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Developing biorefinery in China

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Abstract Biorefinery based on biomass resources is an important approach for the oil refining and petrochemical industry to achieve sustainable development. Two types of biorefinery suitable for China's biomass resources are presented in this paper. With sorgo and cassava as raw material, an ethanol-biorefinery for the production of ethanol-gasoline and chemicals is explored, and with rape seed and cotton seed oil as raw material, a biodiesel-biorefinery for the production of biodiesel and chemicals is also explored. The associated problems and measures taken are discussed in the end.

Keywords ethanol gasoline, biodiesel, biorefinery

At present the energy and raw material supply for the world's economic development are mainly based on coal, petroleum and natural gas. In order to decrease the dependence on such non-renewable sources, many countries have paid much attention to developing and utilizing renewable sources, such as sunlight, wind and biomass. Using the inexhaustive renewable biomass resources to produce liquid fuels and organic chemicals is an important research direction for green chemistry and an important route for the sustainable development of oil refining and petrochemical industry.

1 World's development trends

In 2000 a bio-based economic object was put forward by the American National Research Council at the National Agricultural Biotechnology Association Meeting. It was pro-

posed that in 2020, 10% of liquid fuels and 25% of organic chemicals should be made from plant/crop biomass [1]. In a report by the U.S. Department of Energy [2], the following orientation aims were brought forward: 1) Achieving at least 10% of basic chemical building blocks from plant-derived renewable resources in 2020, and 50% in 2050; 2) Establishing commercial demonstration industry system chains to produce chemicals from plant-derived renewable resources; 3) Building further collaborative partnerships to improve vertical integration and supporting success via enhanced rural development.

The technologies for producing liquid fuels from biomass resources have been commercialized for many years. However, there were no successful technologies for producing commodity chemicals economically from biomass until 2002. Cargill Dow LLC succeeded in developing the technology for producing polylactic acid-based thermoplastics from corn glucose, the energy consumption of which is 30–50% lower than that of corresponding chemical method, and a 14000 t/a plant put into production in 2002 with the investment of 300 million U.S. dollars. Because of this success, Cargill Dow LLC won the chemical engineering achievement prize-Kirkpatrick in 2003 [3]. DuPont Inc. Successfully developed the technology for producing 1,3-propanediol (1,3-PDO) from corn in 2002, which led to the construction of a 45000 t/a commercial plant in the second year [4]. This process includes the production of glucose liquid from wetmilling corn and its conversion to PDO with gene-modified bacteria and yeast. The cost is 30%–40% lower than that of the corresponding chemical method [5].

This commercialization confirmed that it is both technologically and economically feasible to produce commodity chemicals from renewable plant/crop resources. Therefore, kinds of biorefinery concepts based on different biomass resources appeared recently. Cargill Inc. conceived the biorefinery concept based on corn and straw [6]. Corn and straw are processed into starch and cellulose, which then convert to sugars by biochemical conversion, and further to ethanol, succinic acid, 3-hydracrylic acid, lactic acid and sorbierite etc, which are used to produce the final products

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such as fuels, THF, 1,4-butanediol, acrylic acid and polylactic acid. Purevision Technology Inc. put forward the concept of biorefinery based on waste biomass [7]. In a biorefinery, all kinds of waste biomass are milled and separated into cellulose, semi-cellulose and lignin, which are further processed into ethanol (fuel ethanol), adhesive, sorbierite, lactic acid and other chemicals. Pure Energy Corp.'s biorefinery concept was also based on waste biomass [8]. The biomass is milled first, and then hydrolyzed to a kind of slurry that contains glucose, xylose and lignin. The lignin is used to generate steam or electric power. Glucose and xylose are converted to ethanol and other chemicals by further processing. LSU AgCenter conceived the biorefinery concept based on sugarcane [9]. Sugarcane is fermented and its product is distilled first. After passing through molecular sieve, the distillate becomes anhydrous ethanol. The leftovers are then separated and purified to obtain glycerol, inositol and succinic acid etc, and the final residue is used as animal feeds.

2 Developing biorefinery in China

Developing biorefinery should depend on the raw material resources and technological foundation of the country. According to the situation of China, two types of biorefinery were proposed in this paper: 1) A biorefinery based on sorgo and cassava, where bioethanol (fuel ethanol) and chemicals such as ethylene, glycol and ethylbenzene are produced; 2) A biorefinery based on rapeseed oil and cottonseed oil, where biodiesel and chemicals such as biodegradable industrial solvents and lubricants, higher alcohols, and 1,3-PDO are produced.

2.1 Biorefinery based on sorgo and cassava

Ethanol, also known as ethyl alcohol or grain alcohol, can be used either as an alternative fuel or as an octane-boosting, pollution-reducing additive to gasoline. There are four manufacturers devoting themselves to produce fuel ethanol in China with a total production capacity of more than 1 million t/a. They are Zhaodong Corp. (100 thousand t/a) in Heilongjiang Province, Tianhe Corp. (300 thousand t/a) in Jilin Province, Tianguan Corp. (300 thousand t/a) in Henan Province, and Fengyuan Corp. (320 thousand t/a) in Anhui Province.

2.1.1 The production and supply of raw material is the key for fuel ethanol development

At present, the main raw materials for producing fuel ethanol are sugarcane (in Brazil) and corn (in America), others include wheat and sugar beet etc. The key to the further development of ethanol is decreasing its production cost. Therefore, the proper choice of the raw material is very im-

portant. After thorough investigation, sorgo and cassava are identified as the main raw materials that can be used on a large scale to produce ethanol in the near future, while biomass cellulose will be used in the distant future in China.

1) Sorgo

Sorgo or sugar sorghum, which is called "high-energy plant", is a kind of sorghum. Sorgo is also called as "camel in crops" because it is tolerant to drought, waterlogging and saline. Sorgo is adaptable to badlands, saline land and goaf land etc, and can be planted there, so it won't compete with food for farmland. Generally speaking, 4.5 tons of grain and 75 tons of straw that are rich in sugar (about 15%–25%) can be gathered per hectare. There are about 50 million hectares of waste and bad land in China. If only 8% of them, i.e. 4 million hectares are used to plant sorgo, 0.18 billion tons of sorgo straw will be obtained and so 30 million tons of ethanol will be produced.

The technology for producing ethanol from sorgo should adopt the solid-fermentation method, which is low in cost, simple in technique and low in equipment capital investment. This method is useful for countryside to set up minitype ethanol production plant, the crude ethanol (about 65% in concentration) from which can be collected to a large ethanol plant, where the crude ethanol is distilled, dried and further processed.

The cost of ethanol from grain is about 3800 ¥/t, but from sorgo is only 3400 ¥/t. As the market price of gasoline is 4000–4500 ¥/t, the ethanol from sorgo could compete with gasoline in the market. However, it is possible to further reduce the production cost of sorgo ethanol, once the following aims are reached: 1) Stable and high-yield species of sorgo and the relevant planting technique; 2) The technique to keep the sugar of sorgo; 3) high-yield bacteria and high-efficiency reactor in solid fermentation.

2) Cassava

Cassava is wild, easy to plant and tolerant to drought with high yields. It is widely adaptable to the amount of precipitation and can grow in an area with 360 mm–500 mm of precipitation. These make cassava an ideal raw material for ethanol production. When there is a lack of grain its price is high, some Chinese facilities that use grain to produce ethanol import dried cassava flake from Southeast Asia to produce ethanol.

Cassava planting can use not only farmland but also badlands. Even if badlands are used, aborative cultivation is not needed for cassava. In China, there are about 13 million hectares of badlands in Guangxi, Guangdong, Hainan, Fujian and Yunnan, and thereinto, 10 million hectares in Guangxi only. If 20% of the badlands are exploited to plant cassava, 80 million tons cassava will be gathered, from which 11 million tons of ethanol will be produced.

Although we have made great progress and gained much experience in cassava ethanol production, there are still many problems to be solved to reduce the cost, including: 1) Developing stable and high-yield species of cassava and the relevant planting technique; 2) Developing modified planting and storage technique to reduce the loss of starch; 3)

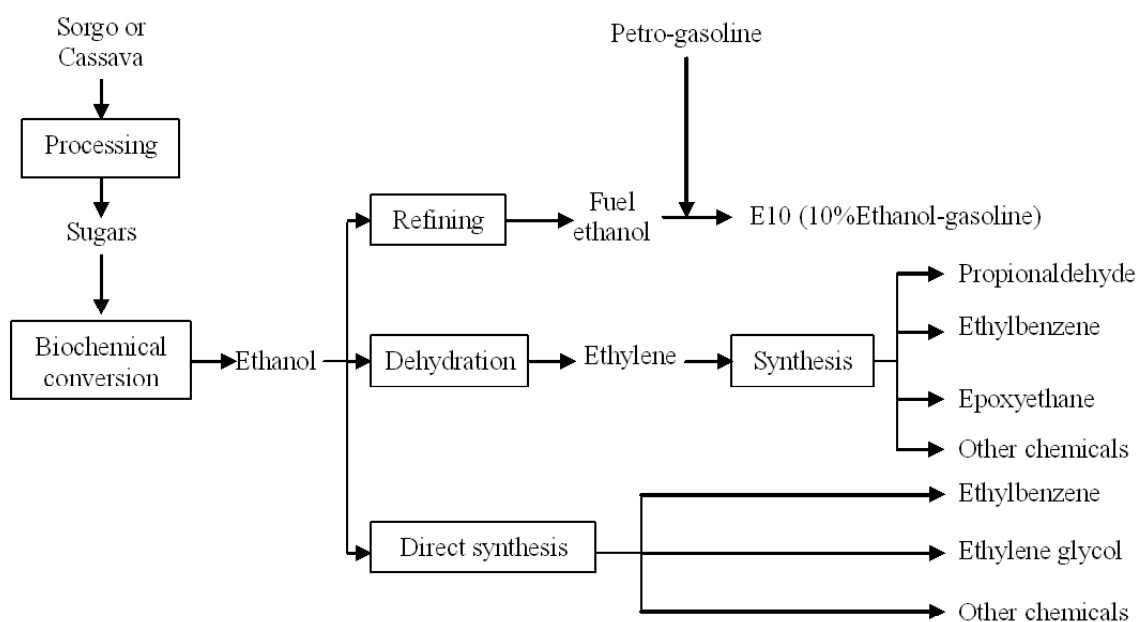


Fig. 1 Scheme of fuel-ethanol refinery

Developing the microzyme tolerant to ethanol and high temperature to raise the fermentation concentration and temperature etc.

2.1.2 Fuel ethanol refinery

Not only fuel ethanol but also chemicals in fuel ethanol refinery as shown in Fig. 1.

In the figure, sorgo or cassava is processed into sugar first, and then converted to crude ethanol by biochemical conversion. The crude ethanol is refined and concentrated to anhydrous ethanol, which is blended with petro-gasoline by the ratio of 10% to produce E10 gasoline. There are two ways to make chemicals from ethanol. The first one is ethanol dehydration to produce ethylene, from which as a widely used raw chemical material, many chemicals such as acetone, styrene and ethylene oxide can be made. The second one is direct synthesis of some chemicals from ethanol, such as ethyl benzene and glycol.

Much research should be completed first before fuel ethanol refinery is established, as described below. 1) In the sugar fermentation step, it is needed to develop excellent fungus species and high-efficiency reactor; 2) In the crude ethanol concentration step, the rectification technique and equipment can be further optimized, such as adopting membrane separation; 3) In the ethanol dehydration step, developing fluidized bed-based ethanol dehydration technique to replace fixed bed technique is needed; the advantage of the technique is that the ethylene product is of high purity and can be used as raw material to directly synthesize basic organic chemicals, but it must be further refined when used for producing polyethylene. In order to decrease the dehy-

dration temperature, molecular sieve catalysts are being developed in the world; 4) There is still much work to be done in the direct synthesis of chemicals from ethanol.

At present, fuel ethanol is the main product of fuel ethanol plants, but chemicals are also produced in some of the plants. The main chemical is ethylene, the cost of which is less than 6800 ¥/t, lower than that of petro-ethylene whose cost is more than 7000 ¥/t. Since the price of crude oil increasing rapidly, using ethanol to produce ethylene, which is used as raw material for chemical production, can thus obtain high profits. However, although the cost of bio-ethylene is lower than that of petro-ethylene, bio-ethylene has no advantages over petro-ethylene in terms of the scale of production. The scale of petro-ethylene plants has reached 200–400 thousand t/a, but only 50–100 thousand t/a is suitable for bio-ethylene, because its scale is limited by the collection, transportation, storage and seasonal growth of the raw material.

2.2 Biorefinery based on rapeseed oil and cottonseed oil

Biodiesel, which is defined as the monoalkyl esters, mainly methyl esters (FAME), of long-chain fatty acids derived from renewable biological sources, such as vegetable oils and animal fats, is considered as a possible substitute or extender of the conventional diesel fuel. The production capacity of biodiesel in China is more than 100 thousand t/a. Most of the biodiesel is produced today by Hainan Zhenghe Bioenergy Corp, Sichuan Gushan Oil & Fat Chemical Corp and Fujian Zhuoyue New Energy Development Corp. They all use waste edible oil or saponifiable oil as raw material and have the production capacity of 10–20 thousand t/a each.

Recently, Yuanhua Energy Technique Corp. has invested 36 million Yuan RMB to set up a 30 thousand t/a biodiesel plant in Fujian Province. In addition, it was reported that several foreign corporations came to China to set up biodiesel plants. A U.S. company will invest 50 million U.S. dollars to set up a 50 thousand t/a biodiesel plant in Shanghai [10]. An Austrian company will set up a 250 thousand t/a biodiesel plant in Weihai, Shandong Province [11], and an Italian company will set up a 200 thousand t/a plant in Jiayusi, Heilongjiang Province [12].

2.2.1 *The production and supply of raw material is the key for biodiesel development*

Generally speaking, the price of vegetable oil accounts for 70%–85% of the total cost of biodiesel. The property and composition of vegetable oil affect the process flow scheme and the kinds of products produced, the yield of raw material per acre affects the scale of production (from a few thousand to 200 thousand t/a), and the collection, transportation, logistics radius and the local market size of the oil product affect the location of the plant. Therefore, Watkins suggested performing a four-step feasibility study before planning the construction [13], which begins with an in-depth feedstock market analysis (availability and suitability), followed by an examination of the diesel fuel market segment and an analysis of potential customers. Next, Watkins recommended the potential investors to analyze the current legal system and look for ways to establish a supportive biofuels policy. Finally, the results of all these analyses lead to the selection of the most appropriate process technology.

Vegetable oil is low-density-energy biomass, which limits the production scale of biodiesel, so the biodiesel production cost can't compare with that of petro-diesel hydrogenation unit which is usually 1–2 million t/a in scale. However, a biodiesel plant has the advantage of much lower investment and rapid construction. Considering the collection and transportation of the raw materials, the plant should be set up near the harbor or railroad if the production capacity is larger than 50 thousand t/a. However, if the raw material isn't easy to collect, or its amount is not very large, only plants of few thousand to 20 thousand t/a can be considered, and they should be set up near the producing area, or mobile production equipment is adopted. The supply of vegetable oil is seasonal, so different kinds of the raw materials should be used to ensure the continuous production for the whole year.

Because China has a large population, the selected raw materials of biodiesel should not affect the edible oil market. Based on the results of investigation, rapeseed oil, cottonseed oil, imported soybean oil and wild-plant oil can be used as the raw materials for biodiesel, but for large scale production only rapeseed oil and cottonseed oil can be used in the near future.

1) Rapeseed oil

Rape is a good oil crop with wide adaptability, wide uses

and high economy value. Most rape are planted in winter. There are about 9 million hectares of farmland not in use during winter in China. This farmland can be used to grow rape and produce biodiesel, and it is possible to produce more than 3 million tons of biodiesel a year. China has excellent rape species and many species have been widely used, such as Qinyou-2, Rongyou-3, and Huaza-4 etc. China also has the optimal technique of rape planting. Canola oil is the raw material for producing B100 biodiesel, and it can be planted in China too.

2) Cottonseed oil

China produces the most cotton and cottonseed in the world. The cottonseed output was 9 million tons in China in 2004, and the corresponding amount of cottonseed oil is 1.8 million tons, but the oil statistic consumption of that year is only 0.89 million tons. The difference is possibly caused by 1) low-level technique in oil expression; 2) oil loss in the process of removing gossypol; 3) not all the cottonseed was expressed to produce oil. When used as edible oil, cottonseed oil is not as good as soybean oil and canola oil etc, and the ratio of cottonseed oil in edible oil market will decrease continuously. A lot of cottonseed oil will become excess produce and it can be used as raw material of biodiesel. There are three cotton sections in China: the Northwest section, the North China section and the section of lower and middle reaches of the Yangtze River. The three sections all have cotton collecting stations, and the cottonseed can be collected there too, making it easy for collecting cottonseed for use in biodiesel production.

The important factor for biodiesel production is the price and steady supply of vegetable oil. In order to increase the competitiveness of biodiesel in the fuel market and accelerate its development, the present price of vegetable oil should decrease to a lower level. New rape or cotton species is needed. Methods of planting, harvest, storage and transportation etc should be improved, and both the oil crop and seed should be utilized. In this way, the biodiesel plants can obtain low price and enough raw materials in the future.

Another key problem for biodiesel production is the processing technology. The base-catalyzed transesterification technology is now widely used, however it has the following drawbacks [14]: it is energy intensive, recovery of glycerine is difficult, the catalyst has to be removed from the product, alkaline waste-water requires treatment, and free fatty acids and water interfere with the reaction. In order to minimize the influence of these problems the Research Institute of Petroleum Processing (RIPP) of Sinopec is developing two technologies: the high-pressure transesterification technology and the reaction–separation coupling transesterification technology.

High-pressure transesterification technology has the following advantages: simple pretreatment of raw material, wide adaptability to various raw material, no catalyst used, and high concentration glycerol produced etc. Low quality raw material such as waste edible oil and high quality raw material such as crude rapeseed oil or cottonseed oil all can be processed by this technology, and the production scale

may vary from 10–20 thousand t/a to 50–200 thousand t/a. In the reaction-separation coupling transesterification technology, the transesterification reaction, glycerol separation and methanol distillation are coupled in one set of equipment. This technology has the following advantages: short process scheme; short reaction time (10–30 min), high conversion (~100%) and FAME selection (~99%) and easy separation of glycerol from crude products etc. This technology is suitable for building 50–200 thousand t/a plant with steady supply of rapeseed and/or cottonseed oil.

The most important current task is to commercialize these advanced technologies, and industrial demonstration units should be built first.

2.2.2 Biodiesel refinery

A biodiesel refinery produces not only biodiesel but also chemicals, which is shown in Fig. 2.

Rapeseed or cottonseed oil reacts with methanol to produce fatty acid methyl esters and glycerol. FAME is biodiesel and generally blended with 80–98 percent petro-diesel for engine use. After further refinement, FAME can also be used as biodegradable solvents, such as used in paint strippers replacing methylene chloride, printing ink press cleaners replacing toluene, adhesive removers replac-

ing acetone and graffiti removers replacing mineral spirits [15]. In addition, FAME is a chemical intermediate for manufacturing many commodity chemicals such as higher alcohols.

All these chemicals have higher prices, and will increase the profits of biodiesel plants. The chemicals made from FAME has formed a new growing industry in USA. The production and sales status of soybean methyl ester-derived products in USA in 2004 is shown in Table 1.

Glycerol is an important chemical product and has versatile uses. The main application area is in food and beverage, pharmaceutical, cosmetic, tobacco, paper making and printing, and textile industries etc. The new use for glycerol is to make 1,3-PDO. With the increased production of biodiesel, more and more glycerol is produced in the world, and thus used as raw material to produce 1,3-PDO, di-propyl glycol etc.

Before a new biodiesel refinery is set up, besides the fuel market, local market survey of related chemical products should be done to determine what will be manufactured in the biorefinery. The biodiesel production capacity also affects the choice of products manufactured. The direct utilization of FAME and glycerol is generally chosen in a 10–20 thousand t/a plant, more value-added commodity and fine chemicals can be manufactured in a 50–200 thousand t/a plant.

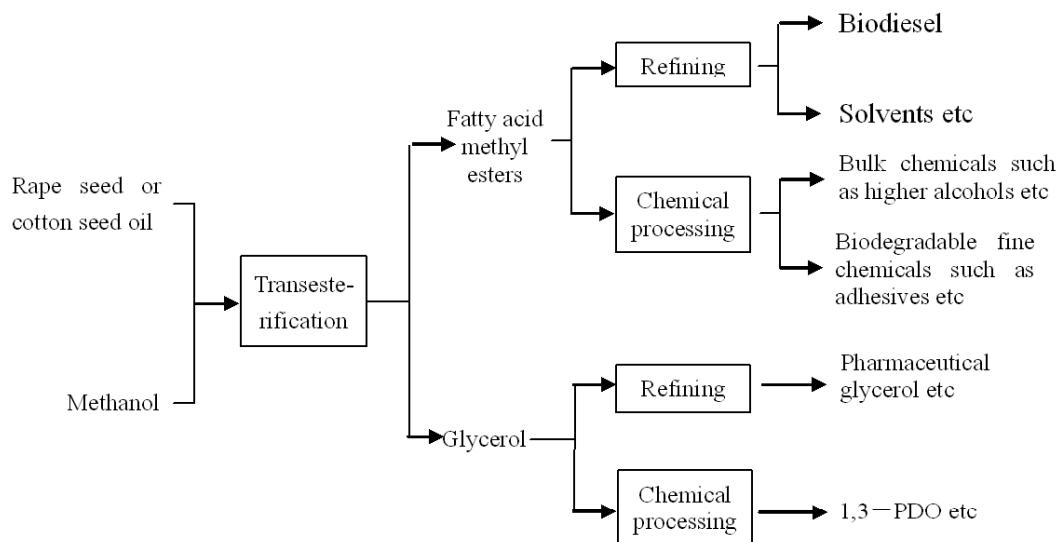


Fig. 2 Scheme of the biodiesel refinery

Table 1 The production & sales status of soybean methyl ester-derived products in USA [16]

Products	Producer and suppliers	Products	Producer and suppliers
Adhesives	2	Agricultural adjuvants	5
Dust suppressants	6	Dielectric fluids	2
Hydraulic fluids	5	Industrial cleaners	29
Industrial lubricants	13	Metalworking fluids	13
Odor reduction	2	Paint strippers	6
Printing inks	29	Printing supplies	3

There is only so much petroleum in the earth, and as time passes, the oil will become increasingly rare, so the petroleum fuels and petrochemical products will turn to the renewable biomass as feedstocks. This transform is already in progress. Let us strengthen the research and development work in China on biorefinery to meet the future challenges.

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