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# NEDO Biodiesel Production Process by Supercritical Methanol Technologies


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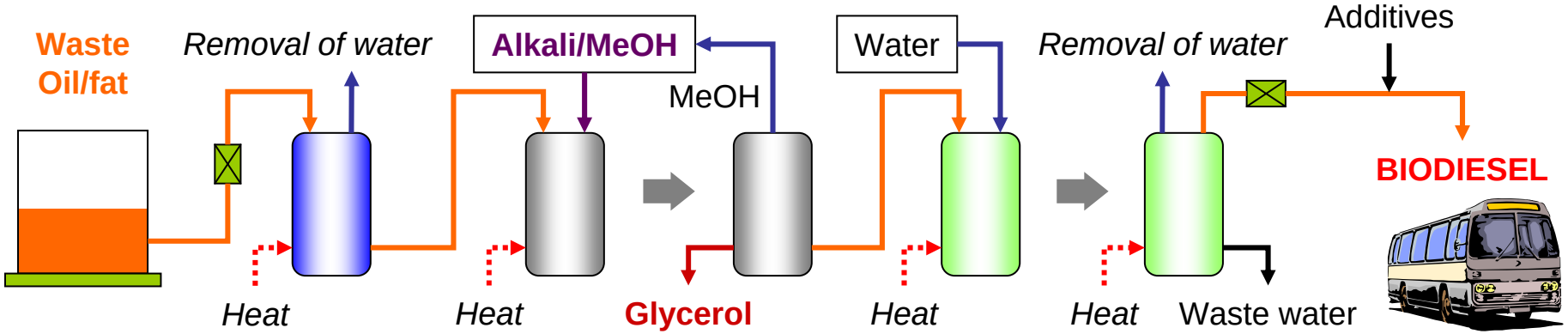
# BDF Activity in Kyoto

220 garbage trucks（B100)
(1.3 million liters/yr)


80 municipal busses　(B20)
(0.2 million liters/yr)

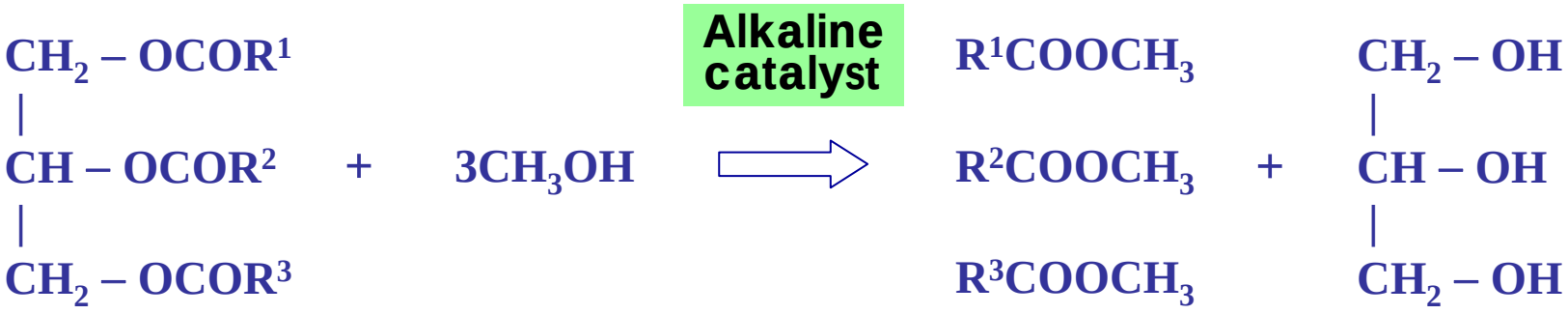
# Biodiesel Production Plant in Kyoto City

- Method : **Alkali-catalyzed**
- Feedstock : **Waste oils/fats (from household sector)**
- Productivity : **5,000 L/day**



# Alkali-catalyzed Method for Commercial Biodiesel Production

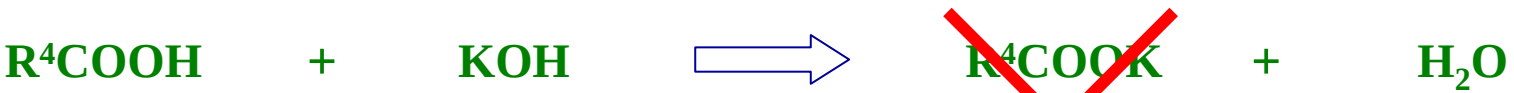
## ◆Transesterification




*Triglyceride*

*Biodiesel*

## ◆Saponification




*Free fatty acid*

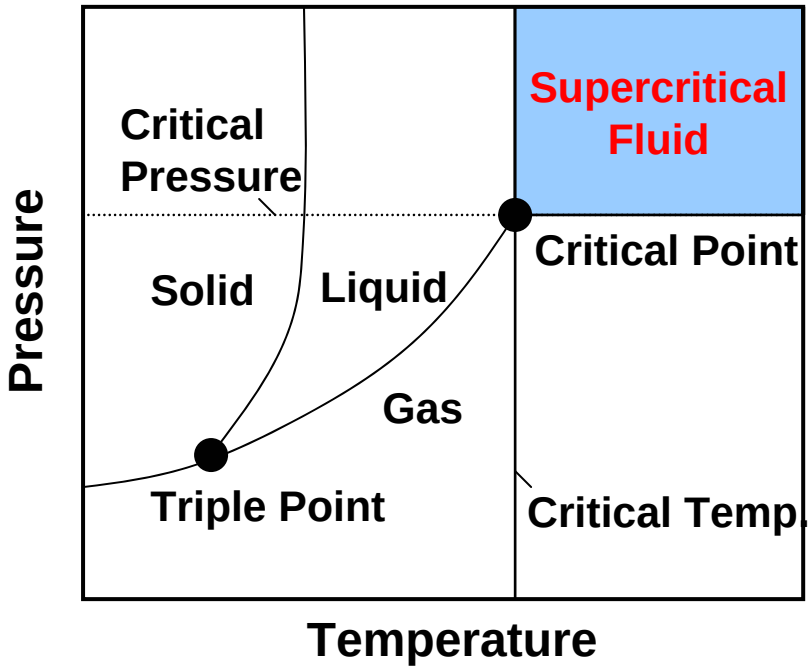
Alkaline catalyst

~~*Saponified product*~~

# Supercritical Fluid

A pure substance may be changed into 3 phases such as gas, liquid and solid. Among these, the critical point exists between the gas and liquid.

Above the critical point, there exists the high-density fluid which cannot be condensed any more, even if temperature and/or pressure are increased. Such a substance is called “supercritical fluid”.



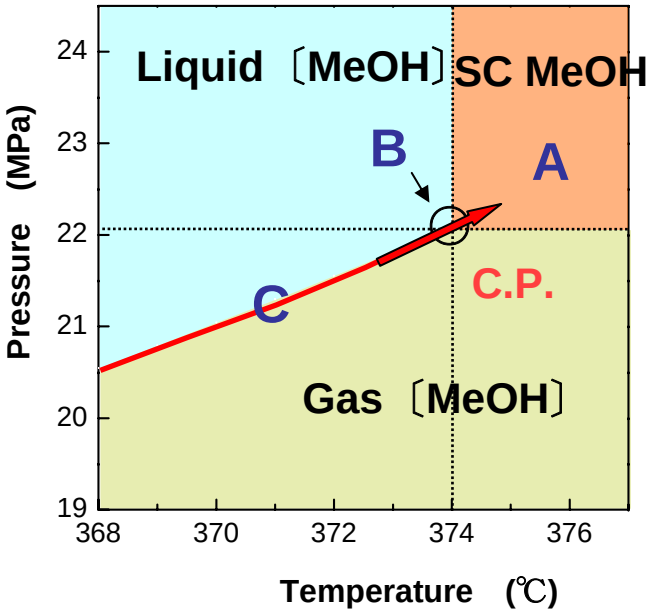

**Temperature-Pressure Relation of the Pure Substance**

◎$H_2O$
Critical Point: 374℃, 22.1MPa

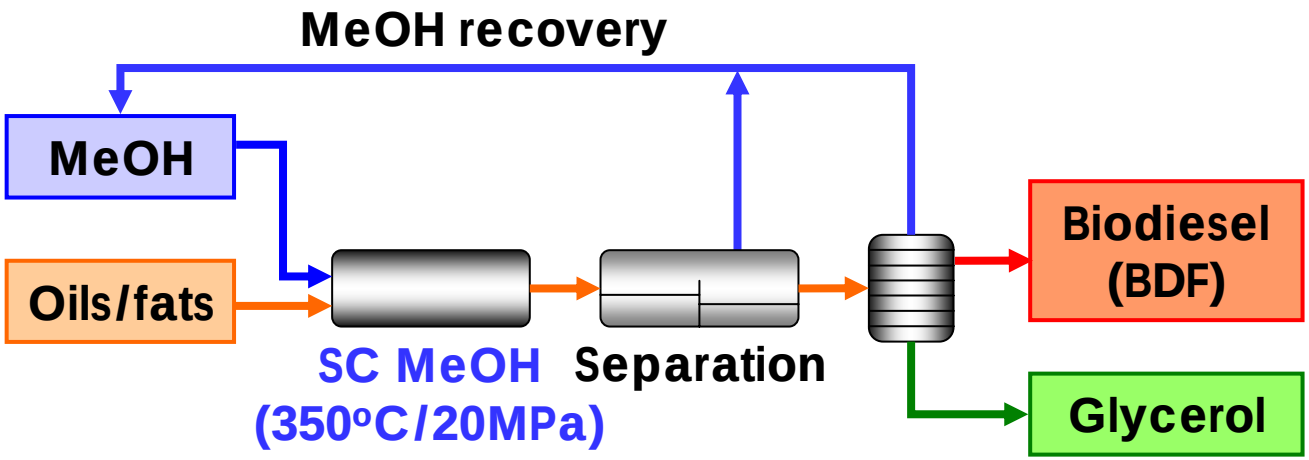
◎MeOH
Critical Point: 239℃, 8.09MPa

Under SC condition,
- Ionic Products: Increased
  ($H_2O$→Hydrolysis)
  (MeOH→Methanolysis)
- Dielectric Constant: Decreased
  (Hydrophilic→Hydrophobic)

# Phase Changes in a Vicinity of Critical Point in MeOH




# One-Step SC MeOH Method
## (Saka Process)




### Transesterification

$$\begin{array}{l} CH_2-OCOR^1 \\ CH-OCOR^2 \\ CH_2-OCOR^3 \end{array} + 3CH_3OH \xrightarrow[\text{No catalyst}]{} \begin{array}{l} R^1COOCH_3 \\ R^2COOCH_3 \\ R^3COOCH_3 \end{array} + \begin{array}{l} CH_2-OH \\ CH-OH \\ CH_2-OH \end{array}$$

*Triglyceride* — *Biodiesel*

### Esterification

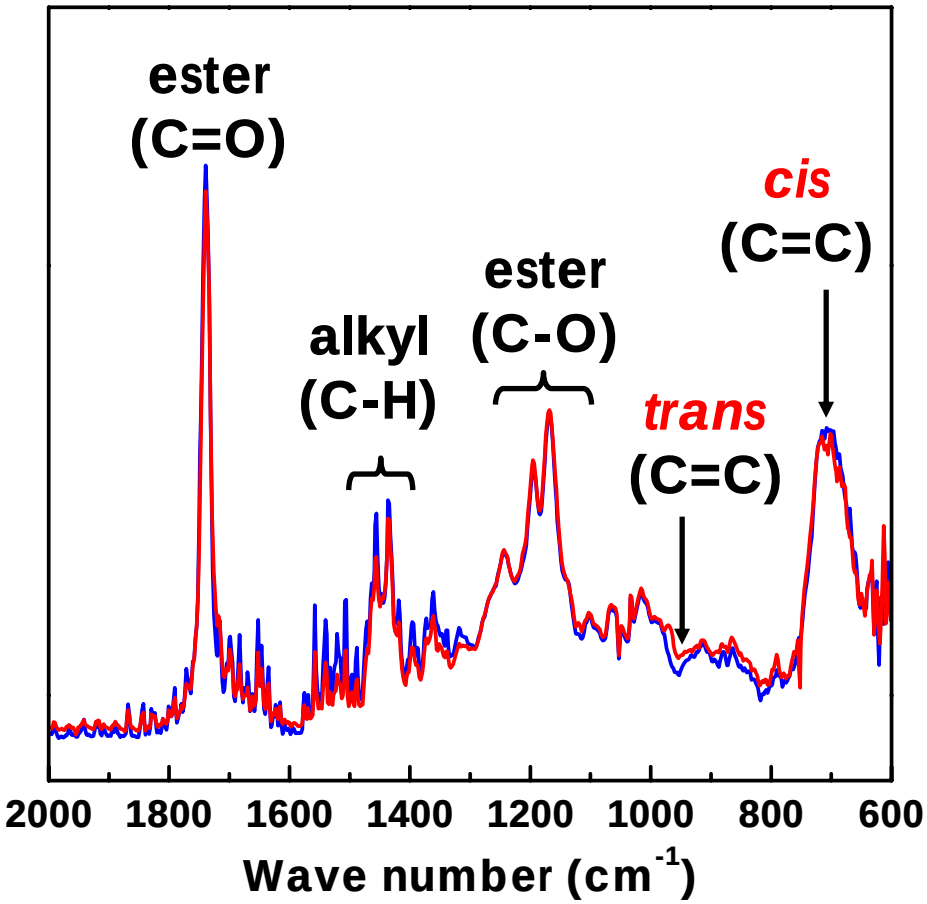
$$R^4COOH + CH_3OH \xrightarrow[\text{No catalyst}]{} R^4COOCH_3 + H_2O$$

*Free fatty acid* — *Biodiesel*

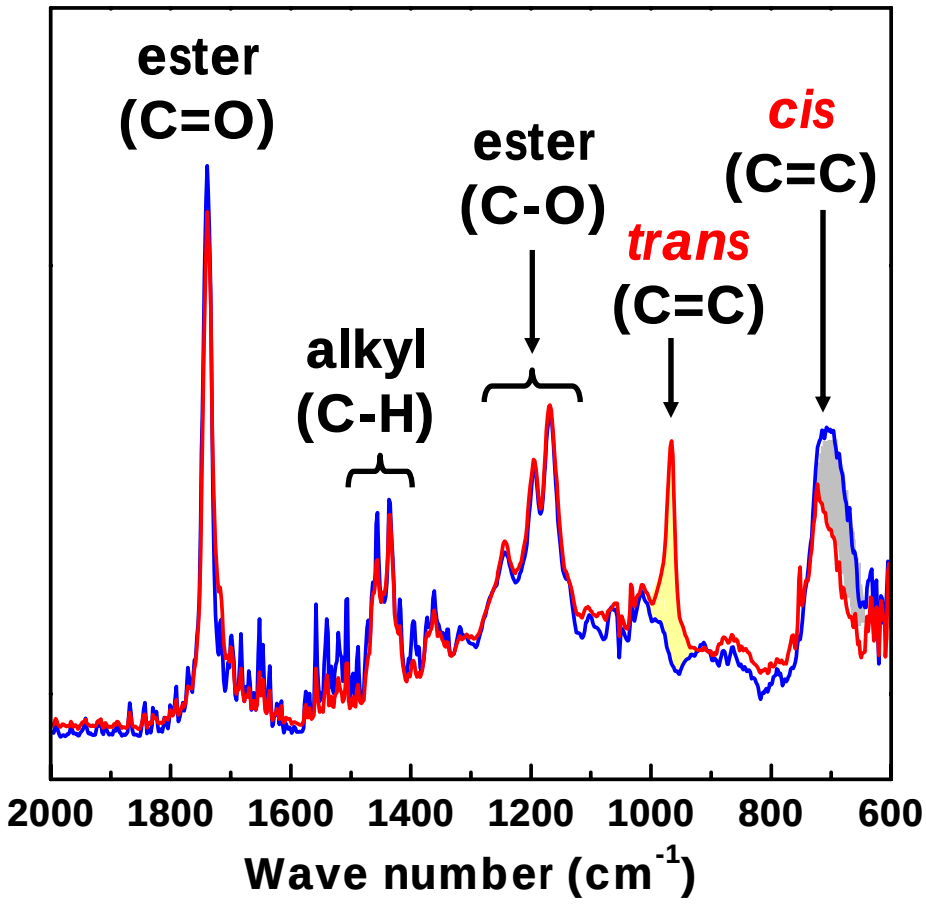
# Thermal Stability of Methyl Linolenate in SC MeOH

— : Untreated — : Treated

## 270°C/20min (Two-step)

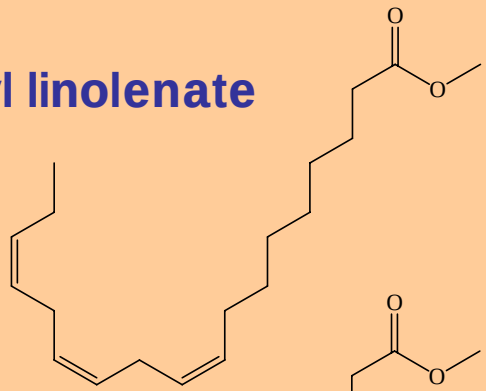



## 350°C/9min (One-step)

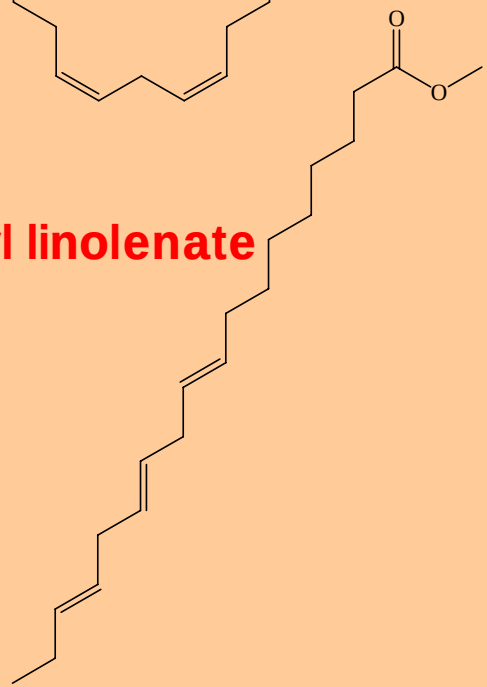


# Isomerization of poly-unsaturated fatty acid methyl esters

*Cis*-
Methyl linolenate



*Trans*-
Methyl linolenate



**Supercritical Methanol**
**(350°C/9min)**

*Cis*-
$T_m$ = - 10℃

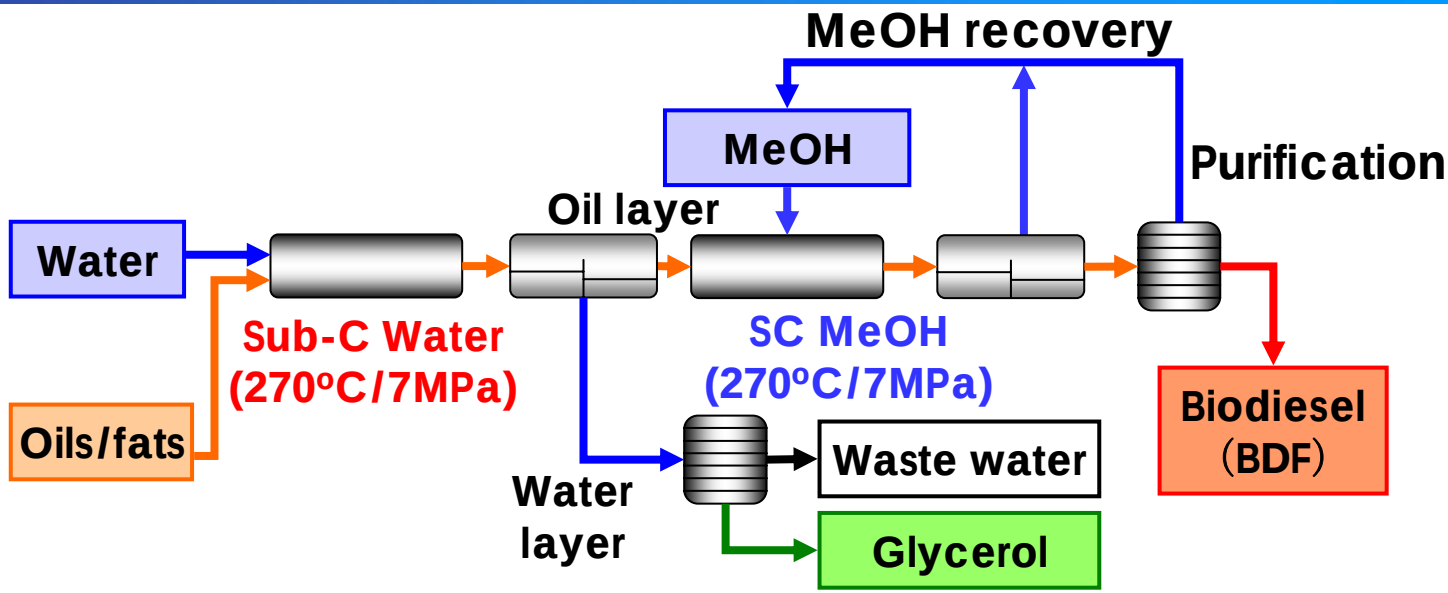
→ partly →

*Trans*-
$T_m$ = 30℃

**An increase in melting point**

→ **Deterioration in cold flow properties (?)**

# Two-Step SCMeOH Method
## (Saka-Dadan Process)




## Step I: Hydrolysis

$$\begin{array}{l} CH_2-OCOR^1 \\ | \\ CH-OCOR^2 \\ | \\ CH_2-OCOR^3 \end{array} + 3H_2O \Rightarrow \begin{array}{l} R^1COOH \\ R^2COOH \\ R^3COOH \end{array} + \begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array}$$

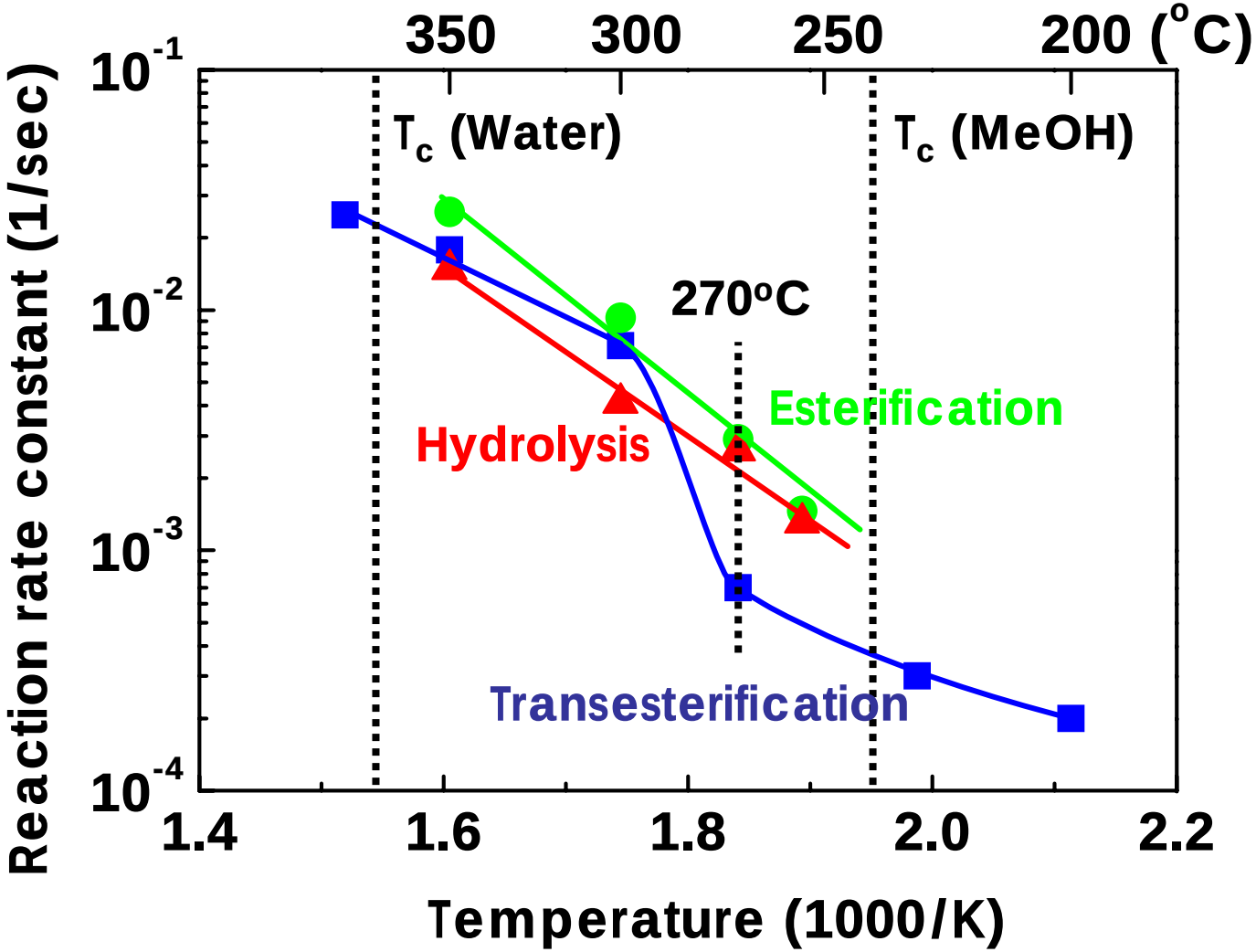
*Triglyceride* *Fatty acids*

## Step II: Esterification

$$R^4COOH + CH_3OH \Rightarrow R^4COOCH_3 + H_2O$$

*Fatty acid* *Biodiesel*

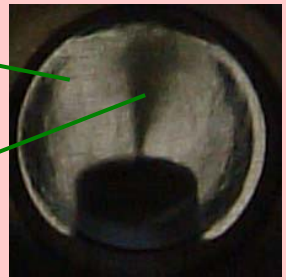
# Arrhenius Plots for Transesterification, Hydrolysis and Esterification of Rapeseed Oil



# Direct Observation through Sapphire Window

MeOH

Oil



240℃

280℃

340℃

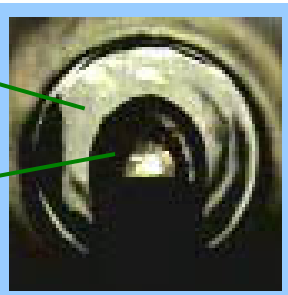
## Transesterification

2 Phase → 1 Phase

(Low Temp) (High Temp)

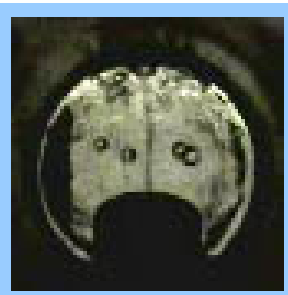
Water

Oil



280℃

300℃



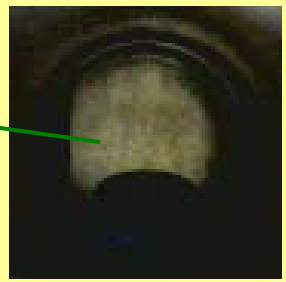
340℃

## Hydrolysis

2 Phase → 2 Phase

(Low Temp) (High Temp)

MeOH + Fatty Acid



160℃

260℃

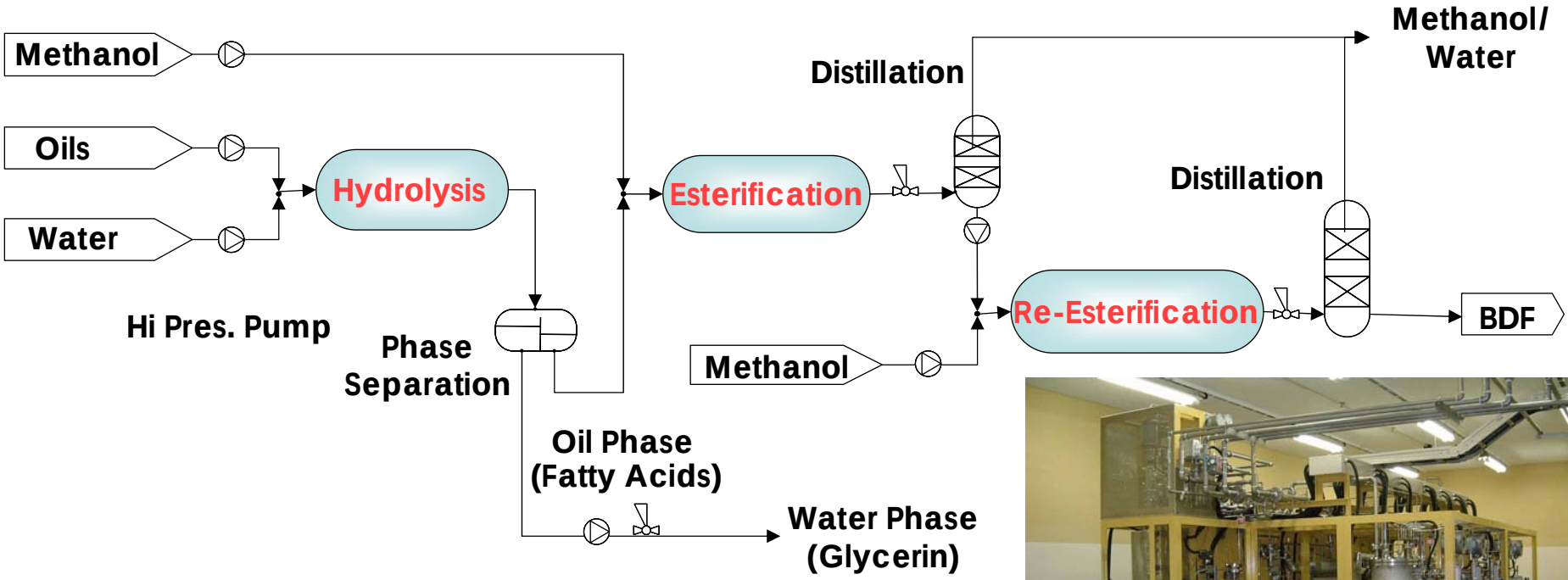
340℃

## Esterification

1 Phase → 1 Phase

(Low Temp) (High Temp)

# Two-Step Biodiesel Production Process
## (Hydrolysis – Esterification – Re-esterification)

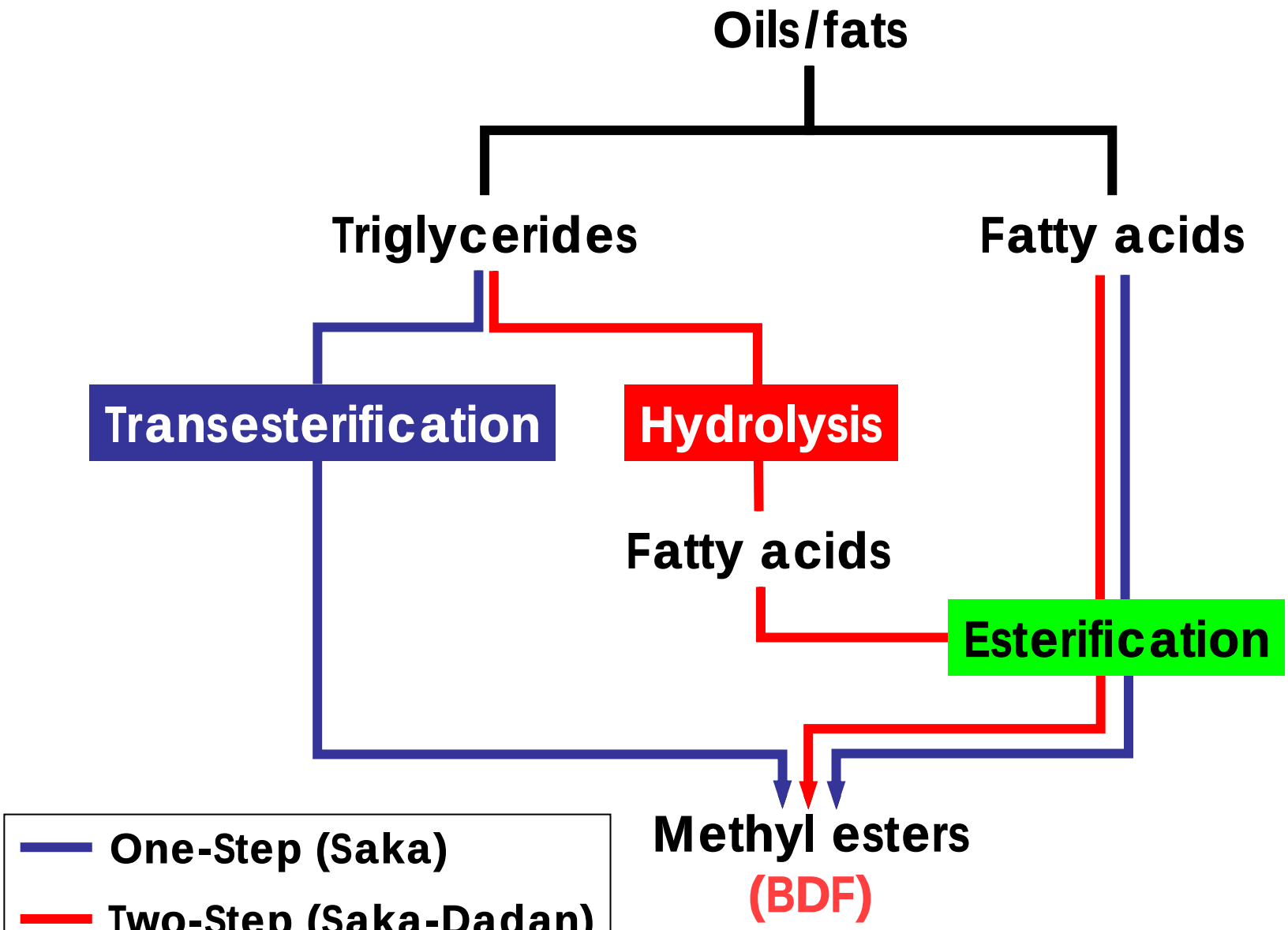



## Step II: Esterification

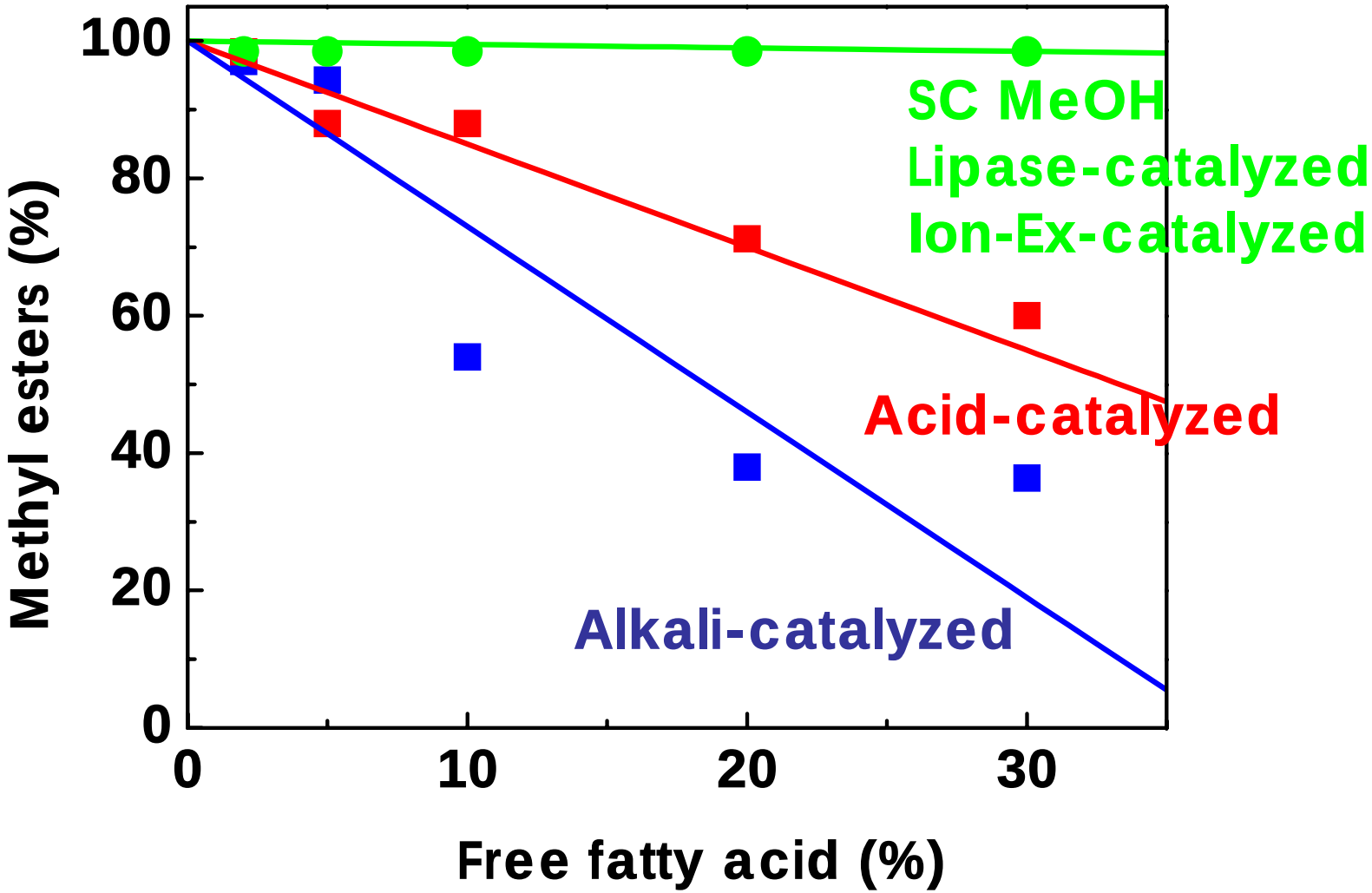
$$R^4COOH + CH_3OH \rightleftharpoons R^4COOCH_3 + H_2O$$

*Fatty acid* *Biodiesel*

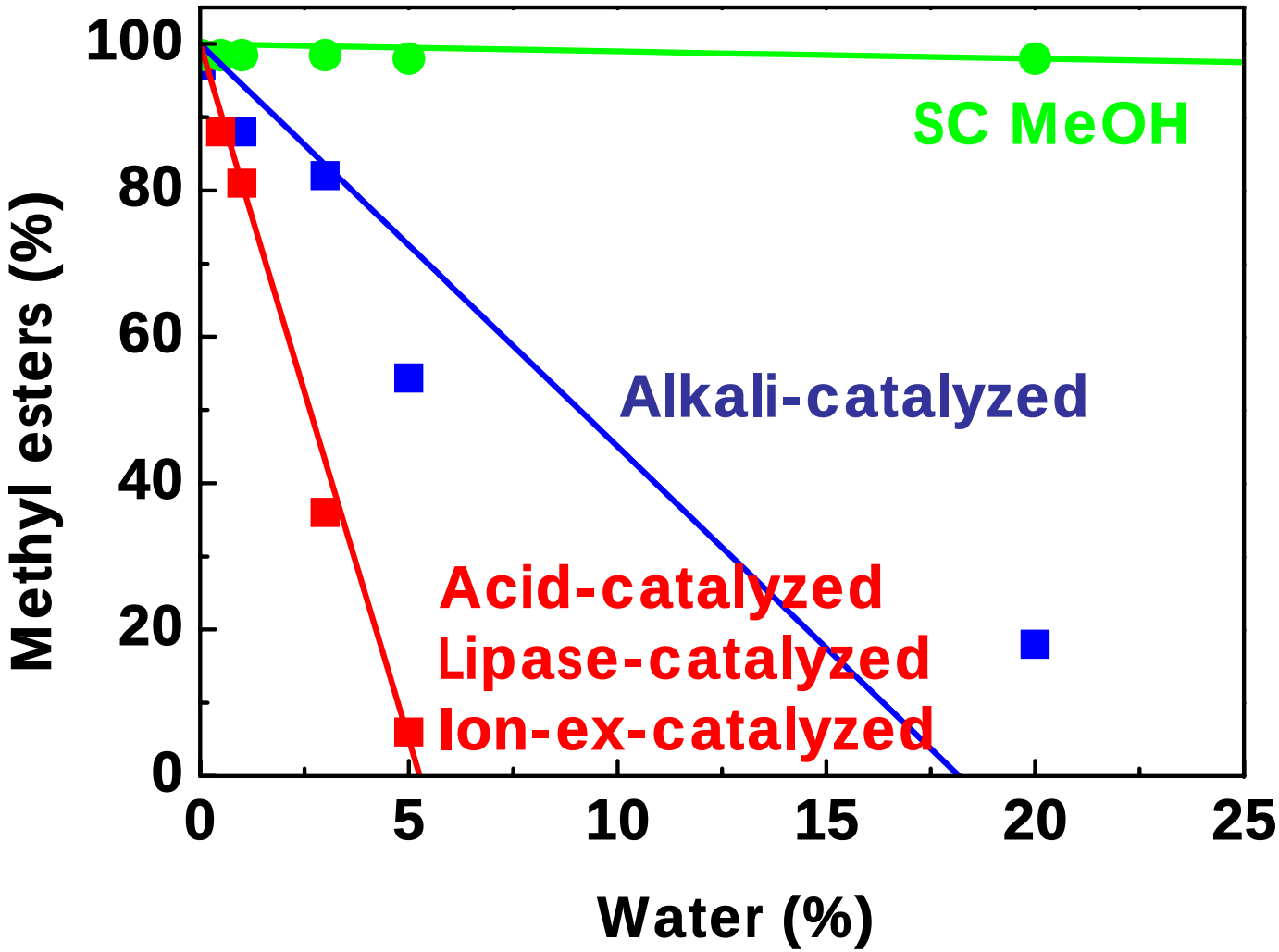
# Reactions Involved in SC MeOH Methods



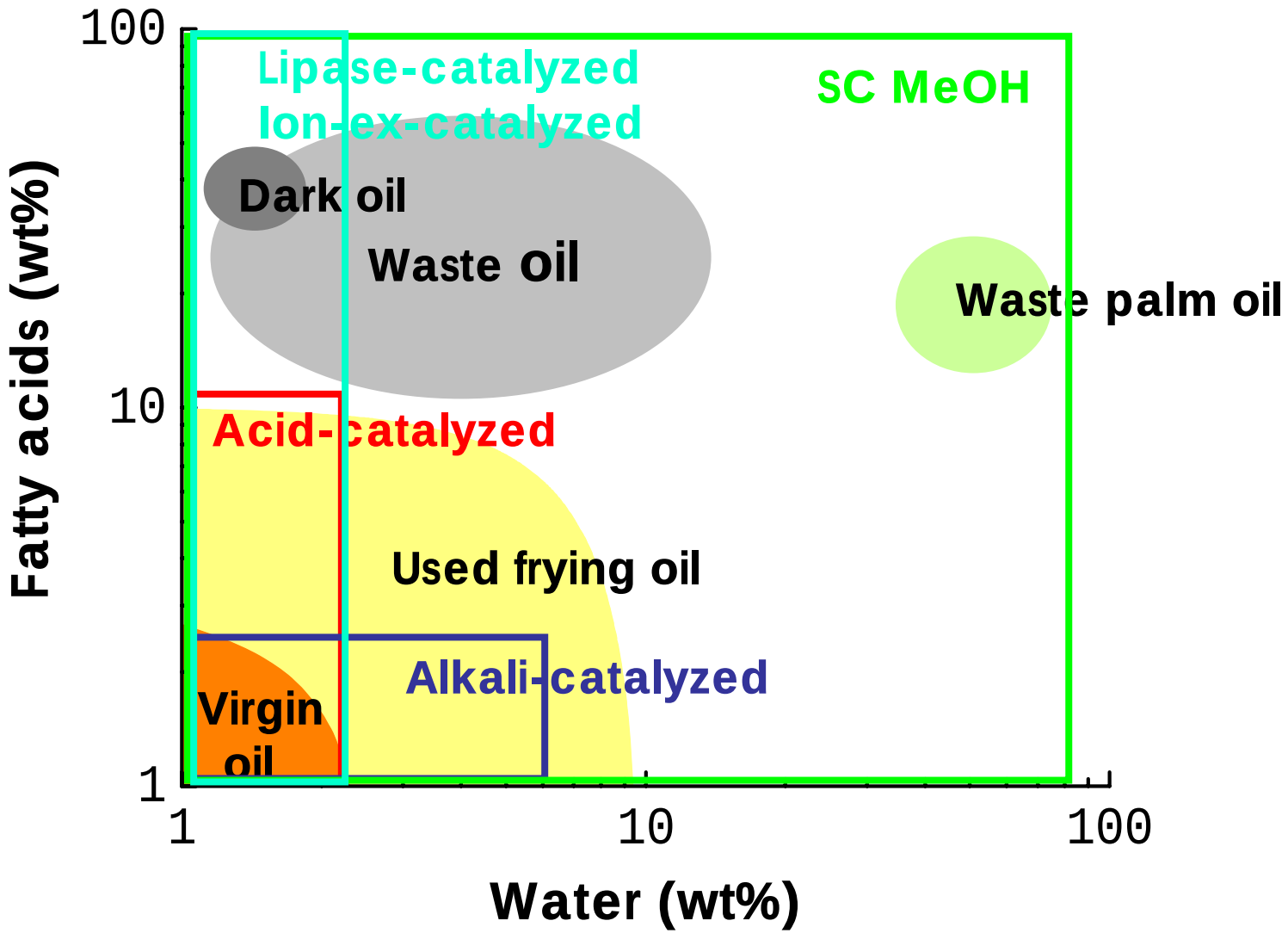
# Effect of Free Fatty Acid on Transesterification/ Esterification by Various Methods



# Effect of Water on Transesterification/Esterification by Various Methods



# Applicable Range of Different Methods in Water and Free Fatty Acid Contents in Various Oils/Fats



# Specification Standards of Biodiesel Fuel

| | Unit | Kyoto | EU | US |
|---|---|---|---|---|
| Density (15°C) | g/mL | 0.86 ~ 0.90 | 0.86 ~ 0.90 | 0.88 |
| Viscosity (40°C) | $mm^2/s$ | 3.5 ~ 5.0 | 3.5 ~ 5.0 | 1.9 ~ 6.0 |
| Pour point | °C | < –7.5 | - | - |
| CFPP | °C | < – 5 | - | - |
| Carbon residue (10%) | % | < 0.30 | < 0.30 | < 0.50 (100%) |
| Cetane number | | > 51 | > 51 | > 47 |
| Water | ppm | < 500 | < 500 | < 500 |
| Flash point | °C | > 100 | > 101 | > 130 |
| MG | % | < 0.8 | < 0.8 | - |
| DG | % | < 0.2 | < 0.2 | - |
| TG | % | < 0.2 | < 0.2 | - |
| G | % | < 0.02 | < 0.02 | < 0.02 |
| Total glycerol | % | < 0.25 | < 0.25 | < 0.24 |
| Methanol | % | < 0.2 | < 0.2 | - |
| Na+K | mg/kg | < 5 | < 5 | - |
| Acidic value | | < 0.5 | < 0.5 | - |
| Iodine value | | < 120 | < 120 | - |


Thank you for your attention!
Kyoto University 21 COE Program
Grant-in-Aid for Scientific Research (B)(2)
NEDO for “High Efficiency Bioenergy Conv Projects”
29 4