

# Technologies for Production of Biodiesel with Focus on Heterogeneous Catalysis

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# OUTLINE

1. Introduction and Current Issues of Biodiesel Industry
2. Technologies for the production of biodiesel
3. Heterogeneous catalyst for the production of biodiesel
4. Conclusion



# Introduction & Issues

1. High cost of Raw Material.
2. Biodiesel Quality
3. Availability of Feedstock
4. Food or Fuel?
5. Sustainability



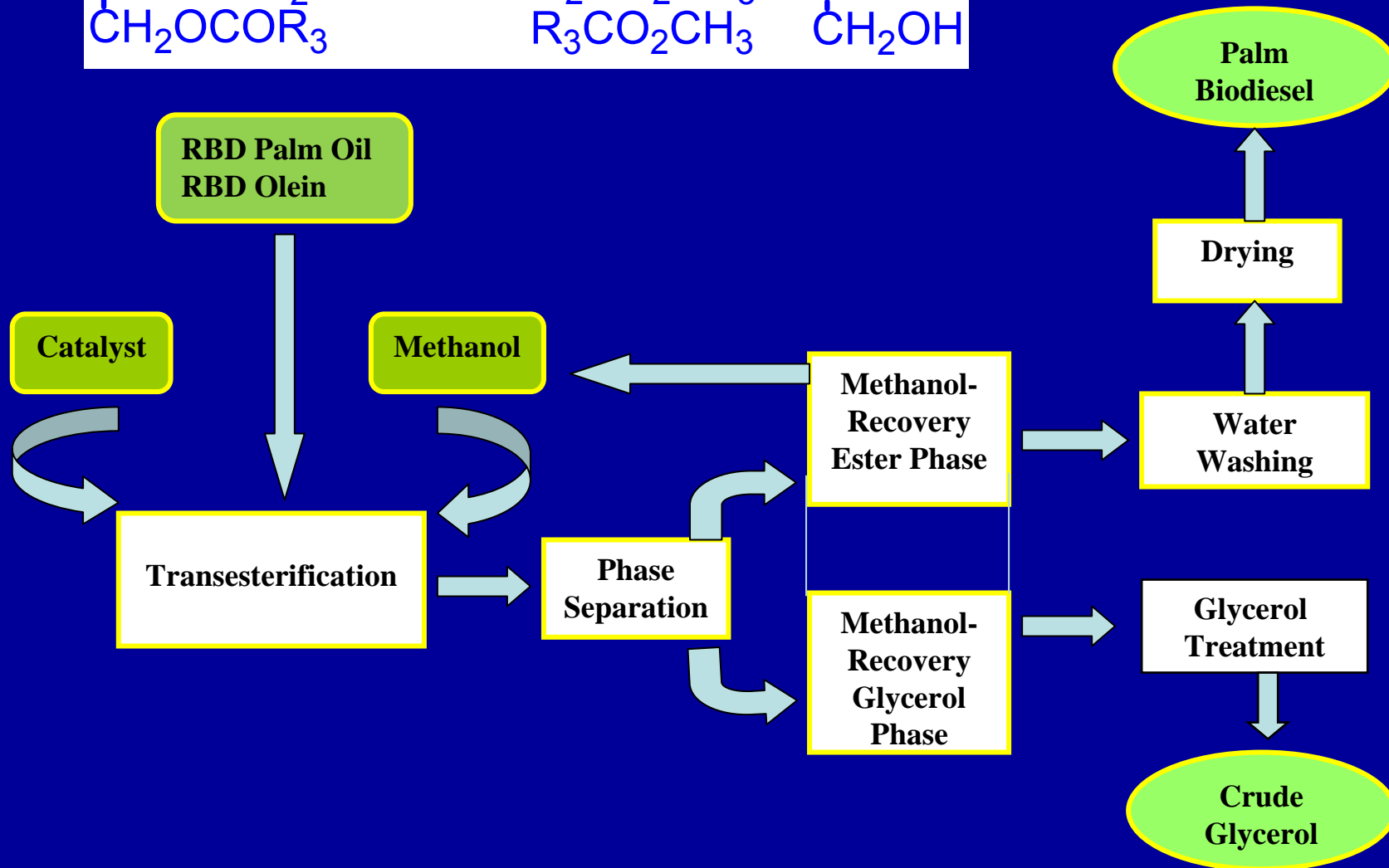
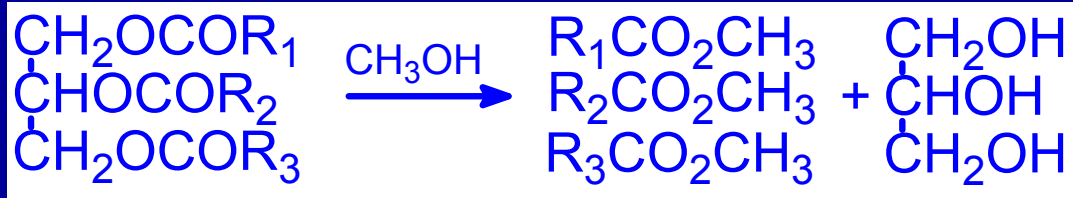
**MPOB Palm Biodiesel Plant**  
**Engineering: Lipochem Sdn. Bhd.**  
**Capacity: 60,000 TPA**  
**Commissioned: May 2007**

# Introduction & Issues

With more vegetable oil crop planting programs coming on stream, there are going to be more oils (edible and non-edible) as feedstock for the production of biodiesel.

- ◆ Is the current biodiesel production process “Green”?
- ◆ Is transesterification going to remain as the main reaction for biodiesel production?
- ◆ Can other processes replace transesterification reaction for the production of biodiesel from vegetable oil e.g. hydrotreating ?

# Biodiesel Process



# Current Biodiesel Production Technologies

- ◆ Transesterification Reaction – Predominantly uses homogeneous base catalysts e.g. sodium methoxide, sodium hydroxide and potassium hydroxide.
- ◆ Differences Between Commercial Processes:
  - Reactor Design: Continuous Stirred Tank Reactor (CSTR), Loop Reactor, Tubular Reactor.
  - Purification Step: Residual catalysts and soap need to be removed from biodiesel and glycerol.

**This is the main drawback of the current process.**

# Biodiesel Purification Process

- ◆ Purification processes: Water washing process and adsorbent treatment process (water-free process):
  - Water washing process – need waste water treatment plants.
  - Evaporate and recover water for re-use: energy intensive.
  - Adsorbent treatment process e.g. Magnesium Silicate – high cost of adsorbent and disposal of spent adsorbents

# Potential Cleaner Process

- ◆ Eliminate catalyst cleaning up step and simplify biodiesel and glycerol purification.
- Heterogeneous catalytic system (solid catalysts)
- Enzymatic transesterification process
- Catalyst-free process: supercritical methanol?



# Enzymatic Transesterification

- ◆ Cost of lipase production is the main hurdle to commercialization.
- ◆ Development of cost-effective system.
  - To maintain lipase activity in the presence of high concentration of methanol and glycerol. Novel operations such as stepwise addition of methanol has been developed (Kaieda *et al.*, 1999).
  - Intracellular lipase as a whole cell biocatalyst could lower the lipase production cost (Fukuda *et al.*, 2001)
  - Solvent-tolerant lipases
  - Genetic engineering: higher level of expression.

**Industrial Application: Promising prospect**

# Transesterification Using Supercritical Fluids

- ◆ Biodiesel production in supercritical methanol
  - Without using any catalyst
  - Short reaction time, 5 mins ( conversion >90%)
  - Temperature: 350 °C, Pressure: 45 MPa
  - Methanol to oil (rapeseed) ratio: 42 to 1
  - Free fatty acids in crude oils and fats could also be converted to methyl esters
  - Main limitations: High investment & energy costs, use of excessive methanol.
- ◆ Industrial application: Further R&D is needed.

Saka & Kusdiana, 2001, *E. S. Song et al., 2007*

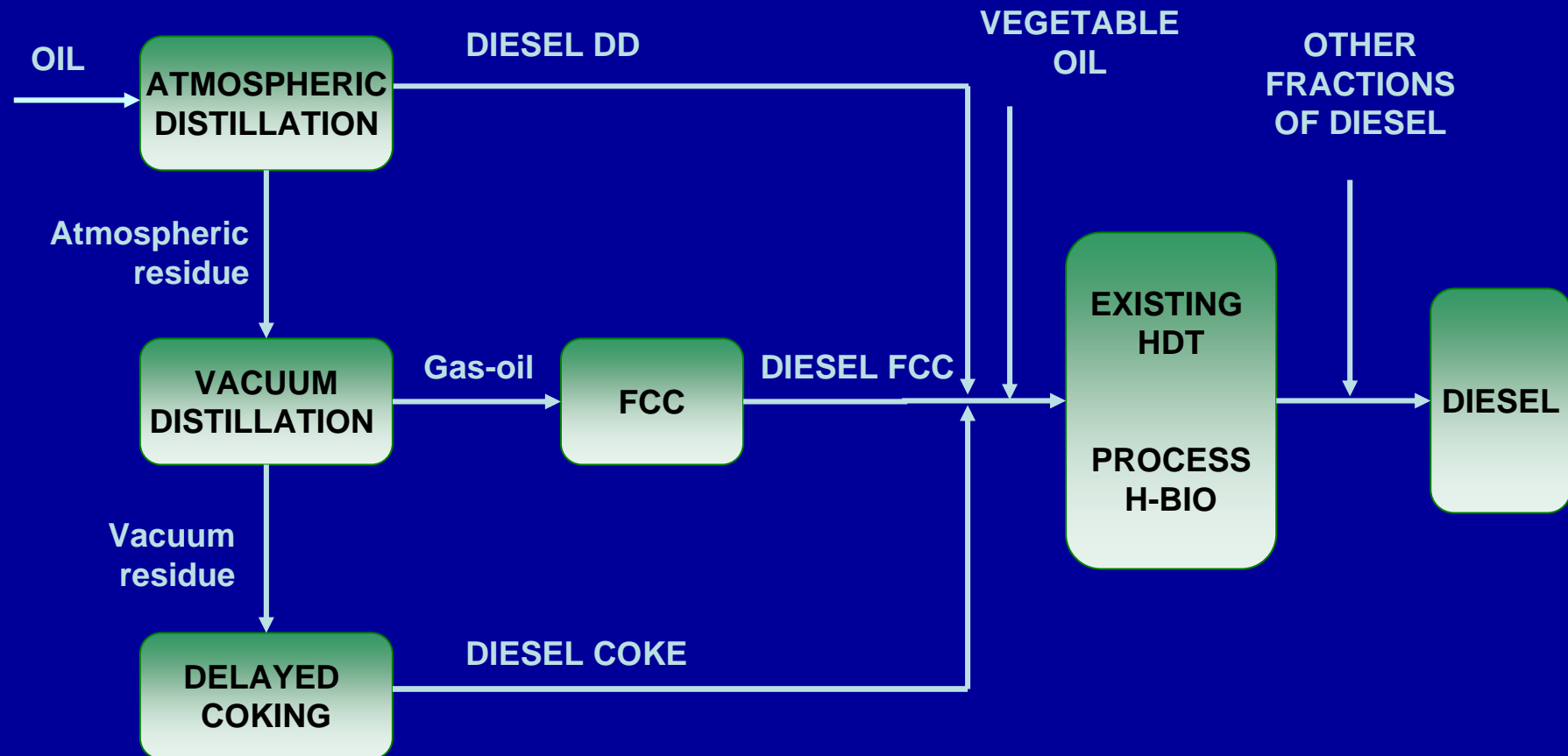
*Clerici & Cheah, ICS-UNIDO Workshop, 2007, Malaysia*

# Hydrotreating

- ◆ Oils and fats are transformed into linear hydrocarbon chains. Propane and water are the by-products.
- ◆ Catalytic hydroconversion under high temperature (300 °C) and pressure (70 atm).

Only viable for big petroleum refineries that already possess HDT.

# Hydrotreating: H-BIO



Source : <http://www.petrobras.com.br>

Clerici & Cheah, ICS-UNIDO Workshop, 2007, Malaysia

# Commercial Biodiesel Process using Heterogeneous Catalyst – ESTERFIP Process



- ◆ A process is licensed by Axens (ESTERFIP)
- ◆ Catalyst: ZnO and ZnAl<sub>2</sub>O<sub>4</sub> on Al<sub>2</sub>O<sub>3</sub>
  - ⇒ Fixed bed process, 210-250°C, 30-50 bar
  - ⇒ 91% FAME at 240°C, 50 bar and 160 min c.t.
- ◆ It is claimed that small amounts of H<sub>2</sub>O and FFA are tolerated

*US 5,908,946 to IFP*

*Clerici & Cheah, ICS-UNIDO Workshop, 2007, Malaysia*

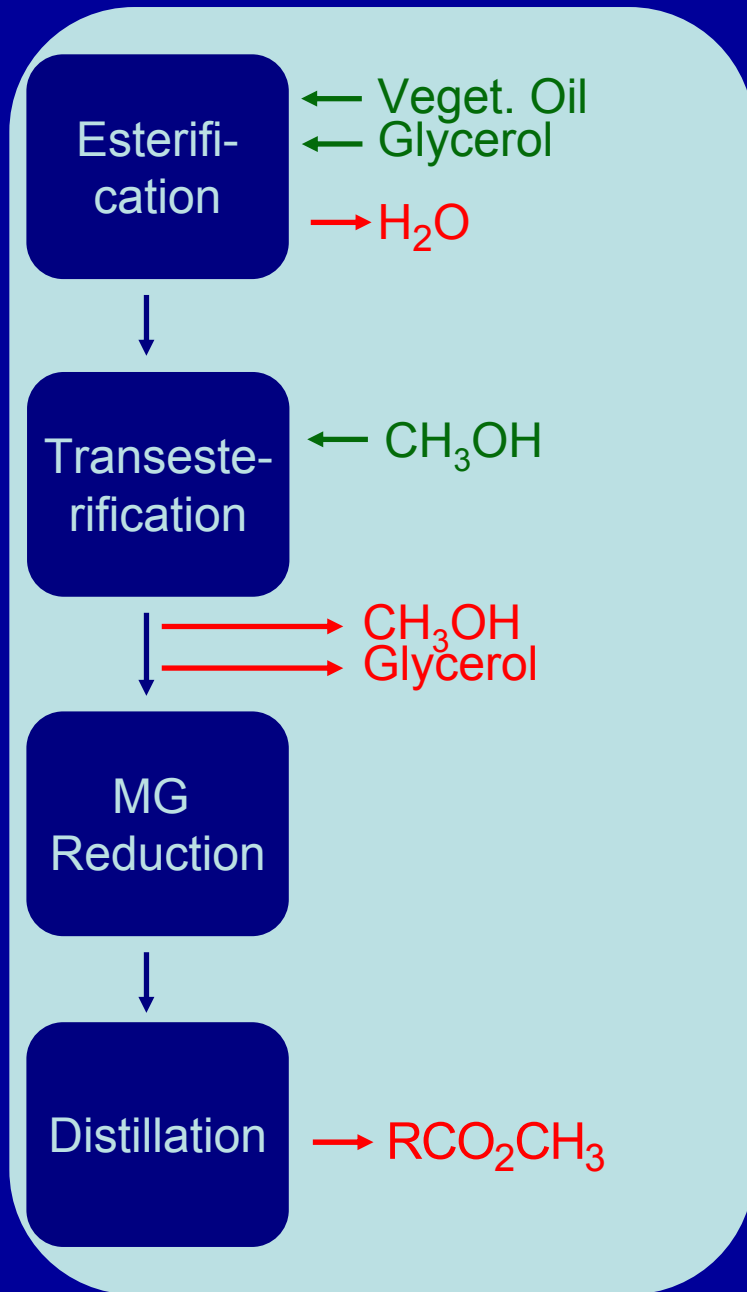
# Commercial Biodiesel Process using Heterogeneous Catalyst – ESTERFIP Process

- ◆ The process is improved in US 6,147,196
  1. FFA in the feed removed by esterification to MG
    - *ZnO/Al<sub>2</sub>O<sub>3</sub>, 220°C, 2h, 1bar, 90% FFA reduction*
    - *Water is eliminated by an inert gas sweep*



2. Crude product heated to 250°C, to convert MG to DG





**Step 1 - 220°C, 1bar, 2h**

**Step 2 - 240°C, 50bar, 160min**

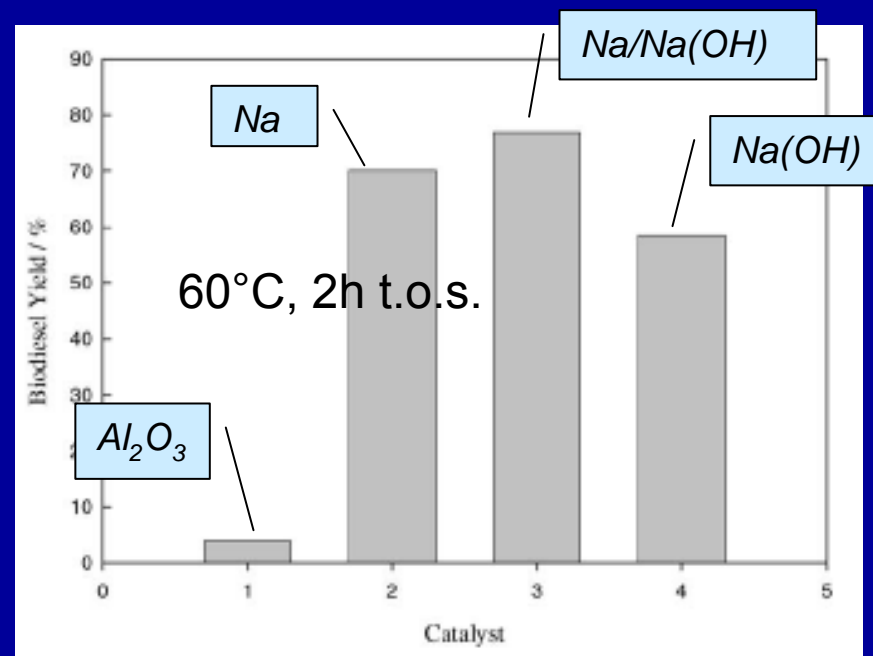
**Step 3 - 250°C, 1bar, 2h**

**Higher capital and production cost:  
High temperature, high pressure and  
more processing steps to achieve  
EN spec.**

# Alkali Metal Oxides



- ◆  $\gamma\text{-Al}_2\text{O}_3$  heated at 320°C with NaOH and Na  
 ⇒ No free Na species detected on the support
- ◆ NaOH/ $\gamma\text{-Al}_2\text{O}_3$  only slightly less active than homogeneous NaOH  
 ⇒ No test to exclude the leaching of NaOH



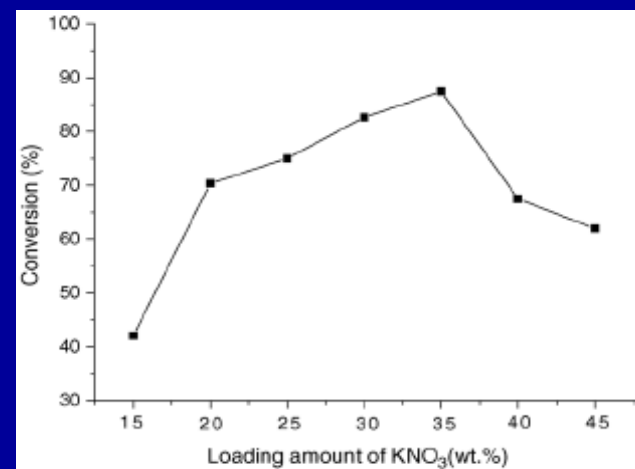
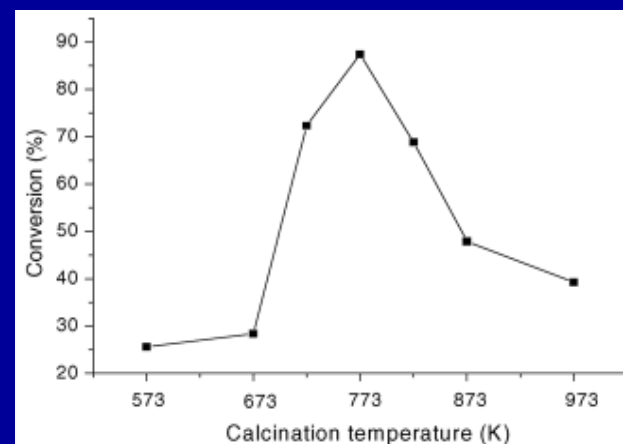


# Alkali Metal Oxides



- ◆ Catalyst: calcined  $\text{KNO}_3/\text{Al}_2\text{O}_3$ 
  - ⇒  $\text{K}_2\text{O}$  and Al-O-K active species
- ◆ Conversion (basicity) depends on calcination T and K loading
  - ⇒ Quite common feature of this class of materials
  - ⇒ It is an evidence of heterogeneously catalyzed process

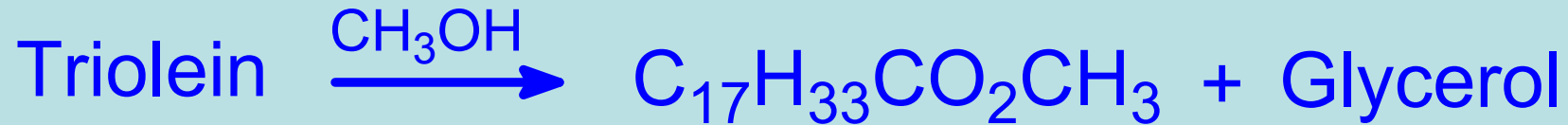
Reflux, 7h



W. Xie et al., 2006

Clerici & Cheah, ICS-UNIDO Workshop, 2007, Malaysia

# Alkali Metal Oxides

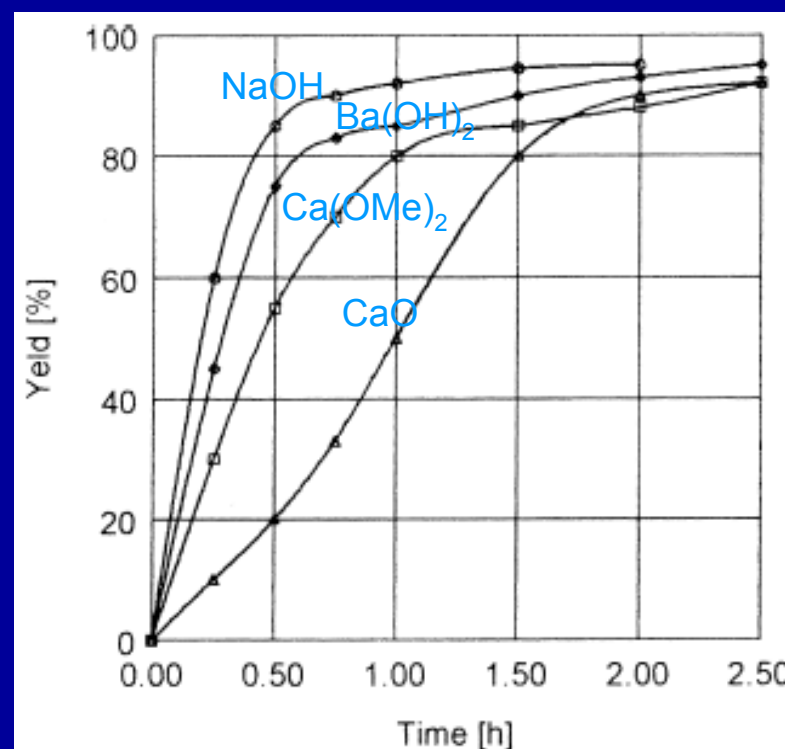


- ◆  $\text{LiNO}_3$ ,  $\text{NaOH}$ ,  $\text{NaNO}_3$ ,  $\text{KOH}$ ,  $\text{KNO}_3$ ,  $\text{RbNO}_3$ ,  $\text{KF}$  supported on  $\text{Al}_2\text{O}_3$  and calcined at  $400^\circ\text{C}$
- ◆  $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  calcined at  $550^\circ\text{C}$
- ◆ Yields  $>80\%$  at  $60^\circ\text{C}$  (except with Rb)
- ◆ It is claimed that the activity was not significantly affected by small amounts of water

## II Group Metal Oxides



- ◆ Basicity: Mg < Ca < Sr < Ba
- ◆ Activity increases with basicity (*and solubility*)
- ◆ Catalysis by homogeneous species is most likely
- ◆ CaO is poorly soluble and poorly active



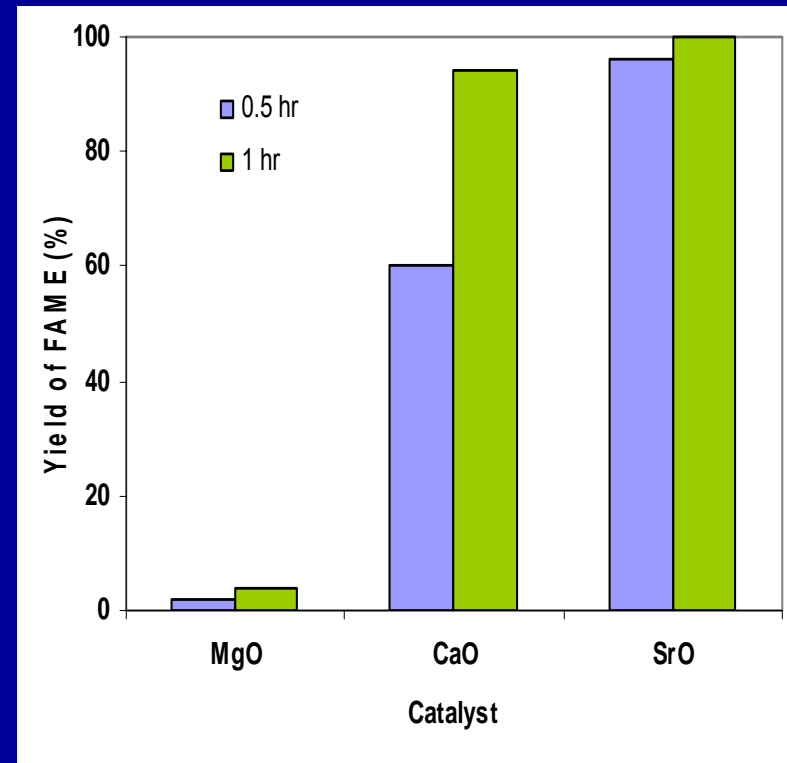
S. Gryglewicz, 2005

Clerici & Cheah, ICS-UNIDO Workshop, 2007, Malaysia

# II Group Metal Oxides



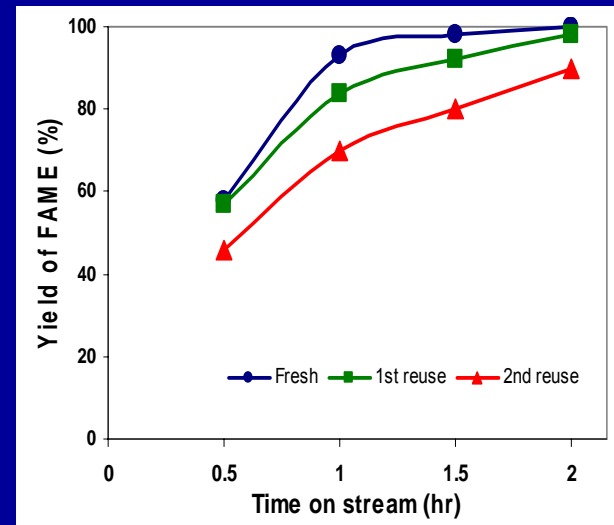
- ◆ Catalyst: CaO, Ca(OH)<sub>2</sub>, CaCO<sub>3</sub>.
- ◆ CaO obtained after calcination of lime stone at 900°C for 1.5hr.
- ◆ Conversion after 1 h: CaO (93%), Ca(OH)<sub>2</sub> (12%), CaCO<sub>3</sub> (0).
- ◆ Comparing CaO with MgO (calcinated at 500°C) and SrO (calcined at 1050°C: SrO)
- ◆ Basic strength (MgO < CaO < SrO) seemed to be determinant for catalytic activity



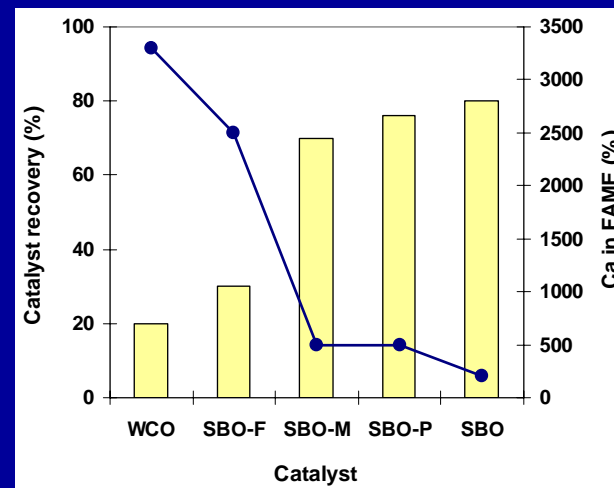
# II Group Metal Oxides



- ◆ CaO can be reused without serious deactivation for transesterification although the yields of FAME decrease.



- ◆ Leaching of Ca was observed.

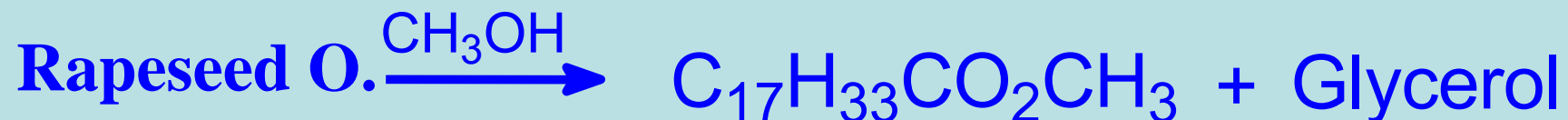


# II Group Metal Oxides



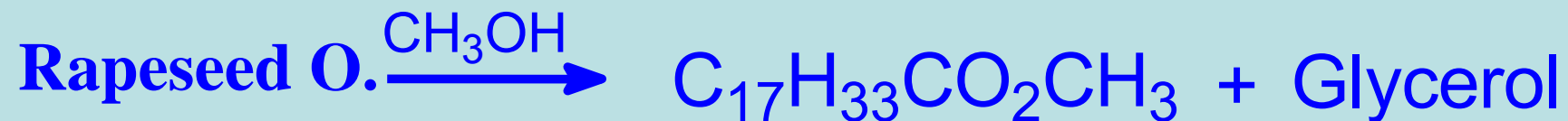
- ◆ Transesterification of SBO to FAME using CaO as catalyst . Conversion exceeded 95%.
- ◆ Reaction condition: Reaction time (3h), Temp. (65 °C), Catalyst dosage (8%), Methanol to oil ratio (12:1), Water content in methanol (2.3%).
- ◆ CaO maintained sustained activity even after being repeatedly used for 20 cycles

# Alkali-doped Metal Oxides



- ◆  $\text{LiNO}_3/\text{CaO}$ ,  $\text{NaNO}_3/\text{CaO}$ ,  $\text{KNO}_3/\text{CaO}$ , and  $\text{LiNO}_3/\text{MgO}$  calcined at  $600^\circ\text{C}$  for 5hr
- ◆ Conversion  $>90\%$  at  $60^\circ\text{C}$ , reaction time: 3h
- ◆ Conversion for  $\text{CaO}$  (no doping)  $< 70\%$ .
- ◆ It is claimed that there was a clear correlation between base strength and activity. Base strength is the most important factor.
- ◆ Catalysts showed good reusability. Conversion do not drop significantly after 5 cycles.
- ◆ However, leaching of catalyst was observed: Na(52ppm), K(32ppm), Ca(200-400ppm) and Mg(30ppm).

# Alkali-doped Metal Oxides

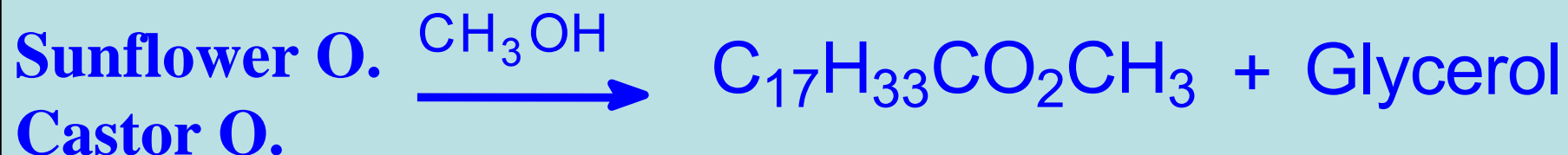


Remaining glycerides after 180 min reaction, compared to EU standard

Catalyst	Monoglyceride	Diglyceride	Triglyceride
KNO <sub>3</sub> /CaO (calcined)	2.5	1.1	0.7
LiNO <sub>3</sub> /MgO (calcined)	2.2	0.9	0.1
EN 14214	0.8	0.2	0.2

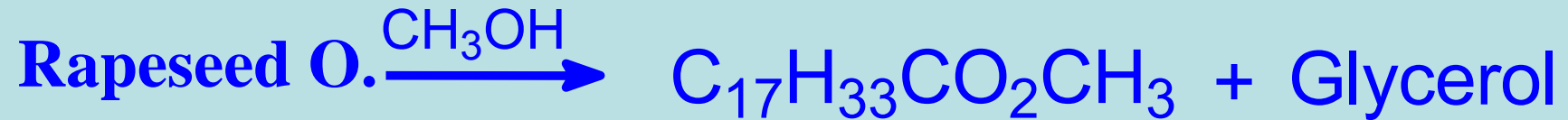


## II Group Metal Oxides



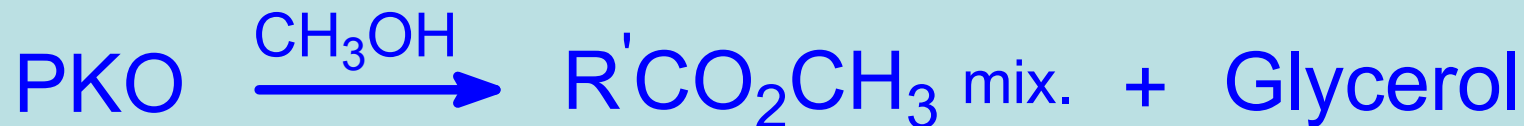
- ◆ CaO supported on porous silica (SBA-15, MCM-41, fumed silica)
- ◆ A sample containing 14 wt% of CaO supported on SBA-15 the most active for transesterification process
- ◆ Conversion reached 95% (sunflower oil) and 65% (castor oil) at 60°C after 5 hr and 1 hr of reaction time, respectively, with 1:12 molar ratio of the oil to MeOH.
- ◆ It is claimed that no leaching of active phase occurred – strong interaction between CaO and silica.

# Metal Oxides



- ◆ 13 metal oxides containing Ca, Ba, Mg & La were evaluated as heterogeneous base catalyst to produce biodiesel
- ◆ The Ca containing catalysts ( $\text{CaTiO}_3$ ,  $\text{CaMnO}_3$ ,  $\text{Ca}_2\text{Fe}_2\text{O}_5$ ,  $\text{CaZrO}_3$  &  $\text{CaO-CeO}_2$ ) showed highest activities.
- ◆ Yields reached 79-92% at 60°C for 10 hr with 1:6 molar ratio of the oil to methanol
- ◆ High durability of catalytic activity found for the  $\text{CaZrO}_3$  and  $\text{CaO-CeO}_2$  with FAME yield >90% and have potential to be applied in biodiesel production

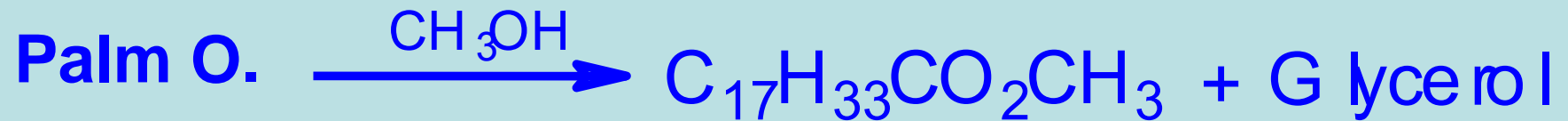
# Other Metal Oxides



				<i>Acidic</i>	<i>Basic</i>	
Catalyst	-	ZnO	ZrO <sub>2</sub>	KNO <sub>3</sub> / ZrO <sub>2</sub>	SO <sub>4</sub> <sup>2-</sup> / ZrO <sub>2</sub>	SO <sub>4</sub> <sup>2-</sup> / SnO <sub>2</sub>
Yield (%)	41	78	49	66	86	81

- ◆ Zn, Zr, Sn oxides tested for transesterification of CCO and PKO (200°C)
- ◆ K<sup>+</sup> loading increases the activity of ZrO<sub>2</sub>
- ◆ Leaching phenomena with sulfated oxides

# Metal Oxides



- ◆ 1.5% potassium (K) loaded-calcined Mg-Al hydrotalcite at 500°C for 2 hr
- ◆ FAME content of 96.9% and yield of 86.6% at 100°C for 6 hr using 30:1 MeOH to oil mol ratio and 7wt% catalyst

# Metal Oxide Catalysts

- ◆ Information on metal oxides used as transesterification catalysts is getting interesting (exciting).
- ◆ Preliminary results recommend further studies
  - ⇒ Good activity at relatively mild conditions
- ◆ Following issues appear as most important
  - ⇒ Activity enhancement by doping/pretreatment
  - ⇒ Leaching of soluble species – Catalyst stability and reusability.
  - ⇒ Conversion > 99% - To meet EN spec. on mono-, di- and triglycerides
  - ⇒ Leaching of soluble species will also lead to off-spec biodiesel.

# Metal Oxide Catalysts

- ◆ Suggestions on other potential basic catalysts may come from:
  - ⇒ The literature on metal oxides modified by alkali metals
  - ⇒ Solid catalysts used in base-catalyzed organic reactions
- ◆ Acidic materials are numerous, intrinsically more stable and better studied than solid bases.
- ◆ Acid catalysts should not be excluded *a priori*

# Conclusion

- ◆ Potential Green and Cleaner Processes: Heterogeneous catalysts and enzymatic transesterification.
- ◆ For heterogeneous catalyst, current results (a process, papers) recommend further studies on early Groups  $M_xO_y$  catalysts
  - ⇒ Open issues: nature of support, metal doping, leaching
- ◆ Some attention could be given to other materials