New Biodiesel Process and Technology Provided by Us

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What is biodiesel and its benefit in general ?

Biodiesel(BD) fuel has been tested extensively for emissions and compatibility with existing engines and meet fuel property standards.

Biodiesel met include:

- Development and meet of a fuel standard (ASTM,EN,JIS)
- Engine manufacturer's acceptance
- Positive public image and acceptance(Renewable/Ecological fuel)
- Contains no petroleum, but can be blended at any level with petroleum-based diesel to create a biodiesel blended fuel.
- Burns in compression-ignition (diesel) engines without having to perform major modifications to the engine.
- Simple to use, biodegradable, non-toxic and free of sulfur and aromatics,not like petroleum

Biodiesel Fuel Advantages

- **A more environmentally friendly alternative to petroleum diesel fuel**
- **An alternative to reduce greenhouse gas emissions such as CO2, carbon monoxide, particulate matter and hydrocarbon emissions. ,but increase NOx emission slightly.**
- **Can be made simply from used oil(WVO/UCO) or unused vegetable oils(VO),off-specification waste oils derived from the food processing industry or from fats, tallow and animal fats and non-food vegitable or tree seed oil(Jatropha,Castor Oil,etc.).**
- **Used as diesel engine fuel(cars/heavy duty construction machines) w/o modification and also for boiler/generator burning fuels(Bioheat).**
- **Compatible with the existing fuel distribution & infrastructure facilities.**
- **Biodiesel reduces emissions by more than 80-90%(with natural gas based methanol,but almost 100% with renewable ethanol based biodiesel).**

Biodiesel said to be poor winter cold weather performance in general.. However, can be used up to -40 or less deg.C(See above),if treated properly by our technology.

Biodiesel Basics and its Problems

- Reaction(called Transesterification) takes place chemically such as
  1(VO)＋3(Methanol)⇒3(BD)+1(Glycerin)
  BD: Biodiesel
- Commonly,traditional (homogeneous) lye (NaOH,KOH) used as catalyst and made BD as product ,and glycerin,soap,etc as byproduct.
- Need purification to remove byproducts through water-washing,or newer dry-processing.
- As the state of arts of technology for BD, heterogenious(solid) catalysts(Metal Oxides, Enzymes) processes are just recently introducing and higher purity BD as well as clean chemical grade-glycerin are produced(no-catalyst and no-soap byproduct separation).
- Metal oxide processes mostly need higher temperature(pressure) to speed-up reaction kinetics

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As extensive evaluation works were performed in past a few years, solid catalysts were future way as our next-generation biodiesel process.

Results become EnZymatic catalyst were selected as the best among them.

Main differences between biodiesel made using chemical Lye and EnZyme Solid Catalyst (1)

The differences are highlighted in the table below.

EnZymatic Process

- **Reaction temperature: low as 10-35°C.**
- **Feedstock(FFA:Free Fatty Acid): Any purity of FFA feedstocks up to 100% .**
- **No effect on biocatalysis at water content <5%,so that low grade methanol/ethanol can be used.**
- **No-Soap byproduct.**
- **Biodiesel yield >98+% .**
- **Glycerin quality is transparent salt free & high quality.**
- **No catalyst removal and may no or only simplified Dry washing depending on fuel purity requirements.**

Conventional Lye Process

- **55-70°C (higher energy).**
- **Reduced up to 2~3%(by acid or lye treatment for greater than 3%FFA) .**
- **Need pre-treatment de-hydration /FFA removal/higher water-free methanol.**
- **Makes soap with FFA.**
- **Typically, 96%(98%+ by our MSR:Milli-seconds reactor).**
- **Blackish-brown; pH >7; low quality; contains salt and others.**
- **Final product requires Wet/Dry washing to remove catalyst/soap.**

Main differences between biodiesel made using chemical Lye and EnZyme catalyst (2)

Enzymatic Process

- **Recyclable Catalyst for one year**
- **Methanol recovery :No or less excess methanol,which is enough for water content <5%.**
- **Waste generation:Extremely low**
- **Catalyst requirement /Ton:0.3 kg**
- **Cost of catalyst/kg of BD:$0.05-0.07**
- **Capital cost:Low. Roughly 50% for conventional technologies**
- **Environment: Non-toxic**
- **Other operating costs:Very low**

Conventional Process

- One time for each reaction
- Large excess of methanol (water content prohibited) . Requires stripping from final product
- Significant waste generation: catalyst, glycelin, soap,water
- 13-15 kg
- $0.09-0.11
- High in general(Very low by our MSR;milli-Seconds Reactor)
- Toxic chemicals
- High(Low by MSR)

The State of Arts,Newest Lye process, still revolutional process

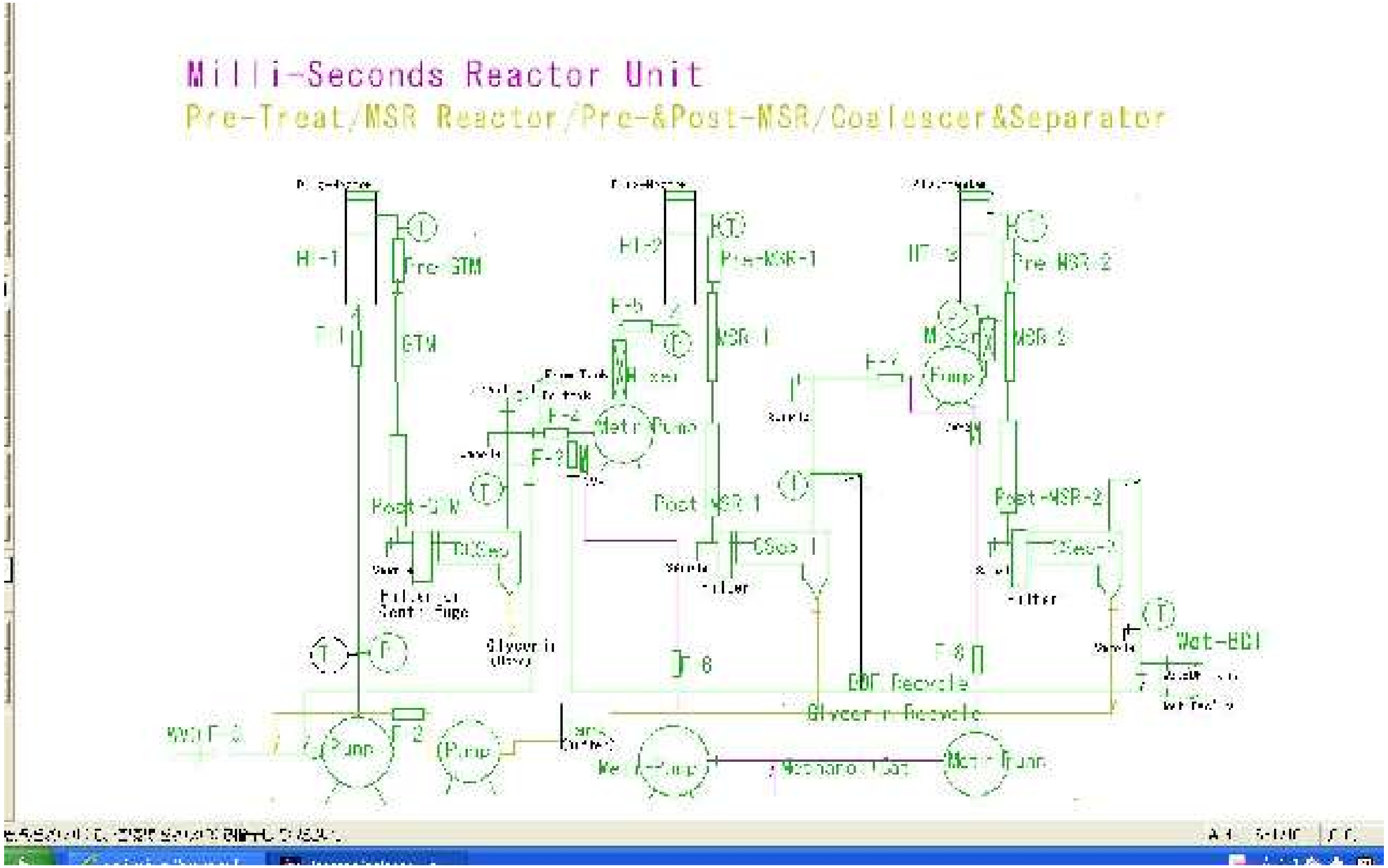
- **Typical lye based process need 2~6 hours of reaction time in batch mode for small to medium sized processor(100~3,000L).**
- **Also typically,need 1-3 hours of residence time for continuous process(large reactor size and cost-up),mostly applied for large plant above 5,000 or 10,000 L/day as minimum .**
- **Our newest state of arts, lye process (MSR:Milli-Seconds Reactor) has capable to :**

  +compleate reaction within 300 to 600 milli-seconds(0.3-0.6seconds).

  +Lowest cost(plant construction and operating expence) and shown small sized process(right) has 5,000-10,000L per day of capacity(dual 3/8" dia x 17" length).

  +Typical methanol requirements are only 15-16%,which is lowest (Another process needs 20~22% typically).

Lye Based Biodiesel MilliSeconds Reactor(MSR) Process Flow



Glycerin byproduct usage of lye catalyst based process

1)As chemical feed stocks

-Base lye trans-esterified reation（by additional distillation、cost-up）.

-Higher purity glycerin by newest & state of art solid catalyst process without such complex operations.

2)As disposal or low-grade

-Boiler fuels mixed with petrorium fuel oils.

-Animal feed stocks（Up to 20%）.See picture.

3)As medium value stocks

-Soap making feed as shown.

-Candle feed ,and others.

The State of Arts,Newest EnZymatic Biodiesel Process

Solid catalyst based processes（metal oxide,EnZyme as Catalysts) are still very little in commercialization and ours is a top runner.

Back-ground

・Capable multi-feed stocks(due to feed shortage and have to explore low-grade FFA oil), and non-food feed stocks(jatropha,palm residue oils,which contain higher fatty acid). Don't applicable by current lye base processes beyond FFA 3-4% .

・Need cost reduction pressure as whole

For plant construction(simple process and lowest cost).

For lowest energy requirement(30~35 deg.C).

For lowest methanol consumption (~15%),which occupay 60~65% of BD operating cost.

and also used or lower grade alcohol(~80%) can be used.

Higher grade glycerin (only by demethanol and dehydration),which contributes to reducing BD cost more (Revenue by sale).

Proposed EnZymatic Technology Overview

- **Breakthrough development of modified and methanol-resistant enzymes enabling industrial use of immobilized enzymes in the process of biodiesel production..**
- **Adaptation of enzymes (lipases) for use in organic synthesis.**
- **Immobilization of enzymes for industrial applications, which is achieved by binding the enzymes to specific solid carriers(resin).**
- **Technology overcomes the major drawbacks of enzyme catalysts in biodiesel production such as:**

+High cost of the enzymes and slow reaction rate.

+Use of solvent to enhance the contact between oil and methanol for speed-up reaction rate(Highly active in solvent-free systems)..

+The methanol-resistant modified EnZymes developed(Mostly,has to be used higher cost ethanol).

+Tolerate low-grade raw materials(oil,methanol or also ethanol,if available) and cost less compareing others.

+Can be used in both multiple batch&continuous processes for long time cycles.

Enzymatic Biodiesel Analysis Data from Soybean Oil

Specification	Units	Test Method	Europe EN 14214	USA ASTM D6751	Results EnZymeCatalyst
Density 15° C	g/cm³	ASTM D 1298	0.86-0.90		0.885
Viscosity 40° C	mm²/s	ASTM D445	3.5-5.0	1.9-6.0	4.2
Distillation	% @ ° C			90%,360° C	
Flash Point	° C	ASTM D93	120 min	130 min	180
Sulphur	mg/kg	ASTM D2622	10 max	15 max	<10
CCR 100%	% mass			0.05 max	400
Carbon Residue	% mass	ASTM D4530	0.03 max		<0.3
Sulphated Ash	% mass	ASTM D874	0.02 max	0.02 max	
Water	mg/kg	ASTM D2709	500 max	500 max	320
Total Contamination	mg/kg	ASTM D5452	24 max		<10
Max CU Corrosion	3h/50° C	ASTM D130	1	3	<1
Oxidation Stability [110° C]	Hours	EN 14112	6 min		
Cetane Number		ASTM D613	51 min	47 min	
Acid Value	mg KOH/g	ASTM D664	0.5 max	0.8 max	0.22
Methanol	% mass	EN 14110	0.2 max		<0.01
Ester Content	% mass	EN 14103	96.5 min		96.6
Monoglyceride	% mass	EN 14105	0.8 max		0.538
Diglyceride	% mass	EN 14105	0.2 max		0.06
Triglyceride	% mass	EN 14105	0.2 max		<0.001
Free Glycerol	% mass	EN 14105	0.02 max	0.02 max	0.005
Total Glycerol	% mass	EN 14105	0.25 max	0.24 max	0.183
Iodine Value		EN 14111	120 max		127
Linolenic Acid Methyl Ester	% mass	EN 14103	12 max		5.9
Polyunsaturated Methyl Esters	% mass		1 max		
Phosphorous	mg/kg	ASTM D4951	10 max	10 max	<0.1
Alkalinity	mg/kg				
Group I Metals [Na, K]	mg/kg	EN 14109	5 max		<0.1
Group II Metals [Ca, Mg]	mg/kg	EN 14538	5 max		<0.1

Glycerin Quality Results & discussion

Quality analysis of enzymatically formed glycerin vs chemically formed glycerin

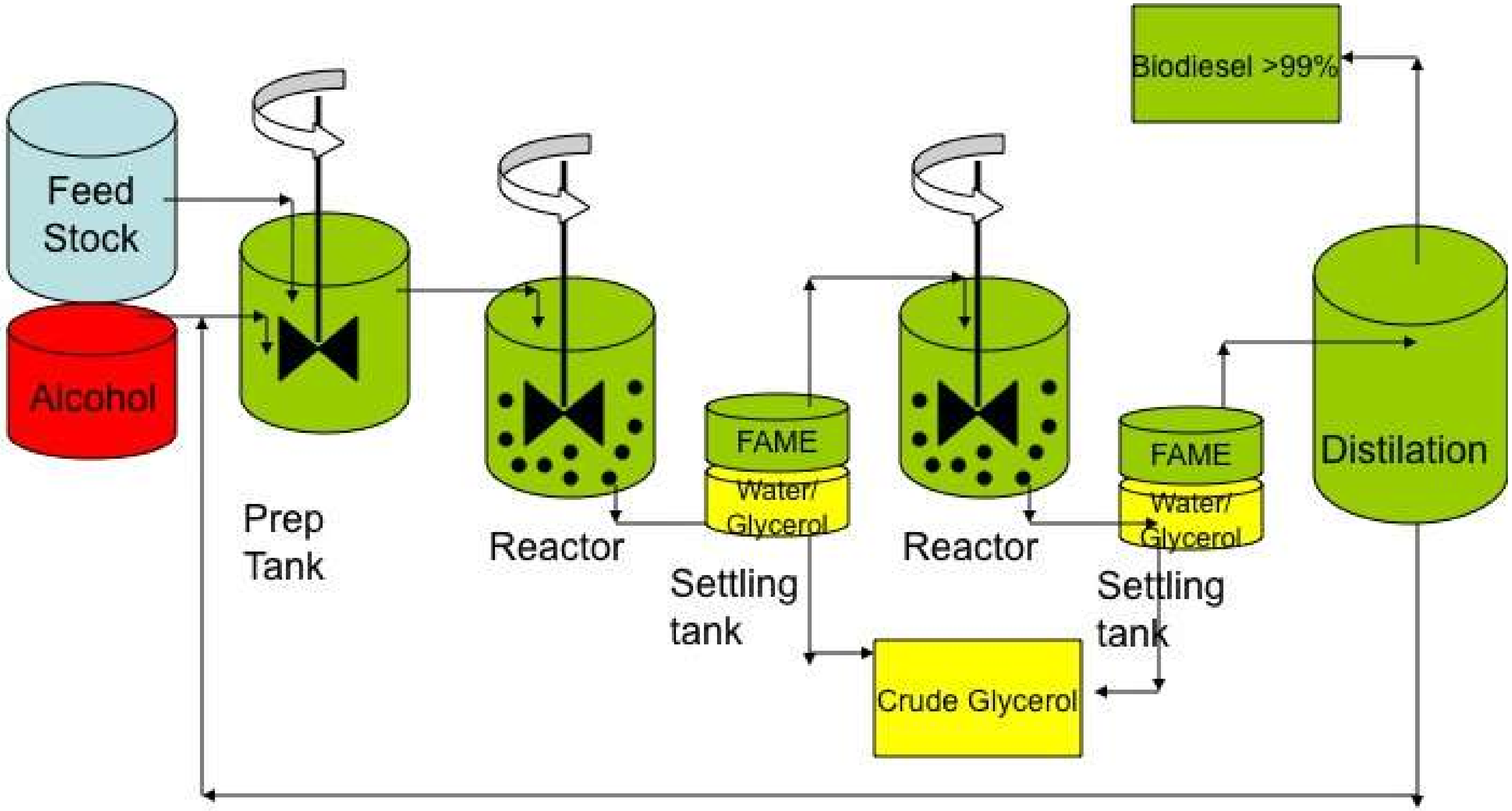
Chemically	Enzymatically	Property
Very brown	Transparent	Appearance
44% - 54%	78%	Glycerin content
8.9 – 10.5	6.0 – 6.2	pH
27 - 53%	3%	Methanol content
1 - 4%	7%	Water content
7%	0.1%	Sulphated ash

Enzymatically formed glycerin

Chemically formed glycerin

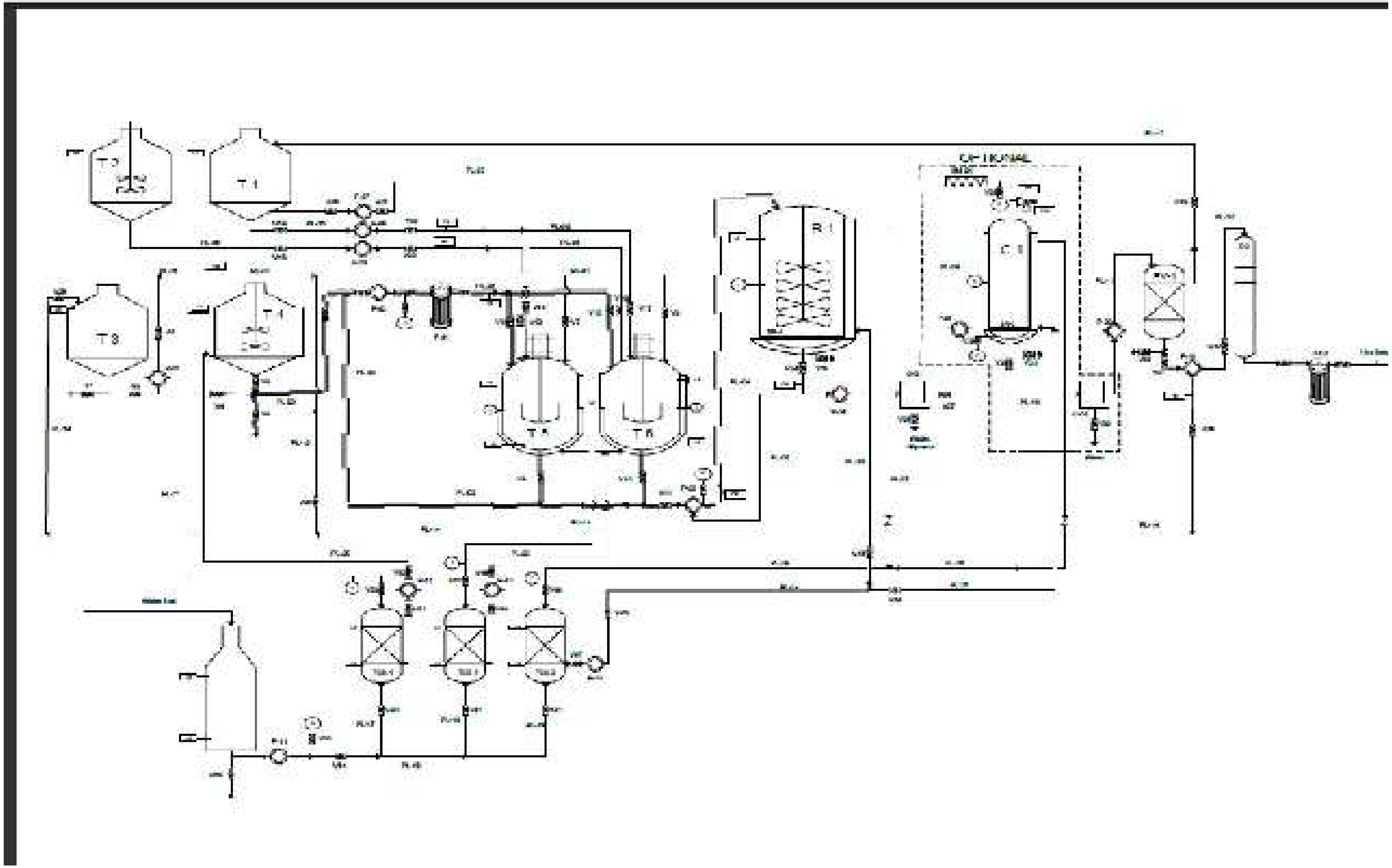
The results of the analysis confirmed that the enzymatically formed glycerin is of much better quality than the glycerin formed via conventional chemical process

Proposed State of Art Enzymatic Process Overview (1)



Proposed State of Arts Enzymatic Process Overview (2)

P&I diagram examle



Enzymatic Biodiesel Plant Running Examples (15 ton/day)

Enzymatic Biodiesel Plant underconstruction Example (35 ton/day)

Proposed EnZymatic Process Summary

We believe the proposed EnZymatic process is:

- the most advanced state of art & cutting edge technology and also being field proven biodiesel process.
- used for the most wide and multi-feedstocks(0-100%FFA,virtually all feedstocks available), as well as waste vegitable oil(Ca'nt find elsewhere !).
- the highest purity biodiesel fuel as well as glycerin are obtained.
- the easiest plant operation and simplest process flow .
- the most cost competive and economical process and can keep your competiveness & investment for long time future.
- Our Japanese manufacturing excellence&quality control(QC) standard&practices and extensive knowledge&expertise in biodiesel.

End of Presentation

Thank you

by Akira Hirai