

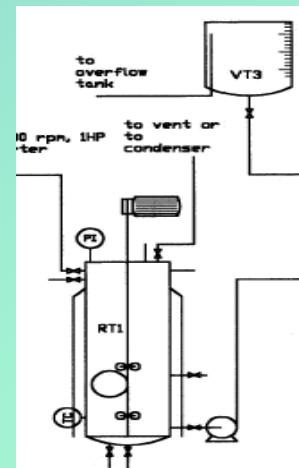
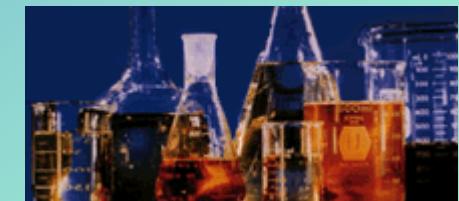
CHALLENGES IN BIODIESEL PRODUCTION

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Naples, 12 December 2005



- Our University – School
- Biodiesel General
- Production Processes
- Our research targets
- Thermal Process
- Catalytic Process
- Enzymatic Process
- Pilot Plant
- Conclusions





- Oldest and most famous T. U. in Greece
- Founded in 1836
- Comprises the Schools of :
 - *Chemical Engineering*
 - *Civil Engineering*
 - *Architecture*
 - *Mechanical Engineering*
 - *Electrical Engineering*
 - *Mining and Metallurgical Engineering*
 - *Naval Architecture and Marine Engineering*
 - *Rural and Surveying Engineering*



Founded in 1917

Consists of the Sections :

- ✓ Chemical Science
- ✓ Process Analysis and Plant Design
- ✓ Material Science and Engineering
- ✓ Synthesis and Development of Industrial processes

Incoming students : 140 per year

5 years studies

Courses : 9 Semesters

Diploma Dissertation : 1 Semester

Research Targets and Activities

Simulation, Design and Development of
Chemical and Biochemical Processes

Fields of applications

Hydrotreatment of Petroleum Fractions

Diesel Hydrodesulphurization

Naphtha Hydrodesulphurization

Benzene Hydrogenation

Biofuels Production

Biodiesel production processes

Bioethanol plant design

Simulation of :

- Laboratory Reactors
- Pilot Reactors
- Industrial reactors

Scale up / Scale down studies

Reactor miniaturization

CATALYTIC PROCESSES

Homogeneous Catalysis

a. Bases (NaOH , KOH , CH₃ONa)

Methanol / Oil = 6 / 1(mol / mol); Reaction Temperature 61 – 64 °C

b. Acids

Methanol / Oil = 30 / 1 (mol / mol); Reaction Temperature 61 – 90 °C

Heterogenous Catalysis

a. Basic catalysts (CaO , MgO , Ca(OH)₂ , Mg(OH)₂)

Methanol / Oil = 6 / 1 (mol / mol); Reaction Temperature 150 – 210 °C

b. Acid catalysts (Zeolites, superacids)

Methanol / Oil = 6 / 1 (mol / mol); Reaction Temperature 150 – 210 °C

THERMAL PROCESS

Methanol / Oil = 6 / 1 (mol / mol); Reaction Temperature 150 – 210 °C

ENZYMATIC PROCESS

Methanol / Oil = 1-1.2 / 1 (mol / mol); Reaction Temperature 30 – 45 °C

Homogeneous Basic Catalysis

- Production of soaps from FFA and water in Oil
- Glycerine needs cleaning
- Biodiesel needs cleaning from catalyst
- Catalyst consumption

Homogeneous Acid Catalysis

- High Methanol / Oil ratios
- Prolonged reaction time
- Corrosive environment due to the presence of acid
- Biodiesel, Glycerine need cleaning from catalyst

Heterogeneous Catalysis

- High Reaction Temperature, Pressure

Thermal Process

- High Reaction Temperature, Pressure

Enzymatic Process

- High Biocatalyst Cost / Low reaction rates

Processes Investigated

Thermal

Heterogeneous Catalysis

Enzymatic

Feedstocks

Cotton seed Oil / Acid Cotton Seed Oil
(60,000 tn/year)

Sun flower Oil
(10,000 tn/year)

Soya bean Oil
Imported

Used cooking Oils (Olive Oil etc)
(20,000 tn/year)

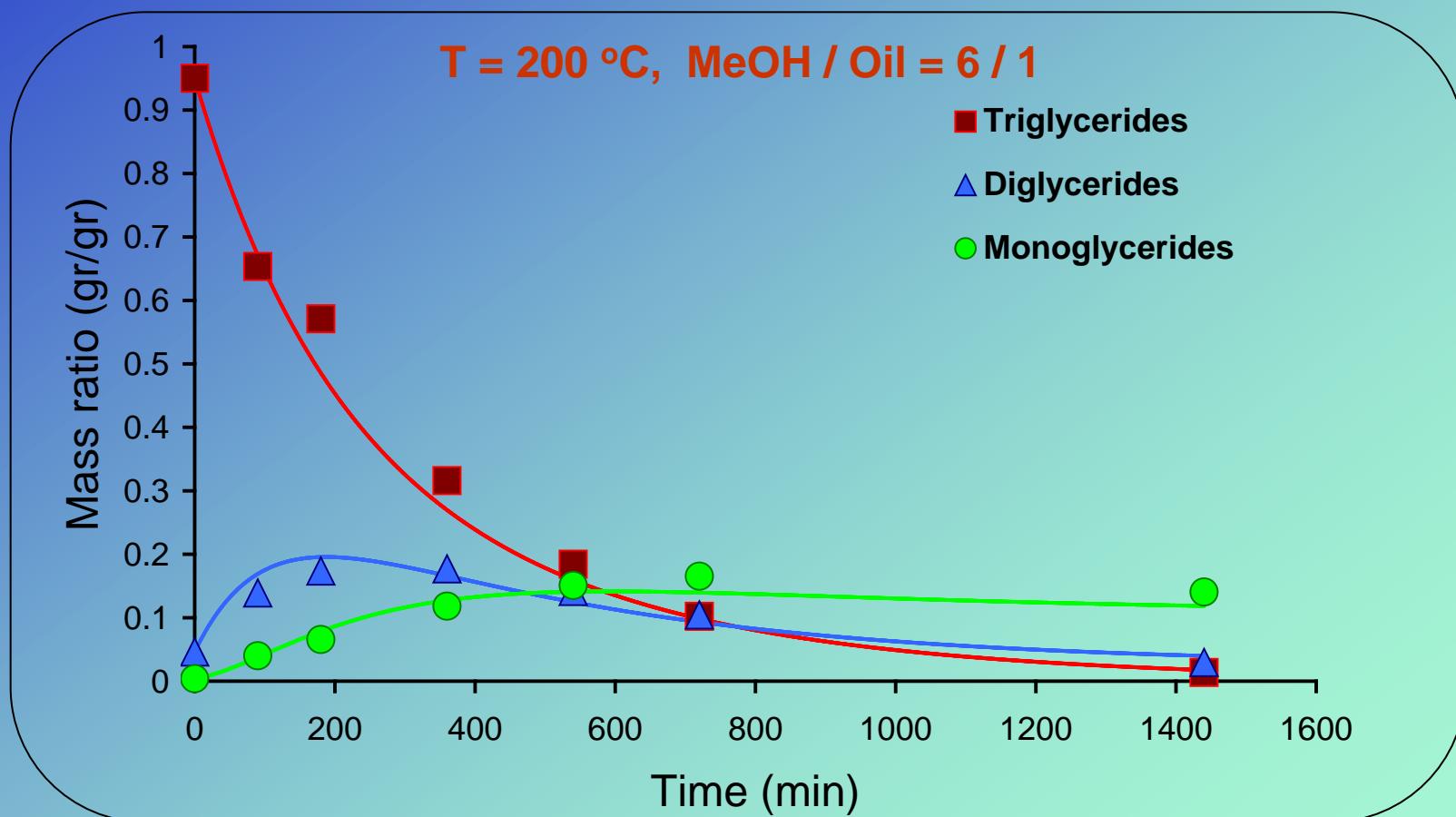
Waste Animal Fats
(20,000 tn/year)

EXPERIMENTATION

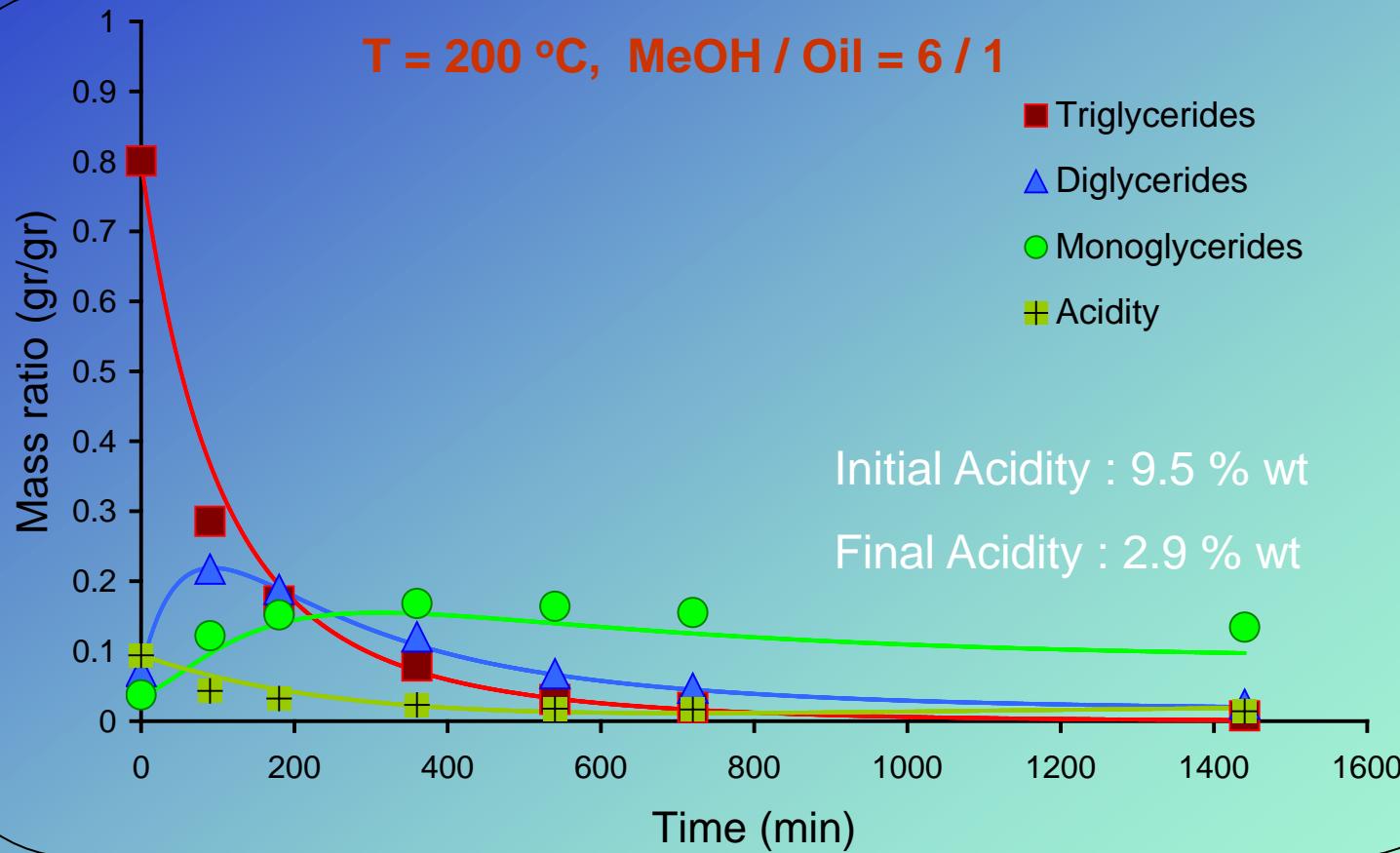
- *Batch Reactor*
- *Sampling during operation*
- *Reaction Temperature : 170 – 220 °C*
- *Reaction Pressure : 12 – 40 bar*



Refined Cotton seed Oil

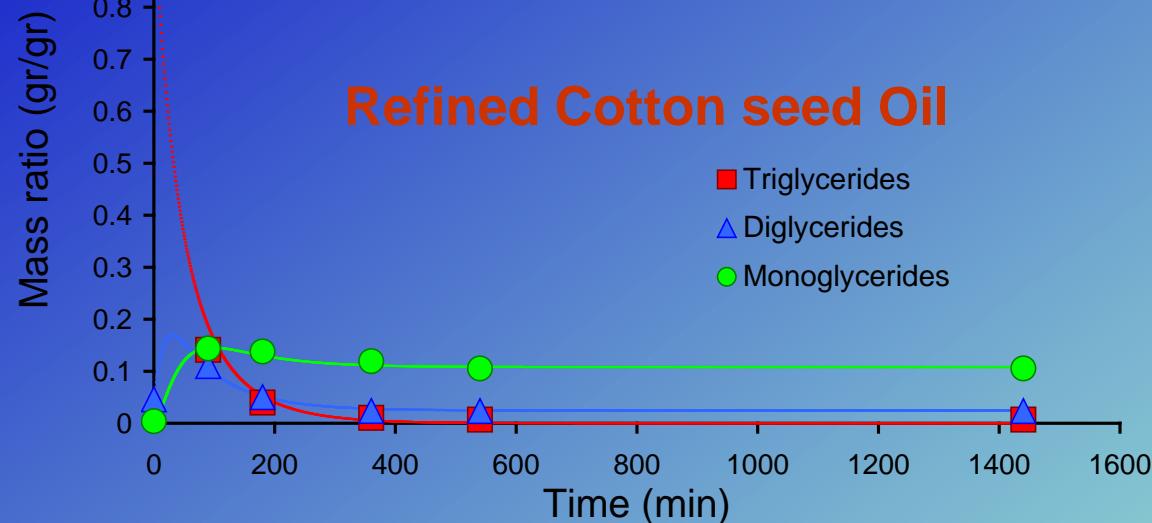


Acidic Cotton seed Oil

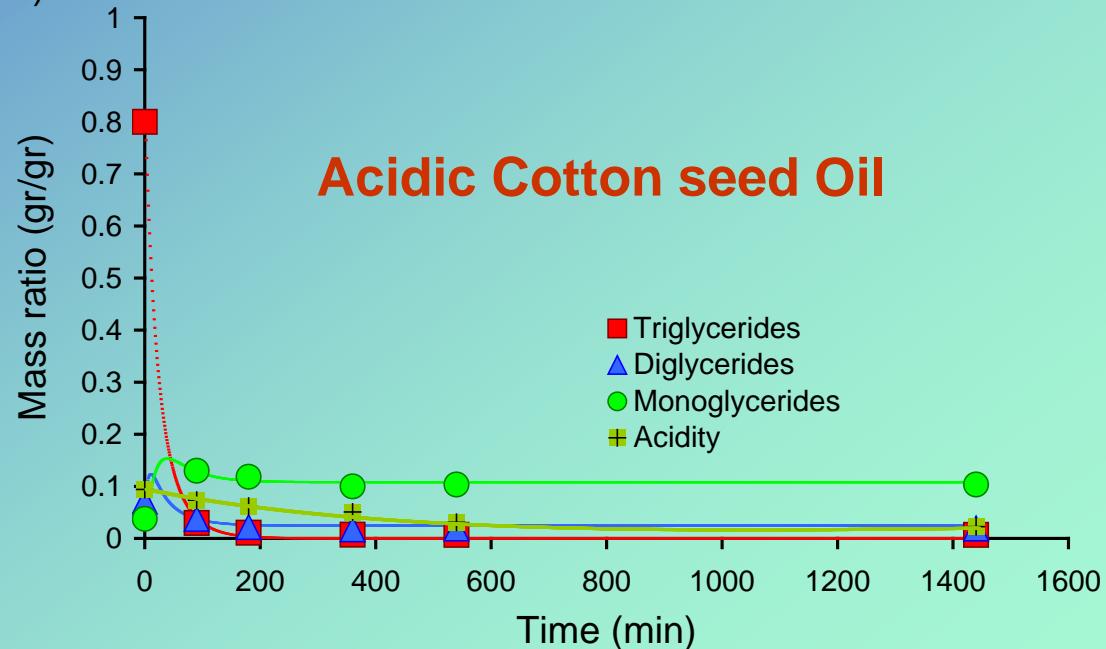


T=200°C , methanol / oil 6:1 , 1wt.% Catalyst (HAS)

Refined Cotton seed Oil



Acidic Cotton seed Oil



Initial Acidity : 9.5 % wt

Final Acidity : 2.9 % wt

1. Batch reactor

- ◊ Homogeneous mixture with constant density ($d_{\text{mixture}} = \text{constant}$)
- ◊ Isothermal – single phase mixture, apparent constant rates

2. Three reactions first order with respect to each reacting component

- ◊ Irreversible Triglycerides reaction



3. Equilibrium

- ◊ Reversible Di- and Mono-glycerides reactions



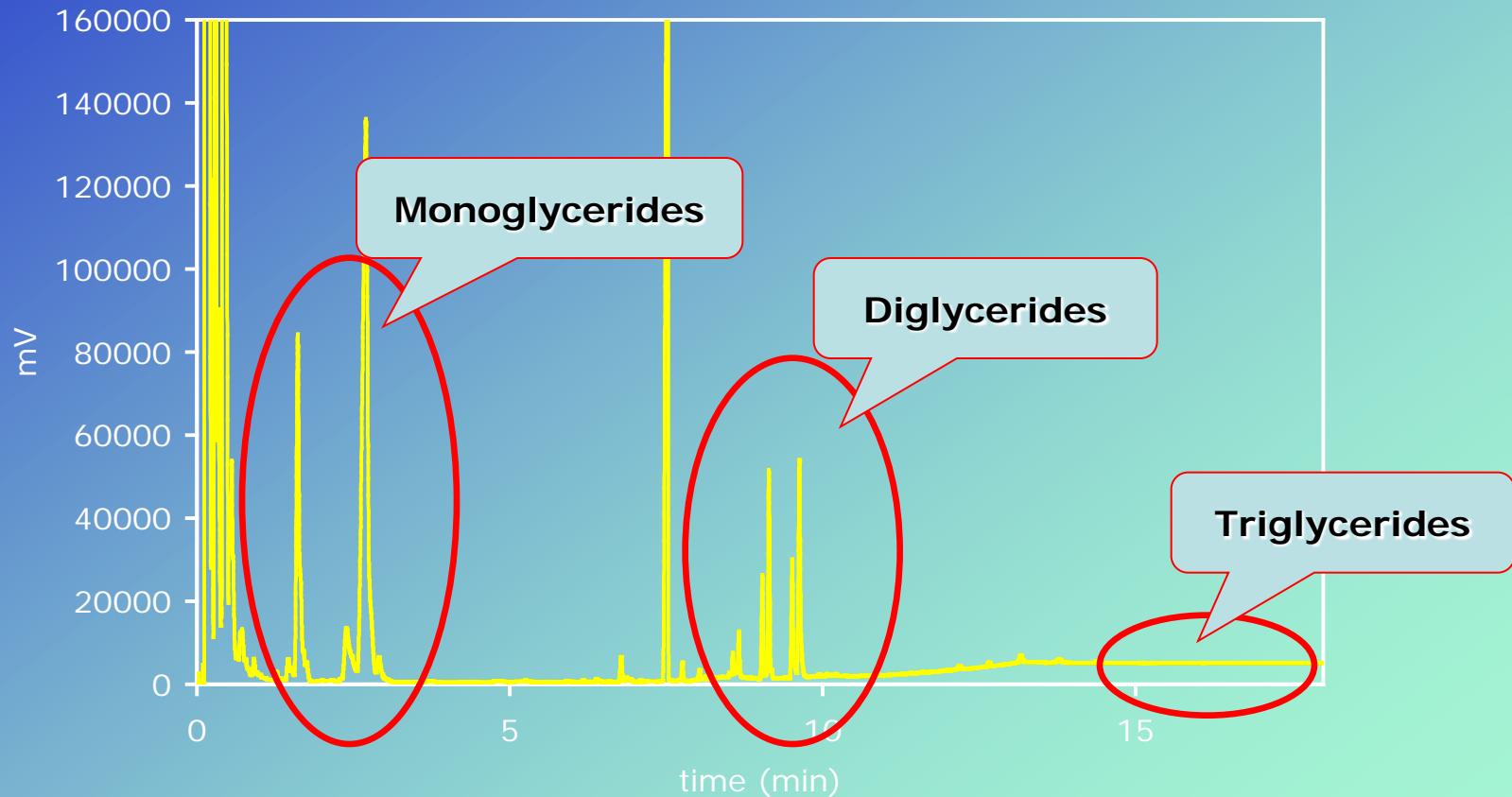
$$K_{\text{eq},2} = \frac{K_2}{K_{-2}} = \frac{C_{\text{MG}} \cdot C_{\text{ME}}}{C_{\text{DG}} \cdot C_{\text{MeOH}}}$$

$$K_{\text{eq},3} = \frac{K_3}{K_{-3}} = \frac{C_{\text{GL}} \cdot C_{\text{ME}}}{C_{\text{MG}} \cdot C_{\text{MeOH}}}$$

Temp. = 200 °C

Molar Ratio

Glycerin : Methyl esters : Methanol = 1 : 3 : 3



1. Triglycerides

Acid oils (High FFAs)
Refined oils

$$\frac{dC_{TG}}{dt} = -K_1 \cdot C_{TG} \cdot C_{MeOH} - K_{1ox} \cdot C_{TG} \cdot C_{MeOH} \cdot C_{ox}$$

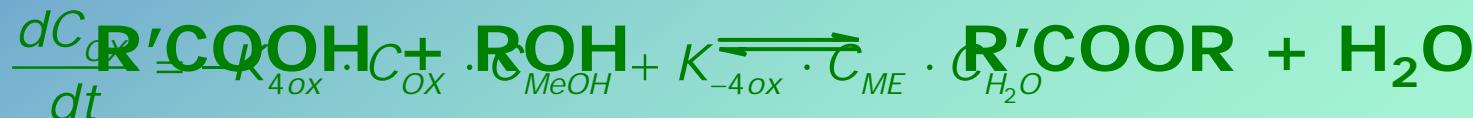
2. Diglycerides

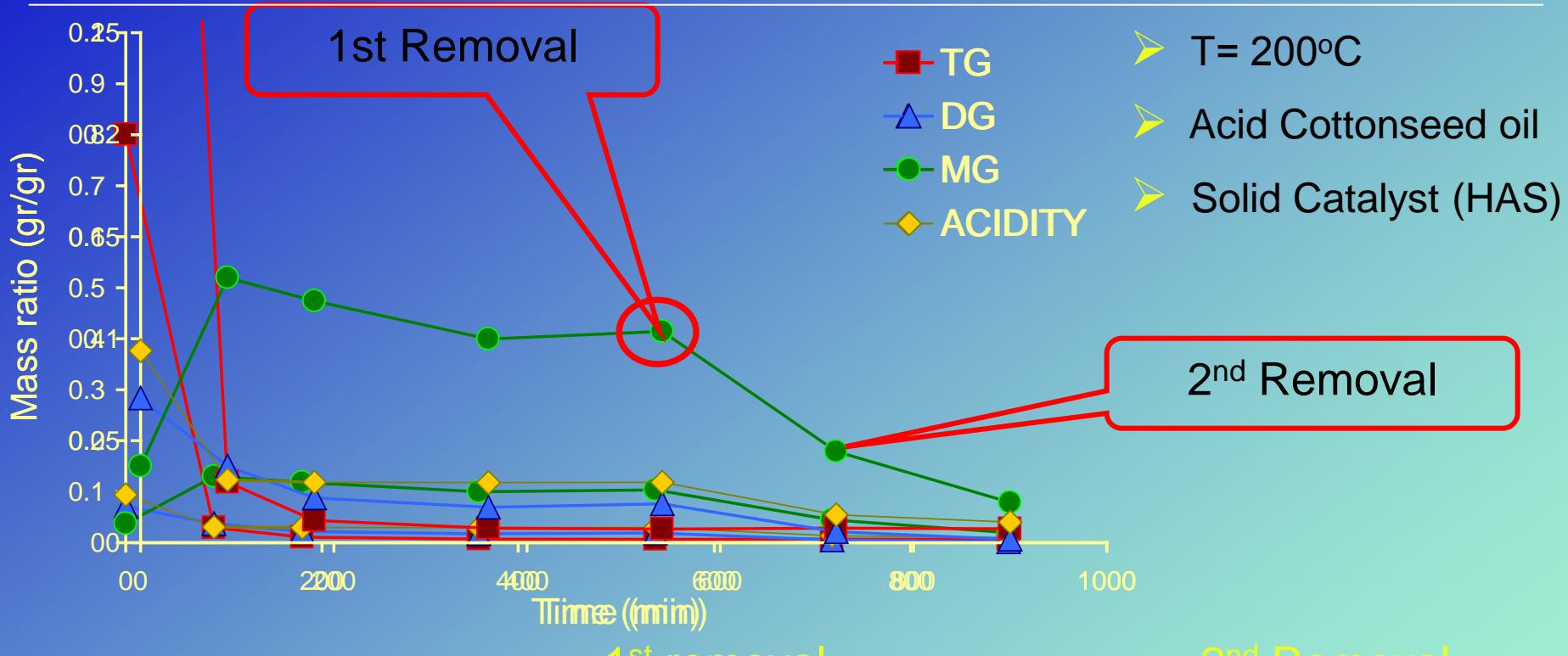
$$\begin{aligned} \frac{dC_{DG}}{dt} = & K_1 \cdot C_{TG} \cdot C_{MeOH} + K_{-2} \cdot C_{MG} \cdot C_{ME} - K_2 \cdot C_{DG} \cdot C_{MeOH} \\ & + K_{1ox} \cdot C_{TG} \cdot C_{MeOH} \cdot C_{ox} - K_{2ox} \cdot C_{DG} \cdot C_{MeOH} \cdot C_{ox} \end{aligned}$$

3. Monoglycerides

$$\begin{aligned} \frac{dC_{MG}}{dt} = & K_2 \cdot C_{DG} \cdot C_{MeOH} + K_{-3} \cdot C_{GL} \cdot C_{ME} - K_{-2} \cdot C_{MG} \cdot C_{ME} - K_3 \cdot C_{MG} \cdot C_{MeOH} \\ & + K_{2ox} \cdot C_{DG} \cdot C_{MeOH} \cdot C_{ox} - K_{3ox} \cdot C_{MG} \cdot C_{MeOH} \cdot C_{ox} \end{aligned}$$

4. Acidity

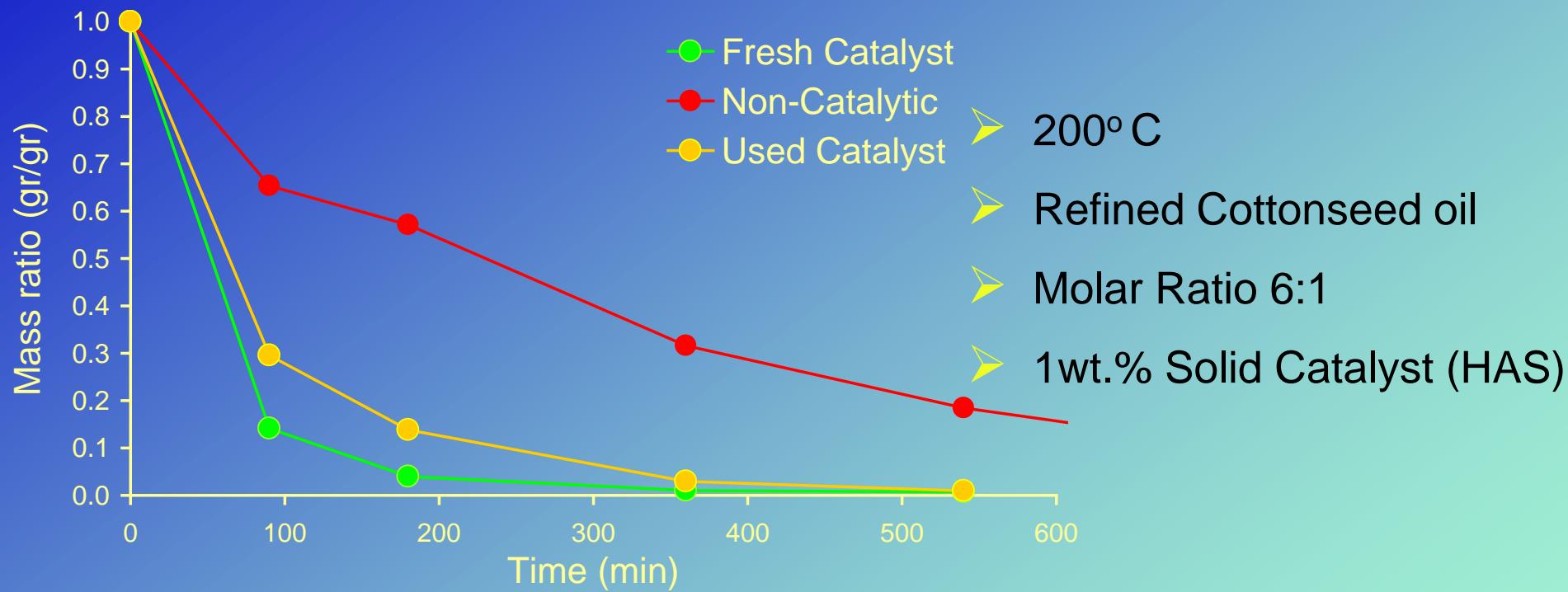




$C_{TG} = 0.0\text{wt.\%}$
 $C_{DG} = 1.8\text{wt.\%}$
 $C_{MG} = 10.0\text{wt.\%}$
 Οξύτητα = 2.9wt.%

$C_{TG} = 0.0\text{wt.\%}$
 $C_{DG} = 0.5\text{wt.\%}$
 $C_{MG} = 4.5\text{wt.\%}$
 Οξύτητα = 1.4wt.%

$C_{TG} = 0.0\text{wt.\%}$
 $C_{DG} = 0.2\text{wt.\%}$
 $C_{MG} = 2.0\text{wt.\%}$
 Οξύτητα = 1.0wt.%

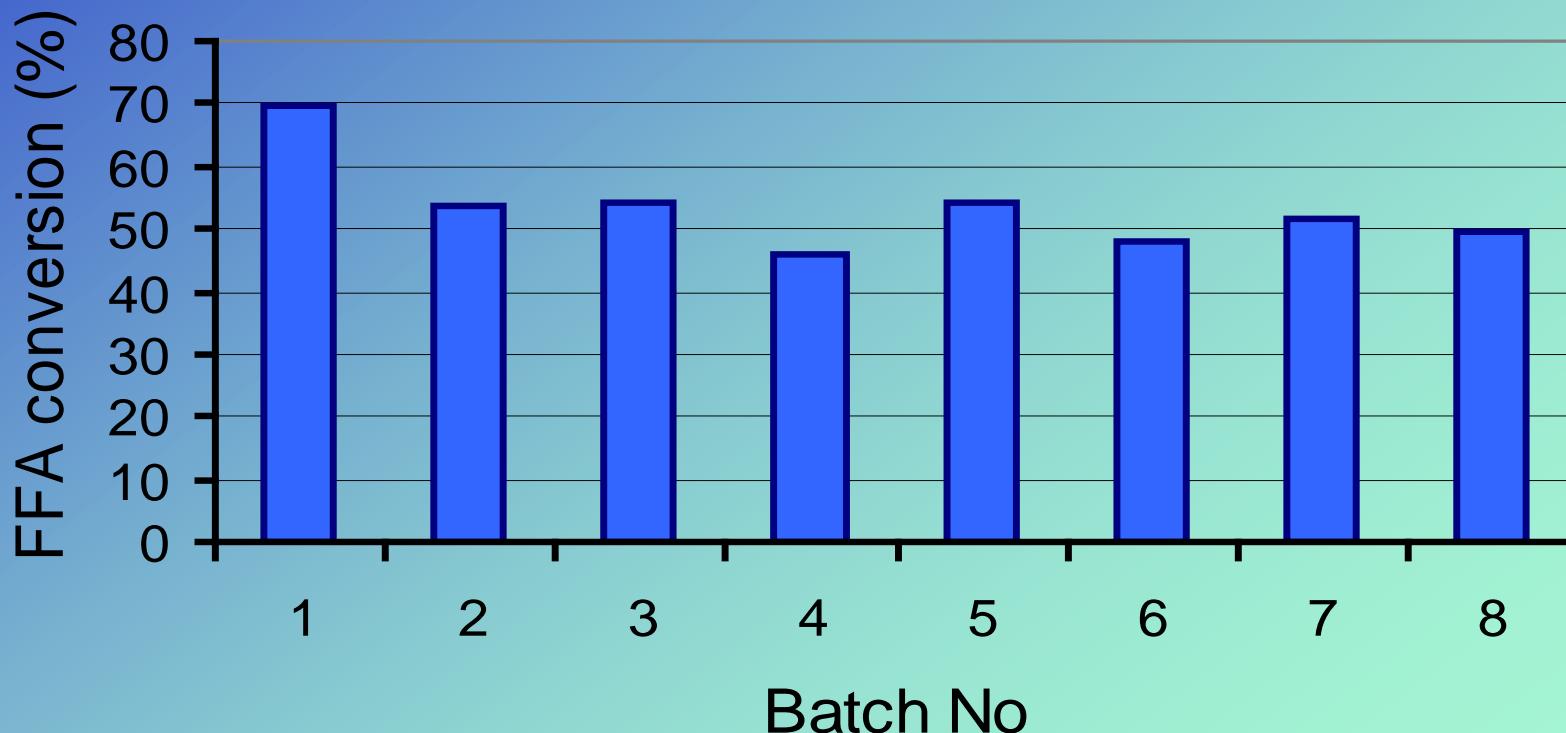


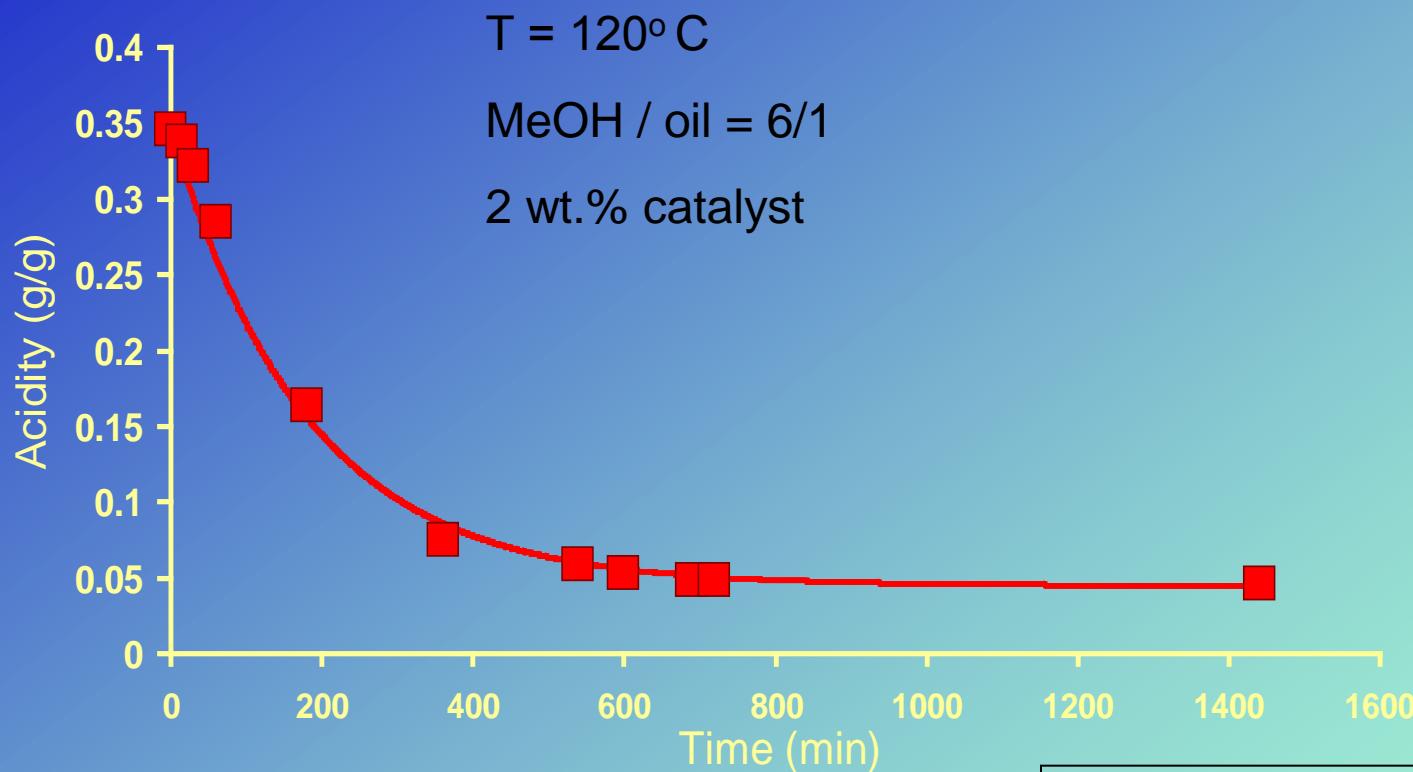
Experimental Results

- Super Acid Oil
 - Refined - Cooked Palm oil
 - Crude Animal Fat
- }
- $C_{TG} = 0.0 \text{ wt. \%}$
- $C_{DG} = 2.0 - 2.5 \text{ wt. \%}$
- $C_{MG} = 10.0 - 11.0 \text{ wt. \%}$

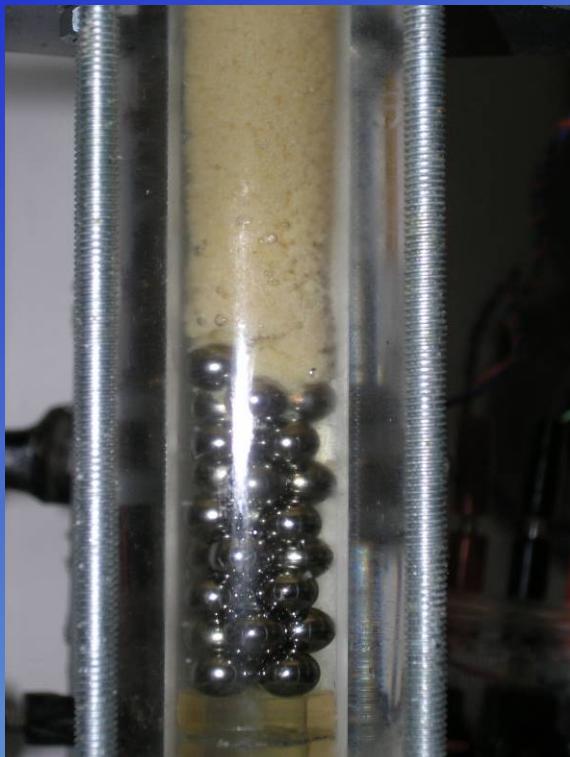
- Feedstock : high FFA oil (acidity 38.1wt.%)
- Molar ratio methanol / oil : 6 / 1
- Catalyst : superacid resin (1wt.% and 2wt.%)
- Reaction temperatures : 90°, 100°, 110°, 120°C
- Purpose : study the deactivation of the catalyst,
examine the influence of mass transfer phenomena,
find the kinetic and equilibrium parameters

- Continuous catalyst reuse
- Reaction temperature, 110°C
- Molar ratio methanol / oil, 6:1
- 1wt.% superacid catalyst
- Reaction time, 12h

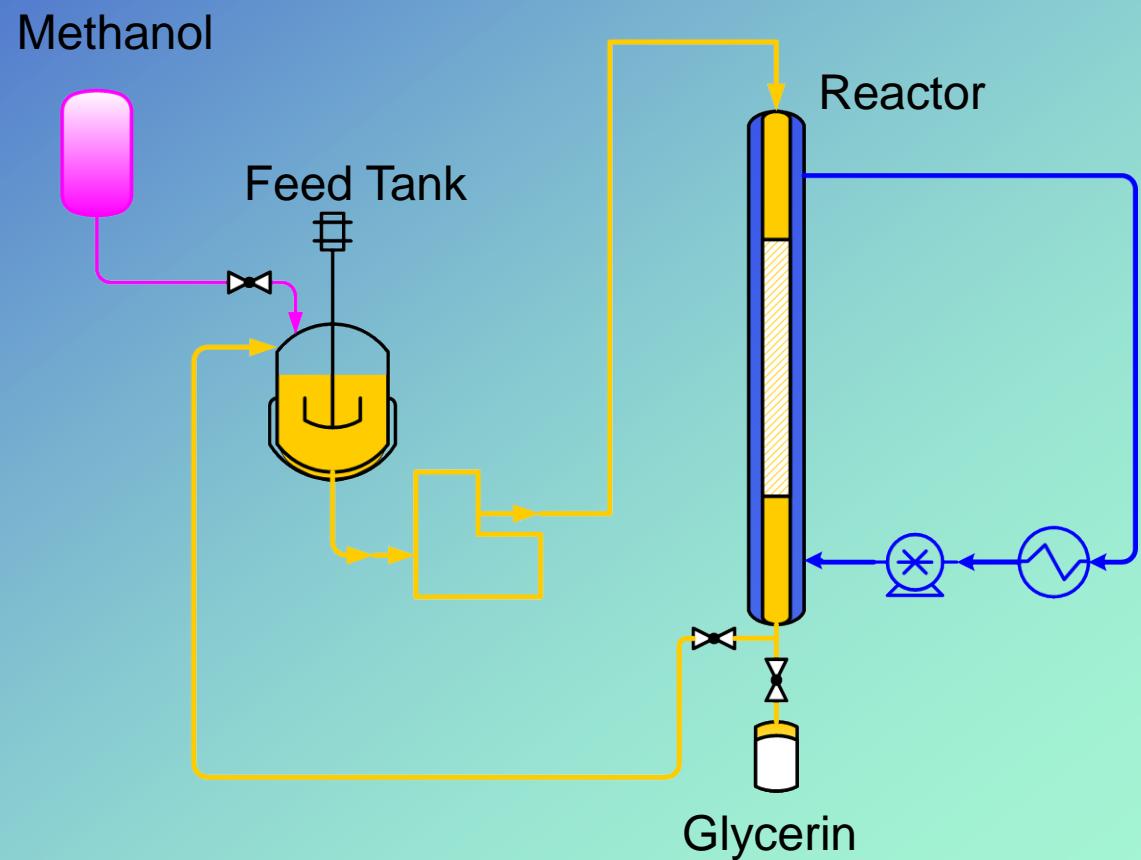




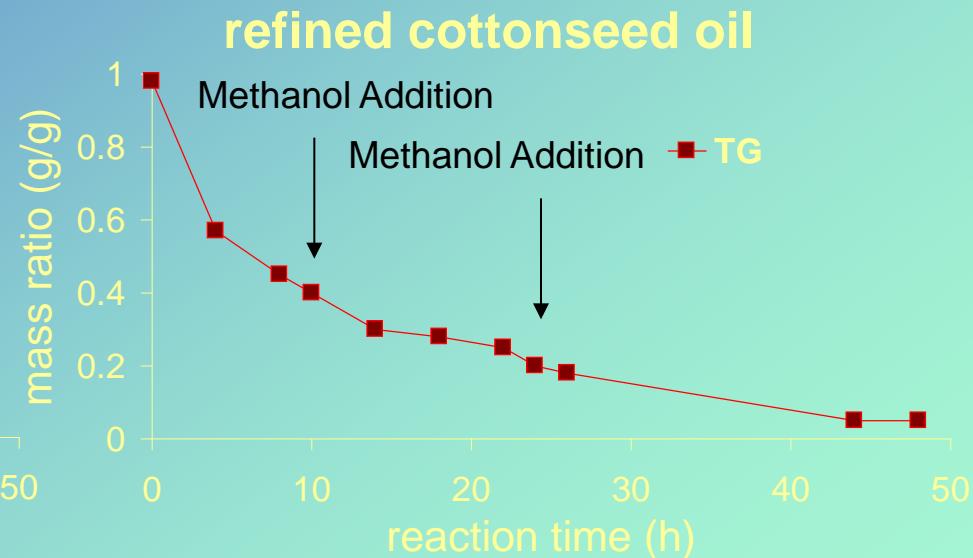
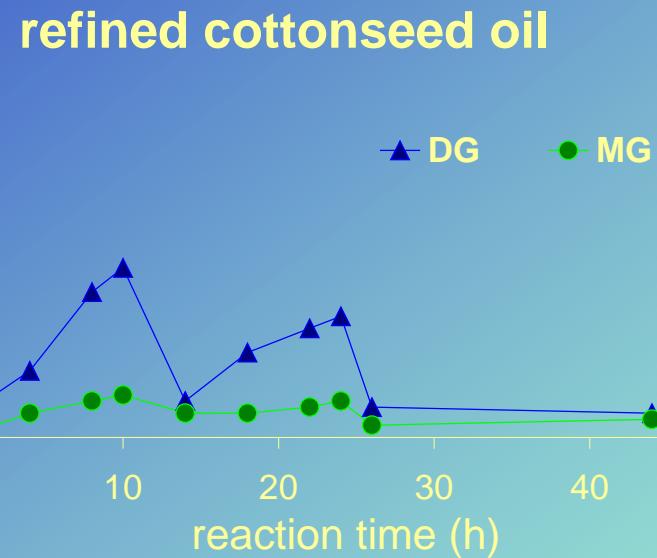
$$k_{\text{ox}} = 44.771 \text{ gmix}^2/\text{min}\cdot\text{mol}\cdot\text{gcat}$$
$$k_{-\text{ox}} = 45.522 \text{ gmix}^2/\text{min}\cdot\text{mol}\cdot\text{gcat}$$



Flow Sheet



System: Semi - Batch reactor
Oil : Refined cottonseed oil
Alcohol : Methanol
Gradual addition of Methanol up to Methanol / Oil = 3 / 1
Batch size : 10 g
Temperature : 35 oC;
Biocatalyst : 4 %w/w Novozym 435



Reactor Volume: 20lt.

Temperature: 62 – 64 °C

Catalyst: 1 wt.% KOH

Alcohol: 6/1 MeOH



Glycerol Removal

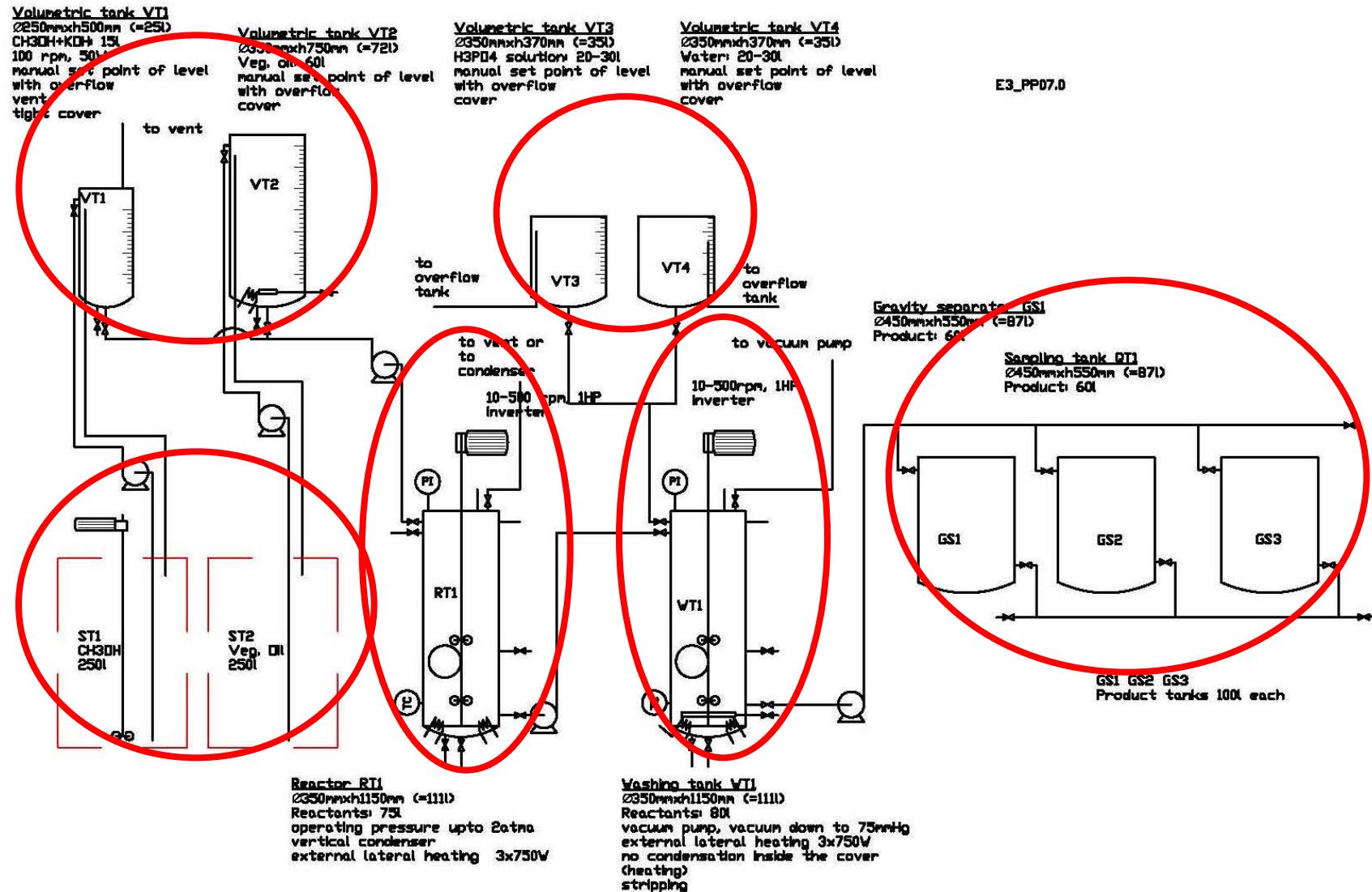
Naples, 12 December 2005



FEED STOCKS
Refined Soybean oil
Neutralized Cottonseed oil



Biodiesel Collection





Properties of our Biodiesel derived from Cottonseed oil

| Property | Unit | min | max | Biodiesel |
|-------------------------------------|-----------------------------|--------|---------|----------------|
| Ester content | %(m/m) | 96.5 | - | 98.58 |
| Density at 15°C | kg/m ³ | 860 | 900 | 883 |
| Viscosity at 40°C | mm ² /s | 3.5 | 5 | 4.2 |
| Flash point | °C | 120 | - | 172 |
| Sulfur content | mg/kg | - | 10 | 7 |
| Cetane number | | 51 | - | 52.03 |
| Water content | mg/kg | - | 500 | 335 |
| Copper strip corrosion (3h at 50°C) | Rating | Class1 | Class 1 | 1a |
| Oxidation stability 110°C | Hours | 6 | - | 6.9 |
| Acid value | mg _{KOH} /g | - | 0.5 | 0.15 |
| Iodine value | gr _{iodine} /100gr | - | 120 | 105.6 |
| Linolenic acid methyl ester | % (m/m) | - | 12 | 0.2 |
| Polyunsaturated methyl esters | % (m/m) | - | 1 | 0 |
| Monoglyceride content | % (m/m) | - | 0.8 | 0.6 |
| Diglyceride content | % (m/m) | - | 0.2 | 0.07 |
| Triglyceride content | % (m/m) | - | 0.2 | 0 |
| Group metals (Ca, Mg) | mg/kg | - | 5 | < 0.6 / < 0.05 |
| Group metals (Na, K) | mg/kg | - | 5 | 0.08 / 0.15 |
| Phosphorus content | mg/kg | - | 10 | 0.5 |

| SAMPLE | N.A. | Additive 1 | Additive 2 | Additive 3 |
|-------------------------------|--------|------------|------------|------------|
| Biodiesel from Sunflower oil | 1.63 h | | | |
| ≈ 0.03 % | | 2.12 h. | 3.60 h. | - |
| ≈ 0.06 % | | 1.48 h. | 5.45 h. | 1.7 h. |
| ≈ 0.25 % | | 3.55 h. | 15.5 h. | 3.15 h. |
| ≈ 0.60 % | | 4.97 h. | 23.8 h. | 5.38 h. |
| Biodiesel from Cottonseed oil | 6.03 h | | | |
| ≈ 0.03 % | | 6.15 h. | 8.62 h. | - |
| ≈ 0.06 % | | 6.85 h. | 11.8 h. | 3.62 h. |
| ≈ 0.25 % | | 8.63 h. | 22.4 h. | 6.50 h. |
| ≈ 0.60 % | | 11.1 h. | 38.6 h. | 8.02 h. |



Oxidation Stability according to EN-14214

Oxidation Stability Limits : 6.00 h.

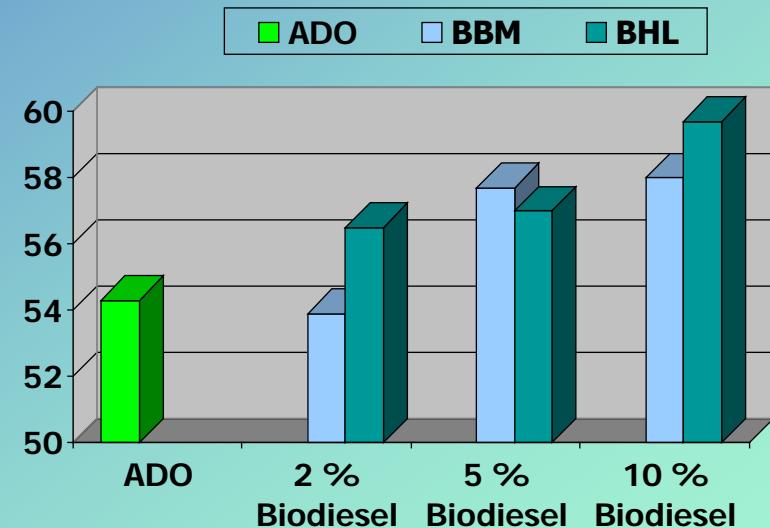
| SAMPLE | CETANE NUMBER |
|---------------|---------------|
| ADO | 54.3 |
| BBM | 52.3 |
| BHL | 50.9 |
| ADO + 2% BBM | 53.9 |
| ADO + 5% BBM | 57.7 |
| ADO + 10% BBM | 58.0 |
| ADO + 2% BHL | 56.5 |
| ADO + 5% BHL | 57.0 |
| ADO + 10% BHL | 59.7 |

ADO : Diesel

BBM : Biodiesel from Cottonseed oil

BHL : Biodiesel from Sunflower oil

Improvement of Cetane Number
with the addition of Biodiesel



- ✓ New, cost effective processes can be developed for Biodiesel production
- ✓ Thermal, non-catalytic reaction is a promising way either to pretreat acidic feeds or to produce biodiesel
- ✓ Solid catalysts can be applied for biodiesel production either from acidic or from refined oils
- ✓ The enzymatic process appears as the most promising for development if cheaper biocatalysts can be produced