

# **Non-Catalytic Alcoholysis Process for Production of Biodiesel Fuel - Its Application and Economical Efficiency -**



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農研機構



# Contents

- **Materials for Production of Biodiesel Fuel in Japan and Southeast Asia**
- Problems with Conventional Alkaline Catalyzed Alcoholysis Reaction Process for Production of Biodiesel Fuel
- Advantages of Non-Catalytic Alcoholysis Reaction for Production of Biodiesel Fuel
- Research on Non-Catalytic Alcoholysis Reaction for Biodiesel Fuel Production in Japan
  1. Supercritical Methanol Method
  2. Superheated Methanol Vapor Bubble Method



## ● **Materials for Biodiesel Fuel in Western Countries:**

Europe: Rapeseed Oil

U.S.A.: Soybean Oil

## ● **Biodiesel Fuel Production in 2004:**

Germany: 1 090 000 t

France: 500 000 t

Italy: 420 000 t

Austria: 100 000 t

Spain: 70 000 t

Denmark: 44 000 t

U.K.: 15 000 t

U.S.A.: 83 000 t

References:

The EU's Vegetable Oil Industry Federation

The European Biodiesel Board

The National Biodiesel Board

# Promising Materials for Biodiesel Fuel Production in Japan and Southeast Asia - Lipids Which Do Not Compete with Edible Use -

- ◆ Used Edible Oil (Japan)
- ◆ Lipids Contained in Waste Effluent from Oil Milling Process and By-Products from Oil Refining Process (Japan, Southeast Asia)
- ◆ Crude Oils from Industrial Crops Such as Jatropha (Southeast Asia)



# Jatropha (*Jatropha curcas* L.)

- ◆ Jatropha is an oil crop which can grow in marginal land such as eastern part of Indonesia where precipitation is less than 400 mm/y. Oil content of Jatropha seed is 30 – 40%.
- ◆ Jatropha oil contains toxin and unsuitable for human consumption. Therefore, utilization of Jatropha oil as material for biodiesel fuel does not affect supply and price of edible oil.
- ◆ If crude Jatropha oil can be converted into fatty acid methyl ester with low cost, it will be a promising material for biodiesel fuel. Then, agriculture can be expanded into marginal land by introducing Jatropha plant and the community there will be benefited.



# Productivity of Various Oil Plants

	Oil Productivity (ton oil·ha <sup>-1</sup> ·y <sup>-1</sup> )
Palm	about 4.0
Soybean	0.3 ~ 0.5
Rapeseed	0.5 ~ 1.1
Jatropha	1.0 (Java, Indonesia) 1.0 ~ 2.5 (Lombok, Indonesia) 4.0 (Africa) 1.5 ~ 3.0 (India)



# Characteristics of The Materials Available in Japan and Southeast Asia for Production of Biodiesel Fuel

- ◆ Waste effluent from oil milling factories and by-product from oil refining factories contain considerable amount of free fatty acids.
- ◆ Used edible oil and crude Jatropha oil also contain considerable amount of free fatty acids.

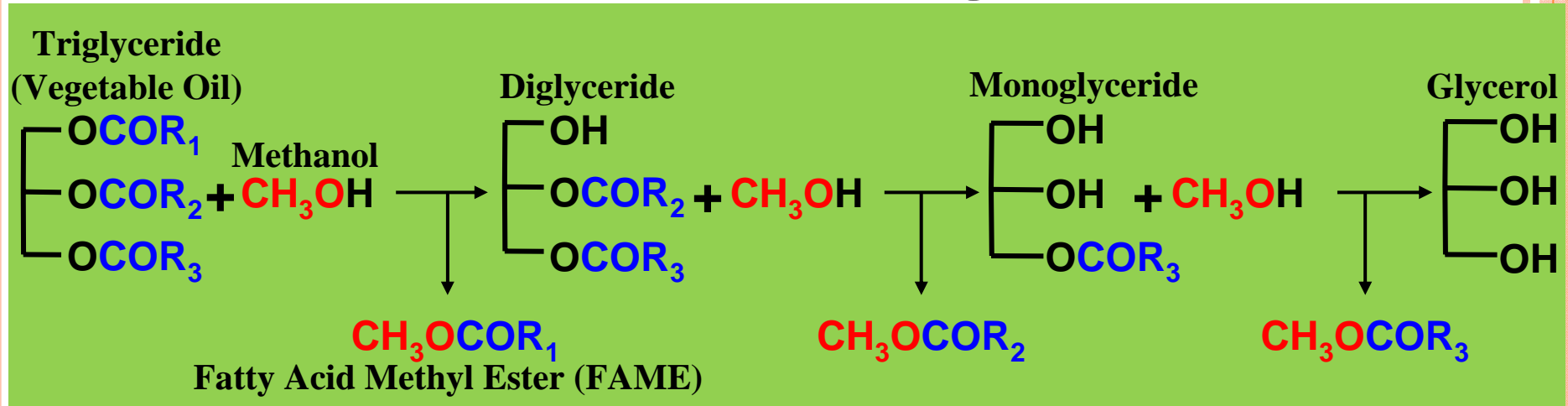


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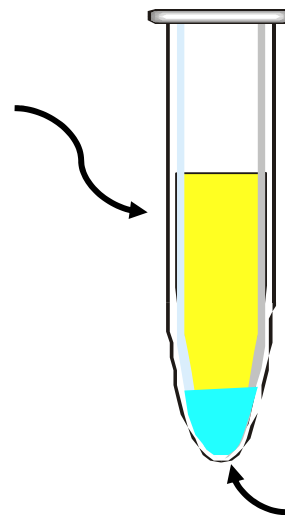
# Alcoholysis Reaction for Production of Biodiesel Fuel from Vegetable Oils



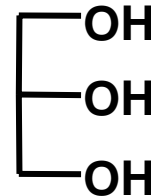
Fatty Acid Methyl Ester (FAME)



Biodiesel Fuel



Glycerol



By-Product

In conventional process, alkaline catalyst such as NaOH and KOH are used to promote the reaction.

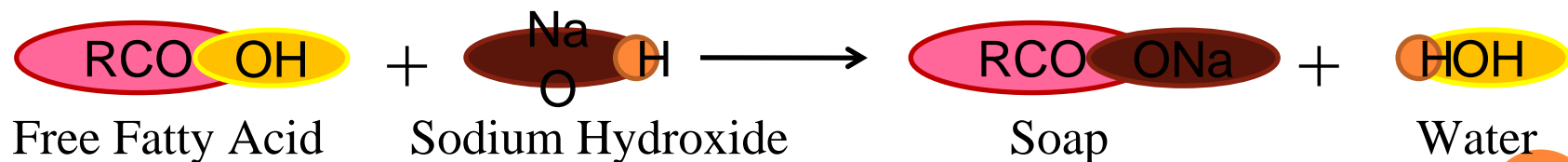
# Problems with Conventional Alkaline Catalyzed Alcoholysis Reaction Process

Alkaline catalysts need to be removed from products after reaction.

**High Cost**

Free fatty acids contained in raw material have to be removed prior to reaction in order to maintain activity of the alkaline catalysts.

**High Cost, Low Yield**



Neutralization of Free Fatty Acid

Alkaline catalyst is converted into soap and inactivated.

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# Advantages of Non-Catalytic Alcoholysis Reaction for Production of Biodiesel Fuel

- Purification process to remove catalyst after reaction is not required.

Configuration of the total system can be simplified and the by-product (glycerol) can be directly utilized in other industry. Then, total cost for production of biodiesel fuel will be reduced.

- Not only triglycerides but also free fatty acid might be converted into fatty acid methyl ester.

Neutralization process for removal of free fatty acid is not required prior to the reaction process. Then, yield of the total system will be improved, and the cost required for the process will be reduced.



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# Methyl esterification reaction in supercritical methanol without using any catalysts

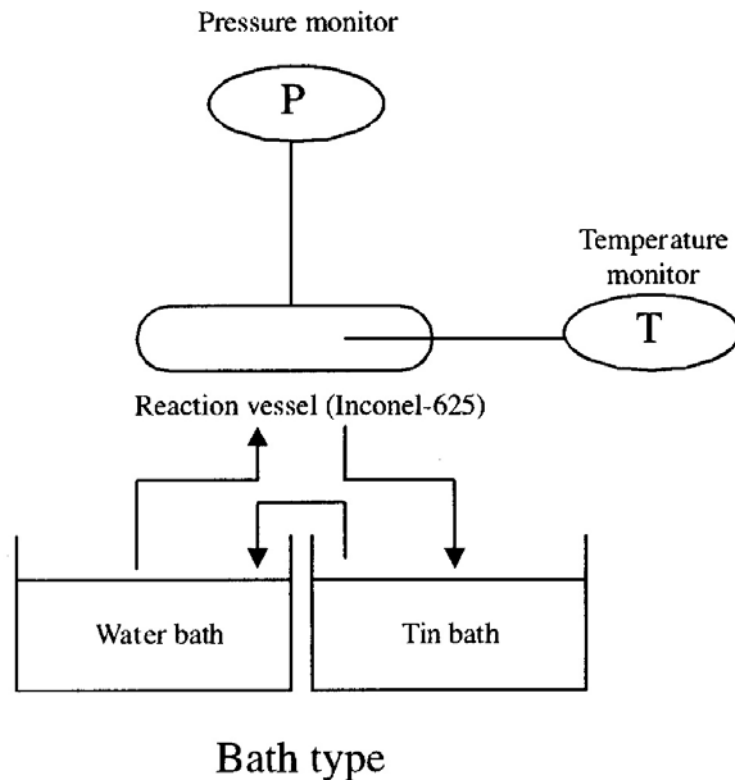


Fig. 1. Supercritical methanol biomass conversion system.

S. Saka and D. Kusdiana;  
*Fuel*, **80**, 225-231 (2001)

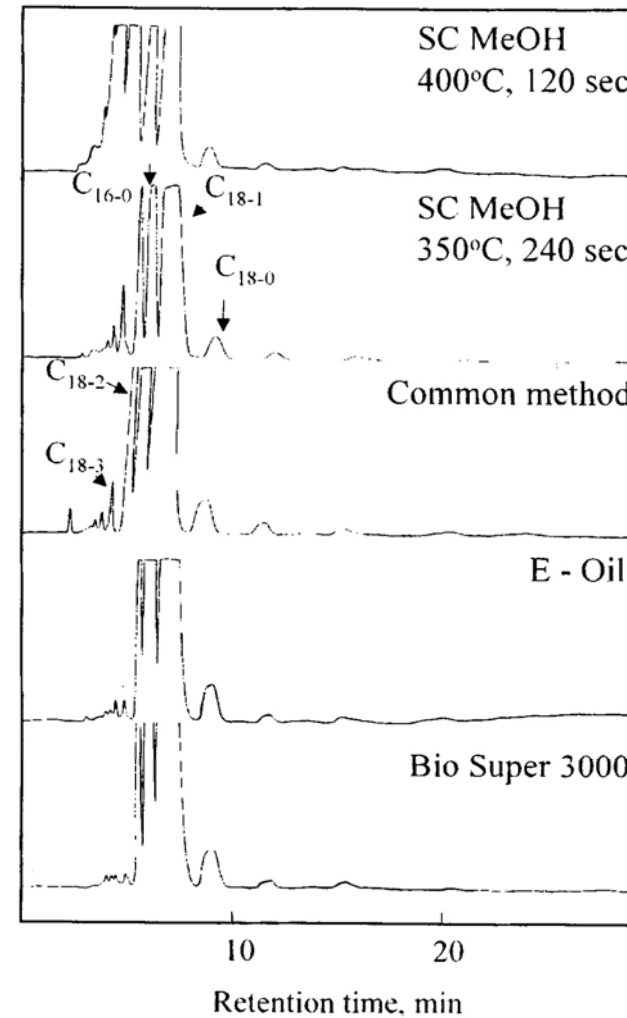
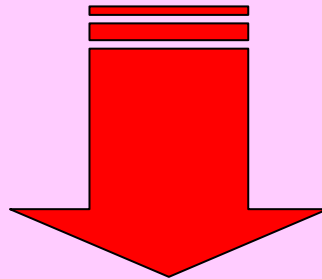


Fig. 6. HPLC chromatograms of methyl esters prepared by supercritical methanol and common method, compared with those of commercial bio-diesel oils.

# Problems with Supercritical Methanol Method

Supercritical Methanol Method requires **high pressure** and **high temperature** for reaction.



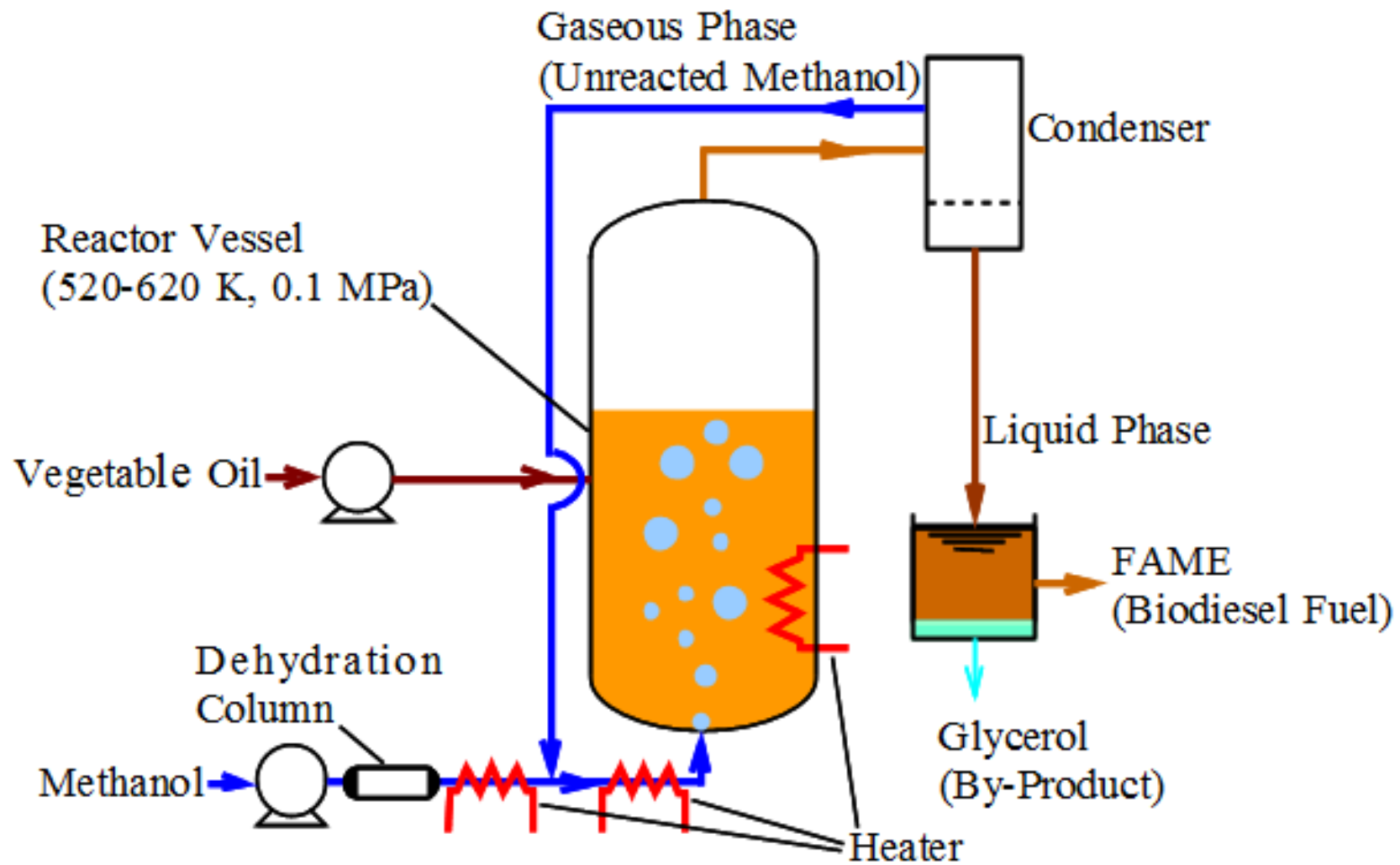
High Initial Cost  
Difficulty in Operation

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# A Schematic Flow Diagram of a Reactor Based on Superheated Methanol Vapor Bubble Method



# Advantages of Superheated Methanol Vapor Bubble Method for Production of Biodiesel Fuel

- Reaction can be conducted under atmospheric pressure condition. Therefore, both initial cost and running cost required for the process can be reduced.

**High safety, Low cost, High Applicability**

**Product Obtained by Alkaline Catalyst Method**



**Glycerol**

Impurities such as alkaline catalyst are contained.  
Limited use

**Fatty Acid Methyl Ester (Biodiesel Fuel)**

**Product Obtained by Superheated Methanol Vapor Method**

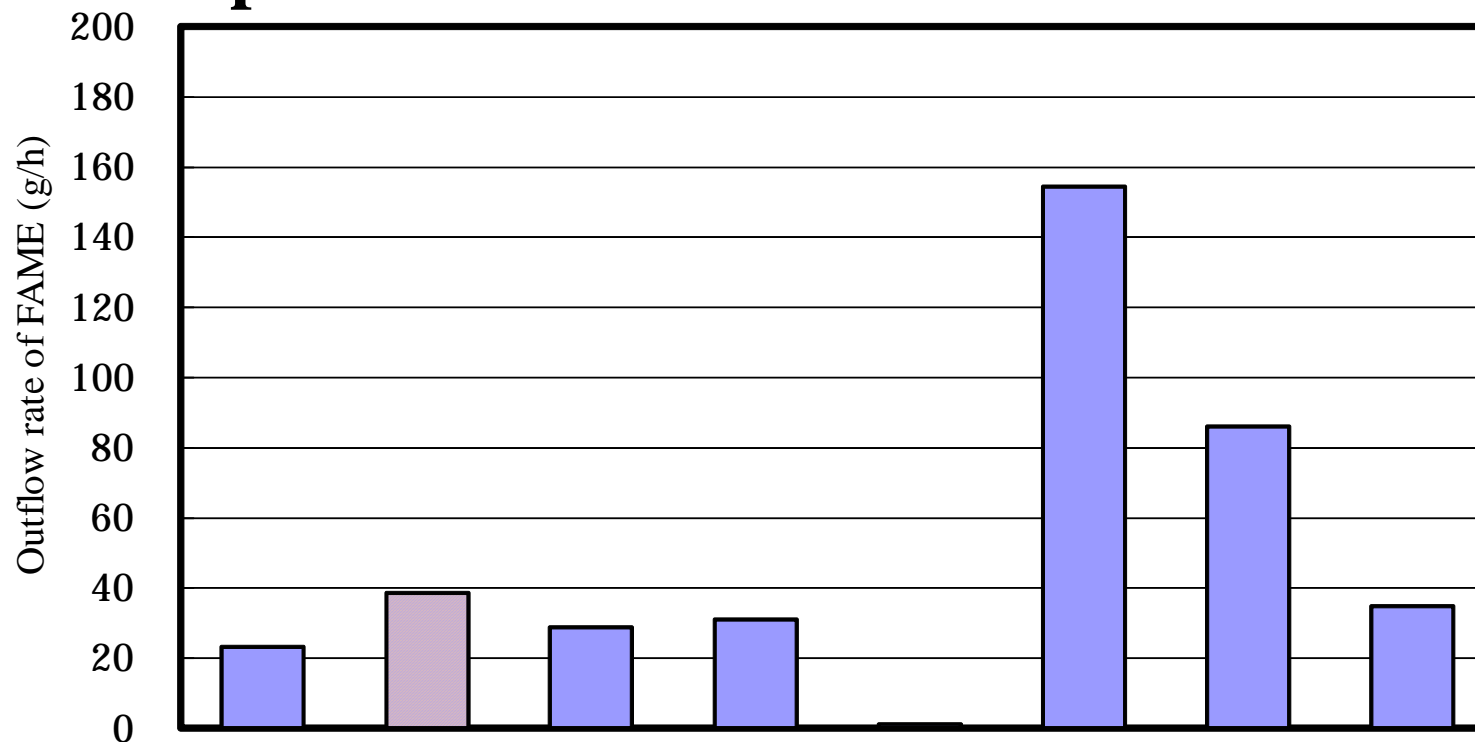


**Glycerol**

Almost no impurity is contained.  
It can be directly utilized in other industry.

# Outflow Rate of FAME into Gaseous Phase

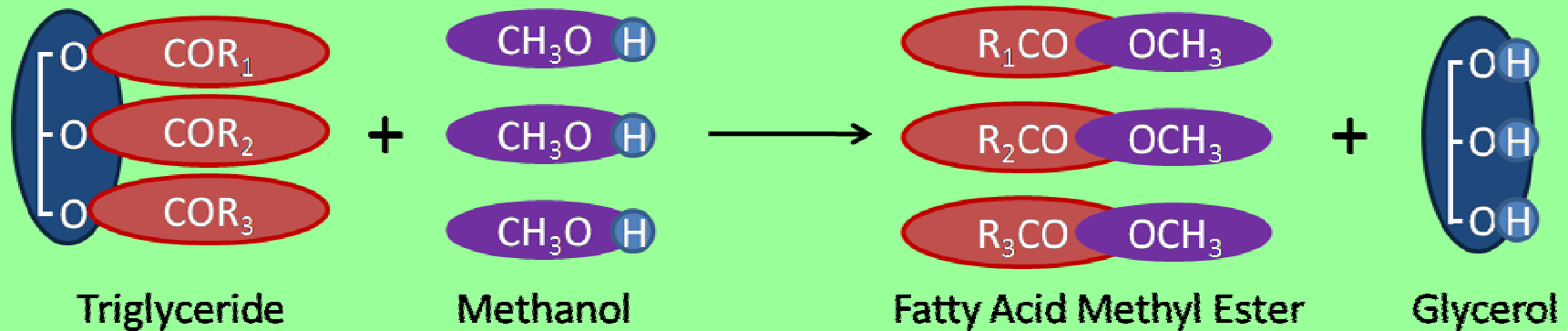
## - Effect of Impurities Contained in Waste Edible Oils -



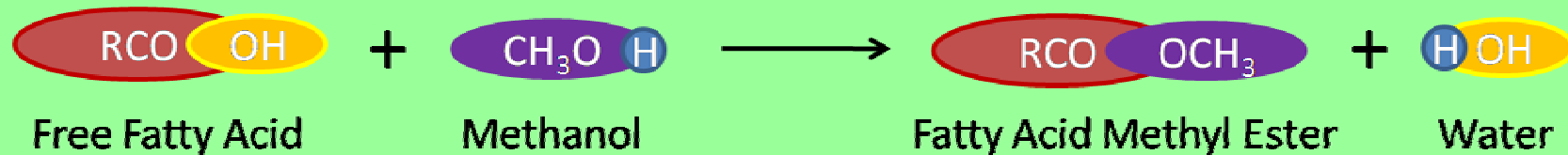
Sample	Fresh Oil (FO)	Used Oil	DG	FO:DG =50:50	MG	Oleic Acid (OA)	FO:OA =50:50	FO:OA =98:2	
Composition	TG	98.7	90.5	13.5	56.0	-	-	49.3	96.4
	DG	1.0	5.0	82.5	41.8	-	-	0.5	1.0
	MG	0.4	4.0	4.0	2.2	100.0	-	0.2	0.4
	FFA	-	0.5	-	-	-	100.0	50.0	2.2
Outflow rate of FAME (g/h)	23.1	38.5	28.8	31.0	1.2	154.4	85.9	34.8	

# Two Simultaneous Reactions Which Proceed in a Reactor with Superheated Methanol Vapor Method

## Formation of Fatty Acid Methyl Ester by Alcoholysis



## Formation of Fatty Acid Methyl Ester by Esterification





**Demonstration Plant for Superheated Methanol Vapor Bubble Method  
(Designed Productivity: 400 L/d)**

# Estimated Cost for Production of Biodiesel Fuel

		Demonstration Plant (146 kL/y)	Practical Scale Plant (6 000 kL/y)	Alkaline Catalyst Method (1500 kL/y)	
			Basic Case	Combination with an incineration facility	
Depreciation Cost	[yen/kg]	39.2	8.6	8.6	36.1
Cost of Repairing	[yen/kg]	0.9	0.2	0.2	0.8
Labor Cost	[yen/kg]	313.9	7.3	-	7.3
Methanol Cost	[yen/kg]	18.0	10	10.0	25.2
Energy Cost (heat)	[yen/kg]	82.7	13.6	-	1.2
Energy Cost (electricity)	[yen/kg]	28.9	9.7	6.4	1.5
Cost of Catalyst	[yen/kg]	-	-	-	4.1
Total	[yen/kg]	483.6	<b>49.5</b>	28.5	<b>76.1</b>
	[yen/L]	396.5	<b>40.6</b>	23.4	<b>62.5</b>

## Future

Results from these research works will reduce the cost required for production of biodiesel fuel, and contribute to prevention of global warming, reduction in consumption of fossil resources and activation of rural area in Japan and Southeast Asia.

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Part of the research work on “Superheated Methanol Vapor Bubble Method” was supported by a grant from the Ministry of Agriculture, Forestry and Fisheries of Japan (Rural Biomass Research Project, BEC-BF010), and implemented in cooperation with;

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