., Ltd.</td>
<td>L-lactic acid</td>
<td>5,000.00</td>
</tr>
<tr>
<td>Jiangxi Musashino Bio-Chem Co., Ltd.</td>
<td>L-lactic acid</td>
<td>4,500.00</td>
</tr>
<tr>
<td>SICHUAN YIBIN WULIANGYE GROUP CO., LTD.</td>
<td>DL-lactic acid</td>
<td>3,000.00</td>
</tr>
<tr>
<td>HeBei XinHua Lactic Acid Co., Ltd.</td>
<td>L-lactic acid</td>
<td>2,200.00</td>
</tr>
<tr>
<td>HuNan AnHua Lactic Acid Co., Ltd.</td>
<td>DL-lactic acid</td>
<td>2,000.00</td>
</tr>
<tr>
<td>HuBei GuangShui National Chemical Co., Ltd.</td>
<td>L-lactic acid</td>
<td>1,500.00</td>
</tr>
<tr>
<td>Jiangsu Senda Biological Engineering Co., Ltd.</td>
<td>DL-lactic acid</td>
<td>1,500.00</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>84,700.00</strong></td>
</tr>
</tbody>
</table>
4. Biomaterials —— L-lactic acid

Radix Puerariae → Puerarin → Starch → Fermentation → PLA → L-lactic acid
Biorefinery of White rice bran

White rice bran is a by-product of rice milled. The amount of white rice bran is about 4,900,000 t.

The composition of white rice bran

<table>
<thead>
<tr>
<th>Moisture (%)</th>
<th>Starch (%)</th>
<th>Protein (%)</th>
<th>Oil (%)</th>
<th>Fiber (%)</th>
<th>Others (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.57±0.01</td>
<td>48.38±1.59</td>
<td>9.96±0.12</td>
<td>8.43±0.1</td>
<td>1.92</td>
<td>13.75</td>
</tr>
</tbody>
</table>
Biorefinery of White rice bran

1t WRB → Hydrolysis → Separation → Supernatant* → Bio-based Chemicals

Residue → Extract → 0.084t Oil → Oil, Biodiesel

Residue → 0.22t Feed** → Protein

*0.47t Glucose
**Protein > 42%
The raw material cost was estimated to be ¥2300/t L-lactic acid when using white rice bran.

The biorefinery of white rice bran have applied Chinese patent (200910086085.9)
图1 3-羟基丁酸和3-羟基已酸共聚物 PHBHVx 的一些应用
美国 PolyOne 公司用天安 PHBV 材料制成的环保产品在欧洲销售

图 1 天安 PHA 产品 PHBV 的制成品
天津国韵生物材料公司万吨PHA产房建设中
Biomaterials —— 1, 3-Propanediol

- Crude glycerol waste stream of biodiesel process
  - Up-stream processing
    - Pre-treatment

- Cheap waste streams of starch and dairy industry

- Bioreactor - biotechnical process with bacterial strain
  - Fermentation medium
    - Down-stream processing
      - By-product
        - Biogas production

- High grade specialty product 1,3-propanediol
1, 3-propanediol fermentation in 300 L bioreactor
Bio-energy Industry in Tianguan – 1,3-Propanediol (PDO)/PTT

5. 秉承绿色理念，开发1,3-丙二醇及PTT  Develop 1,3-PDO/PTT guided by ‘Green Idea’

- 淀粉 (Starch)
- 甘油 (Glycerol)
- 葡萄糖 (Glucose)
- 油脂 (Oil)
- 生物柴油 (Biodiesel)

1,3-丙二醇产业链示意图
Sketch of 1,3-PDO Industry Chain
5、秉承绿色理念，开发1,3-丙二醇及PTT

Develop 1,3-PDO/PTT guided by ‘Green Idea’

该产品既是一种重要的化工原料，又是一种附加值较高的高新技术产品，在高分子聚合领域具有广阔的发展前景，是新一代聚酯PTT的主要原料，在替代石油资源化工产品领域具有巨大潜力。

1,3-PDO is an important chemical material with high value-added. It is broadly used in the field of polymer polymerization, and is the monomer of the new polyester PTT, which could be the alternative to chemical products from fossil oil.
秉承绿色理念，开发1,3-丙二醇及PTT

### PTT纤维与其它纤维性能比较表

<table>
<thead>
<tr>
<th>项目</th>
<th>PTT</th>
<th>PET</th>
<th>PA6</th>
<th>PA66</th>
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</thead>
<tbody>
<tr>
<td>膨松性及弹性</td>
<td>++</td>
<td>中</td>
<td>中</td>
<td>良</td>
</tr>
<tr>
<td>Wrinkle resistance</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>静电</td>
<td>低</td>
<td>高</td>
<td>高</td>
<td>高</td>
</tr>
<tr>
<td>Static electricity</td>
<td>-</td>
<td>++</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>拉伸回复性</td>
<td>优</td>
<td>差</td>
<td>良</td>
<td>优</td>
</tr>
<tr>
<td>Tensile elasticity and recovery</td>
<td>++</td>
<td>--</td>
<td>--</td>
<td>++</td>
</tr>
<tr>
<td>吸水性</td>
<td>差</td>
<td>差</td>
<td>中</td>
<td>中</td>
</tr>
<tr>
<td>Water absorption</td>
<td>--</td>
<td>--</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>抗日光性</td>
<td>优</td>
<td>良</td>
<td>差</td>
<td>差</td>
</tr>
<tr>
<td>Light resistance</td>
<td>++</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>尺寸稳定性</td>
<td>良</td>
<td>良</td>
<td>良</td>
<td>良</td>
</tr>
<tr>
<td>Dimensional stability</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>染色性</td>
<td>优</td>
<td>优</td>
<td>良</td>
<td>良</td>
</tr>
<tr>
<td>Dyeability</td>
<td>++</td>
<td>++</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>印花适应性</td>
<td>优</td>
<td>中</td>
<td>良</td>
<td>良</td>
</tr>
<tr>
<td>Printing adaptability</td>
<td>++</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>加工及后处理费用</td>
<td>低</td>
<td>高</td>
<td>中</td>
<td>中</td>
</tr>
<tr>
<td>Process &amp; Post-treatment cost</td>
<td>-</td>
<td>++</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>耐污染</td>
<td>优</td>
<td>良</td>
<td>优</td>
<td>优</td>
</tr>
<tr>
<td>Contamination resistance</td>
<td>++</td>
<td>-</td>
<td>++</td>
<td>++</td>
</tr>
</tbody>
</table>

### PTT纤维

PTT (聚对苯二甲酸丙二醇酯)
Poly(trimethylene terephthalate)
Biomaterials — Succinic Acid and PBS

Prior Art
Fossil resources

Bioprocess
Biomass resources

- Sequestration of CO₂, less greenhouse gas emission, lower energy consumption
- Pilot plant for fermentation of succinic acid at Jiangsu Province, mass yield at 70%, productivity at 2.0 g/L·h. End product yield up to 85% by membrane separation
- First commercial plant of PBS of 20 kt/a at Jiangsu
Lang chain Dicarboxylic acid

• Lang chain Dicarboxylic acid C10 – C18
• Applications:
  • synthesis of perfume materials (C13)
  • polyester: polyamide 66
  • heat melting gel for cotton
• Chemical synthesis is very difficult
• Production by bio-transformation
Production of $\text{C}_{13}$ dicarboxylic acid (20000 t/year)
Thank you!