Upgrading Technology of Biodiesel Quality for Meeting New Fuel Standards

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1. Benchmarking of Biodiesel Fuel Standardization

・ERIA energy project-”Standardization of biodiesel fuel in East Asia”

Benchmarking of Biodiesel Fuel Standardization

- Using biodiesel fuel is important from the viewpoint of CO_2 reduction and energy security.
- Impurities and the oxidation of biodiesel fuel caused serious influences on engine performance.

Examples of mechanical defects caused by using "inferior biodiesel fuel"

Injector
(source : JAMA)

Fuel tank
(source: Fuel Policy Subcommittee)

Engine
(source: JAMA)

It is necessary to use "high-quality biodiesel fuel" to prevent these troubles.

Harmonization of standards within East Asia region will facilitate the use and trading of high-quality biodiesel fuel.

Need for harmonized specifications in East Asia

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Items	Units	EU
		EN14214:2003
Ester content	mass%	96.5 min.
Density	kg/m3	860-900
Viscosity	mm2/s	3.50-5.00
Flashpoint	deg. C	120 min.
Sulfur content	mass%	0.0010 max.
Distillation, T90	deg. C	-
Carbon residue (100%) or Carbon residue (10%)	mass%	- 0.30 max.
Cetane number		51.0 min.
Sulfated ash	mass%	0.02 max.
Water content	mg/kg	500 max.
Total contamination	mg/kg	24 max.
Copper corrosion		Class-1
Acid value	mgKOH/g	0.50 max.
Oxidation stability	hrs.	6.0 min.
Iodine value		120 max.
Methyl Linolenate	mass%	12.0 max.
Polyunsaturated FAME (more than 4 double bonds)	mass%	1 max.
Methanol content	mass%	0.20 max.
Monoglyceride content	mass%	0.80 max.
Diglyceride content	mass%	0.20 max.
Triglyceride content	mass%	0.20 max.
Free glycerol content	mass%	0.02 max.
Total glycerol content	mass%	0.25 max.
Na+K	mg/kg	5.0 max.
Ca+Mg	mg/kg	5.0 max.
Phosphorous content	mg/kg	10.0 max.

EU's standard
: Focusing Rapeseed oil only

Coconut FAME
Viscosity ≈ 2.6
Flash point ≈ 107ºC
PNS2020:2003 2.50~4.50
100ºC min.

This level of oxidation stability is not enough to prevent metal corrosion (Luck of oxidation stability in FAME corrodes fuel tank).

Iodine value of conjugated polyunsaturated FAME is low, however its oxidation stability is low (Iodine value is not measure of oxidative instability).

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ERIA Energy Project

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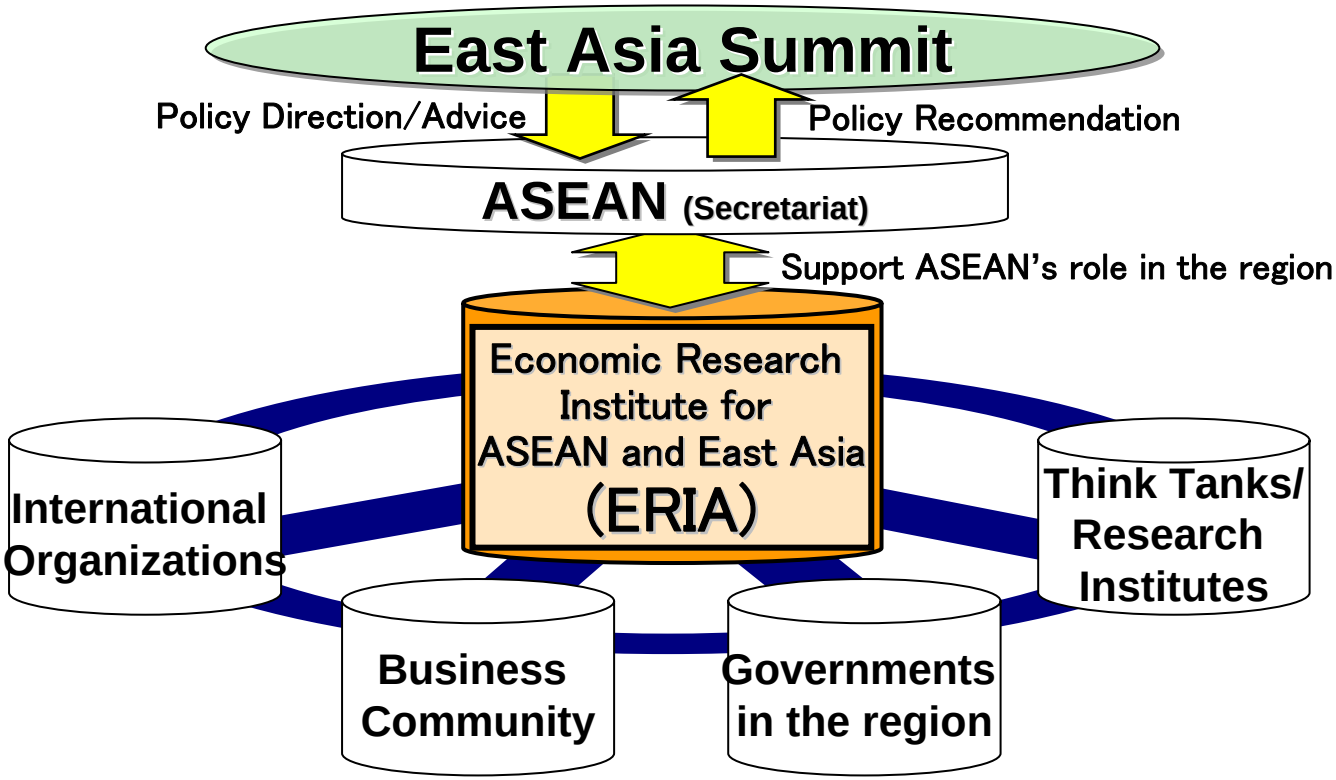
- ERIA is a new kind of international organization to conduct policy research and make policy recommendations to promote economic integration in East Asia.

Intellectual Contribution for Economic Integration in East Asia



・Analysis of Energy Saving Potential in East Asia (IEE, Japan)

・Sustainable Biomass Utilization Vision in East Asia (AIST)

・Standardization of Biodiesel Fuel in East Asia (AIST)

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Schedule (ERIA WG)

FY2007

WG-1
Jul.17-18
Japan

Understanding on the importance of ensuring BDF quality

WG-2
Oct.2-3
Thailand

Study on current situation in each countries

Proposal for common standards

WG-3
Nov.29-30
Japan

Proposal for common standards

WG-4
Feb.21-22
Philippines

Summarize BDF standardization report

FY2008

WG-1
Nov.11-12
Indonesia

Continuous discussions (Oxidation stability, Iodine number, Polyunsaturated FAME, Quality control etc.)

Feasibility study

“Biodiesel Fuel Trade Handbook”

WG-2
Feb. 22-23
Malaysia

Continuous discussions (Oxidation stability, Iodine number, Polyunsaturated FAME, Quality control etc.)

Feasibility study

“Biodiesel Fuel Trade Handbook”

EAS-ERIA Biodiesel Fuel Benchmark Standard

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EAS: East Asia Summit ERIA: Economic Research Institute for ASEAN and East Asia

Items	Units	U.S. ASTM D6751-07b	EU EN14214:2003	Japan JIS K2390:2008	EAS-ERIA BDF Standard (EEBS):2008
Ester content	mass%	-	96.5 min.	96.5 min.	96.5 min.
Density	kg/m3	-	860-900	860-900	860-900
Viscosity	mm2/s	1.9-6.0	3.50-5.00	3.50-5.00	2.00-5.00
Flashpoint	deg. C	93 min.	120 min.	120 min.	100 min.
Sulfur content	mass%	0.0015 max.	0.0010 max.	0.0010 max.	0.0010 max.
Distillation, T90	deg. C	360 max.	-	-	-
Carbon residue (100%) or Carbon residue (10%)	mass%	0.05 max. -	- 0.30 max.	- 0.3 max.	0.05 max. 0.3 max.
Cetane number		47 min.	51.0 min.	51.0 min.	51.0 min.
Sulfated ash	mass%	0.02 max.	0.02 max.	0.02 max.	0.02 max.
Water content	mg/kg	0.05[vol%] max.	500 max.	500 max.	500 max.
Total contamination	mg/kg	-	24 max.	24 max.	24 max.
Copper corrosion		No.3	Class-1	Class-1	Class-1
Acid value	mgKOH/g	0.50 max.	0.50 max.	0.50 max.	0.50 max.
Oxidation stability	hrs.	3 min.	6.0 min.	(**)	10.0 min. (****)
Iodine value		-	120 max.	120 max.	Reported (***)
Methyl Linolenate	mass%	-	12.0 max.	12.0 max.	12.0 max.
Polyunsaturated FAME (more than 4 double bonds)	mass%	-	1 max.	N.D.	N.D. (***)
Methanol content	mass%	0.2 max. (*)	0.20 max.	0.20 max.	0.20 max.
Monoglyceride content	mass%	-	0.80 max.	0.80 max.	0.80 max.
Diglyceride content	mass%	-	0.20 max.	0.20 max.	0.20 max.
Triglyceride content	mass%	-	0.20 max.	0.20 max.	0.20 max.
Free glycerol content	mass%	0.020 max.	0.02 max.	0.02 max.	0.02 max.
Total glycerol content	mass%	0.240 max.	0.25 max.	0.25 max.	0.25 max.
Na+K	mg/kg	5 max.	5.0 max.	5.0 max.	5.0 max.
Ca+Mg	mg/kg	5 max.	5.0 max.	5.0 max.	5.0 max.
Phosphorous content	mg/kg	10 max.	10.0 max.	10.0 max.	10.0 max.

(*) 130deg.C of flashpoint is available instead of measuring methanol content

(**) Meet diesel oil specification

(***) Need data check and further discussion

(****) Need more data & discussion from 6 to 10 hrs.

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WorldWide Fuel Charter (WWFC)

1st Edition of the WWFC Guidelines for Biodiesel was proposed as a draft for comments (July 8, 2008)

Items	Units	EAS-ERIA BDF Standard (EEBS):2008	WWFC Guidelines specifications
Ester content	mass%	96.5 min.	<==
Density	kg/m3	860-900	<==
Viscosity	mm2/s	2.00-5.00	<==
Flashpoint	deg. C	100 min.	<==
Sulfur content	mass%	0.0010 max.	<==
Carbon residue (100%) or Carbon residue (10%)	mass%	0.05 max. 0.3 max.	0.05 max.
Cetane number		51.0 min.	<==
Ash	mass%	-	0.001 max.
Sulfated ash	mass%	0.02 max.	0.005 max.
Water content	mg/kg	500 max.	<==
Total contamination	mg/kg	24 max.	<==
Copper corrosion		Class-1	
Acid value	mgKOH/g	0.50 max.	<==
Oxidation stability	hrs.	10.0 min. (****)	<==
Iodine value		Reported (***)	130 max. May unnecessarily preclude certain feed stocks.
Methyl Linolenate	mass%	12.0 max.	<==
Polyunsaturated FAME (more than 4 double bonds)	mass%	N.D. (***)	1max.
Methanol content	mass%	0.20 max.	<==
Monoglyceride content	mass%	0.80 max.	<==
Diglyceride content	mass%	0.20 max.	<==
Triglyceride content	mass%	0.20 max.	<==
Free glycerol content	mass%	0.02 max.	<==
Total glycerol content	mass%	0.25 max.	0.24 max.
Na+K	mg/kg	5.0 max.	<==
Ca+Mg	mg/kg	5.0 max.	<==
Phosphorous content	mg/kg	10.0 max.	4.0 max.

- Almost similar value to EAS-ERIA BDF standard

-Ash content was proposed.

- Oxidation stability was proposed over 10 hrs.

- Both are for B100 aimed for low level blending with diesel fuel (Never for using as a final fuel!!)

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Research Plan of FY2008

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(1) Discussion (WG meeting)
- Continuous discussions: Oxidation stability (6-10 hr.), Iodine number, Polyunsaturated FAME and so on.
- Determination of how to control the biodiesel fuel quality on each country's real market

(2) Feasibility study
- New inedible feedstocks for biodiesel fuel: Plant tour is planned (Jatropha curcas nursery, experimental plantation plus small scale processing in Indonesia)
- Survey the possibility of inedible materials, i.e. Jatropha, Micro-Algae, etc

(3) Making a "Biodiesel Fuel Trade Handbook"
Including all results of discussion and feasibility study in the handbook

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2. Catalyst technology for Upgrading Biodiesel Fuel Quality

・Partial hydrogenation of polyunsaturated FAME for improvement of oxidation stability

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Desired Technology for Producing High Quality BDF

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(1) Improvement of oxidation stability

- Hydrodeoxygenation (HDO) of vegetable oil
  (NExX-BTL(Neste), 'Green Diesel'(UOP), BHD(Nippon Oil))
- Partial hydrogenation of polyunsaturated FAME

(2) Removal of metal impurities (Na, K, Ca, Mg etc.)

- Washing, adsorption, distillation etc.
- BDF production using insoluble heterogeneous catalysts

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Comparison of Hydrodeoxygenation and Partial Hydrogenation

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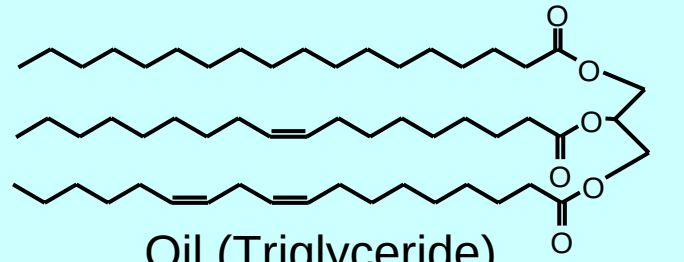
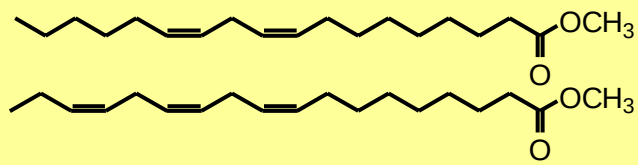
	Hydrodeoxygenation	Partial hydrogenation
Reaction	 Oil (Triglyceride) → Hydrocarbon	 Polyunsaturated FAME → Monounsaturated FAME
Oxidation Stability	High	Relatively high
Reaction Conditions	High pressure (~6MPa) High temperature (>300ºC)	Low pressure (0.1~0.5MPa) Low temperature (80~120ºC)
Research Items	Water-tolerance HDO catalyst Isomerization for Cetane Optimization	Selective hydrogenation catalyst Gas-liquid-solid mixing under Low pressure
Factory	Petroleum refinery (Coprocessing with heavy fraction)	Small Factory at Local Community

Improvement of FAME oxidation stability

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Vegetable oil, waste cooking oil etc.

1st generation BDF

MeOH

Antioxidant

FAME (B100)

Conventional

5%

95%

Petrodiesel

◆Oxidation stability ⇑

◆Sludge formation ??

Mandatory law FAME<5wt%

B5

New Technology

Hydrotreatment

"1.5 generation" BDF

AIST catalyst

5～20%

95～80%

Petrodiesel

Incremental acid value:
Δ<0.12mgKOH/g
@115℃,16h,O_2 flow

Meet mandatory law quality

B5

B20

◆Antioxidant zero or min.

◆Oxidation stability ⇑

◆Sludge formation ⇓

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Japanese Mandatory Law of BDF/Diesel Mixed Fuel

Items	Units	Level
Sulfur content	mass%	<0.0010
Cetane index		>45
Distillation, T90	deg. C	<360
FAME content	mass%	<5
Methanol content	mass%	<0.01
Triglyceride content	mass%	<0.01
Total acid number (TAN)	mgKOH/g	<0.13
Individual organic acid	massppm	<30
Oxidation stability (Incremental acid value)	mgKOH/g	<0.12

This level of oxidation stability is essential to prevent metal corrosion. Even though FAME has 6 hours of oxidation stability, B5 will not be able to meet this requirement.

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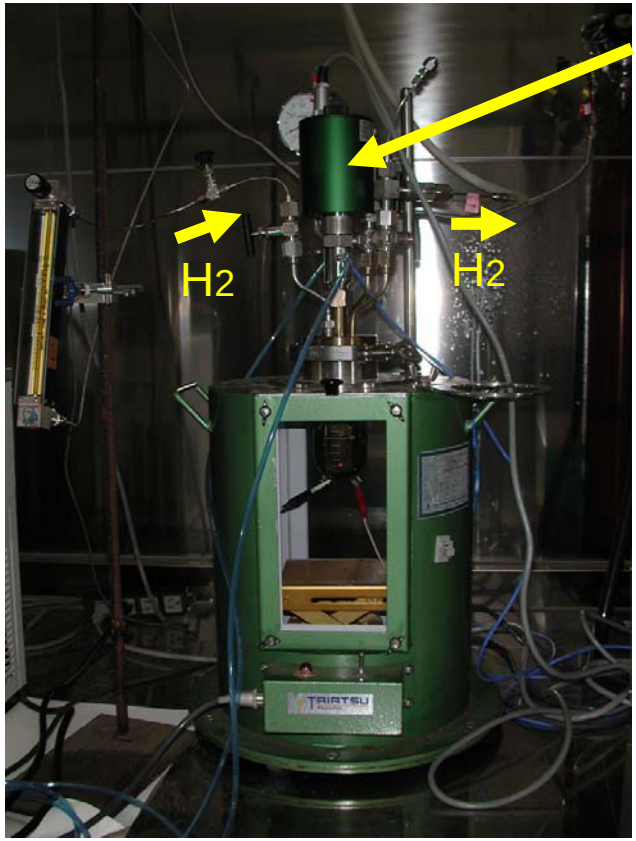
Glass Autoclave for Partial Hydrogenation of BDF



Typical reaction conditions

Temperature: 80 ~ 120 ºC

Pressure: atmospheric ~ 0.5MPa

Oil/Catalyst: 45 ~ 150 (g/g)

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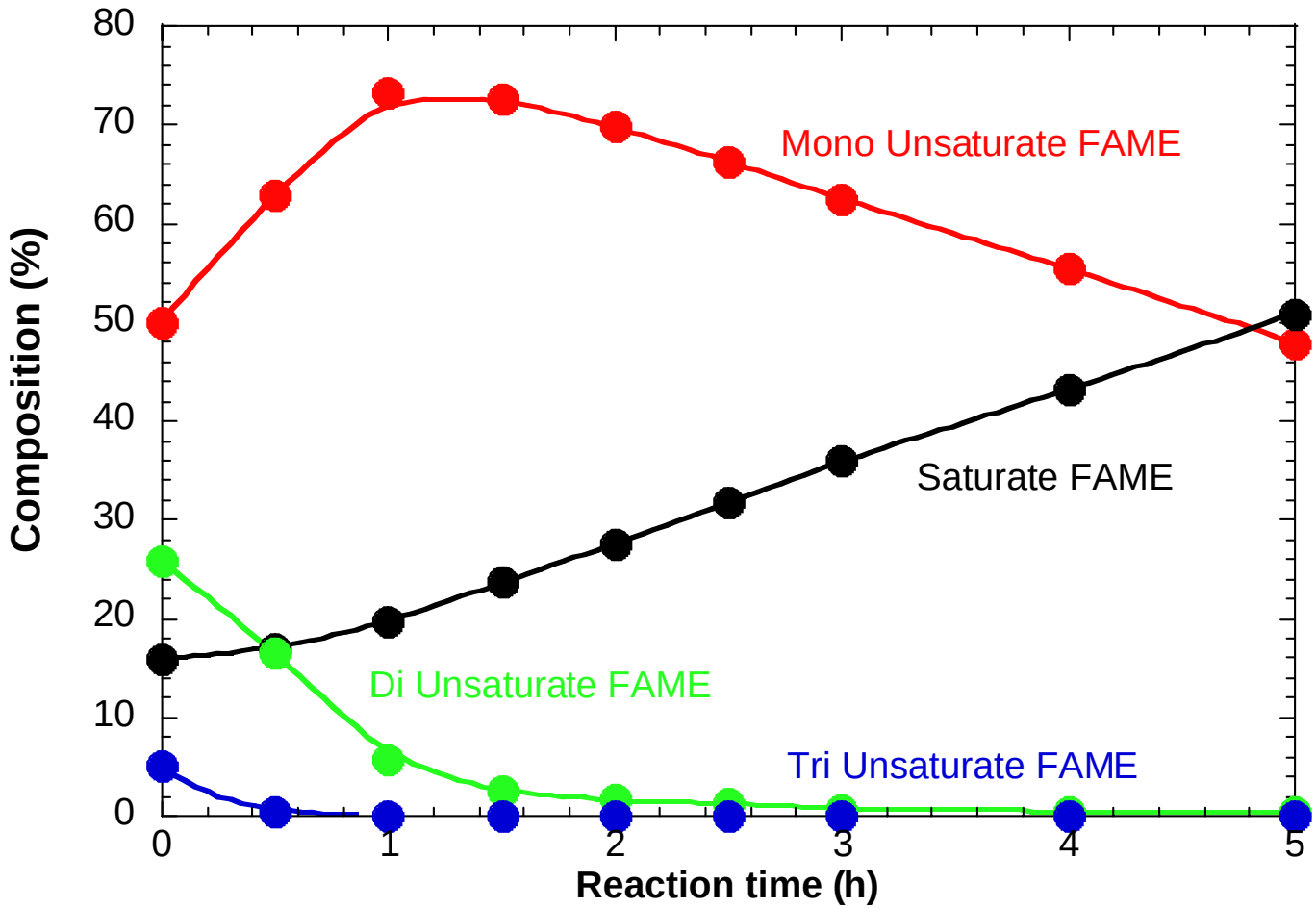
Time Course of Partial Hydrogenation of FAME (Waste Cooking Oil BDF)



Di- and triunsaturate FAME were selectively hydrogenated to mono unsaturate and saturate FAME.

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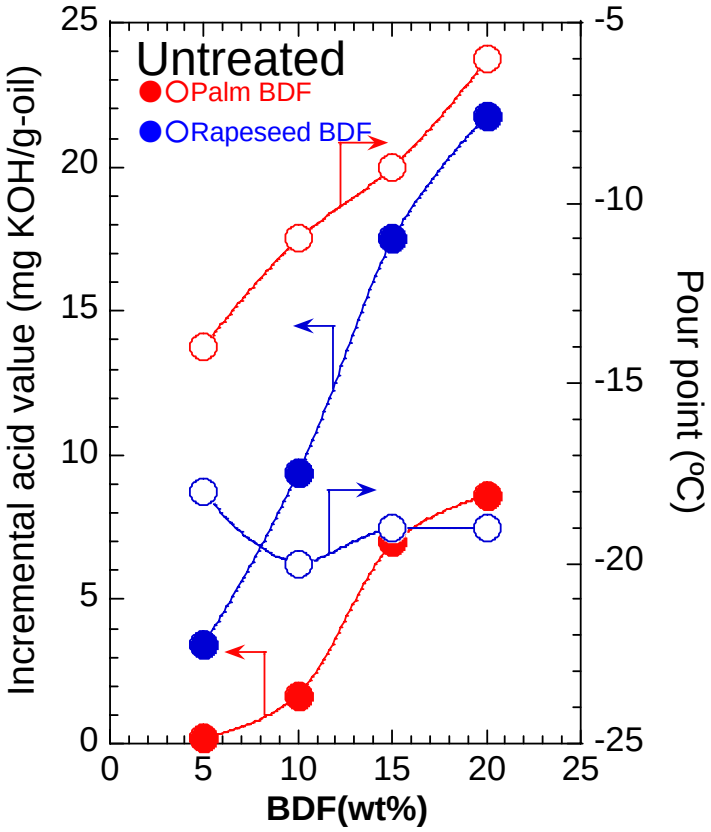
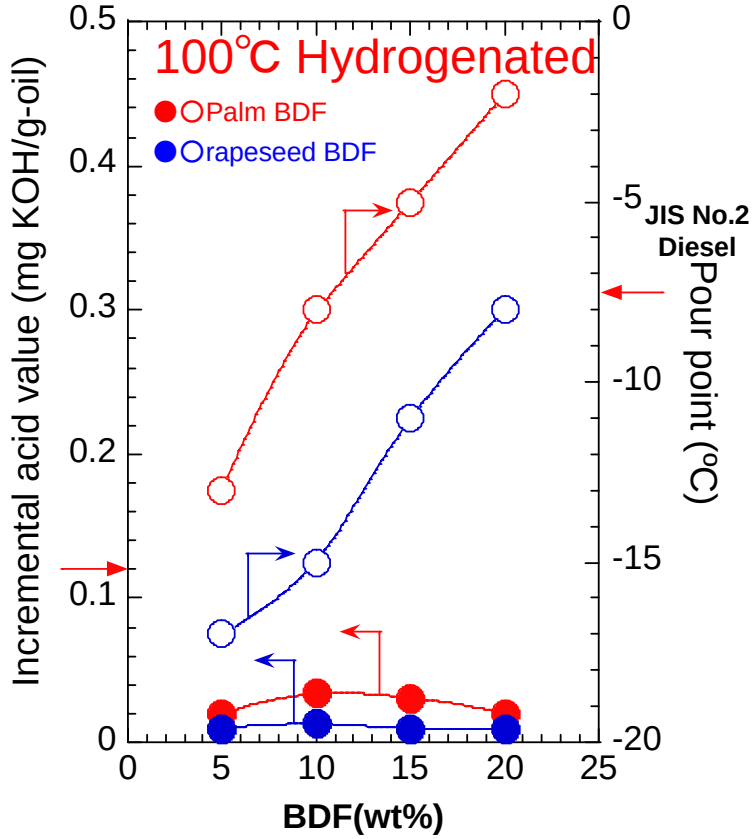
Effect of hydrogenation temperature on oxidation stability and pour point of BDF (B100)

	Temperature (°C)	Rancimat induction time (h)	Pour point (°C)
Crude palm BDF			
	Feed	9.7	12
	40	18.4	12
	80	>24	17
	100	>24	18
	140	>24	26
Rapeseed BDF			
	Feed	3.6	−12
	40	8.9	−6
	80	15.4	0
	100	>24	2
	140	>24	20

Oxidation stability and pour point of BDF increased with increasing hydrogenation temperature.

Oxidation Stability and Cold Flow Properties of Hydrogenated BDF Mixed Fuel





Hydrogenated B5～B20 mixed fuels met the regulation of oxidation stability.
Hydrogenated B5～B20 (rapeseed) and B5～B10 (crude palm) mixed fuels met the regulation of pour point (JIS No.2 diesel).

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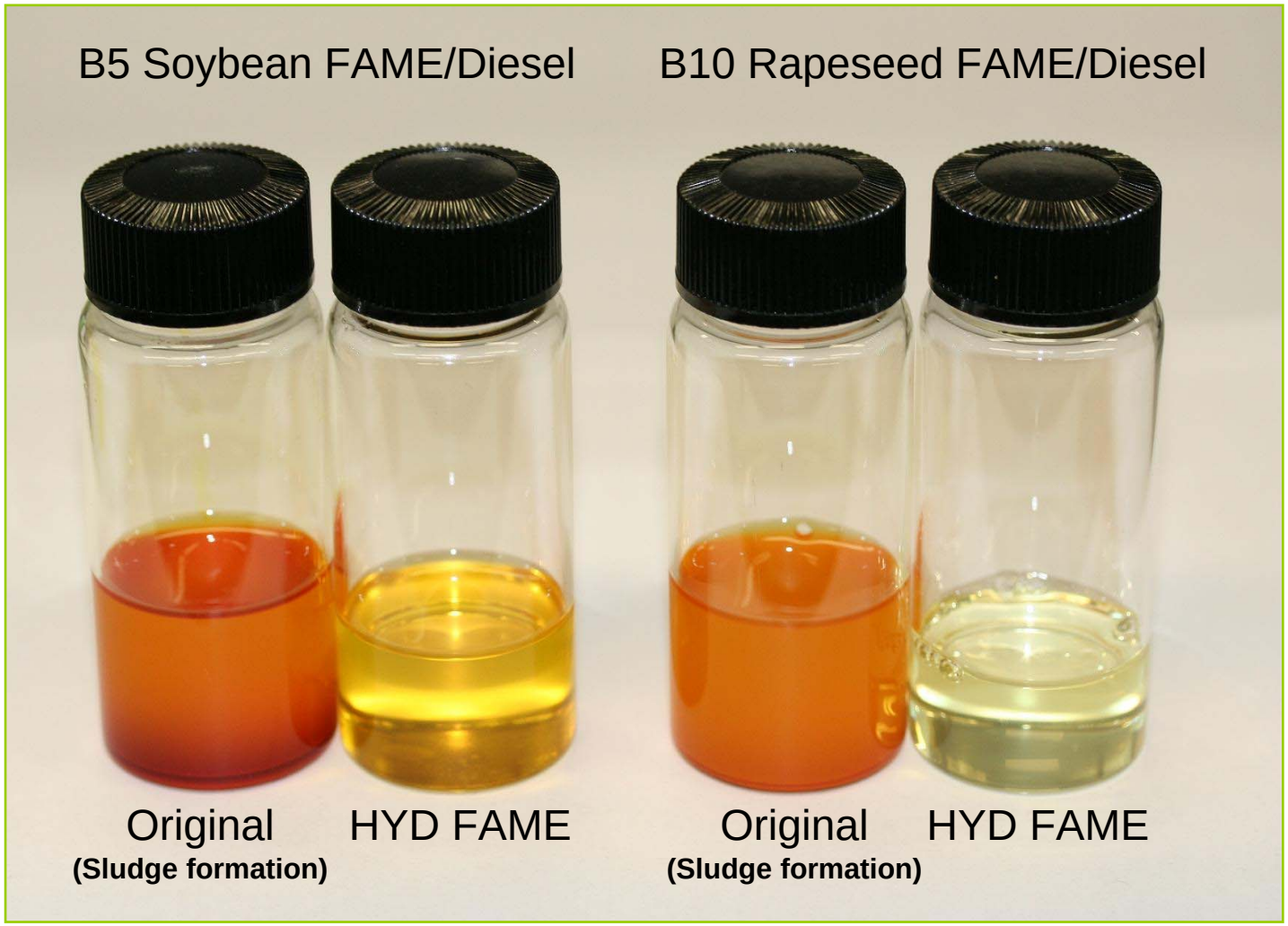
Oxidation Test of Product Oil

(Oxidation condition: 115ºC, 16h, O_2 flow)



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Summary

- A benchmark standard of biodiesel fuel in East-Asia has been discussed by working group members of ERIA project.
- Working group has proposed EAS-ERIA BDF standard aimed for low level blending with diesel fuel.
- Working group continues to discuss about some regulation items of the standard and is planning to make “Biodiesel Fuel Trade Handbook” including all results of discussion and feasibility study in this year.
- Among the regulation items of BDF standard, oxidation stability and ash content will become severer (e.g. WWFC).
- We developed partial hydrogenation method of polyunsaturated FAME to improve the oxidation stability of BDF.
- Oxidation stability of hydrogenated BDF/petroleum diesel blends could meet the Japanese mandatory standards up to the BDF blending ratio of 20 wt%.

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谢谢!

Thank you very much for your attention!