

Bio-energy III, ECI
May 22-27, 2011, Lanzarote, Spain

**Butanol extractive fermentation to
simultaneously produce “properties
improved” biodiesel & butanol in a water
and energy-saving operation way**

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2011-05-26

Bio-energy III, Lanzarote, Spain

Scopes of the presentation

- 1) Objectives**
- 2) Methods**
- 3) Updated results**
- 4) Conclusions**

Bio-energy III, Lanzarote, Spain - Objectives

Important
organic
chemicals &
intermediate

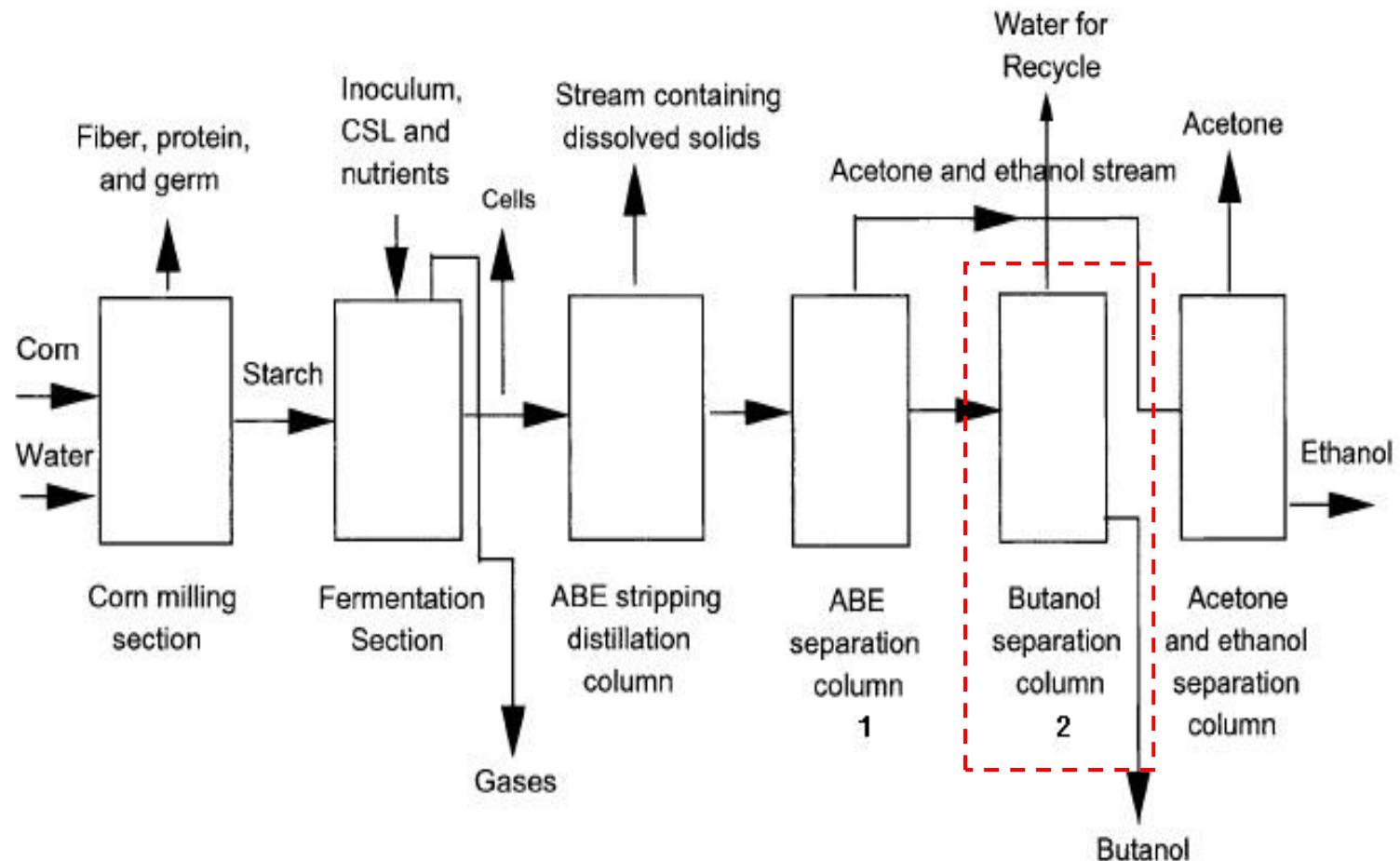
Bio-
Butanol

High
performance
fuel & liquid
fuel additive



Bio-energy III, Lanzarote, Spain - Objectives

Traditional ABE fermentation & purification process



BtOH 13g/l, ACE 6.5g/l, EtOH 2g/l

Bio-energy III, Lanzarote, Spain - Objectives

General comparison of Fossil Diesels & Bio-diesels

Example of the major index	Related Performance	Palm oil methyl ester (One of bio-diesels)	Fossil diesels (#2 diesel US)
Cetane Number (CN)	Ignition delay, combustion, black smoke	49	56
Combustion Heat (MJ/Kg)	Combustion properties Output power	39.8	45.7 Disadvantages
Boiling point (°C)	Ignition at low temp.	+10 °C	-7 °C
S content (wt, %)	Air pollution, environment	0.01	0.07
Total gas exhausts amount (g/Kwh)	Air pollution, environment, global green-house effect	0.421	0.486 Advantages
Available sources	Sustainable/renewable features	Renewable biomass	Fossil sources

Bio-energy III, Lanzarote, Spain - Objectives

Increased CN value of the bio-diesel extracted butanol

中国石油化工股份有限公司金陵分公司质量检验中心

检 测 报 告

委托单位: 江南大学

样品名称: 地沟生物柴油

样品数量: 4 个

送样日期: 2008-01-07

报告编号: WT2008-01-07-26 #

样品编号: WT2008-01-07-26 #

客户编号: -----51.4

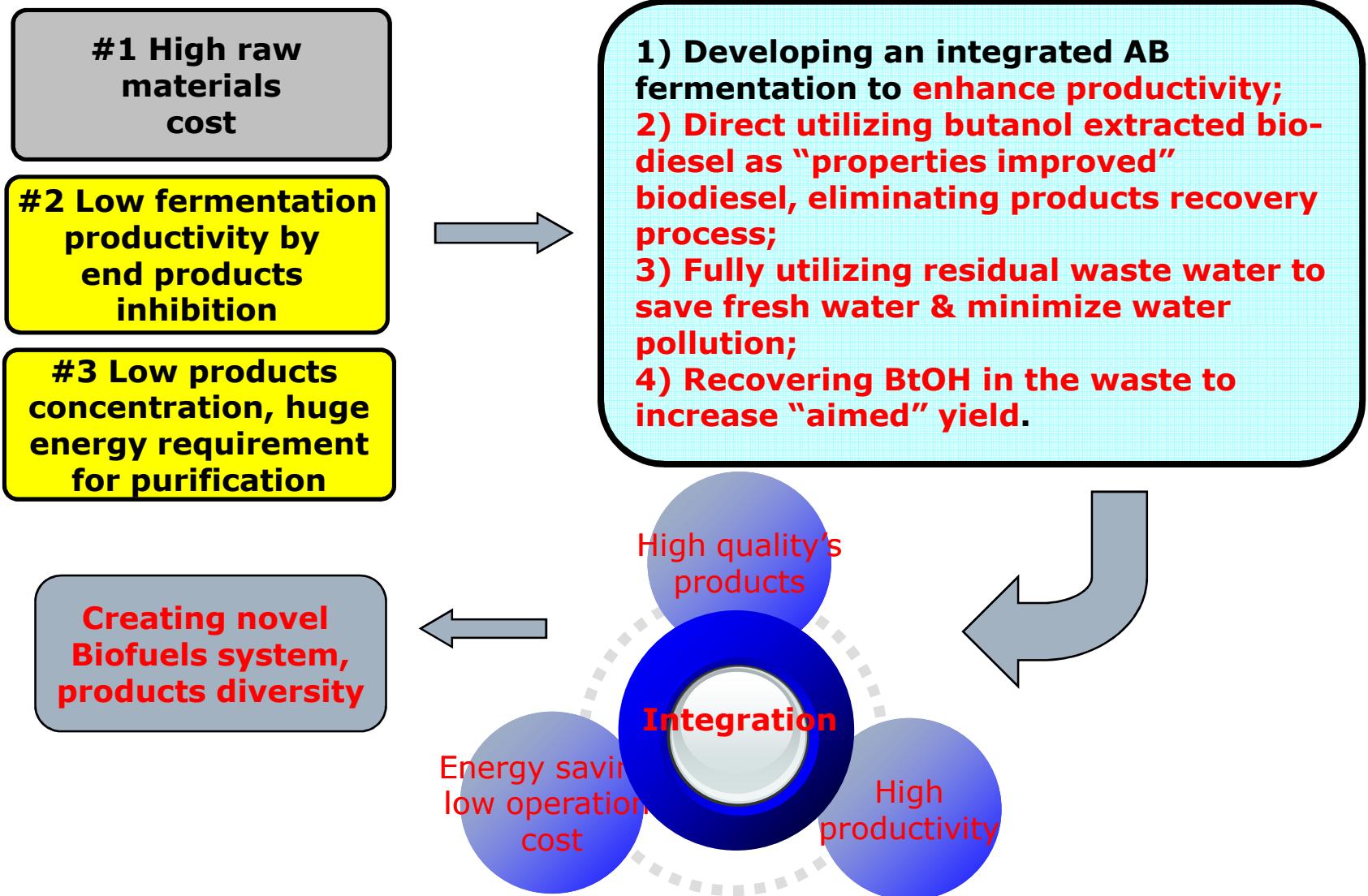
检测日期: 2008-01-08

检 测 结 果

Cetane
Number
(CN)

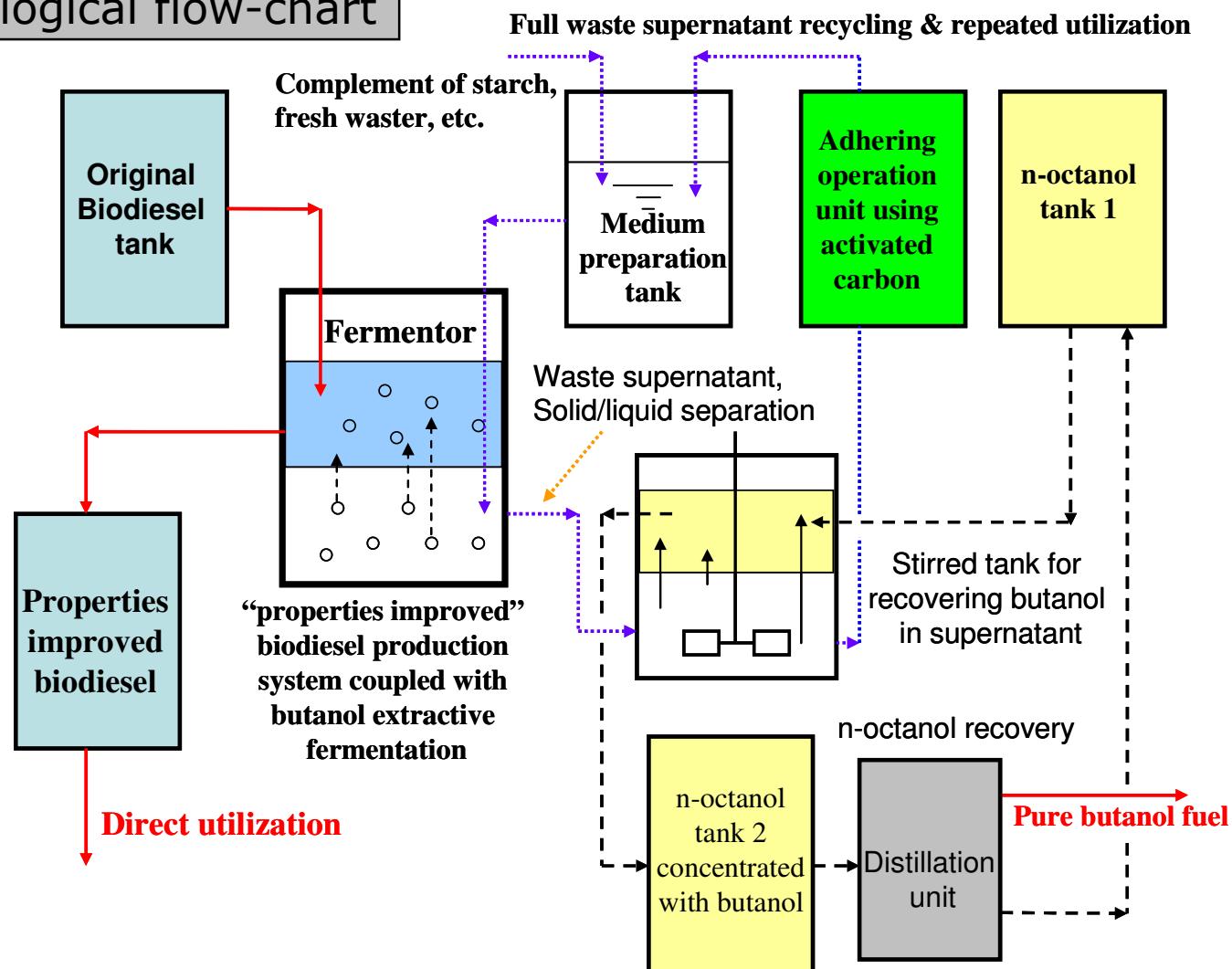
检测项目	检测结果	检测方法
十六烷值, (实测) Original BD	51.4 (A)	GB/T 386
十六烷值, (实测) BD extracted with 12 g/l BtOH	51.4 (B)	GB/T 386
十六烷值, (实测)	49.0 (C)	GB/T 386
十六烷值, (实测)	54.4 (D)	GB/T 386
BD extracted with 12 g/l BtOH but treated with 1.6% Na₂SO₄ dehydration		
BD: Bio-diesel		

Bio-energy III, Lanzarote, Spain - Objectives



Bio-energy III, Lanzarote, Spain - Methods

Technological flow-chart



Bio-energy III, Lanzarote, Spain - Methods

Fermentation conditions

Strain: *Clostridium acetobutylicum* ATCC824

Fermentation medium: corn flour & cassava powders (15%~30%)

Fermentation volume: 2.0~2.5 L

Fermentation extractants: bio-diesels/olyel alcohol, volume ratio 1:1

Fermentation condition: 37°C, strictly anaerobic, static

Initial urea amount: 1% (w/w) of the total sugar

Yeast extracts addition amount: 2.5 g/L-broth

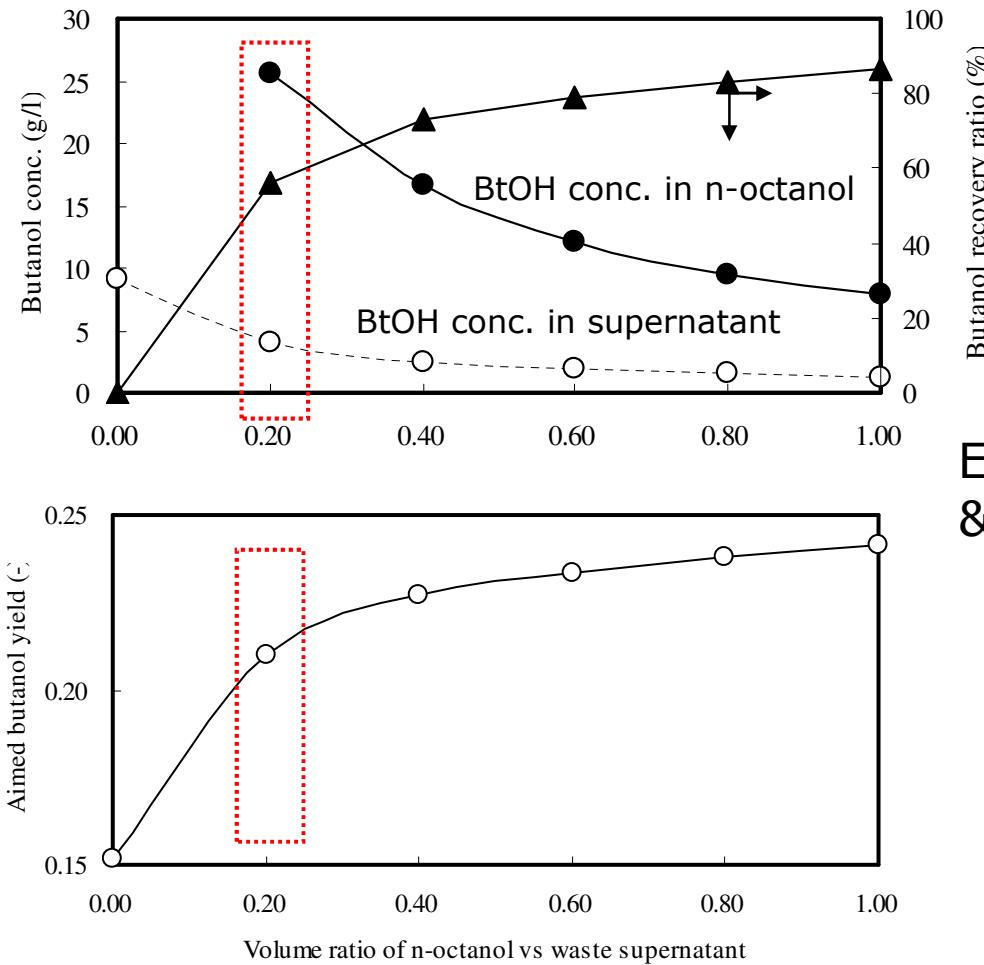
Bio-energy III, Lanzarote, Spain - Methods

Fermentor and instruments



Bio-energy III, Lanzarote, Spain - Results

Using n-octanol to extract BtOH in residual wastes before pretreatment



Ease distillation load
& save purification energy

Aimed BuOH yield =

$$\frac{BtOH^{\text{Bio-diesel}} + BtOH^{\text{n-octanol}}}{\text{Starch consumed}}$$

Bio-energy III, Lanzarote, Spain - Results

Color changes of waste supernatant after adding activated carbon



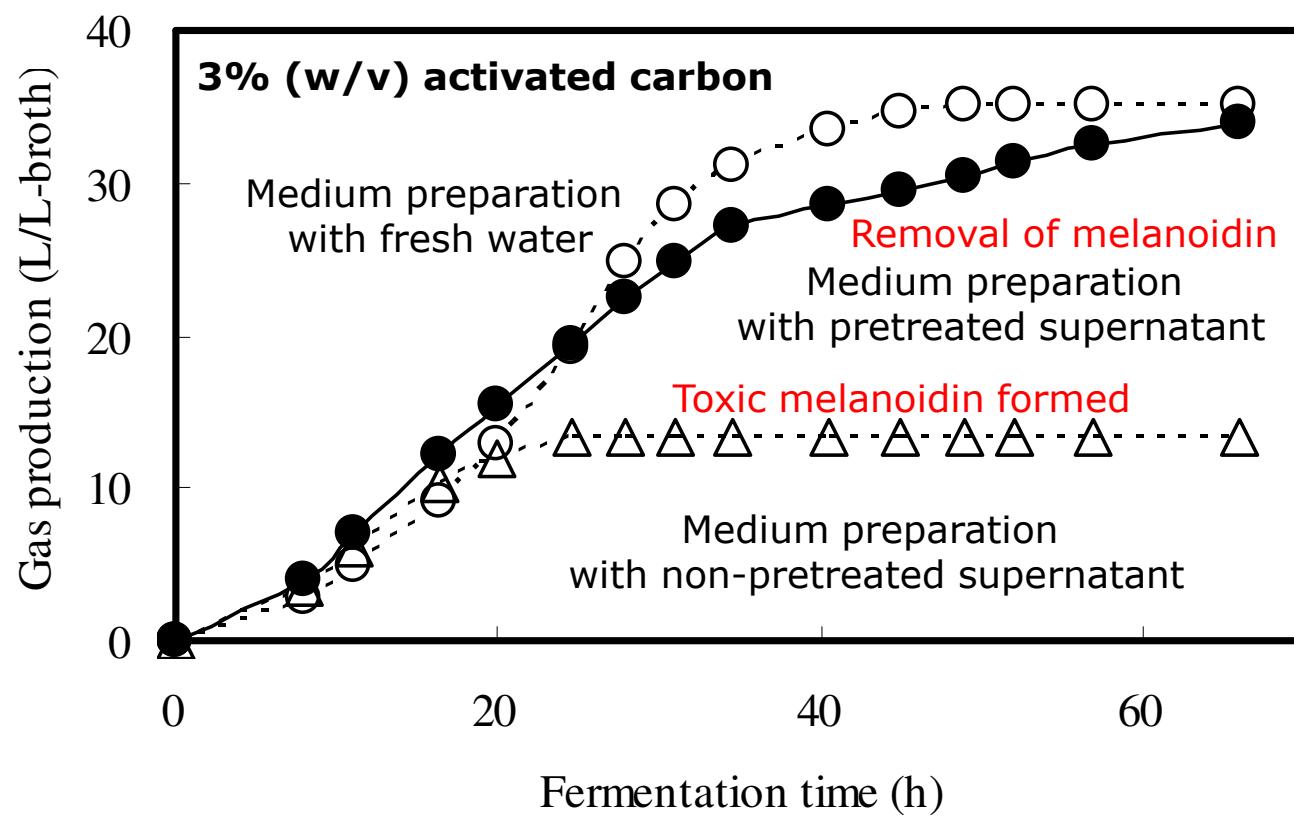
Without activated C treatment



With activated C treatment

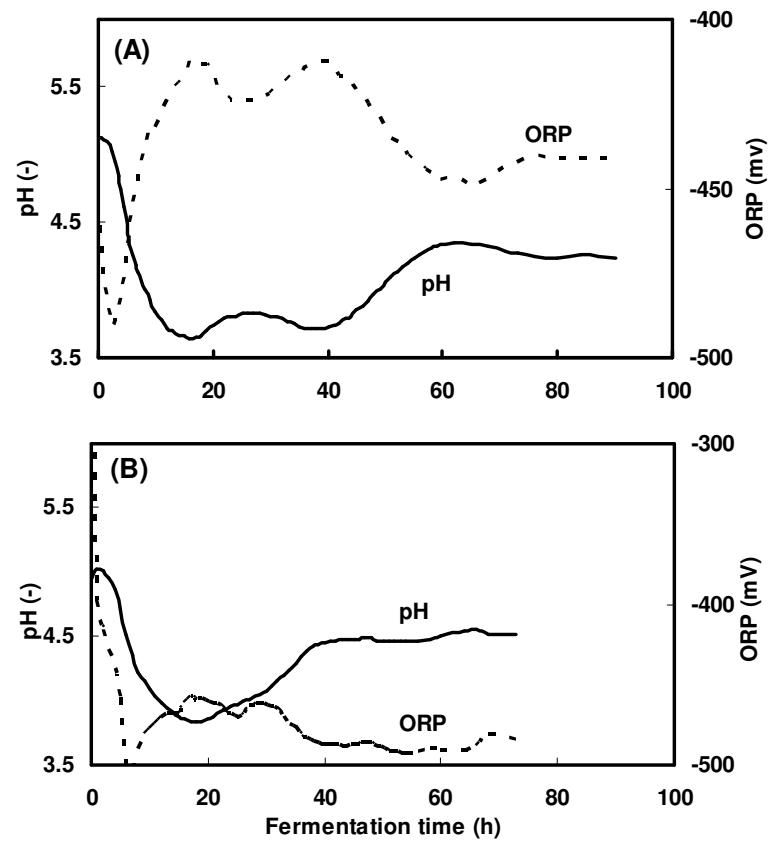
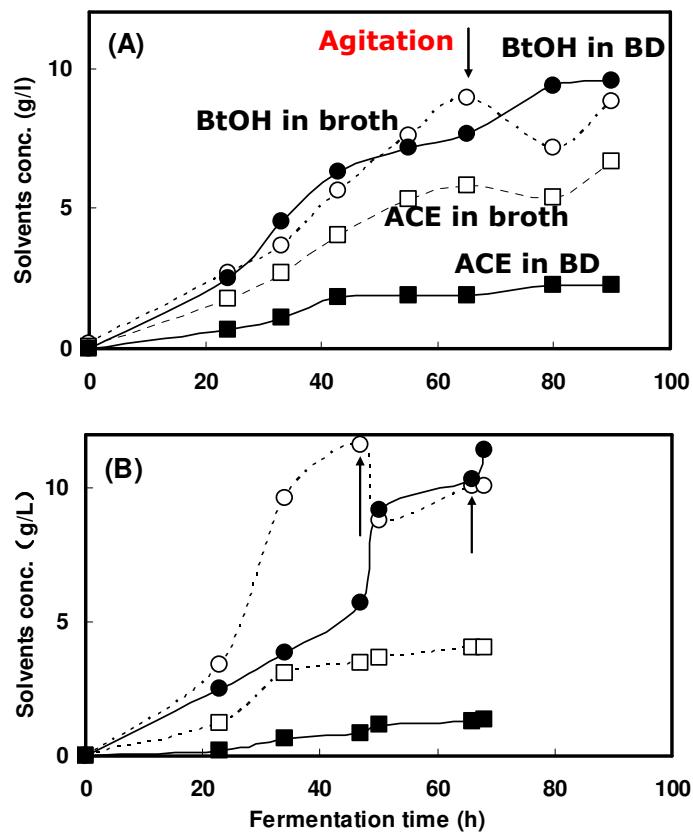
Bio-energy III, Lanzarote, Spain - Results

Pretreatment (residual BtOH extraction + activated C adhere) & full (100%) utilization of supernatant - gas production



Bio-energy III, Lanzarote, Spain - Results

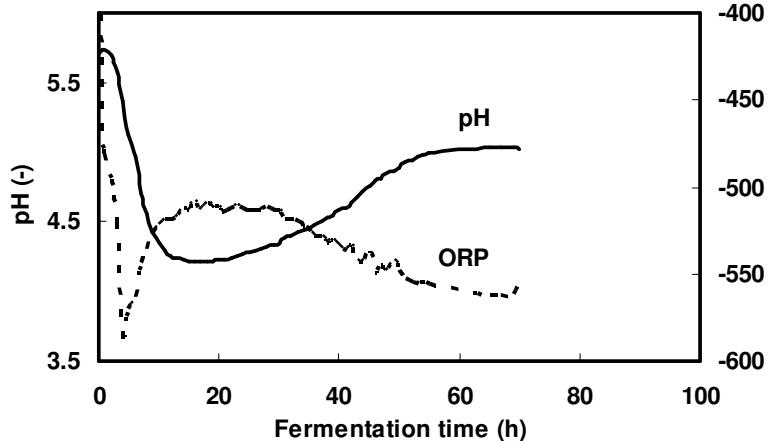
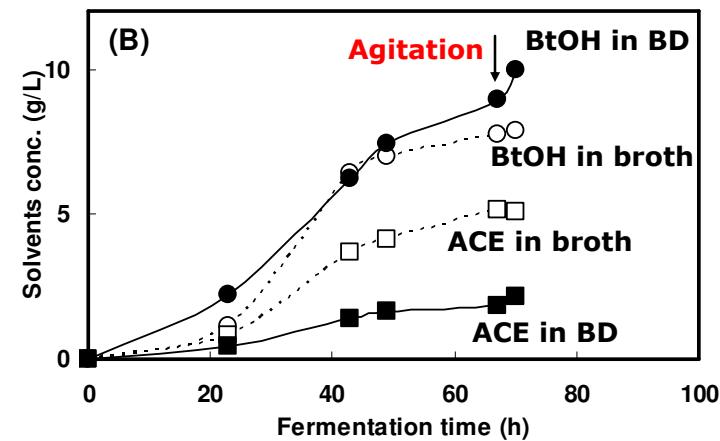
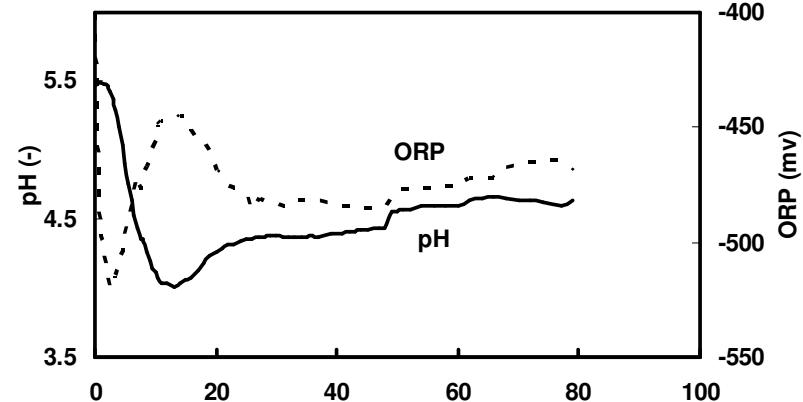
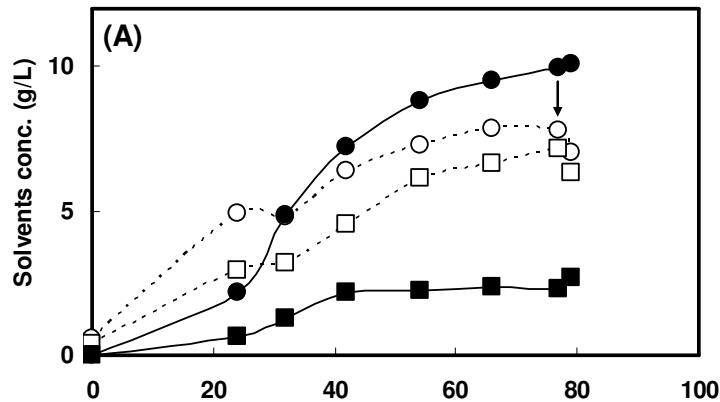
AB fermentation when using fresh water for medium preparation



A: without neutral red addition; B: with 0.1% (w/v) neutral red addition

Bio-energy III, Lanzarote, Spain - Results

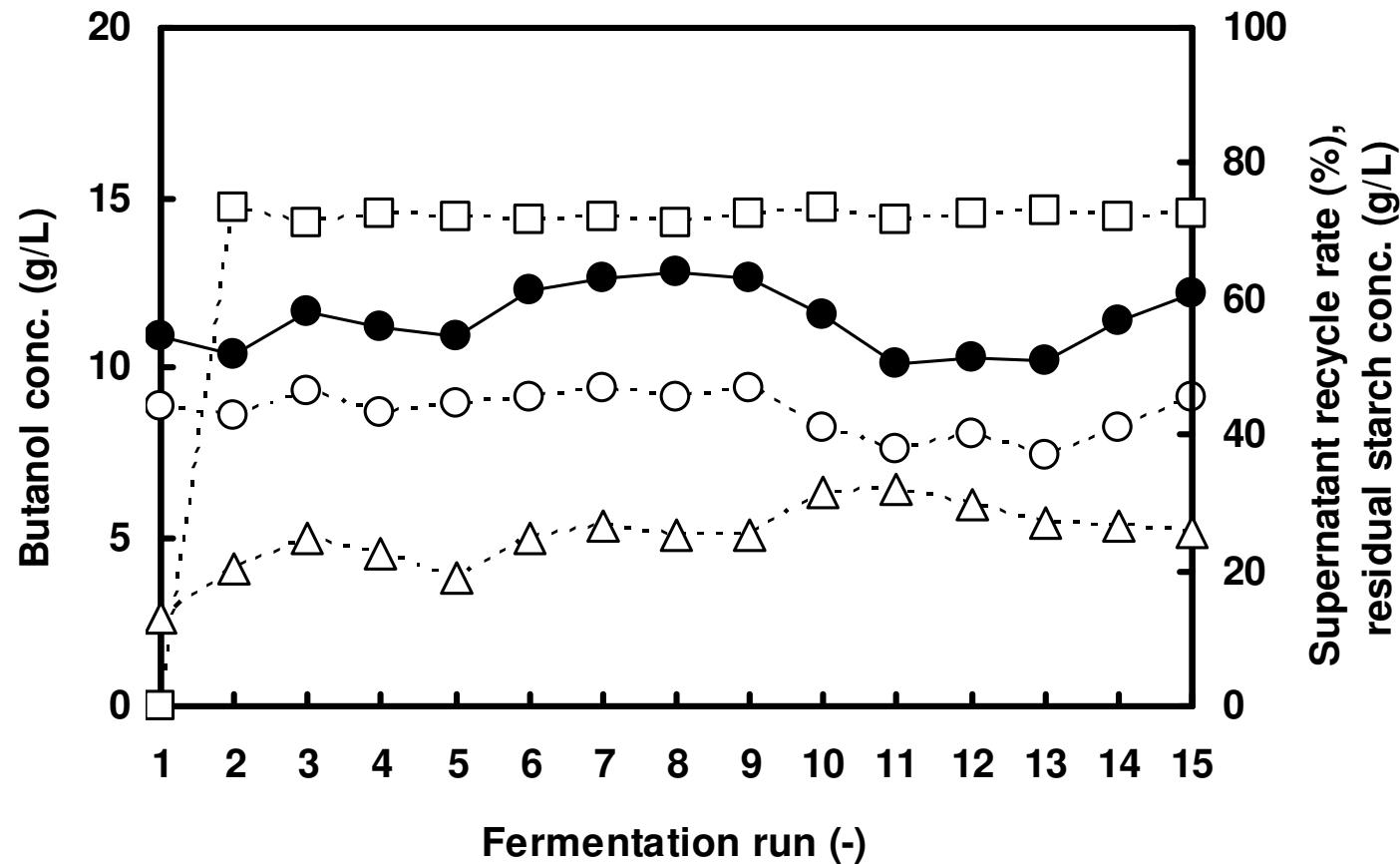
AB fermentation using 100% pretreated waste supernatant for medium preparation



A: without neutral red addition; B: with 0.1% (w/v) neutral red addition

Bio-energy III, Lanzarote, Spain - Results

Repeated utilization of pretreated waste supernatant

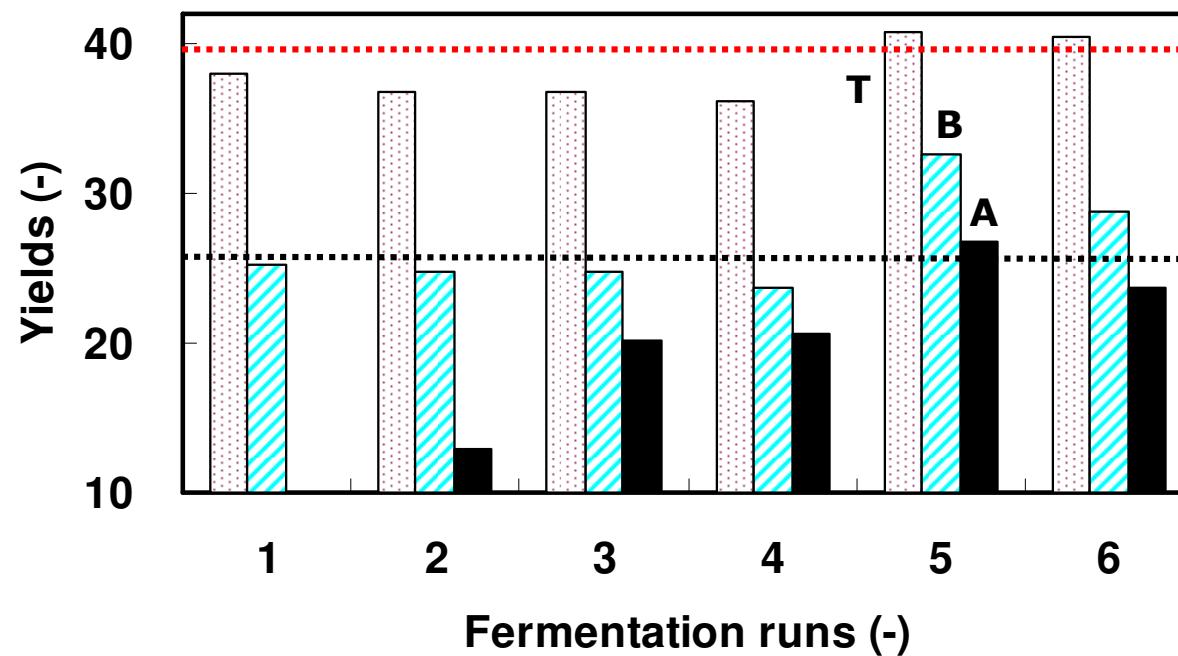


△: residual starch conc.; ○: BtOH in aqueous broth; ●: BtOH in bio-diesel; □: waste recycle ratio

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Yields of total solvents, total butanol and “aimed” butanol in different fermentation runs

Yields of total solvents (T), total butanol (B), and aimed butanol (A)



- 1) Traditional AB fer.;
- 2) Extractive AB fer. using fresh water without recovering residual butanol and using supernatant for the next run;
- 3) Extractive AB fer. with fresh water, recovering residual butanol and using waste supernatant;
- 4) Extractive AB fer. using 100% pre-treated waste supernatant;
- 5) Extractive AB fer. using fresh water for medium preparation with addition of 0.1% neutral red;
- 6) Extractive AB fer. using 100% pre-treated waste supernatant with addition of 0.1% neutral red.

Bio-energy III, Lanzarote, Spain - Results

The performance and comparison of the integrated AB extractive fermentation process

run #	"Properties improved" biodiesel amount (L/L-broth)	BtOH concentration (g/L), in				Starch consumed (g/L)	Aimed BtOH Yields (-)**	Total aimed BtOH amount (g/L-broth)	BtOH/(BtOH+ACE) (in n-octanol, %)	Total BtOH productivity (g/h/L-broth)
		biodiesel	broth	n-octanol	supernatant*					
1	0.00	0.00	11.63	0.00	0.00	46.12	0.00	0.00	0.00	0.18
2	0.97	9.57	8.80	27.20	3.36	74.15	19.86	14.72	80.98	0.21
3	0.96	10.09	7.00	23.50	2.30	72.00	19.98	14.39	88.68	0.22
4	0.97	11.44	10.07	31.10	3.86	66.38	26.09	17.32	92.97	0.27
5	0.97	9.95	7.88	27.30	2.42	61.87	24.42	15.11	91.21	0.25

Run #1: Traditional AB fermentation;

Run #2: AB extractive fermentation using fresh water;

Run #3: AB extractive fermentation using 100% waste supernatant;

Run #4: AB extractive fermentation using fresh water and with 0.1% (w/v) neutral red addition;

Run #5: AB extractive fermentation using 100% supernatant and with 0.1% (w/v) neutral red addition.

Bio-energy III, Lanzarote, Spain - Results

Exploring the possibility of using cassava as fermenting source for bio-butanol production

Corn based sources

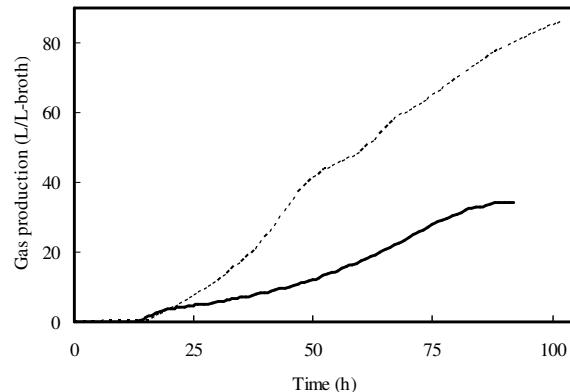
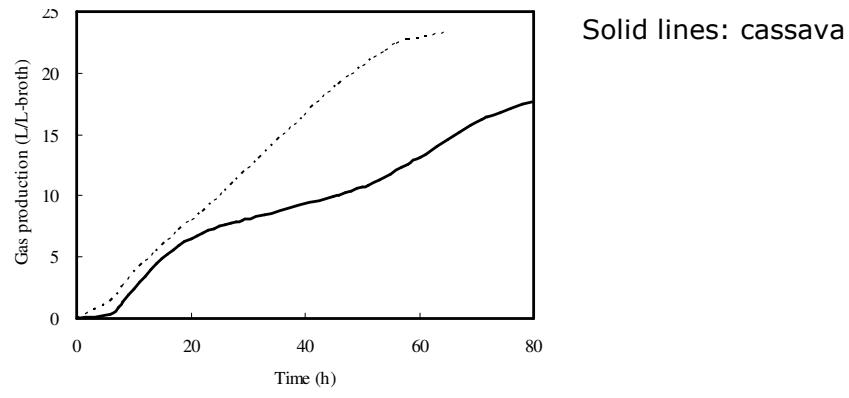
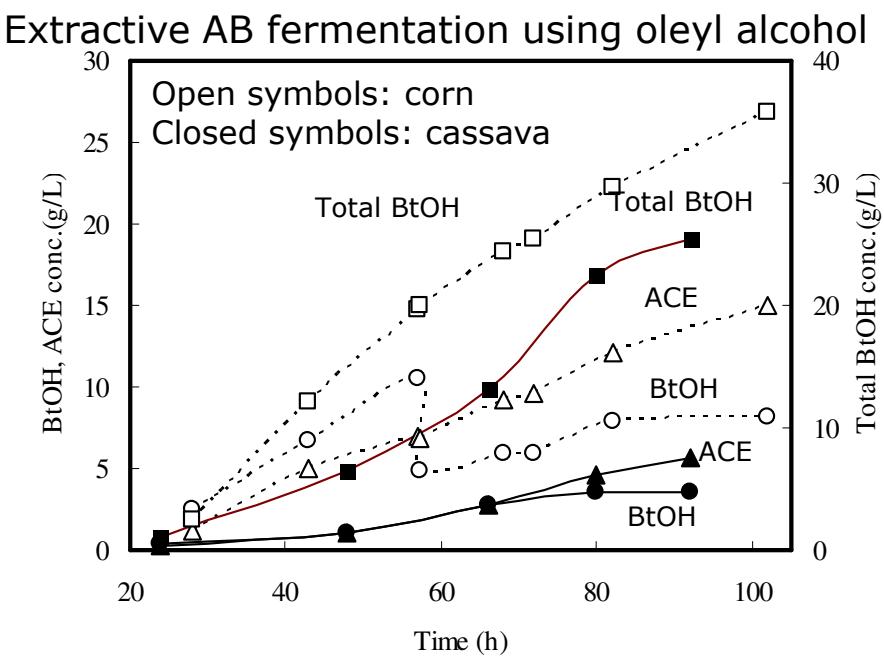
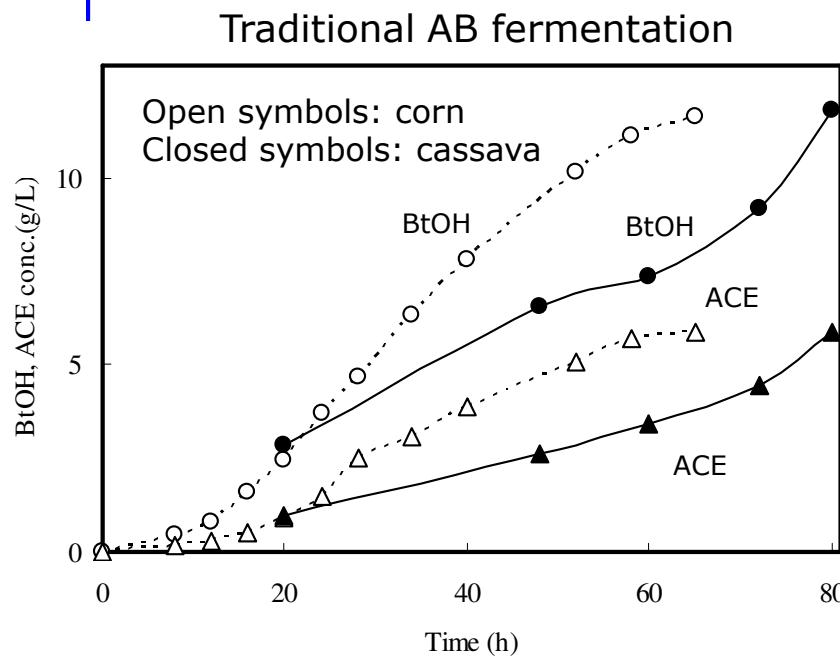
- competition with foods for arable land**

Cassava

- high productivity in in-arable lands even mountain areas**
- non-competition with foods for arable land**
- high starch content, but low protein content, cheap**

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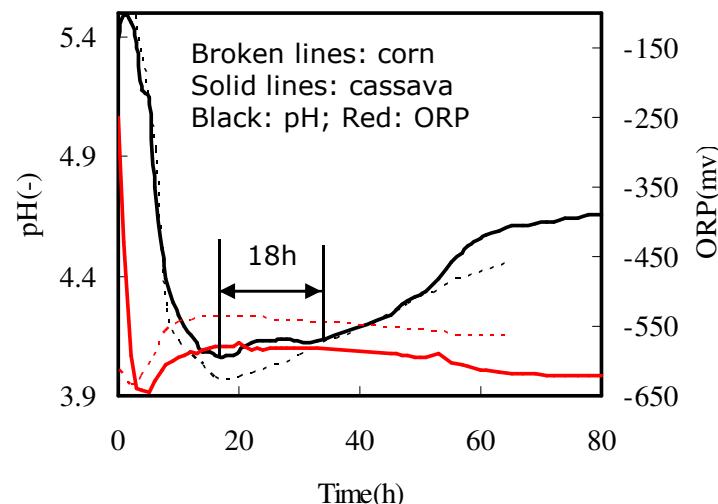
Very low solvents production rates



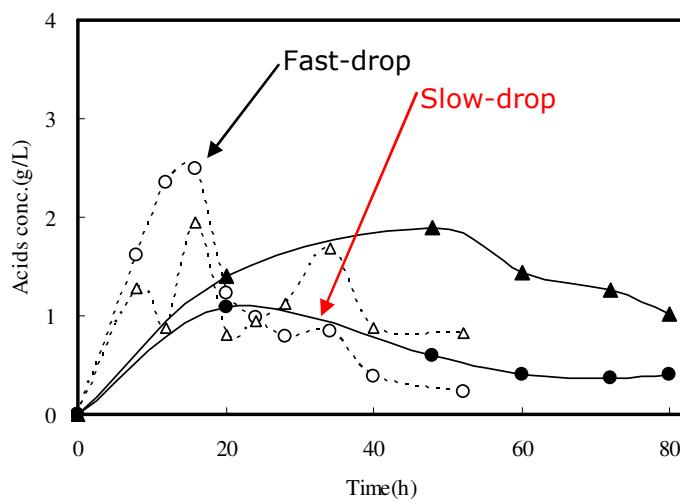
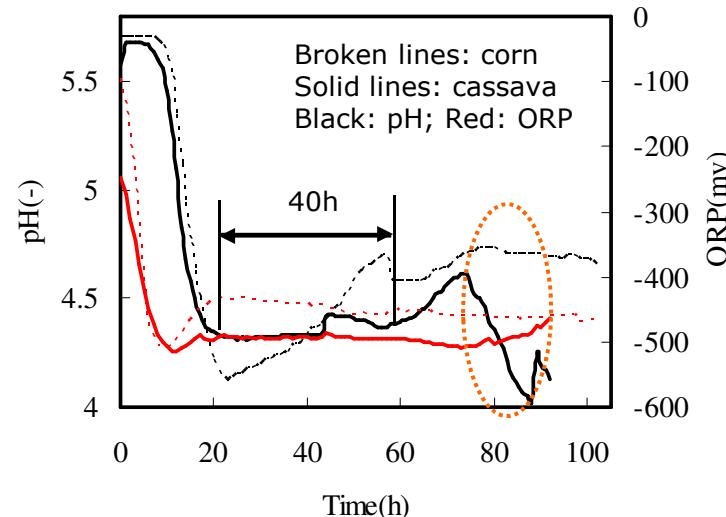
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Long time delay in shifting from acidogenic to solventogenic phase

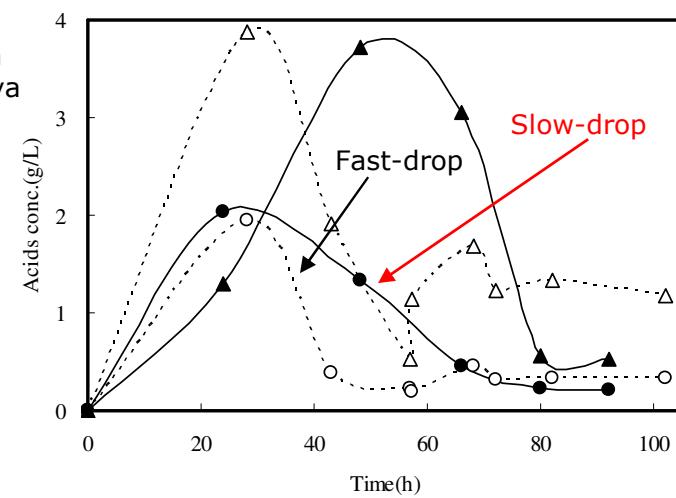
Traditional AB fermentation



Extractive AB fermentation using oleyl alcohol



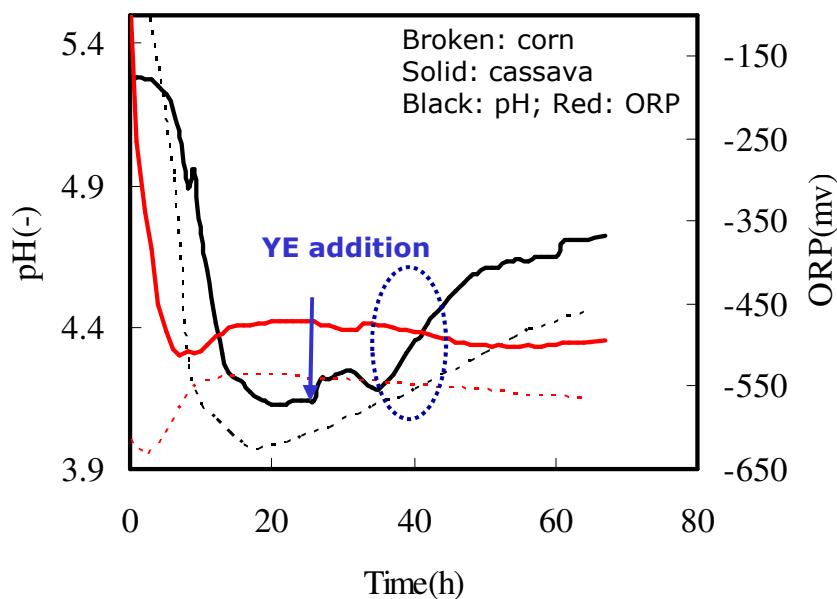
Broken lines: corn
Solid lines: cassava
Circle: butyrate
Triangle: Acetate



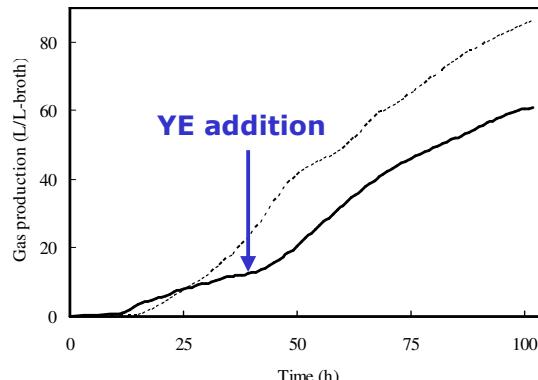
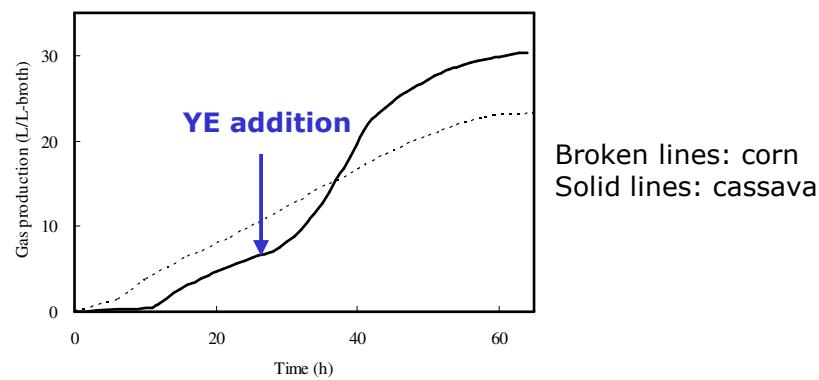
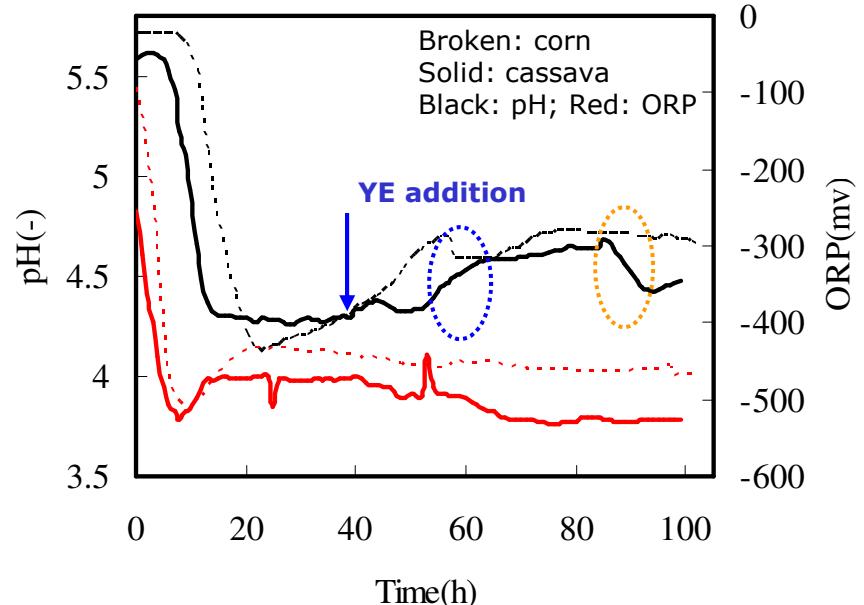
Bio-energy III, Lanzarote, Spain - Results

Yeast extract stimulates bio-butanol production from cassava

Traditional AB fermentation



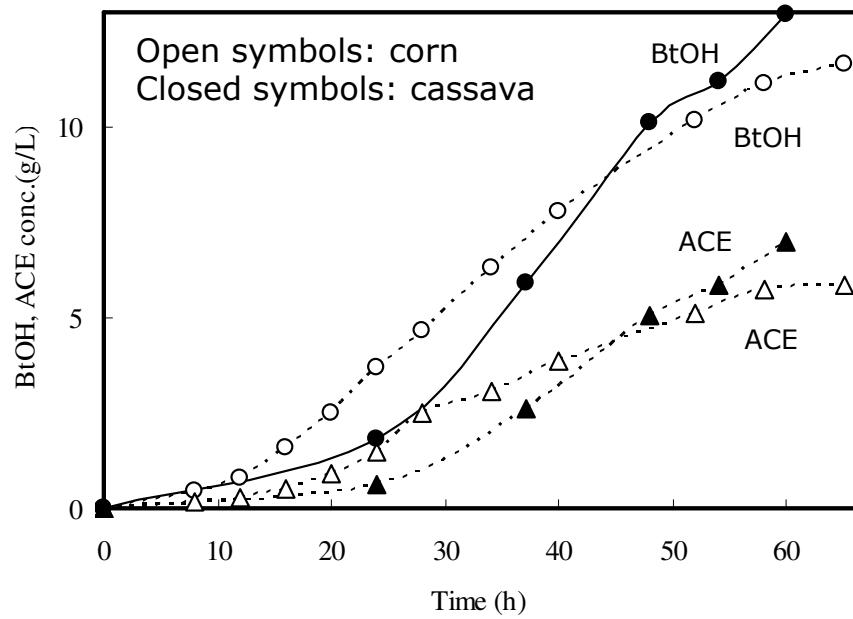
Extractive AB fermentation using oleyl alcohol



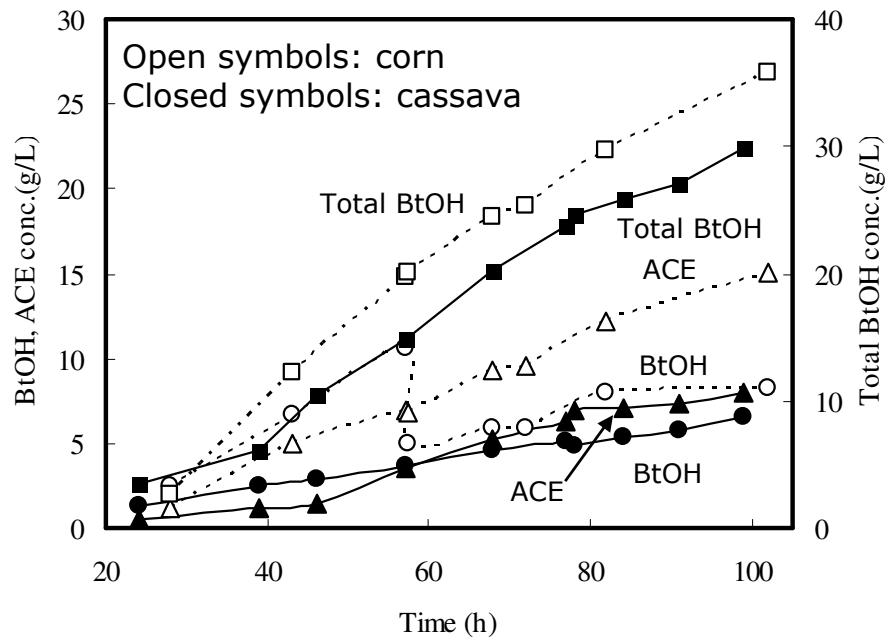
Bio-energy III, Lanzarote, Spain - Results

Yeast extract stimulates bio-butanol production from cassava

Traditional AB fermentation

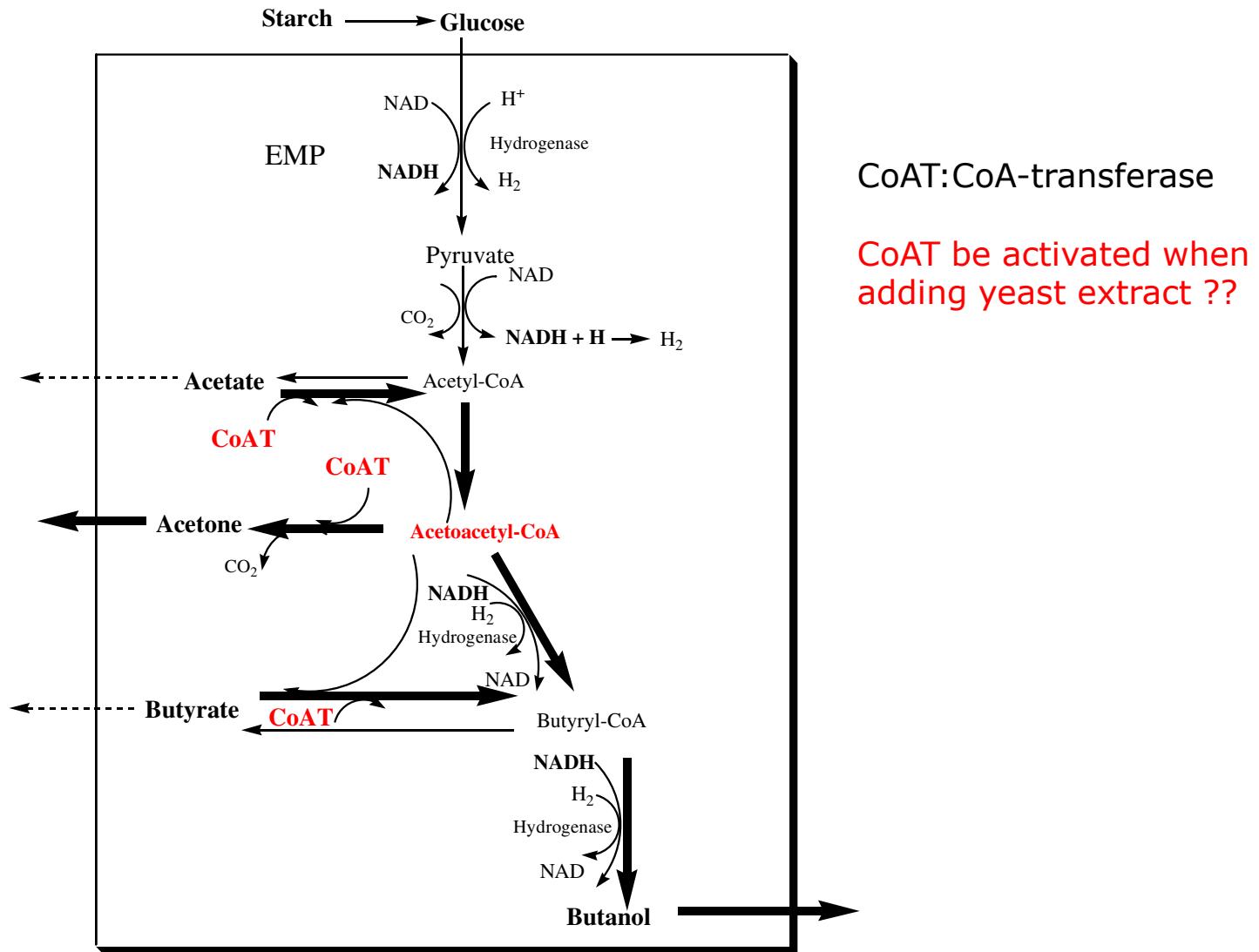


Extractive AB fermentation using oleyl alcohol



Bio-energy III, ECI, Lanzarote, Spain - Results

Yeast extract stimulates bio-butanol production from cassava



Bio-energy III, Lanzarote, Spain - Conclusions

- 1) A novel, integrated fermentation process in production of both "properties improved" bio-diesel for direct use and pure butanol, was proposed.
- 2) Using a small amount n-octanol to recover BtOH in residual wastes before medium preparation, aimed butanol yield increased from 13% to 21%, easing purification load.
- 3) The fermentation residual waste could be 100% re-utilized for medium preparation by pre-treating with 3% activated carbon to remove melanoidin.
- 4) Fully recycling of fermentation residual waste for AB extractive fermentation could be continued for at least 15 runs without performance deterioration.
- 5) Yeast extract stimulates bio-butanol production from cassava.

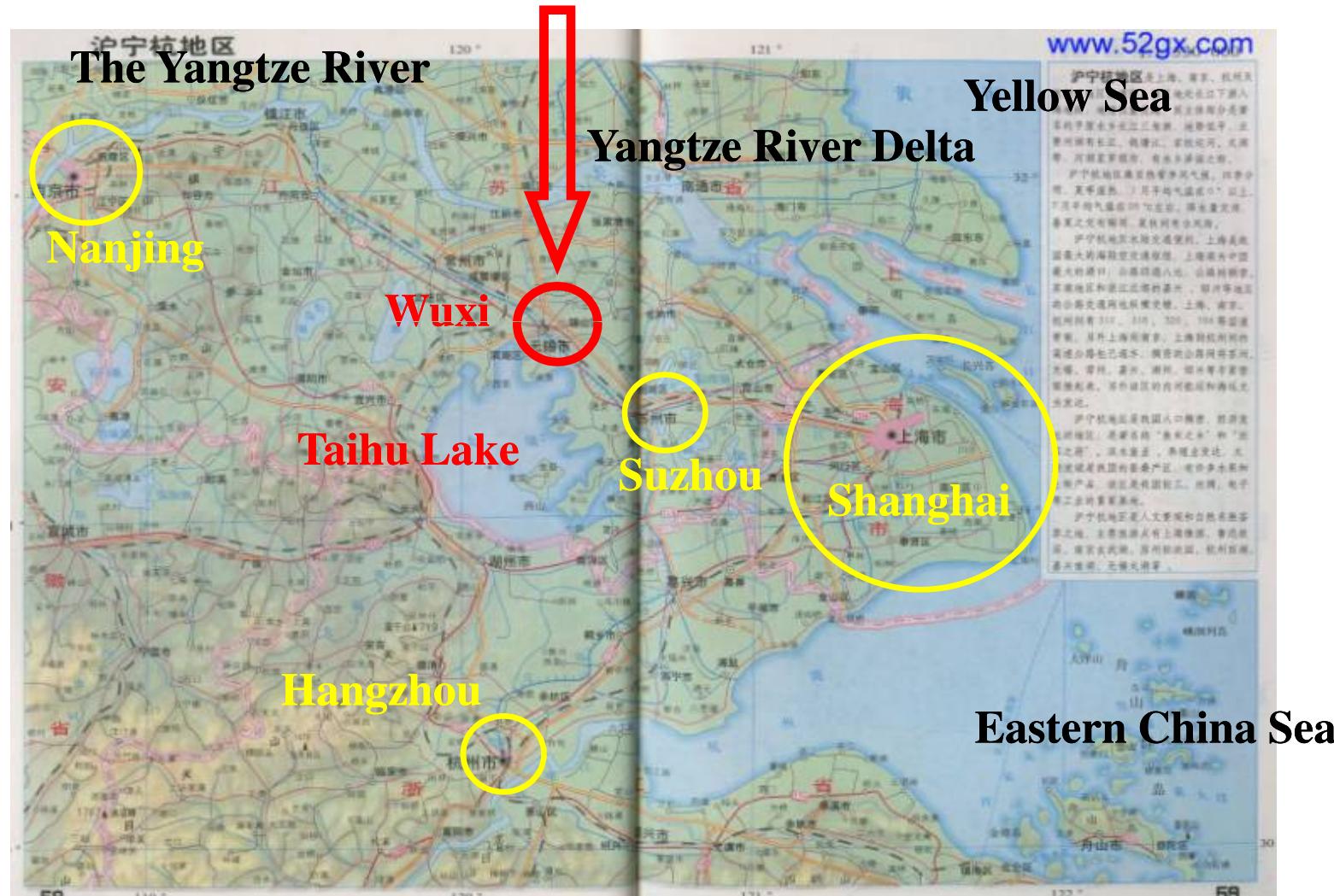
Bio-energy III, Lanzarote, Spain - Acknowledgement

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- **Thanks for the hard experimental works & contribution from following students: Mr. ZG Li, Mr. X Li, Ms. JP Zheng, Ms. L Li.**

Bio-energy III, Lanzarote, Spain

Our location – welcome to visit us for communication/consultation



Bio-energy III, Lanzarote, Spain

Thank you!