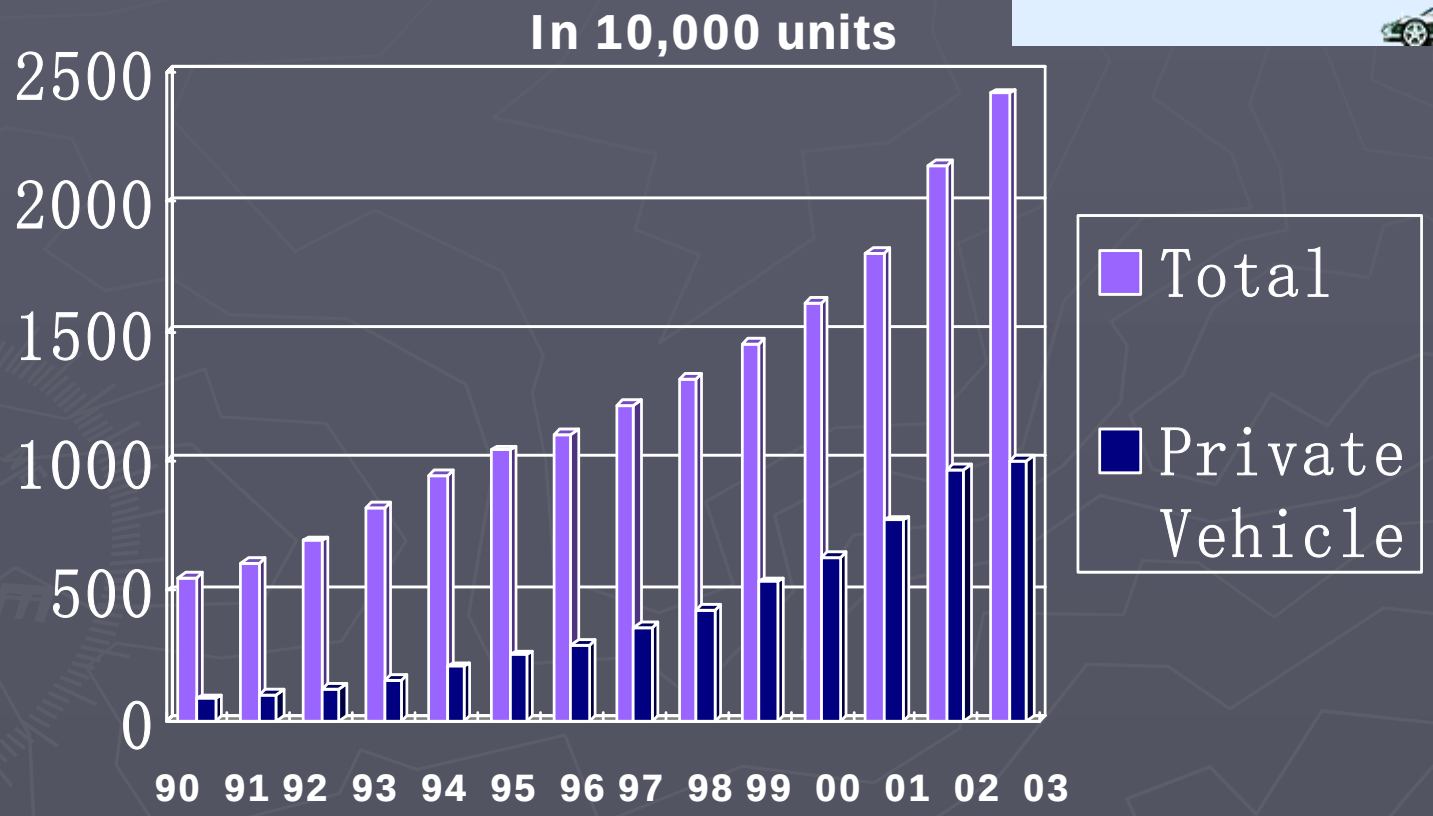
A novel enzymatic route for biodiesel production from renewable oil sources

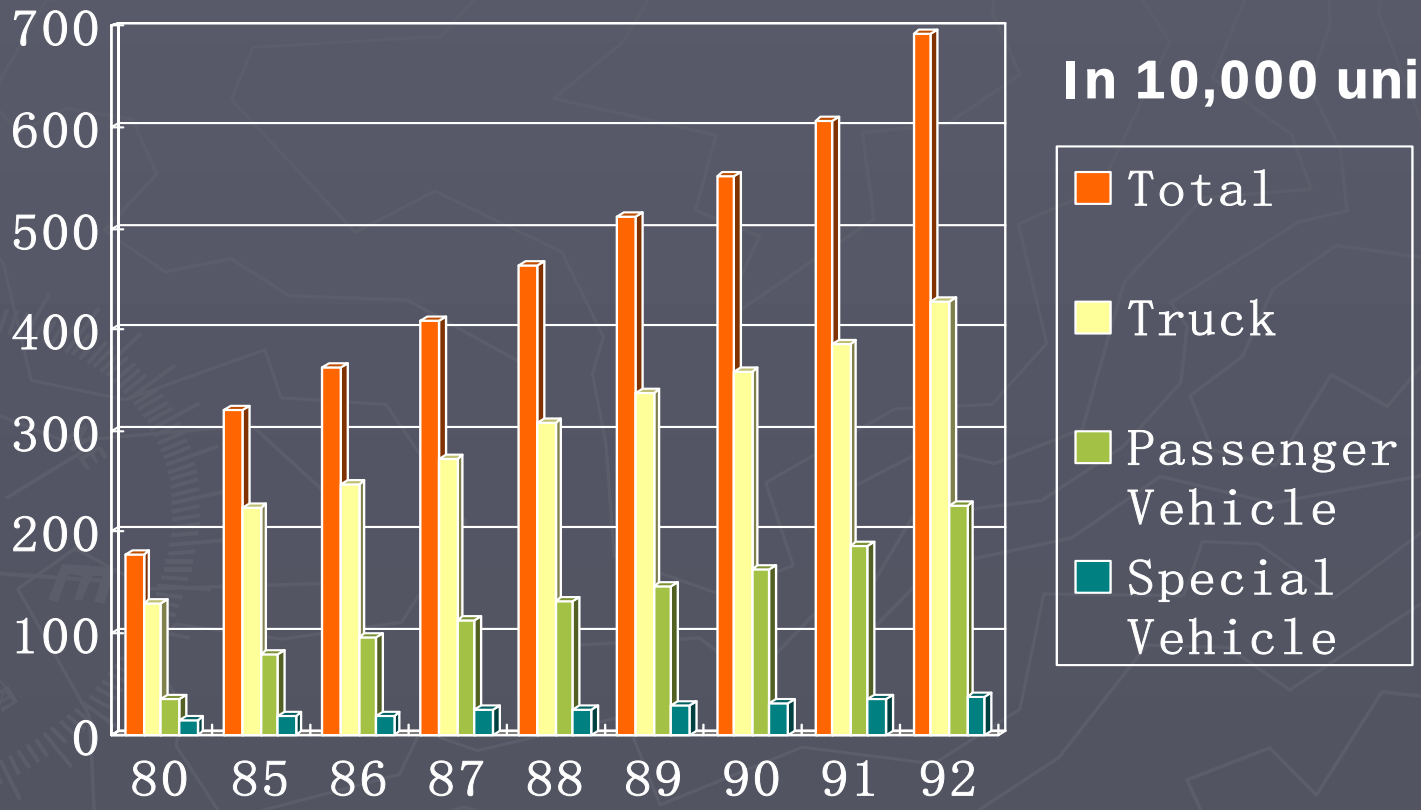
Dehua Liu, Wei Du
Department of Chemical Engineering
Tsinghua University

Automobiles increased so much

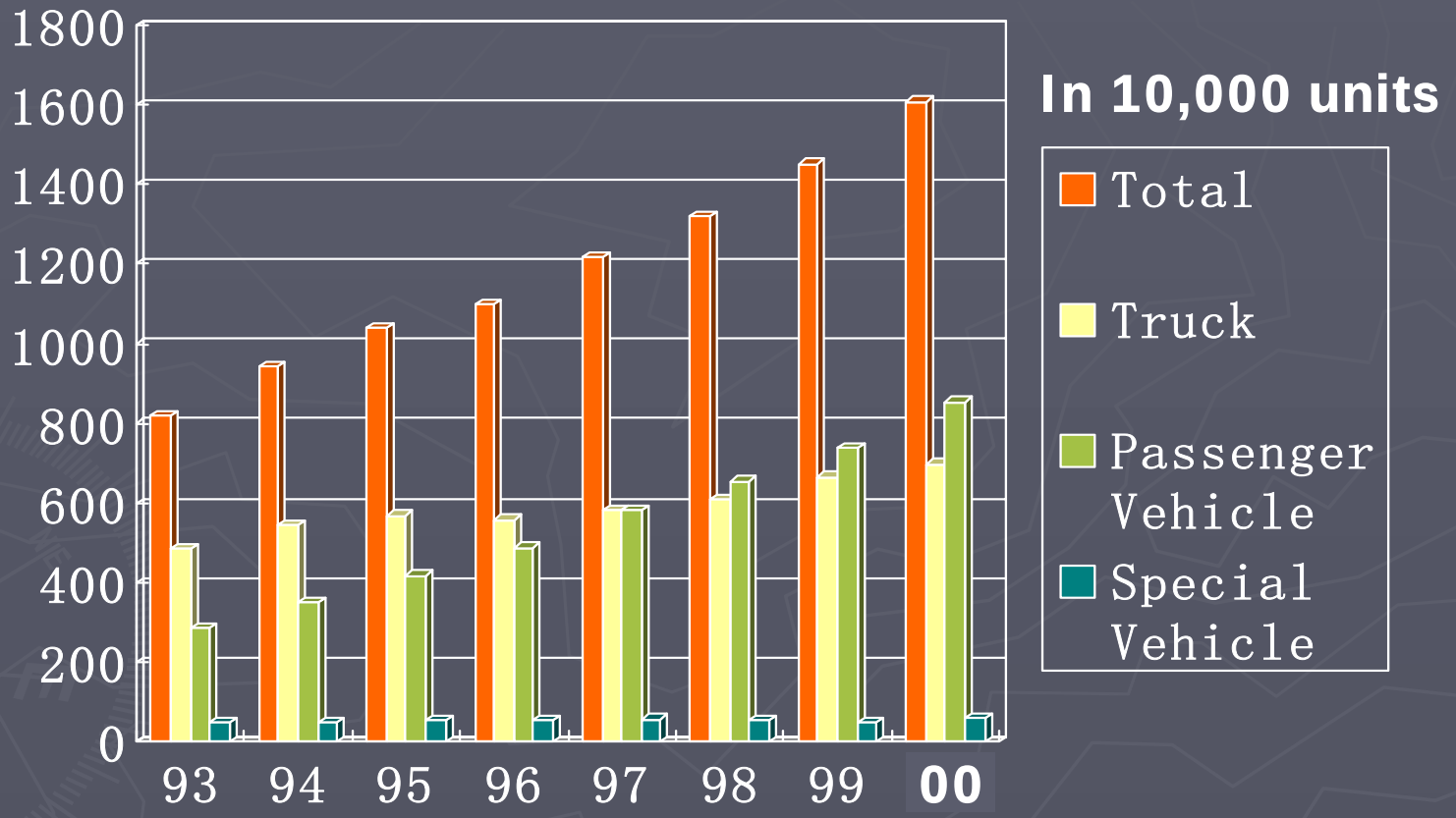


Note: Data are sourced from the State Bureau of Statistic, the same below

Automobiles in Use by Category in Selected Years

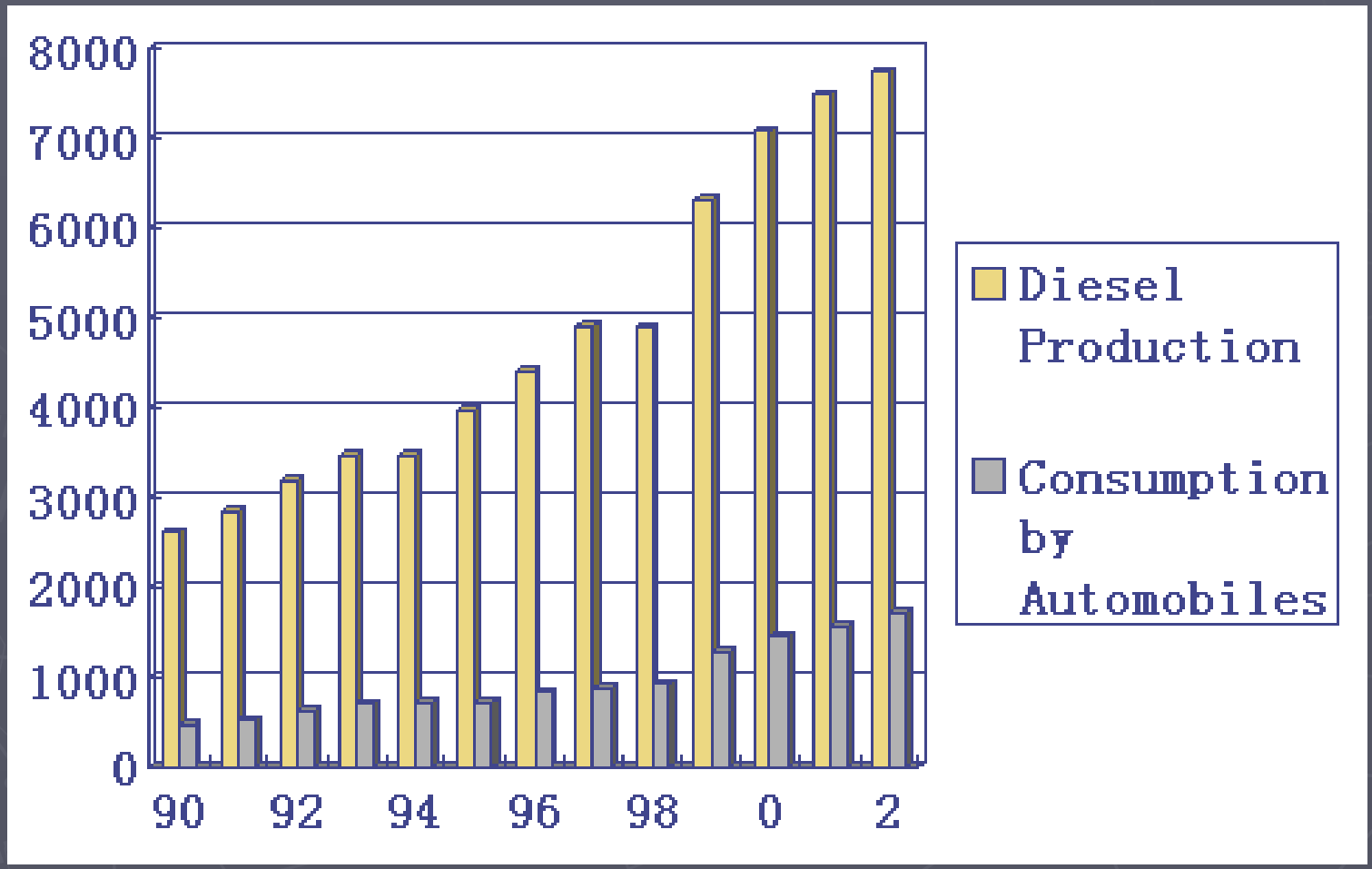


Automobiles in Use by Category in Selected Years II

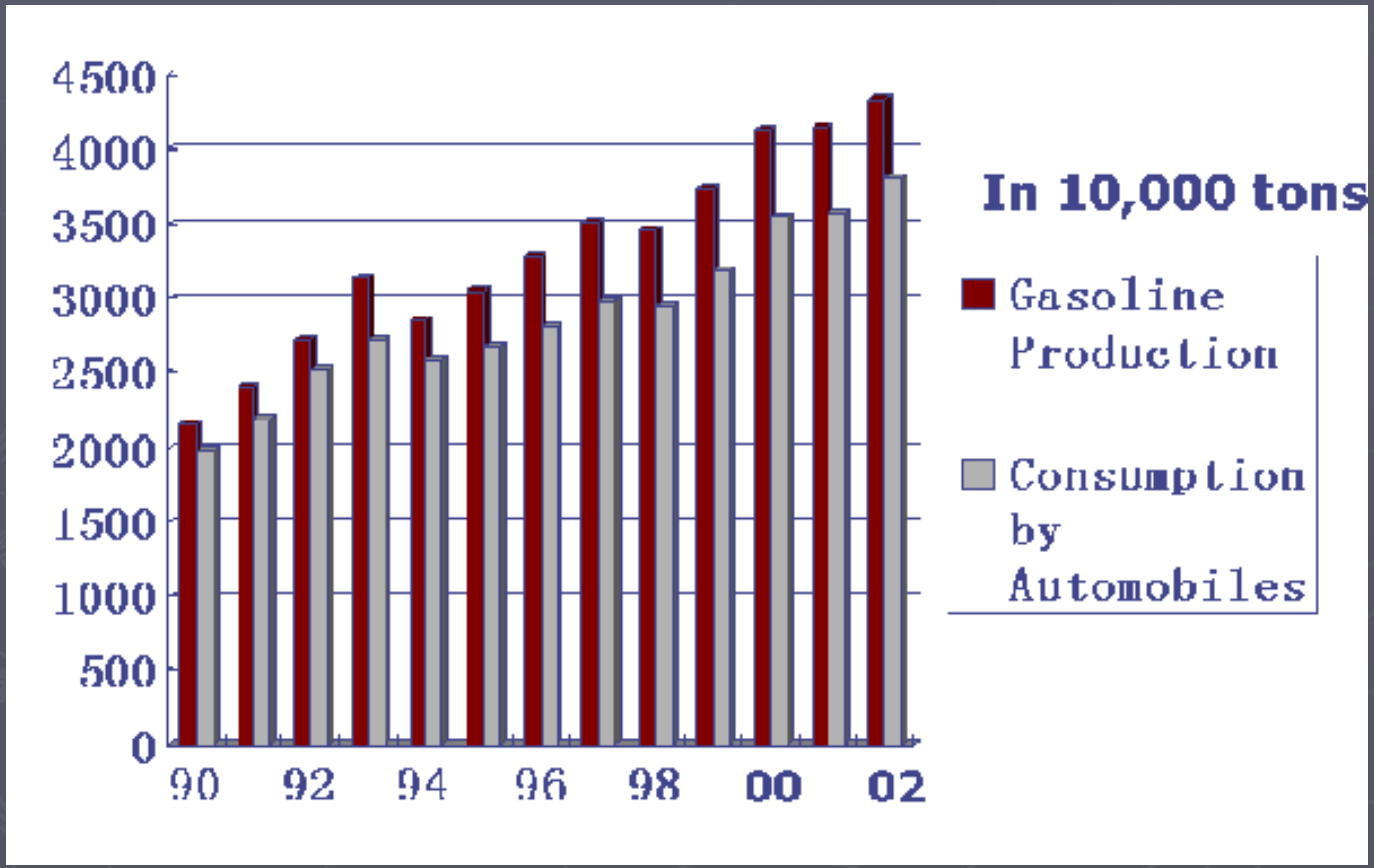


fold	Total	Truck	Passenger vehicle	Special vehicle	Private vehicle
1990compared with 1980	3.1	2.7	4.6	2.3	2.9
2000 compared with 1990	2.9	1.9	5.3	1.8	7.7
2003 compared with 1990	4.4	--	--	--	12.2

Diesel Production and Consumption by Automobiles in Selected Years



Gasoline Production and Consumption by Automobiles in Selected Years



Background

Biodiesel *: defined as "a substitute for, or an additive to diesel fuel that is derived from the oils and fats of plants and animals"*

Environmental benefits
(**particulate ↓ 30%; CO ↓ 50%;**
soot ↓ 80%; aldehyde compound ↓ 30%; SOx ↓ 100%)

Biodegradability

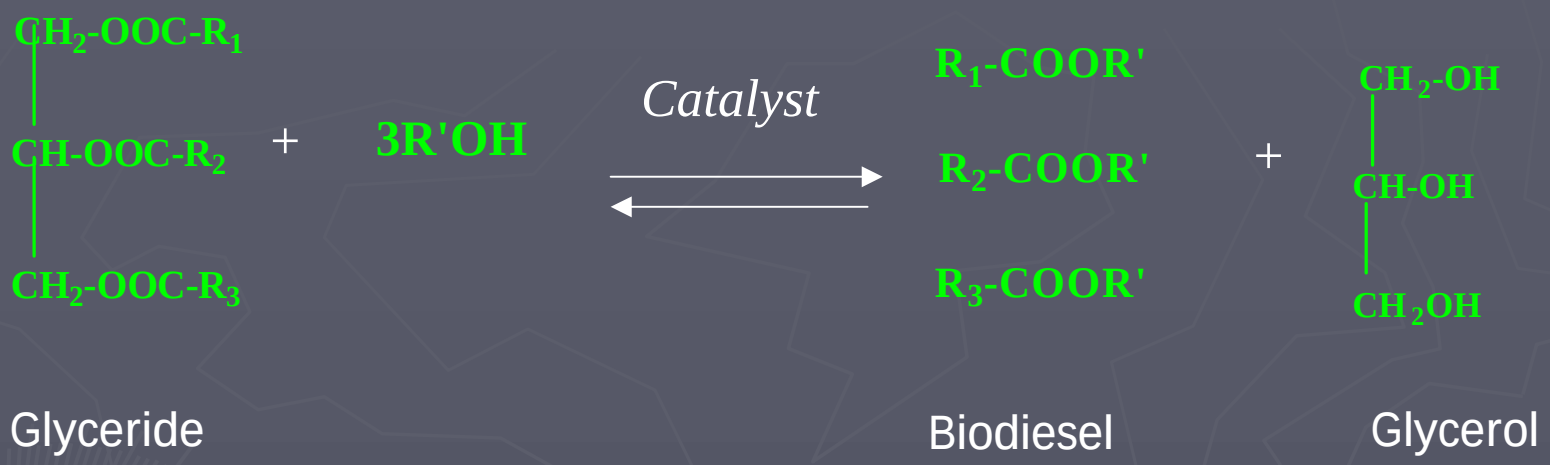
Renewability

→ ***a promising alternative fuel for fossil fuel***

Table 1. Physical and chemical properties of fossil diesel and biodiesel

Standardised properties	unit	Diesel EN 590:1993	Biodiesel (FAME) DIN E 51 606:1997
Density at 15¡ æ	Kg/m^3	820-860	875-900
Viscosity at 40¡ æ	mm2/s/	2.00-4.50	3.5-5.0
Flash-point	¡ æ	>55	>110
sulphur	%(m/m)	<0.2	<0.01
Cetane No.		>49	>49
Other properties		Diesel	Biodiesel
oxygen content	%(m/m)	0.0	10.9
Caloric value	MJ/dm^3	35.6	32.9
Efficiency degree	%	38.2	40.7

Production of biodiesel through transesterification:

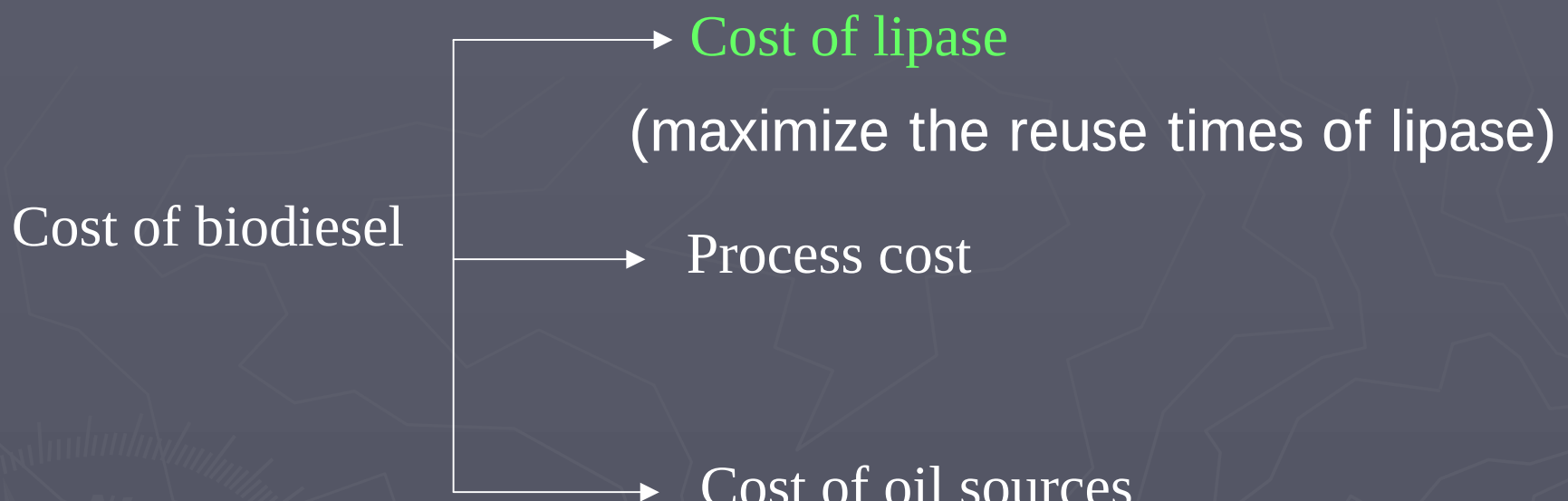


Scheme 1 Biodiesel production through transesterification

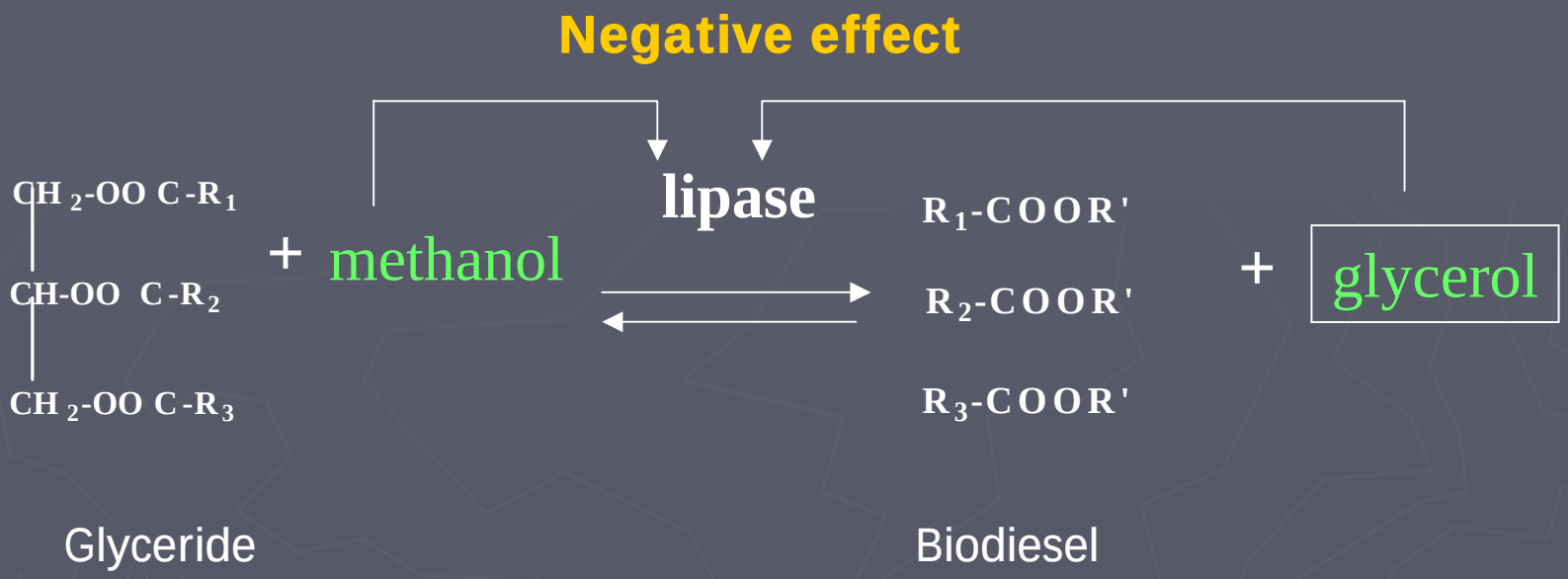
Chemical approaches:

Some unavoidable drawbacks: energy intensive, difficulty in removing the glycerol, free acid and water in oil sources have negative effect on biodiesel production, and not environmental friendly etc.

Enzymatic approaches



The cost of biodiesel, is the main hurdle to commercialization of the product.



Scheme 2 traditional enzymatic approaches for biodiesel production

Major issues:

- ✓*Poor solubility of methanol in oil sources*
- ✓*Methanol deactivates lipase very seriously*
- ✓*By-product glycerol (hydrophilic and very sticky) has negative effect on enzymatic activity.*

→ **Lipase was found to has poor stability and activity during repeated uses**

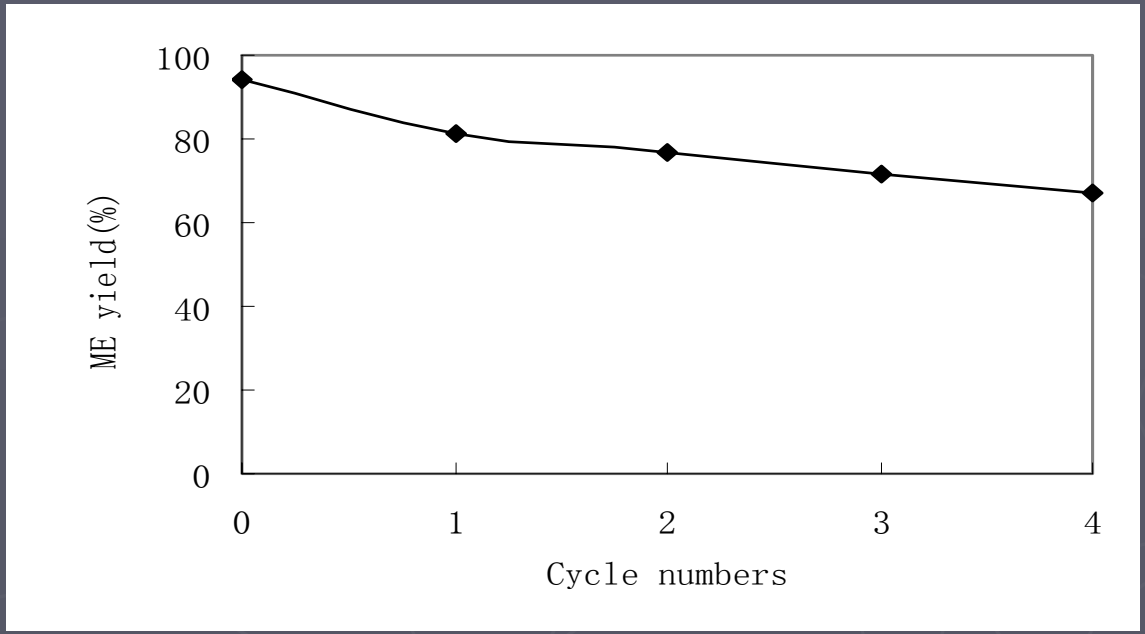
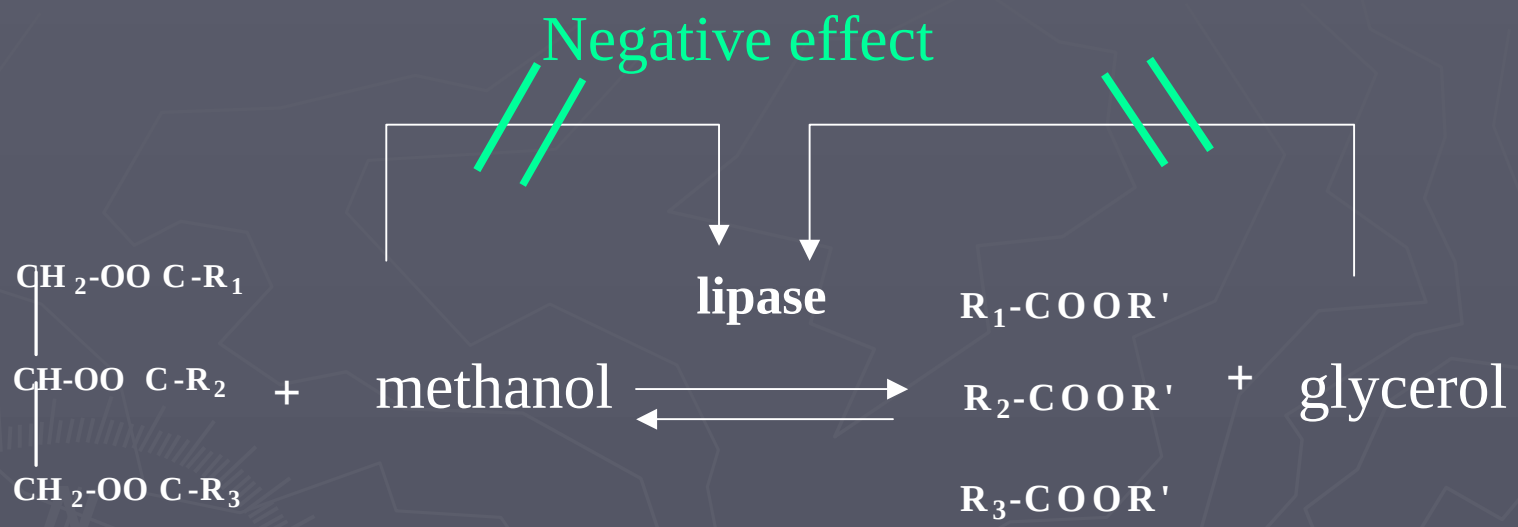


Figure 1 Operational stability of lipase with traditional enzymatic approaches

Reaction conditions: methanol/oil molar ratio 4:1 (soybean oil), 150 rpm, 40 ℃, 30% Novozym 435

Poor stability and activity of the lipase should be due to the negative effect of methanol and glycerol

Novel technology of Tsinghua University for biodiesel production



The negative effect of both methanol and glycerol on enzyme activity could be eliminated with our novel technology for biodiesel production

Patent application: No. 03119600.4 ; No.03150231;

PCT/CN2004/000051

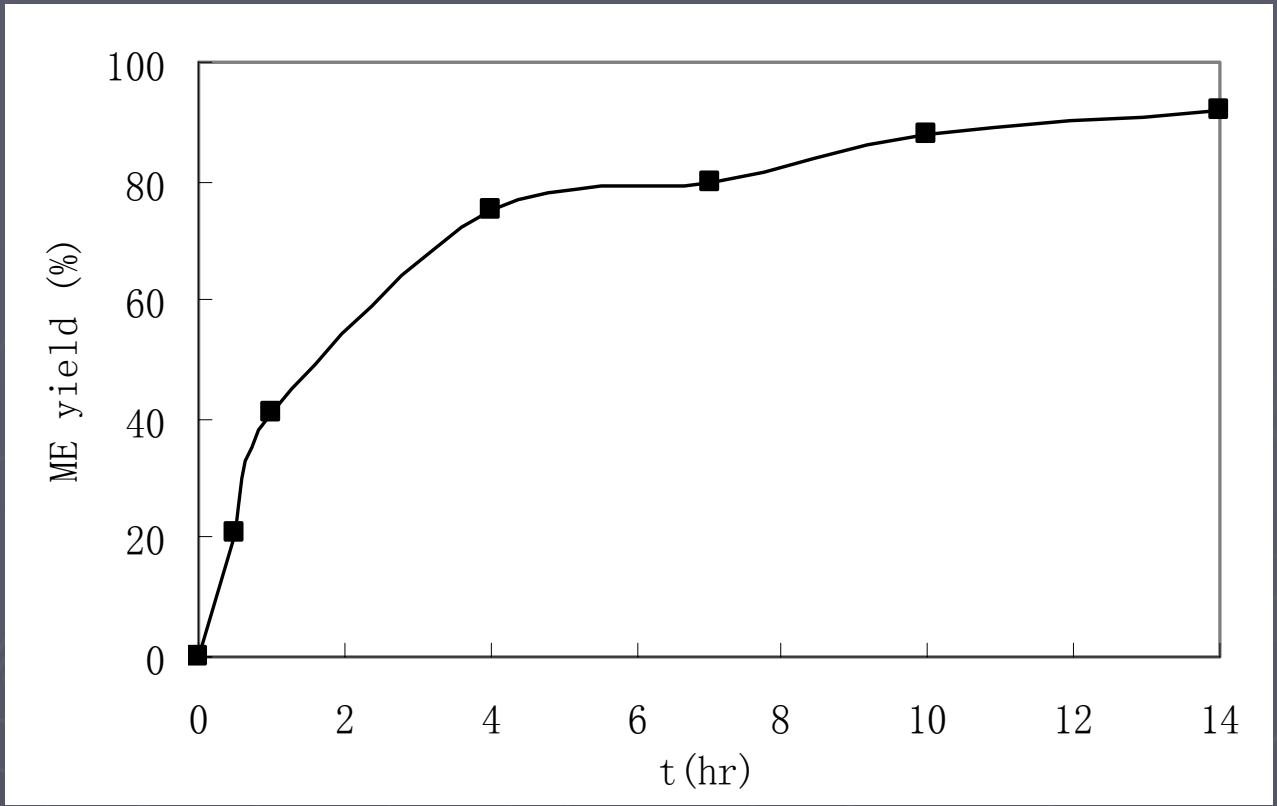


Figure 3 Biodiesel production from refined soybean oil sources

With soybean oils for biodiesel production, a yield of 92% could be obtained in one operative cycle.

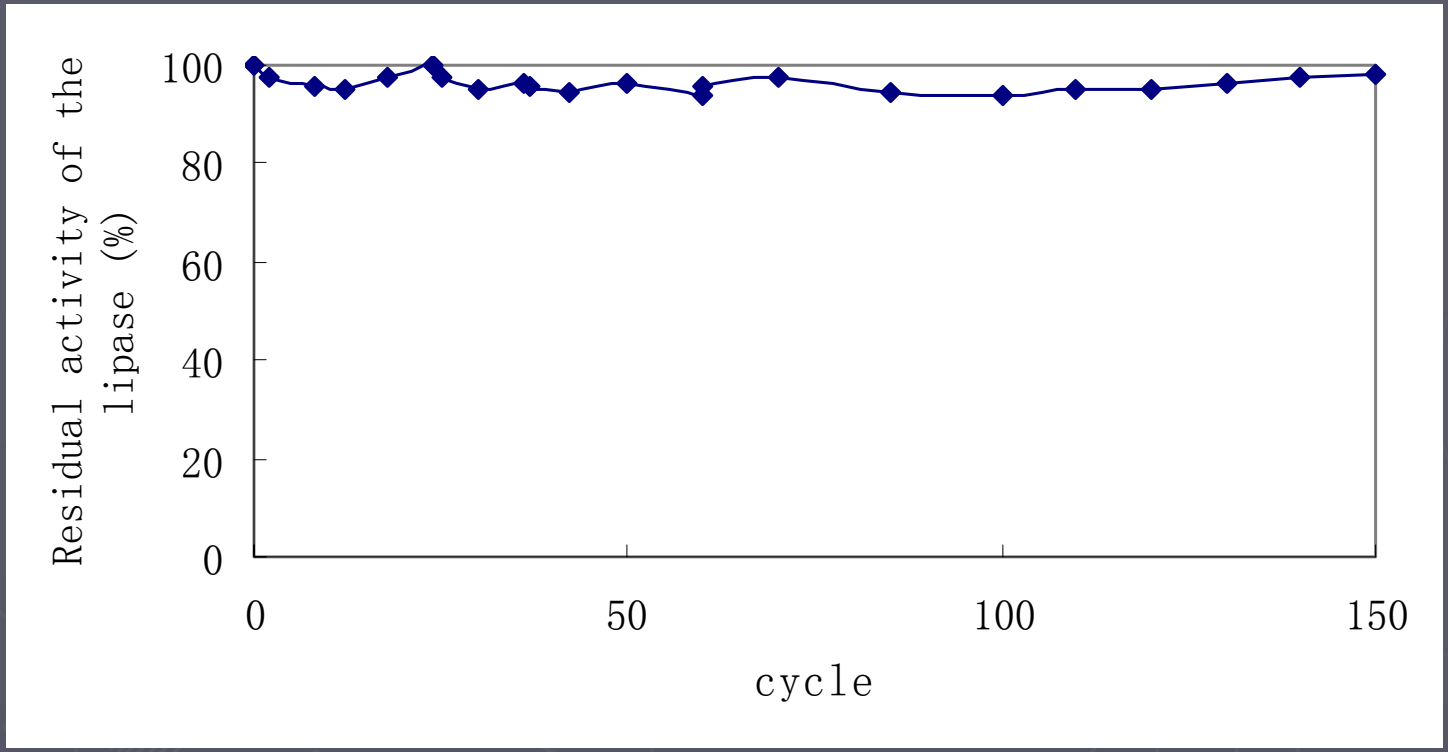


Figure 4 Operational stability of the lipase

Novel technology of Tsinghua University: 150 batches, enzyme activity ~~

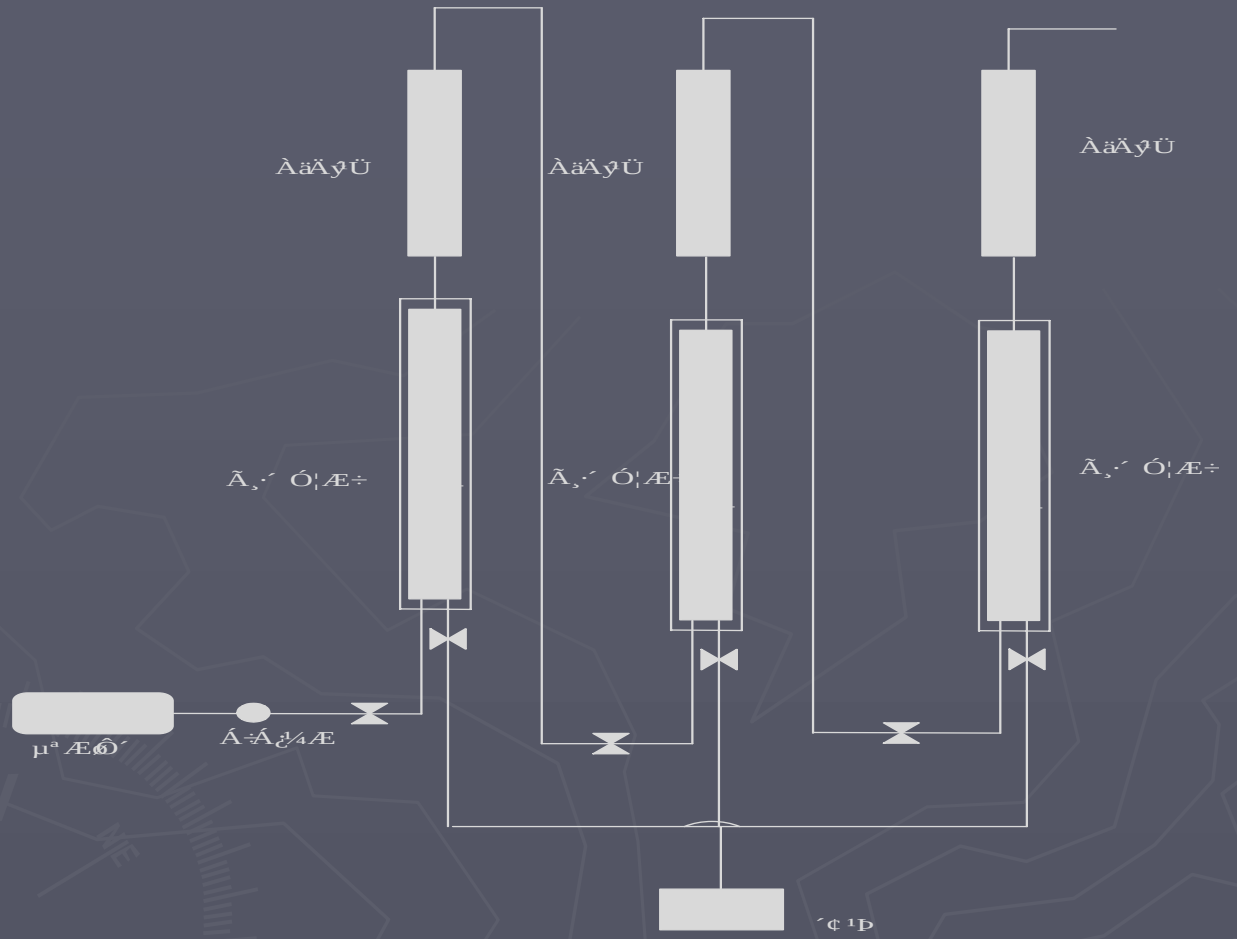
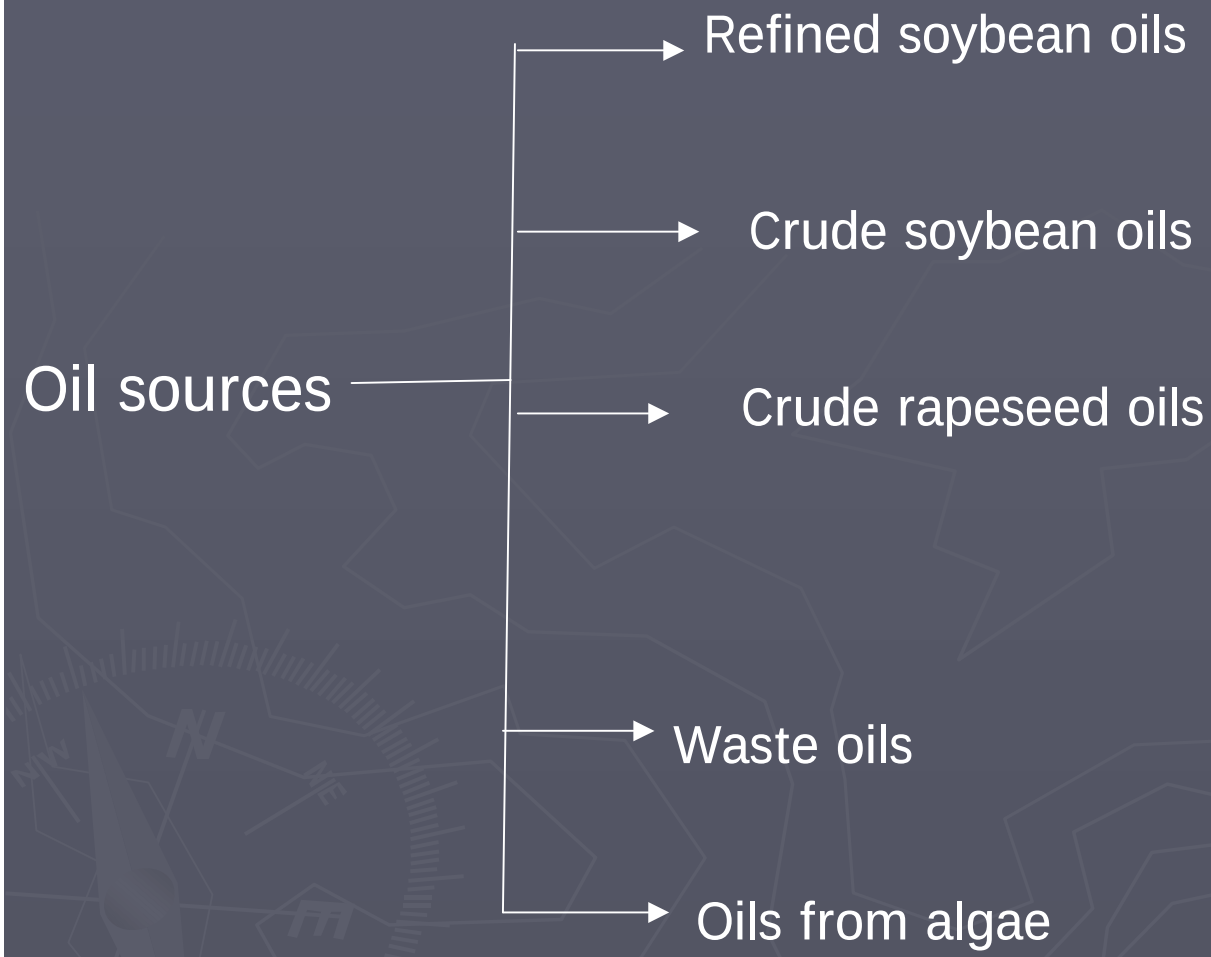


Figure 4 Biodiesel production within bioreactor

The novel process has been operated continuously within bioreactor for over 10 months and there is no loss in enzyme activity detected



These oils can be transformed into biodiesel effectively using our novel technology.

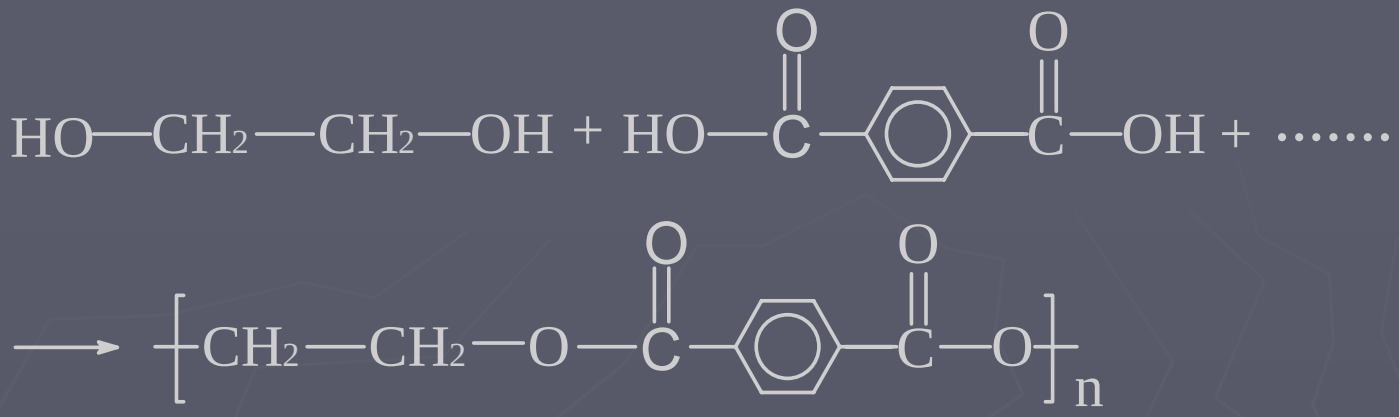
✓Stability and activity of the lipase have been improved significantly:

✓Some cheap oil sources could be used for biodiesel production

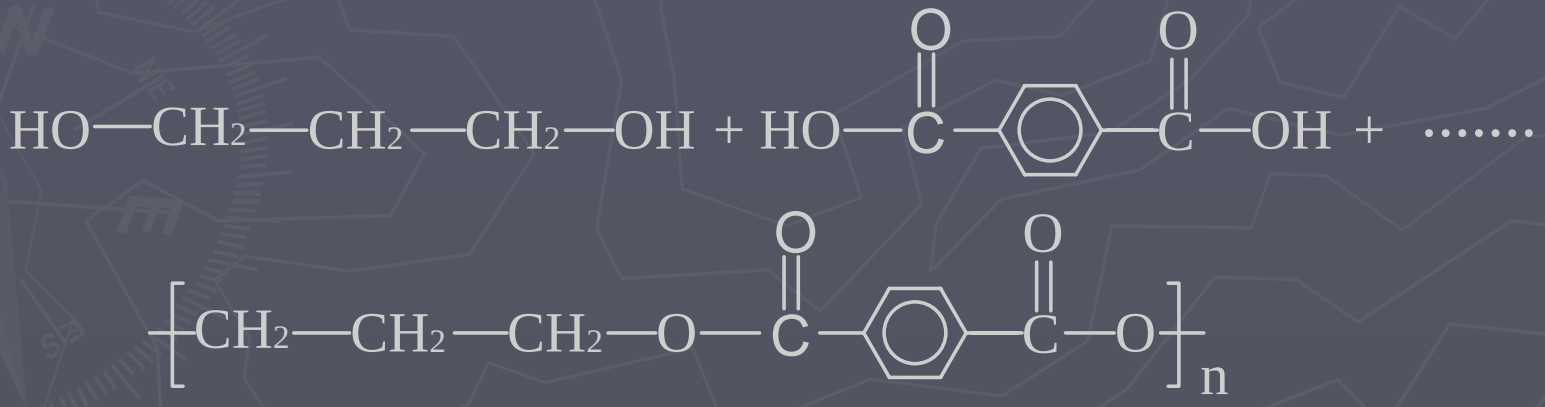
How to deal with the by-product glycerol?

葡萄糖 —耐高渗酵母 供氧发酵→ 甘油 —克氏肺炎杆菌 厌氧发酵→ 1，3-丙二醇

PET分子结构



PTT分子结构



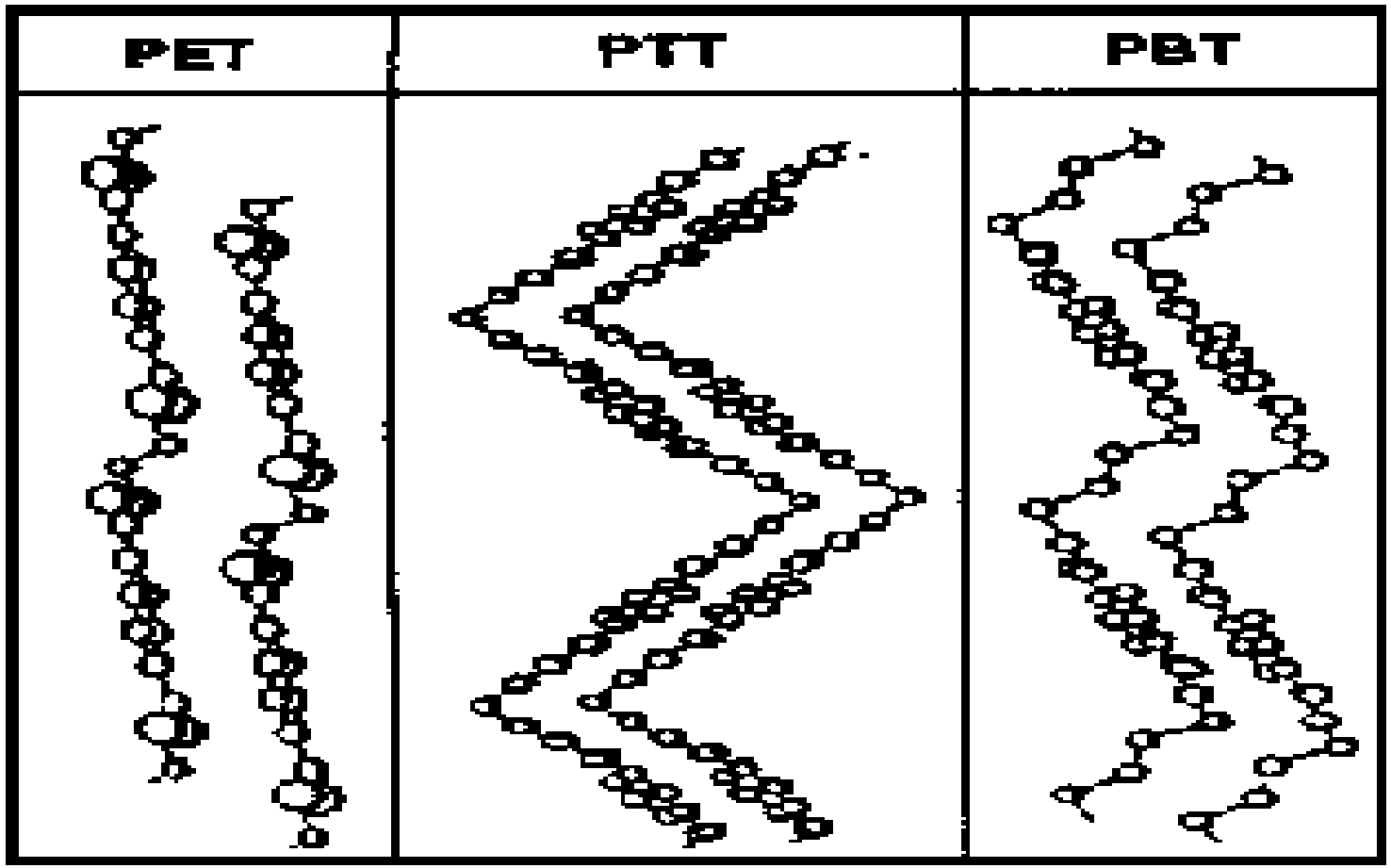
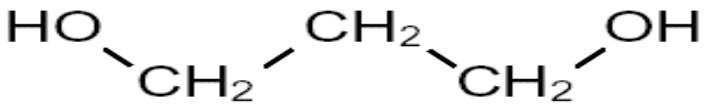


图 1　芳香族聚酯的结构

据对 PET，PBT 和 PTT 纤维的拉伸回复性研究发现回复性大小为：PTT 大于 PBT 大于 PET。

Shell Chemicals*

1,3-Propanediol



Physical properties

CAS Registry Number	504-63-2
Molecular formula	$C_3H_8O_2$
Molecular weight	76.10
Boiling point	214.4 °C (417.9 °F) at 760 mm Hg 103.0 °C (217.4 °F) at 10 mm Hg
Melting point	–26.7 °C (–16.1 °F)
Refractive index, 25 °C	1.4386
Density, 20 °C	1.0526 g cm^{-3}
Viscosity, 20 °C, cP	52
Surface tension, 20 °C	46.2 $Dyne^{-1}cm$
Solubility in water	Complete
Flash point, ASTM D-92	129 °C (265 °F)
Evaporation rate, nBuAc = 1	0.016
Hildebrand solubility parameter, 25 °C	15.2 $(cal\ cm^{-3})^{1/2}$
Fractional polarity	0.47
Hansen solubility parameters, 25 °C	δ_d = 6.1 $(cal\ cm^{-3})^{1/2}$ δ_p = 6.9 $(cal\ cm^{-3})^{1/2}$ δ_h = 13.2 $(cal\ cm^{-3})^{1/2}$

Specified properties**

Property	Minimum Limit	Maximum Limit	Method
Purity, % by GC	99.7	100	SCG-305
Color, Pt-Co	0	20	ASTM-D1209
Water, %w	0	0.1	ASTM-D4672
Appearance; Substantially free of suspended matter	Pass	Pass	ASTM-D4176

Typical properties**

Ash, ppm	<10
Carbonyls, ppm, as C=O	<1000
Chlorides, as Cl, ppm	<0.5
Iron, ppm	<0.1
Acidity, as acetic acid, %w	<0.002

(2003)量认（黑）字（B1045）号　　（2003）黑质监认字（044）号

黑龙江省产品质量监督

检 验 报 告

黑质检字（　委　）　　第 JW-03422 号

受检单位　黑龙江辰能生物工程有限公司

产品全称　1，3—丙二醇

检验类别　委 托 检 验

黑龙江省精细化工产品质量监督检验站

2003 年 12 月 10 日

黑龙江省精细化工产品质量监督检验站

检 验 报 告

产品名称	1，3—丙二醇	样品编号	JW-03422
委托单位	黑龙江辰能生物工程有限公司	样品数量	500mL
规格型号	---	接收日期	2003 / 12 / 03
样品等级	---	签发日期	2003 / 12 / 10
检验依据	气相色谱法、卡尔费休法等	环境条件	20℃，30%RH

检 验 项 目	标准要求	检验结果
1，3—丙二醇（PDO）含量，%		99.92
水分，%		0.020
灰分，%		0.001
色度（钴—铂），号		小于 10
酸度（以乙酸计），%		0.0007
铁含量（以 Fe^{+2} 计），%		未检出
氯化物（以 Cl^{-} 计），%		小于 0.00004
羰基含量（以乙醛计），%		未检出
以 下 空 白		

检验结论					
主检		审检		批准	

质检 鲍春阳

之杨印姝

叶峰印险

检验报告专用章

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- Mr. Zhebo Li


Thanks!