Preparation Technology of Biodiesel and Its Trend

Jiang Jianchun

No. 16, Suojin V Village, Xuwu District, Nanjing City, Jiangsu Province, 210042

Tel: 025-85482488；Email: bio-energy@163.com

http://www.forinchem.com

Outline

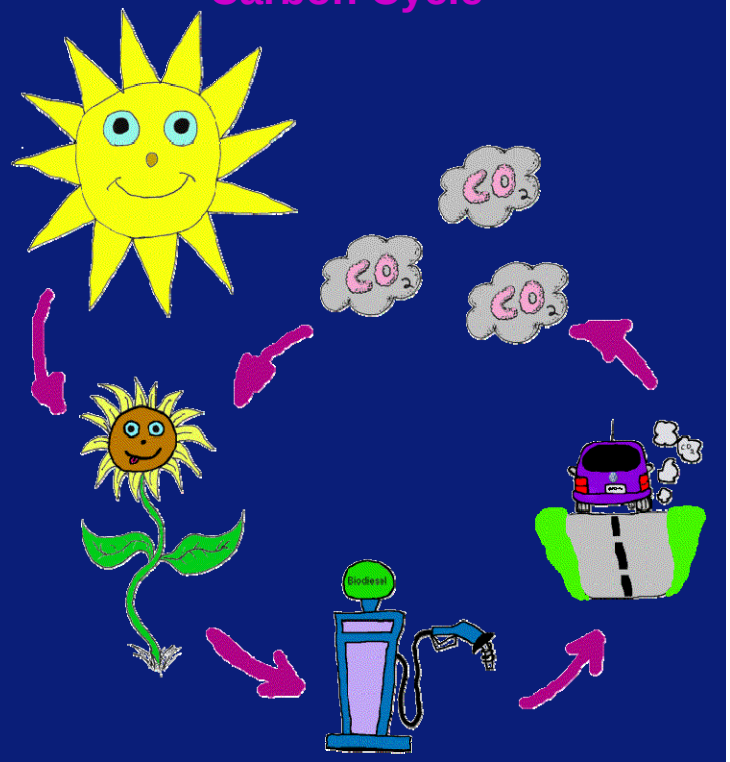
I. Overview
II. Preparation technology of bio-diesel
III. Preparation of bio-diesel and chemical products
IV. Development trend
V. Conclusion

1. Overview

Characteristics of bio-diesel:

- A form of renewable bio-energy;
- Practical and no motor modification is needed;
- Ideal replacement of liquid fossil fuels;
- Pollution-free renewable green energy;
- Environmental-friendly;
- Included in the National Development Plan.

Biodiesel's Closed Carbon Cycle



1. Overview

- The typical definition of biodiesel is long-chain fatty acid methyl esters through synthesis of raw materials—renewable animal and vegetable oil. It is similar to chemical diesel in physical and chemical property and is an environmental-friendly fuel oil which may replace chemical diesel or solve with ordinary chemical diesel at any proportion.
- With the scientific and technological development, we consider to define the biodiesel as: Liquid fuel oil produced by biomass as raw material and through chemical, physical and biological technology with similar nature as chemical diesel, which can replace chemical diesel and used for transportation industry.

1. Overview

Advantages:

- **Meet national development strategy and not fight for land against grain production;**
- **Consider both ecology and benefit;**
- **Extend industrial chain and increase job opportunities, benefit new rural construction;**
- **Rich biological resources in forest trees, which can provide benefits through effective planning;**

Production, import and import dependency of China's oil industry

Year	Net import	Annual consumption	Output	Dependency (%)
1993				
1994	290	14964.72	14674.72	1.9
1995	848	15749.96	14901.96	5.4
1996	1388	17239.81	15851.81	8.1
1997	3385	19604.85	16219.85	17
1998	2920	18937	16016	15.4
1999	4400	20400	16000	21.5
2000	7000	23300	16300	30
2003	9739	26722	16983	36.4
2004	14373	31823.3	17450.3	45.1
2005	13643	31785.22	18142.22	42.9
2006	16287	34655	18368	47
2910	17820	36300	18480	49
2015	18900	37500	18600	50.4
2020	26500	46000	19500	57.6

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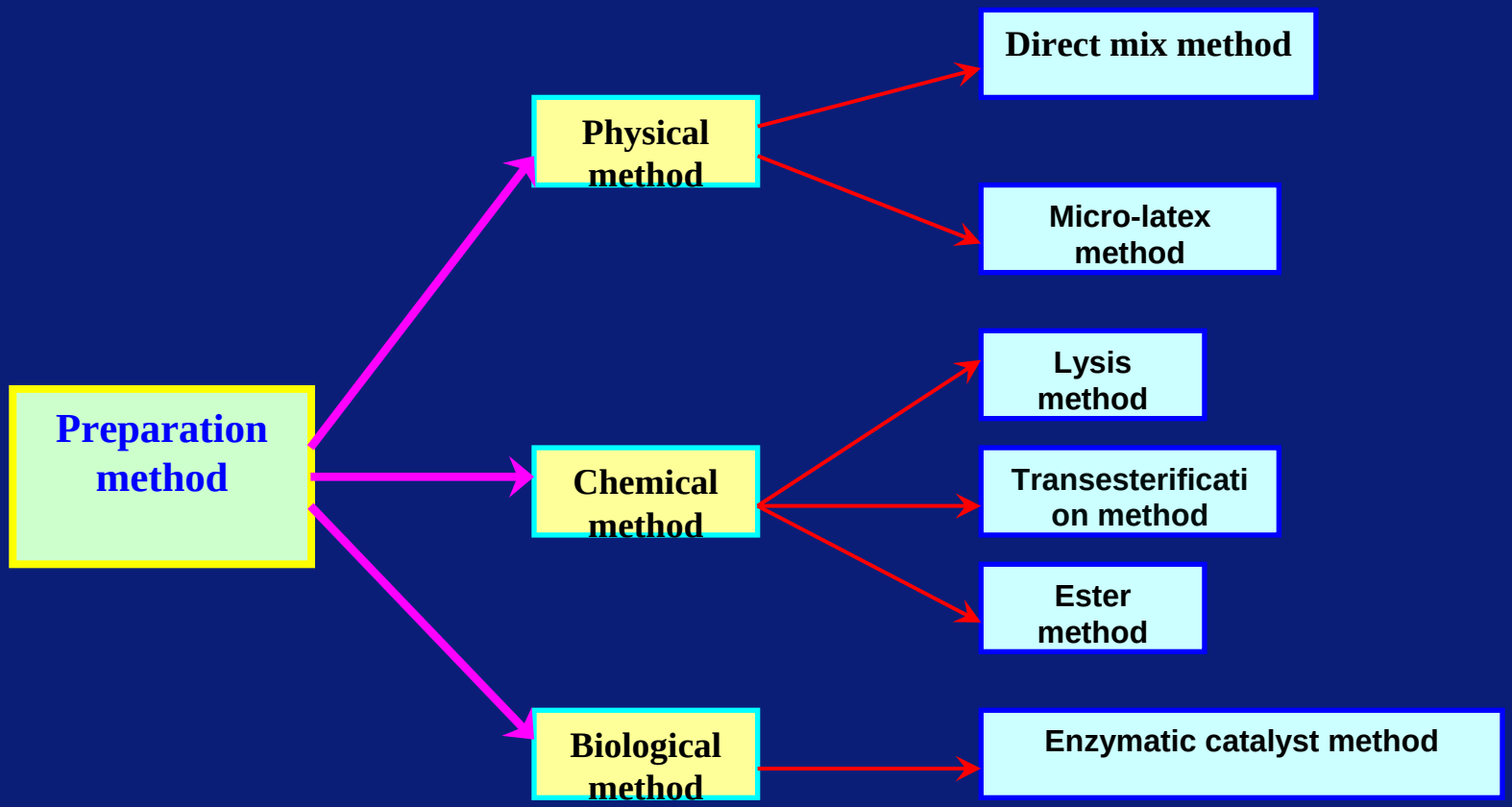
1. Overview

- At present, American annual production capacity of biodiesel remains above 1 million tons; EU has exceeded 2 million tons in 2005; German accounted for 1.5 million tons.
- European Commission plans to achieve 8-10 million tons in 2010 and 12% market share in 2020

1. Overview

- China's biodiesel industry is fallen behind but develops rapidly;
- Currently there are over 30 biodiesel plants, but mainly are small scale ones with production below 20,000 tons per year;
- Some biodiesel plants with 100,000-700,000 tons of production capacity are under construction. According to the statistics in a report, currently 3.5 million tons of production capacity is under construction;
- Raw material is the core factor restrain biodiesel development.

2. Preparation technology of biodiesel



2. Preparation technology of biodiesel

3.1 Physical method

3.1.1 Direct mix method

- In 1983, Adams and others directly sprayed degummed soyabean oil and 2# diesel to the turbo-engine for 600h experiment. When the two were mixed at 1:1 scale, the lubricant thickened and gelled. But the phenomenon did no occur at 1:2 scale, so it can be used as replacement of agricultural machineries.
- Ziejewski and others mixed sunflower oil and diesel at 1:3 scale, measured the mixture viscosity below 40℃ and got 4.88×10-6m^2/s, while ASTM regulated the maximum viscosity shall be lower than 4.0×10-6m^2/s, so the mixture is not suitable to use for long time in the direct-injection diesel engine.

3.1.2 Micro-latex method

Mixing animal and vegetable oil with solvent to get micro-latex liquid is one of the solutions to high viscosity of animal and vegetable oil. Micro-latex is a kind of transparent and thermally stable colloidal dispersion, and a colloidal balance system with 1-150nm diameter mixed by two mutually insoluble liquids and ion or non-ion amphoteric molecules.

In 1982, Georing and others made micro latex by ethanol-water solution and soyabean oil, whose nature is similar to 2# diesel except lower Cetane value.

Zieiewski and others made latex by 53.3% winterized sunflower oil, 13.3% methanol and 33.4% 1-butanol, which did not seriously worsen in 200h durability laboratory experiment, but carbon deposition and lubricant viscosity increase occurred.

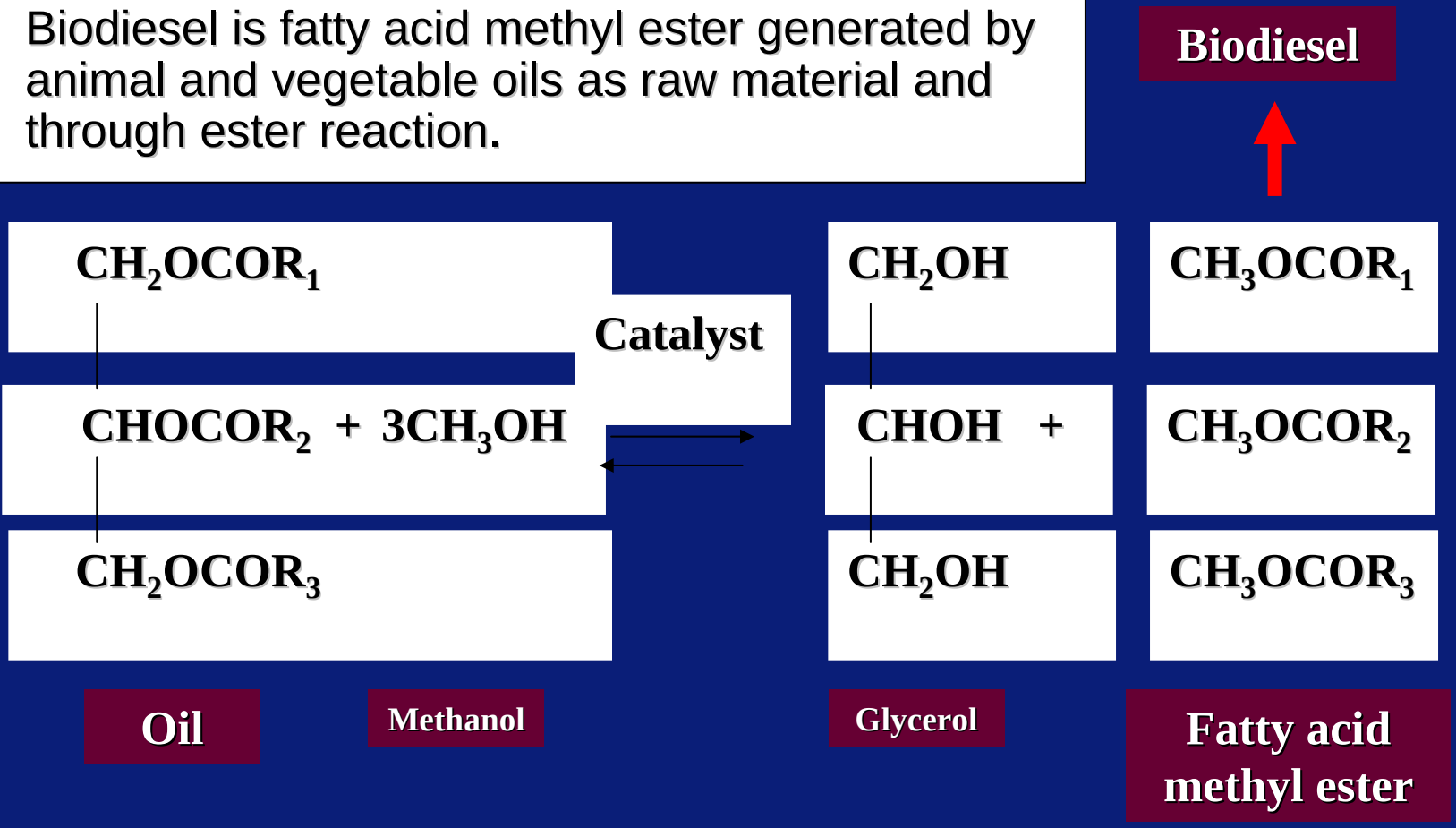
3.2 Chemical conversion

3.2.1 High temperature lysis method

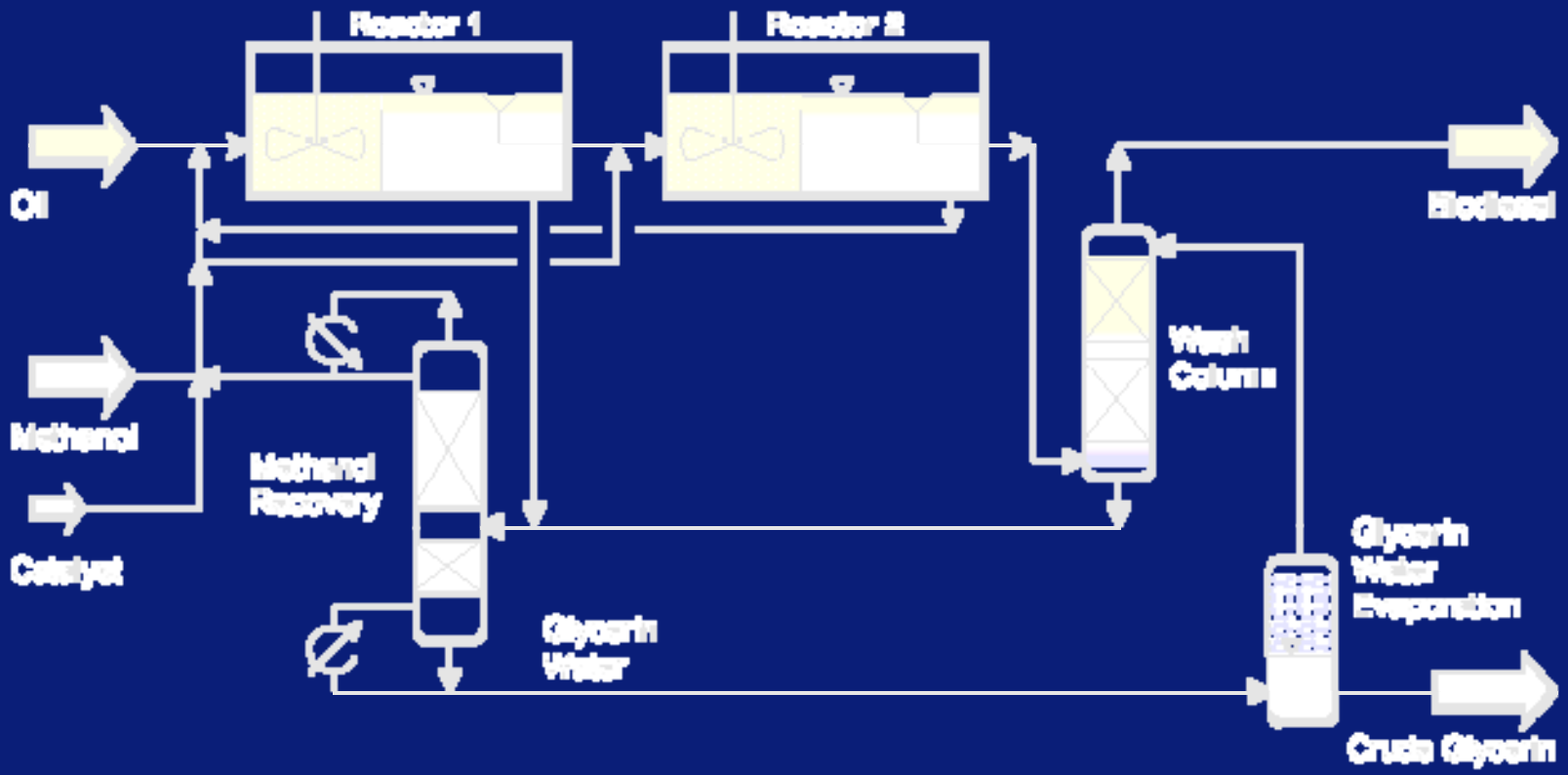
- Thermal lysis quickly breaks the organic high polymer in substances into short-chain molecules with the effect of thermal or thermal catalyst, and maximize carbon and gas to get fuel oil.
- The thermal lysis of vegetable oil aims at synthesizing petroleum. The alkyl and alkene contents are found high in products from thermal lysis of soyabeam oil, the viscosity of lysis products drops by over 3 times in contrast with ordinary soyabean oil, but the figure is still far higher than the viscosity of ordinary diesel, while cetaine and thermal value are similar with ordinary diesel. Coco oil and palm oil can produce gaseous, liquid and solid products after catalyzation and lysis under 450℃ with the catalyst SiO_2/Al_20_3, this biodiesel is very similar to ordinary diesel in terms of nature.
- Thermal lysis is easy in operation, raw material is fully used, but the equipment is expensive, the reaction products are difficult to control, unsaturated hydrocarbon content in products is high, and the oxygen is lost in the form of CO2 after thermal lysis.

(2) Biodiesel

- Biodiesel is fatty acid methyl ester generated by animal and vegetable oils as raw material and through ester reaction.



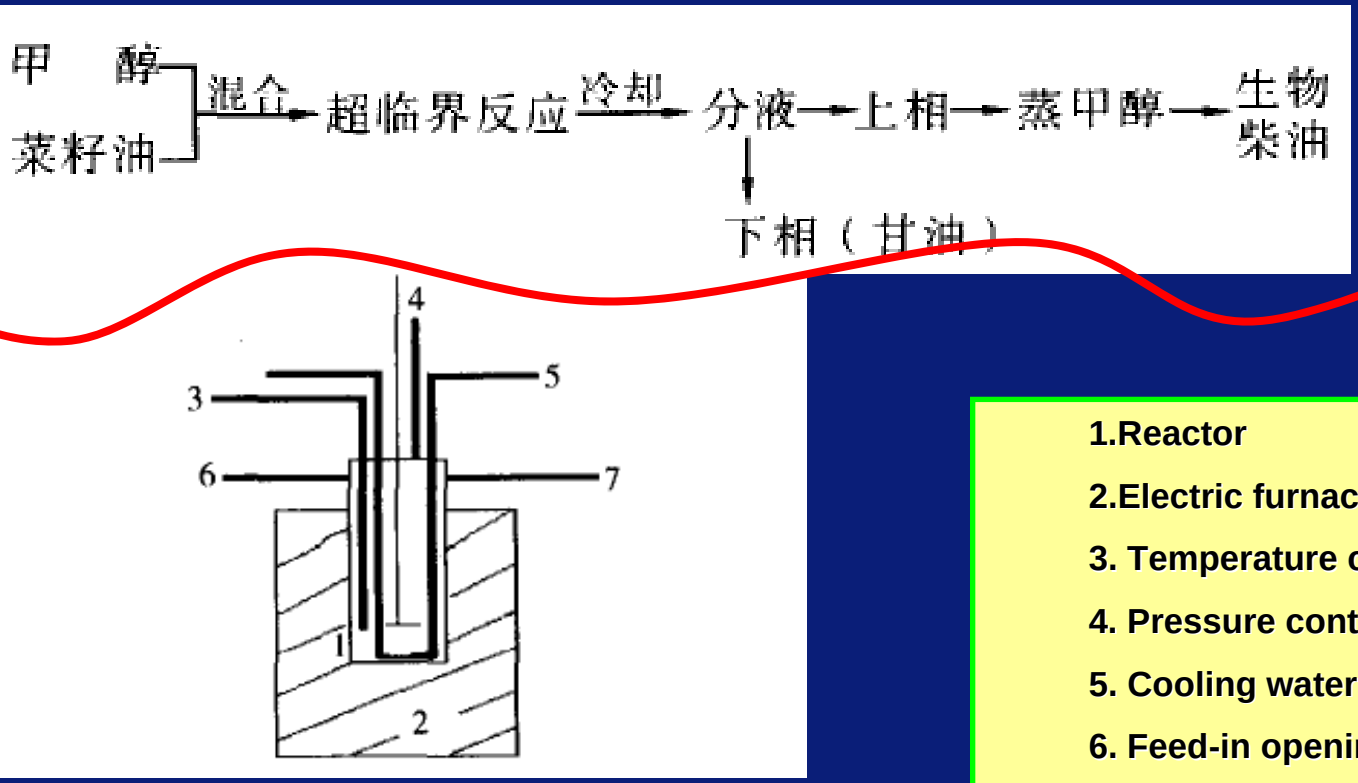
（2）Biodiesel



Biodiesel technology with liquid acid and alkali as catalyst

3. Status quo of industrialized development of biomass energy

3.2.3 super-critical method



Sketch of biodiesel preparation with super-critical methanol method

1.Reactor
2.Electric furnace
3. Temperature controller
4. Pressure controller
5. Cooling water
6. Feed-in opening
7. Feed-out opening
8. Mixer

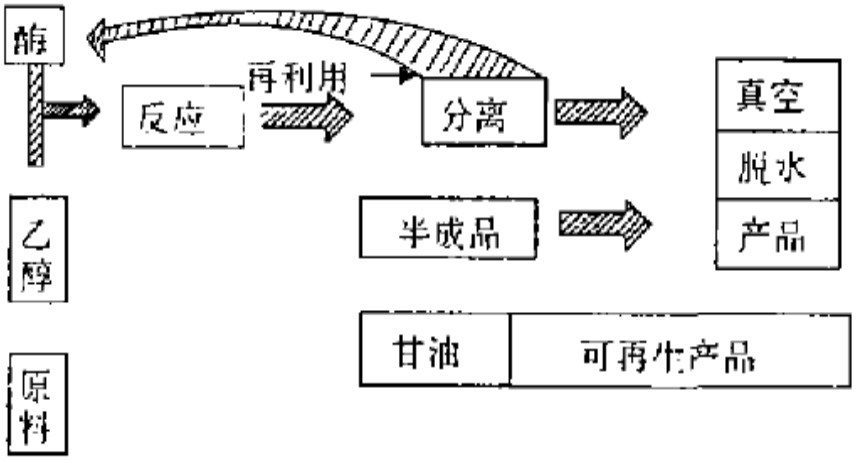
3. Status quo of industrialized development of biomass energy

3.2.3 Super-critical method

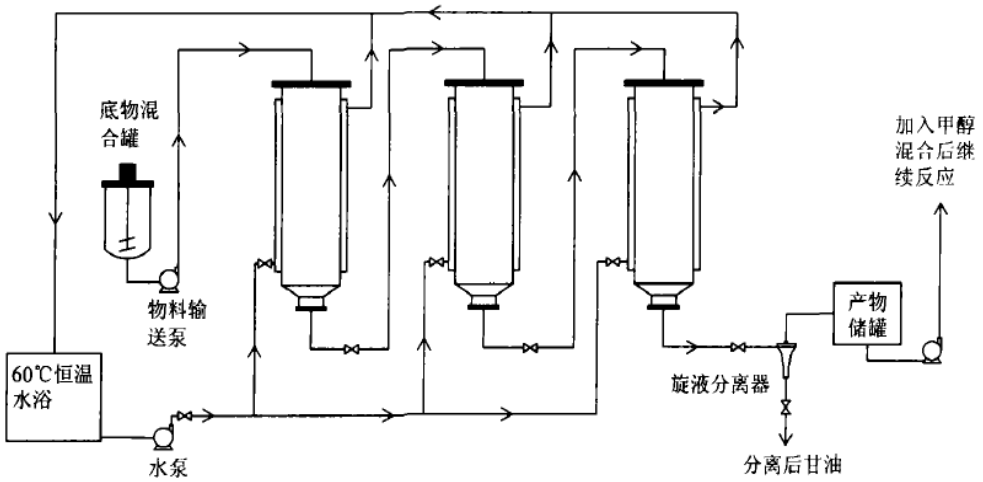
- Preparing biodiesel by super-critical flow technology overcomes the disadvantage of tradition transesterification method. Currently the super-critical preparation technology of Yokogawa Chemical was applied in practice, producing fatty acid methyl ester through action between soyabean oil or colza oil and super-critical methanol.
- Biodiesel requires highly on raw material; the production requires high temperature and high pressure; production cost and energy consumption and industrialization degree all remain high; project is needed to magnify the research and verification of economic feasibility.

3. Status quo of industrialized development of biomass energy

3.3 Use bio-enzyme to catalyze transesterification

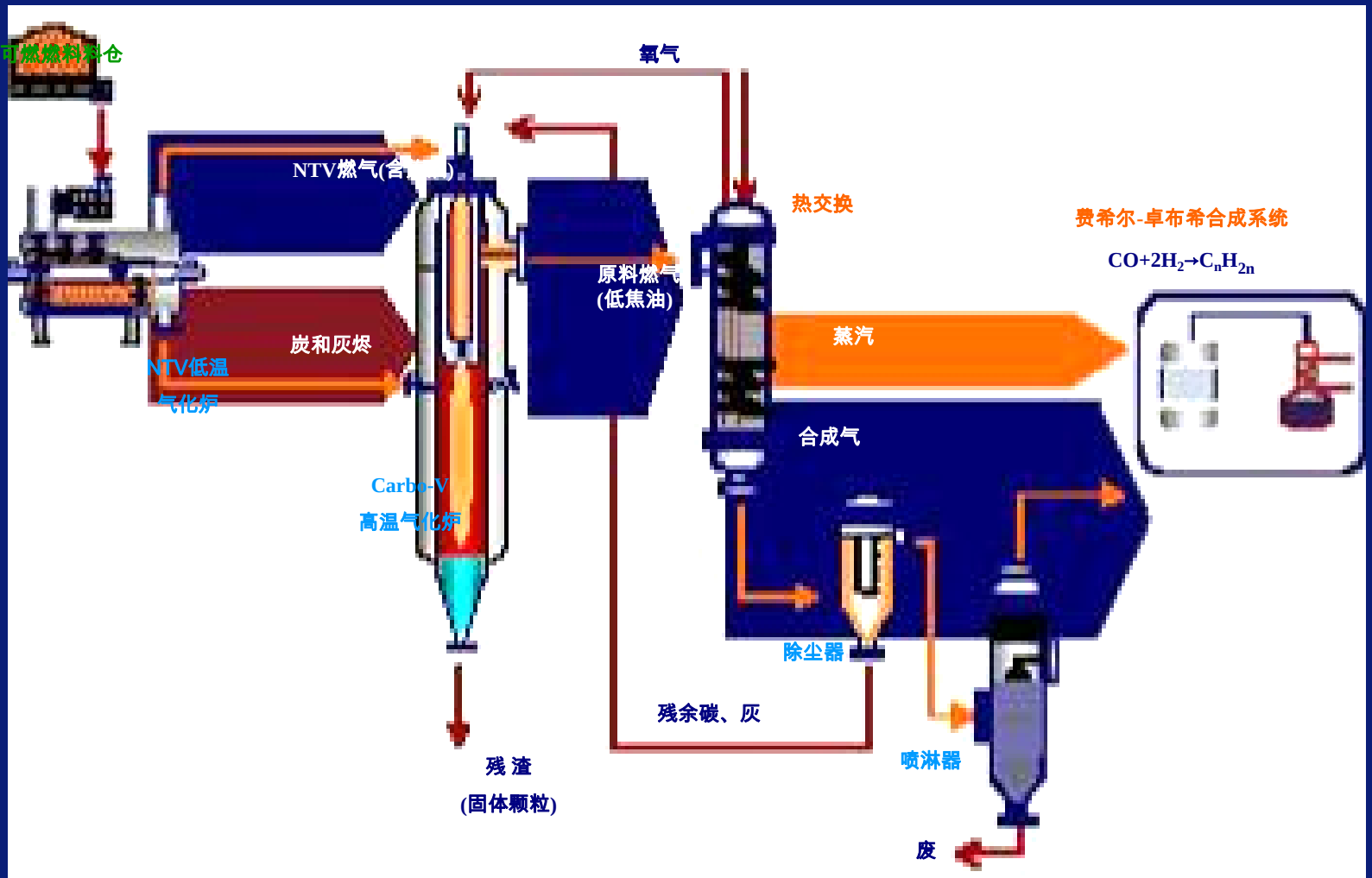


Biodiesel production technology by enzyme method



Fixed-beds reactor produces biodiesel

3.4 New synthetic technology of biodiesel



Sketch of production of synthetic automobile fuel by gasified biomass in Choren

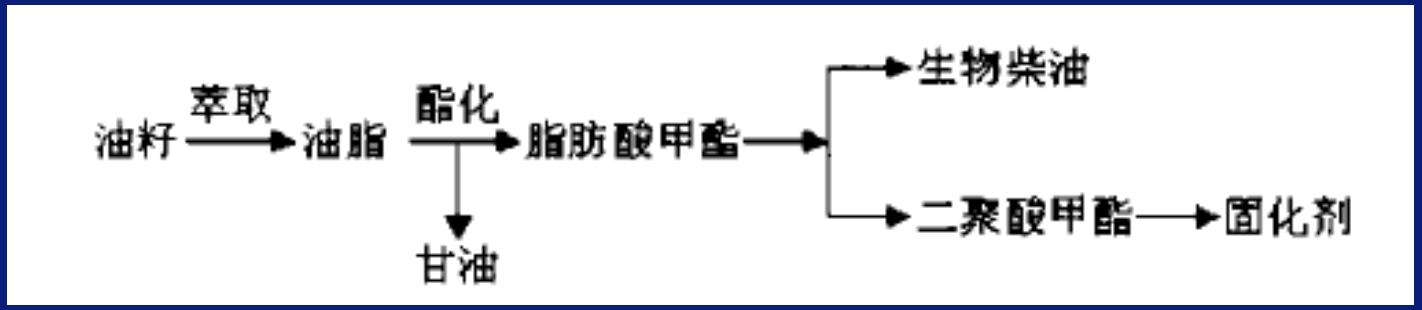
3.5 Other technologies

- Use trickle bed reactor to study the reaction of oil alcoholysis, the production rate of fatty acid methyl ester goes beyond 95%. This method overcomes some disadvantages of remittent mix reaction vessel, not only reducing power consumption and production cost, but also realizing continuous production.
- Prepare fatty acid methyl ester through esterification reaction by adding aether co-solvent and generating single phase with glycerol trioleate and methanol.
- THF, as the inertia co-solvent, can be turned into tri-plural mutual soluble system with waste frying oil and methanol, then synthesize biodiesel. Compared with non-average-phase synthesis method, it can create single-phase mutual soluble system, which can significantly reduce reaction temperature, shorten reaction time and lower thermal consumption, but also can reduce catalyst use, release catalyst's corrosion to equipment and the difficulty in post-treatment of products.

- Use ethylene glycol monomethyl ether and refined soyabean oil to synthesize a new biodiesel--Ethylene Glycol Monoethyl Ether Soyate single ester.

3.5 Other technologies

- American LASTELLA JOSEPH P studied on realizing economical and effective biodiesel fuel production by using continuous flow process to enable raw material oil pass through a series of mixing tanks and separation tanks, but sulphur shall be used in the reaction, this requires highly on equipments.
- The Institute of Chemical Industry of Forest Products of Chinese Academy of Forestry Science researched and developed economical and practical comprehensive processing and utilization technology to prepare biofuel and byproduce chemical products



Comprehensive utilization of biodiesel and chemical products

- Make full use of different chemical structures in oil: e.g. there is double bond structure, under certain conditions, position isomerism caused by proton transfer and geometrical isomerism easily occur. Under the effect of high temperature, the formed isomerism may further experience isomerism, and become conjugated double bonds in trans configuration, rapidly Diels-Alder react with other double bonds and form dimer.
- Get high value-added products by separating effective elements in oil.

Ingredient analysis of several raw material oils

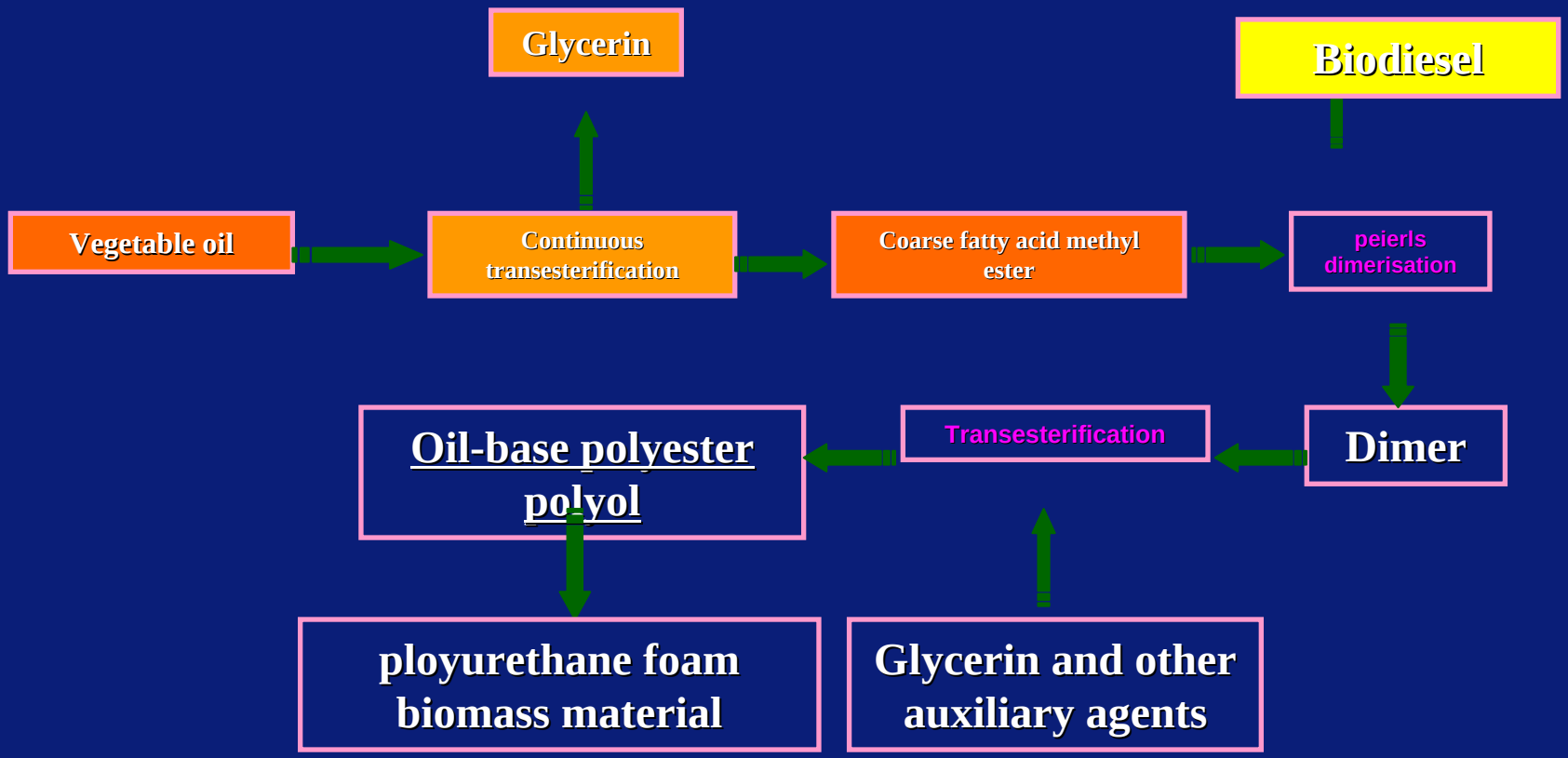
No.	Fatty acid	Crude colza oil	Colza salad oil	Hogwash oil	Kosteletzktya virginica oil	Acidified soyabeam oil
1	Palm oil	5.5434	4.9690	14.6631	24.7104	24.320
2	Stearic acid	1.7756	2.0335	3.4999	1.8934	2.380
3	Oleic acid	33.1390	55.3824	38.7934	13.8600	17.84
4	Linoleic acid	17.0686	20.5901	41.2127	43.3087	51.55
5	Linolenic acid	6.9591	8.5477			
6	Erucic acid	16.1791	0.8894			
7	Other	19.3352	7.5879	1.8309	11.2300	3.91

Comprehensive utilization of biofuel and chemical products

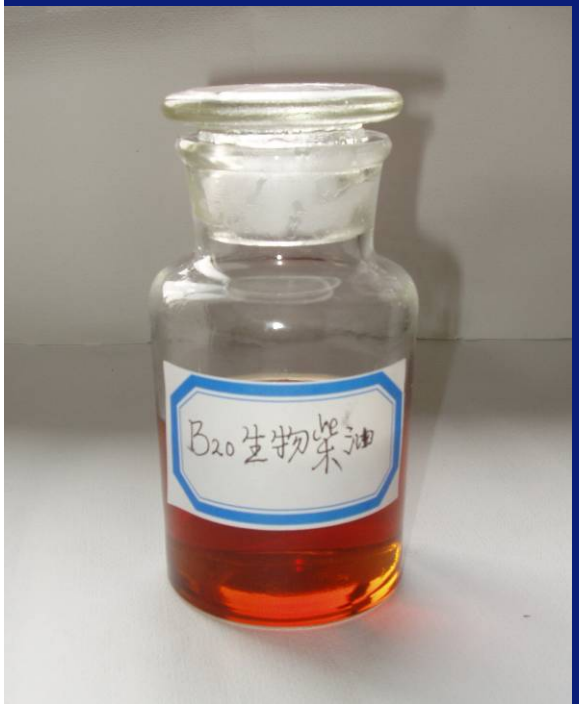
Objective: Aiming at the poor comprehensive economic benefits and big raw material quality difference existing in domestic biofuel production, develop comprehensive production technology of biodiesel and chemical products which can be made by wide ranges of raw materials, realize the industrialized target of econimical and practical preparation of biodiesel to partly replace petro-chemical fuels and reduce environmental pollution (Realize comprehensive utilization of energy material and improve economic practicality)

Diesel and chemical products

Technological flow



◆B20 biodiesel, the price of biodiesel raw materials can be increased



Itemh	Technical requirement	Unit	B20
Density, 20℃	820-860	kg/m^2	836
kinematic bunching viscosity ，40℃	3.0-8.0	mm^2/s	4.7
Flash point (closed slot)	≥55	℃	98
Condensation point	≤4	℃	-2
Carbon content (quality point)	≤0.05	%	0.025
Ash (quality point)	≤0.01	%	痕迹
10% carbon residue (quality point)	≤0.3	%	0.15
Mechanical impurity	无	/	无
Cetane value	≥49	/	50.5
Sheet copper corrosion，50℃，3h	≤1	级	1

B20 biodiesel basically meets the Standard of Diesel for Automobile Use GB/T19147-2003 in terms of performance index.

（1）Infrastructure construction

Raw material and finished products warehouse and irrigated area 5600m²

（2）Product line construction

Bird-eye View of the Product Line

（2）Product line construction

Product line of biodiesel

（2）Product line construction

ransfer oil furnace

DCS auto-control

Nitrogen generator

ilm evaporator

Rectification tower

Filter

Test report

Item	Result	Method
Density 20℃ , kg/cm^3	877.3	GB/T 1884
Distilled process: Initial distillation point, ℃ 10% evaporation temperature℃ 50% evaporation temperature ℃ 90% evaporation temperature ℃ Final distilled point ℃ 350℃ distilled, mL	334 337 343 / / 76.0	GB/T 6536
Sulfur content, (UV fluorescence method), %(m/m) kinematic bunching viscosity (40℃) mm^2/S Flash point (closed slot), ℃ Freezing point, ℃ Carbon residue (Conradson method), % Ash, % (v/v) Water content, % (v/v) Mechanical impurity, % Cold filtration point Sheet copper corrosion (50℃，3h), grade Cetane value	0.005 7.93 > 140 — — — Mark — — < -3 60	GB/T 380 GB/T 265 GB/T 261 GB/T 510 GB/T 268 GB/T 508 GB/T 260 GB/T 511 GB/T 0248 GB/T 5096 GB/T 386

Record of energy consumption and product yield rate

Material	Colza oil	Methanol	Catalyst
	1000 kg	320 kg	10 kg

Feed-in time	0.33hr
Heating time（25-100℃）	0.5hr
Dehydration time	1hr
Response time	2hr
Static time	Overnight
Methanol recycling time	2 hr
Feed-out time	0.2hr
Time consumption	6hr

Power consumption:110kwh Energy consumption: 60 kg diesel Water consumption: 2m^3 Worker's salary: RMB100yuan

Product: Biodiesel (Theoretic weight 1004kg) Crude

Stand experiment of biodiesel

- When diesel engine is consuming biodiesel specimen, the diesel engine can operate properly without any irregular phenomenon.
- Under the precondition of constant power, the fuel consumption of diesel engine increased when using biofuel, but the thermal efficiency obviously increased when working under part of loads, and the fuel consumption efficiency increased.
- When using two kinds of fuel oils, the emission index of diesel engine can meet the emission limit at Phase II of EPA. Compared with diesel, the CO of biodiesel reduced by 24.1%, THC reduced by 51.1%, PM reduced by 63.72%, and NO_X increased by 17.96% in contrast with the emission.
- The standard-meeting margin of CO, HC and particles emission of diesel engine increased in contrast with ordinary diesel, in the following in-depth research, discuss how to appropriately delay the oil supply oil angle advance of diesel engine and study the combustion mechanism of biodiesel in depth to reduce NO_X emission, so that to reduce the creation of harmful emissions from the diesel engine.

Main technical characteristics and innovations

- Use the byproduct dimer and blycerin from the production of biodiesel to prepare polyol adipate, while improving the cost-effectiveness and obtaining the polyurethane intermediates, enabling comprehensive utilization of oils from different sources without any organic waste discharge, as well as meeting the objective of clean production.
- Use oil-based polyester polyhydric alcohol prepared by dimer, blycerin and other polyhydric alcohols through transesterification to separate fatty acid methyl ester free from double bonds for use as biodiesel, which does not influence the product performance, its effective function groups can fully replace petroleum polyester and polyaether polyhydric alcohol without influencing the heat insulation and size stability of polyurethane products.

Main technical characteristics and innovations

- Use independently designed pipeline reactor with special structure, quickly mix and detract raw material liquid after peierls dimerisation and transesterification, improving reaction speed, shortening reaction time and saving energy consumption so as to realize the objective of continuous production.
- Use independently developed green catalyst to accelerate oil products dimerization, transesterification and rosin dienes addition, dehydrated esterification, which improves the safety in operation, reduces environmental pollution caused by catalyst, realize continuity of reaction and minimized energy consumption so as to achieve the objective for clean production.

- **Favorable economic returns:**
  - **Oil RMB6000 yuan/ton, waste oil price is even lower;**
  - **PO: RMB13000 yuan/ton, purified anhydride acid : RMB11000 yuan.**
  - **Petrochemical polyester and polyaether polyhydric alcohol: RMB 14000 yuan/ton;**
  - **The project products: Assume the price as RMB 12000 yuan/ton, which are competitive on market.**

- **Applied for 8 national patents, of which 2 have been authorized and 1 has been publicized:**
  - **Preparation method of biodiesel by natural oil**
  - **Preparation method of biodiesel by equal-phase continuous reaction**
  - **Preparation method of dimer fatty acid polyhydric alcohol and application to polyester foam**
  - **A method to prepare Monoglycerid Ester by waste oils**
  - **Method to prepare fatty acid polyaether polyhydric alcohol by recycled oils and its uses**
  - **Rosin polyester polyhydric alcohol used for hard polyurethane foam plastics and its preparation method**
  - **Rosin polyaether polyhydric alcohol used for hard polyurethane foam plastics and its preparation**

5. Conclusion

Development opportunity of biomass energy:

Environmental problems increased by GHG forced people to emphasize limitation on use of fossil energies.

Fossil energy, especially oil resource, hardly meets demand due to its limitedness.

traffic

life demand

power

....*supply* products

5. Conclusion

- At present, the national requirement for liquid biofuel development is to develop liquid fuel replaceable for vehicle fuel;
- It is urgent to solve the raw material supply of biodiesel: quantity, variety, cost price, maturity of production technology (including development of new technology);
- Increase economical feasibility of biodiesel, reduce its damage to motor lubricate and corrosion, improve its stability and fluidity under low temperature.

5. Conclusion

- Biodiesel, as the replacement of automobile liquid petroleum fuels, is the future development target;
- Currently locate at technological demonstration and mature engineering technology stage, not suitable to establish factories with several hundred thousands of production capacity;
- Set up different industrial demonstration product line according to different areas as prophase demonstration and accumulation for future large scale promotion (the twelfth five-year plan period)

5. Conclusion

- Forestry biomass resource is rich and renewable;
- The only renewable energy which can be converted to liquid fuel;
- Energy product market is very wide;
- Research and develop replacement of oil energy to replace the comprehensive utilization of petro-chemical products;
- Establish demonstration projects of appropriate scale according to different area and resources, accumulate experience and data;

The forest biodiesel industry development aims at comprehensive use of biomass energy and oil energy replacement material.

Welcome leaders and experts to visit our institute!

THANK YOU !