“Upgrading of the conventional FAME into H-FAME”

In

Thailand-Japan collaboration on “Innovation on production and automotive utilization of biofuels from non-food biomass” in Science and Technology Research Partnership for Sustainable Development (SATREPS, JST-JICA Joint Collaboration Program)

Dr. Yuji YOSHIMURA

Leader/Research Director of Project, Prime Senior Researcher,
National Institute of Advanced Industrial Science and Technology (AIST),
Japan

Dr. Paritud BHANDHUBANYONG

Project Director of Project, Thailand

NAC 2013, April 1, 2013, Bangkok

Demands for gradual shift to non-food biomass

Food biomass *(well prepared feed production/logistics)*

Biofuels production

Biodiesel

Biofuels distribution

Biofuels end use

Use of petroleum infrastructure, and without modification of vehicle

Energy security

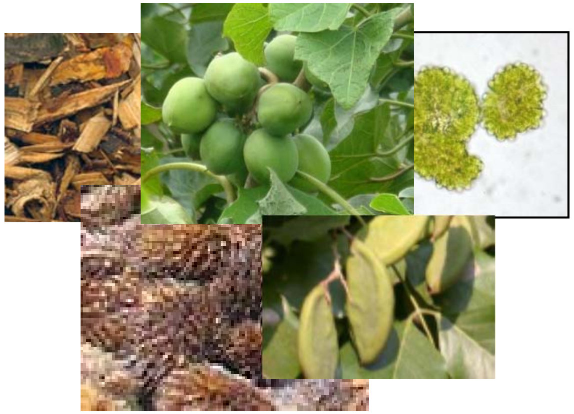
Growth of agricultural/ forestry industries

CO2 reduction

National policy

competitive with food supply chain

Non-food biomass



◆***Limited production and supply chain***

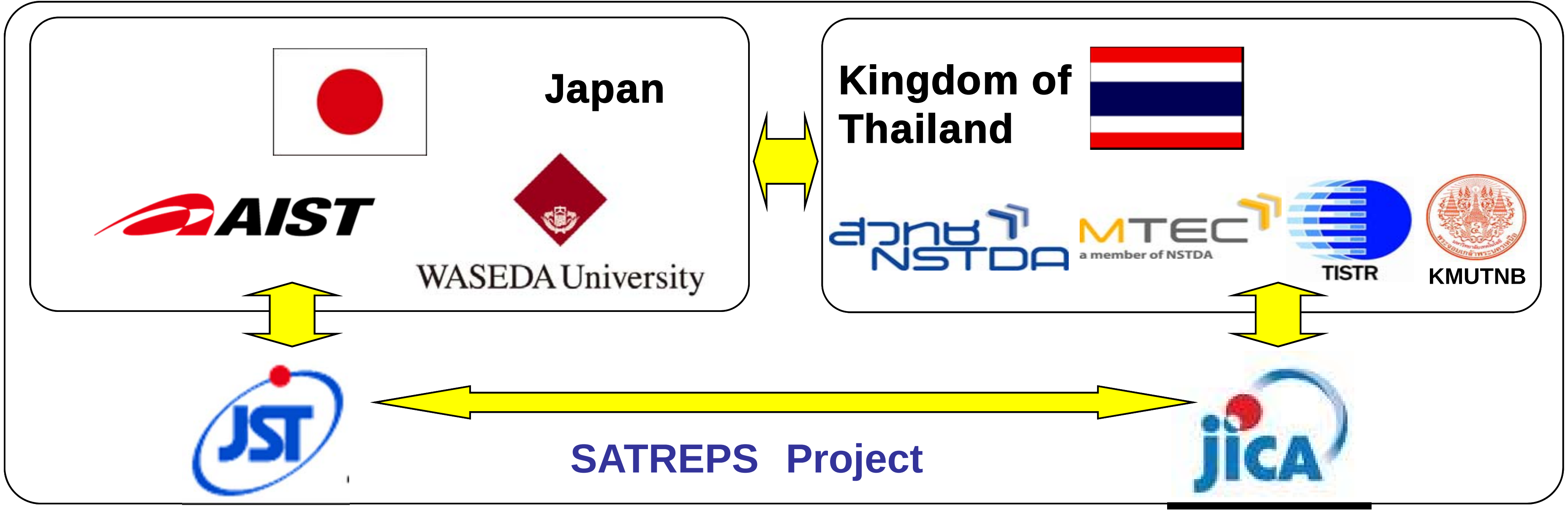
◆***Need to develop the new/modified biomass conversion technologies***

◆***Limited quality assurance to meet with standards***

◆***Limited information on its vehicle use***

Drop-in oil

Innovation on production and automotive utilization of biofuels from non-food biomass (FY2010 - FY2014)



SATREPS Project

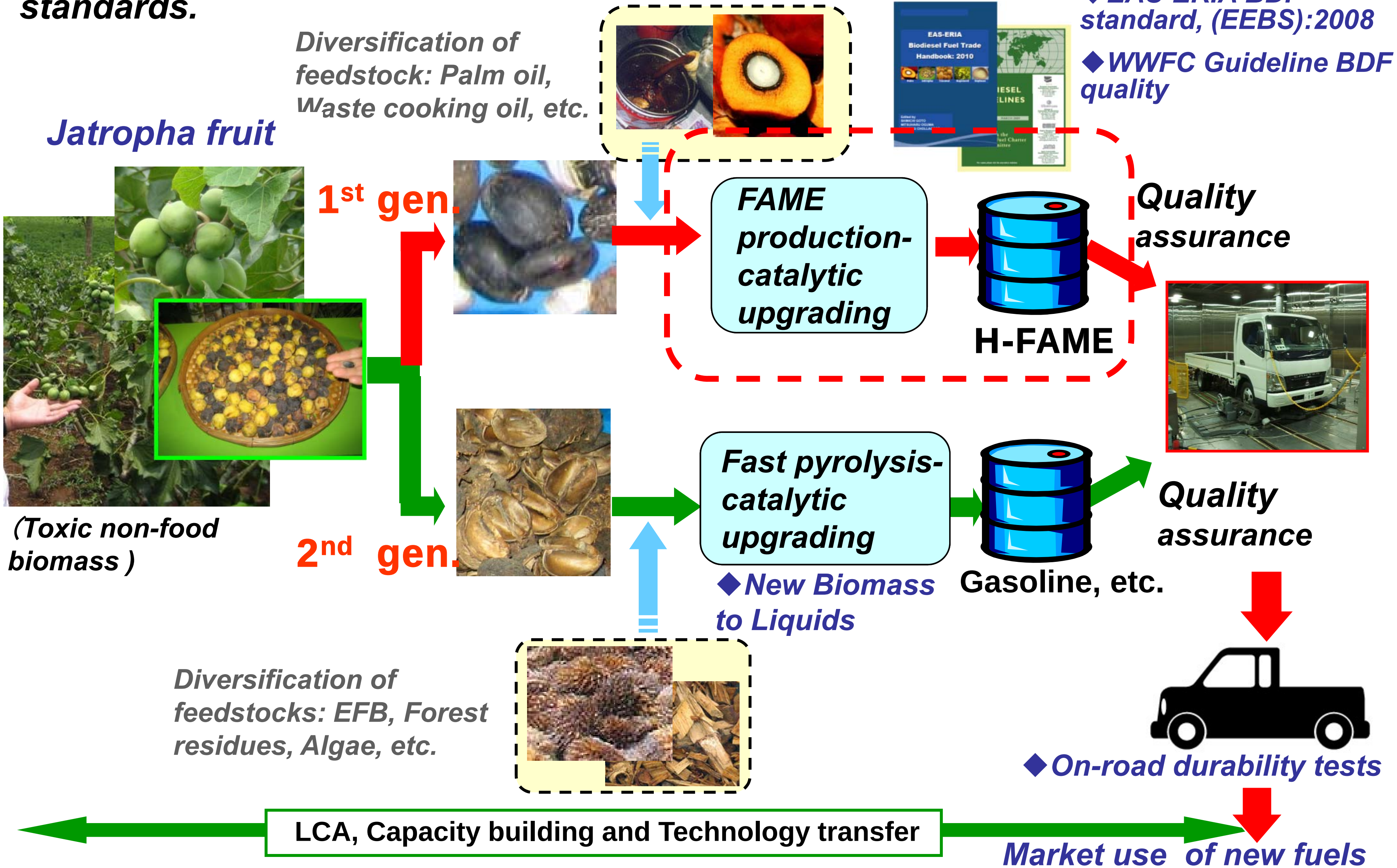
R/D signing ceremony on Feb.25,2010

R&D of Jatropha to transportation fuels

- National Institute of Advanced Industrial Science and Technology (AIST)
- Waseda University
- Japan Science and Technology Agency (JST)
- Japan International Cooperation Agency (JICA)
- National Science and Technology Development Agency (NSTDA)
- Thailand Institute of Science and Technological Research (TISTR)
- King Mongkut's University of Technology NB

Outline of JST-JICA project

To develop the novel non-food biomass conversion technology for producing drop-in oils that meet with the automotive fuel standards.



Jatropha fruit

(Toxic non-food biomass)

1st gen.

2nd gen.

Diversification of feedstock: Palm oil, Waste cooking oil, etc.

FAME production-catalytic upgrading

H-FAME

Quality assurance

◆EAS-ERIA BDF standard, (EEBS):2008

◆WWFC Guideline BDF quality

Fast pyrolysis-catalytic upgrading

Gasoline, etc.

Quality assurance

◆New Biomass to Liquids

Diversification of feedstocks: EFB, Forest residues, Algae, etc.

◆On-road durability tests

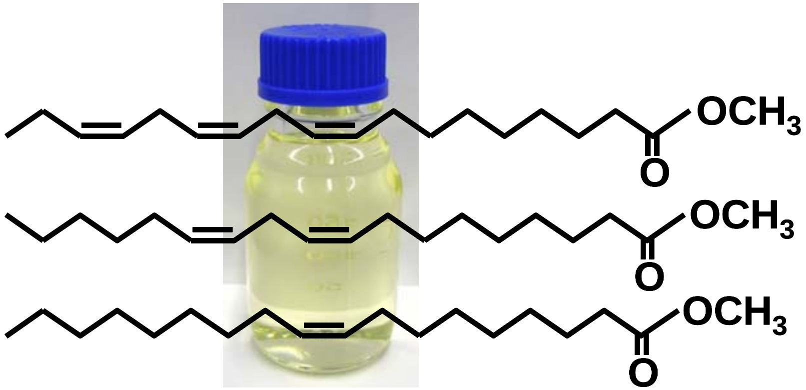
LCA, Capacity building and Technology transfer

Market use of new fuels

Contents:

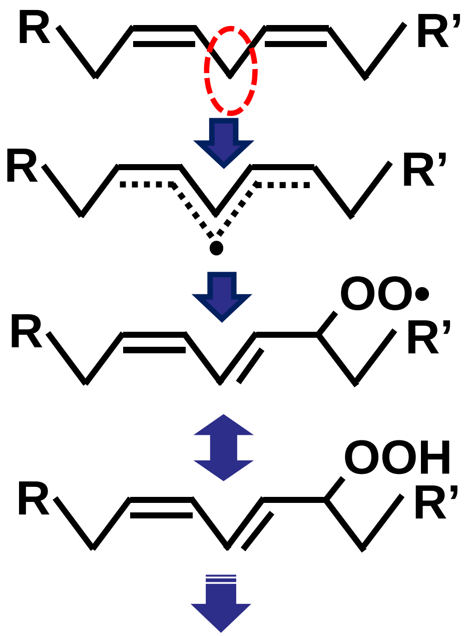
1. Importance of FAME oxidation stability
2. How to improve the FAME fuel quality
3. How to produce the partially hydrogenated FAME (H-FAME), i.e., a chemically upgraded FAME
4. Materials compatibility and engine performances of H-FAME
5. Feasibility study of H-FAME

1. Importance of FAME oxidation stability



Fatty acid methyl ester (FAME)

- ◆ World wide use as diesel alternative
- ◆ Blending use, B5,B7,etc.
- ◆ Standards for B100, B5, B7, etc.
- ◆ Worry on impurities, its oxidation stability and high-concentration use of FAME.



FAME is potentially easy to be oxidized !

Organic acids and sludge formed after oxidative degradation in the use of inferior FAME and in the inappropriate anti-oxidant addition

harmful effects

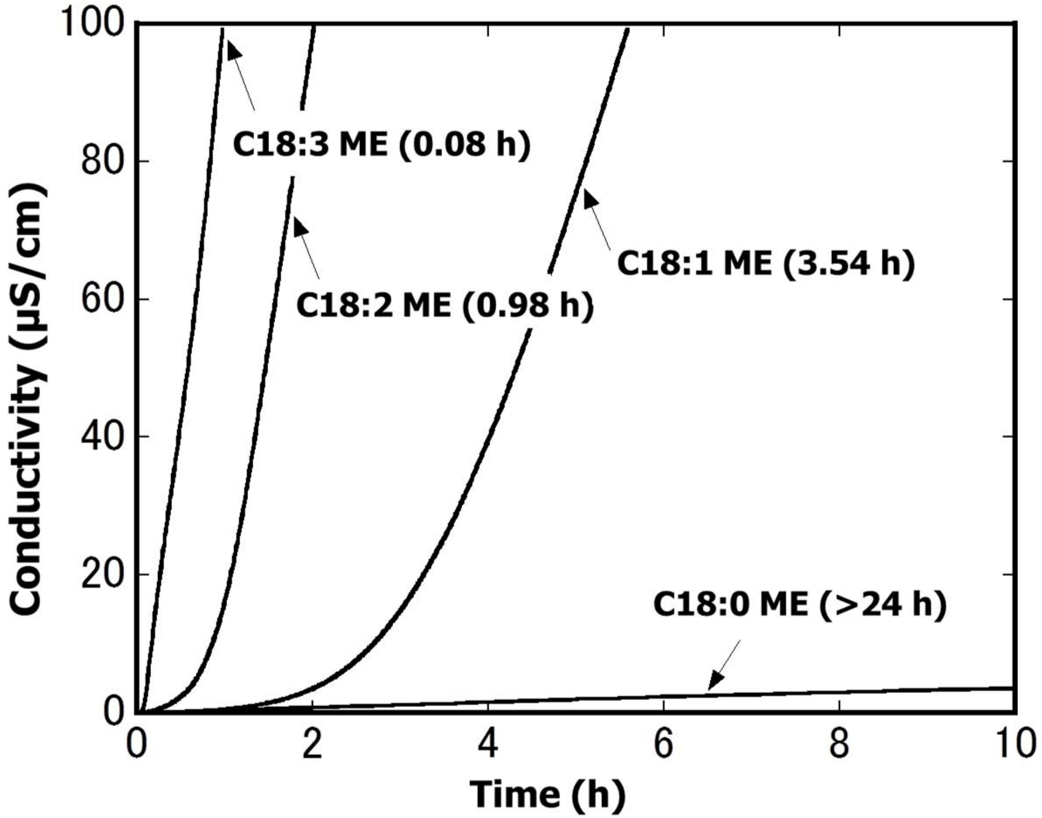
Injector
(source : JAMA)

Fuel tank
(source: Fuel Policy Subcommittee)

◆ *Oxidation stability is an important item for FAME quality assurance*

1-1. Oxidation stability of FAME components

Main components of FAME:
Tri-unsaturated FAME (C18:3)
Di-unsaturated FAME (C18:2)
Mono-unsaturated FAME (C18:1, C16:1)
Saturated FAME (C18:0, C16:0, C14:0, C12:0)



Oxidation stability of various FAME measured by Rancimat

Y.Abe, et. Al., J.Jpn.Petrol.Inst., 52(5), 359-360(2009)

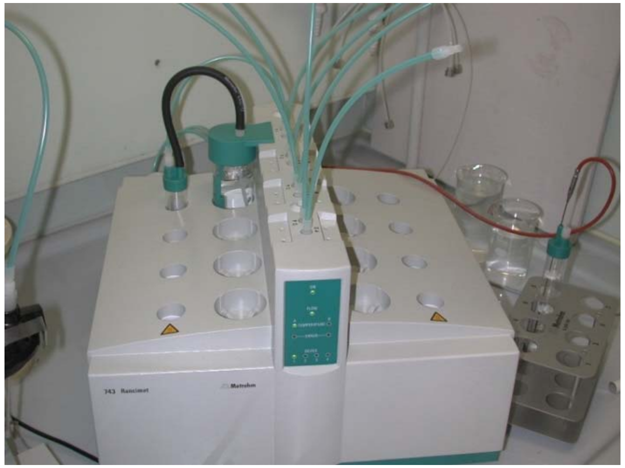
- ***Ease of oxidation and formation of acids after oxidative degradation: C18:3>C18:2>C18:1>>C18:0***
- ***Sludge formation: C18:3***

Reported oxidation rates for FAME: 98 (C18:3)>41(C18:2)>1(C18:1)

"The biodiesel handbook", AOCS press, 2005

- **FAME oxidation stability will depend on feedstock, i.e., dependence of quality assurance on feedstock.**

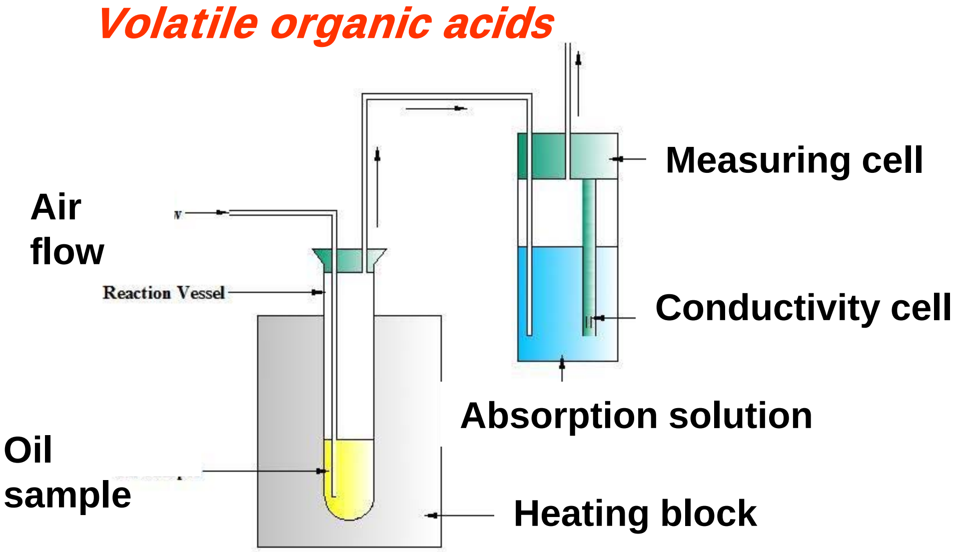
How to measure the oxidation stability of FAME



Rancimat apparatus

PetroOXY apparatus

- ◆ ***Induction time when the pure oxygen pressure is reduced by 10% is an index of oxidation stability (e.g., >65 min)***



Volatile organic acids

Measuring cell

Air flow

Reaction Vessel

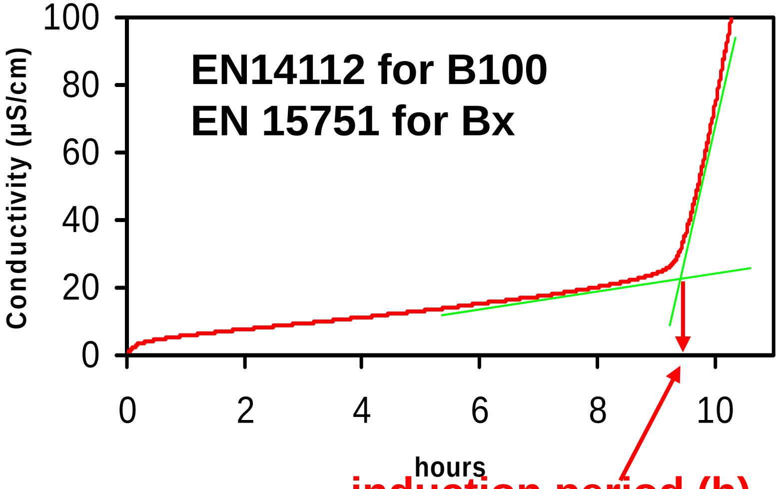
Conductivity cell

Absorption solution

Oil sample

Heating block

Temperature 110 ˚C, Air flow rate 10 L/h

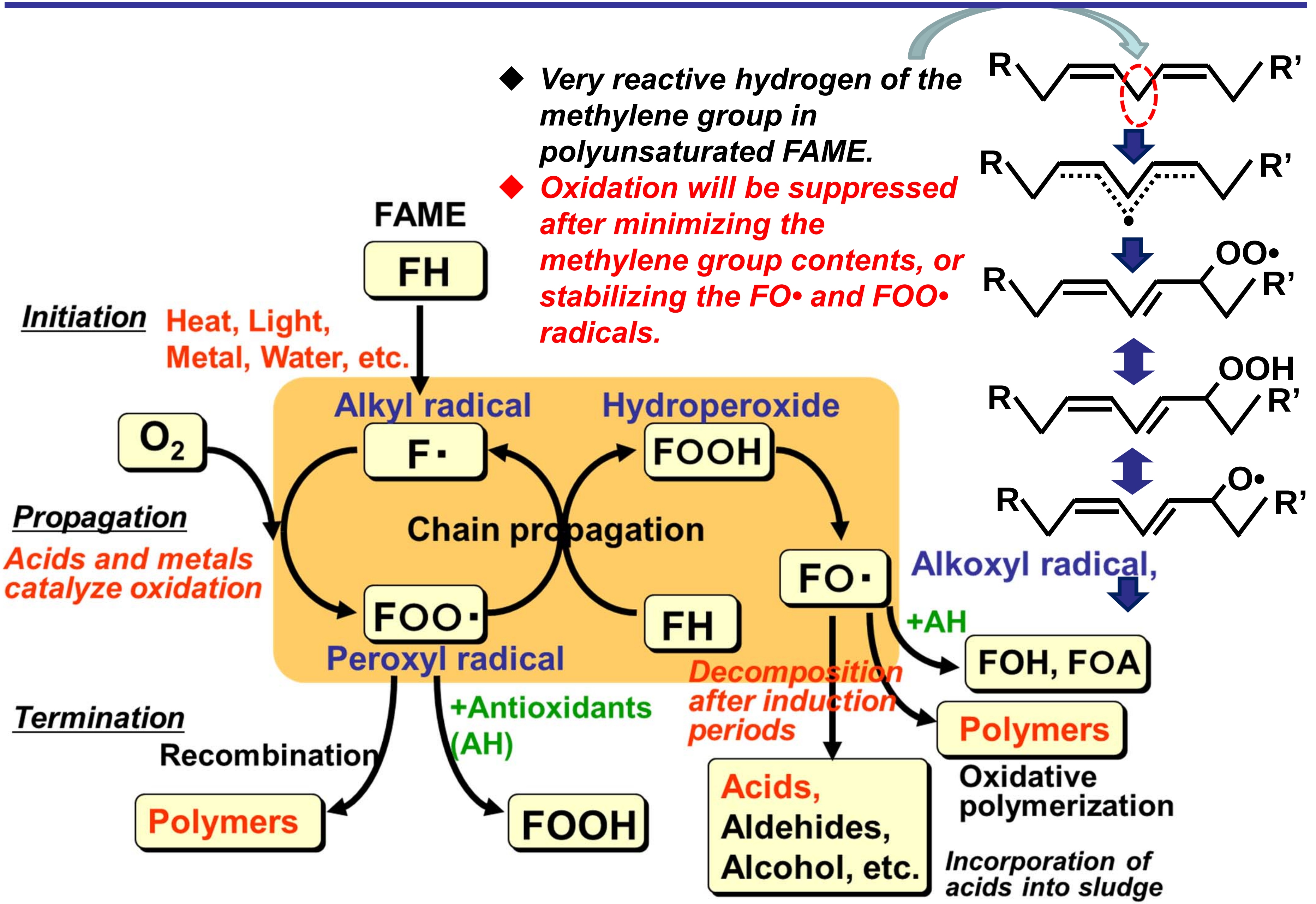


EN14112 for B100
EN 15751 for Bx

induction period (h)

- ◆ ***Induction time is an index of oxidation stability (e.g., >10 h)***

1-2. Possible oxidation mechanism of FAME



- *Very reactive hydrogen of the methylene group in polyunsaturated FAME.*
- *Oxidation will be suppressed after minimizing the methylene group contents, or stabilizing the FO• and FOO• radicals.*

FAME

FH

Initiation Heat, Light, Metal, Water, etc.

Propagation

Acids and metals catalyze oxidation

O_2

Alkyl radical

F·

Hydroperoxide

FOOH

Chain propagation

FOO·

Peroxyl radical

FH

FO·

Alkoxyl radical,

+AH

FOH, FOA

Polymers

Oxidative polymerization

Incorporation of acids into sludge

Decomposition after induction periods

Acids, Aldehides, Alcohol, etc.

Termination

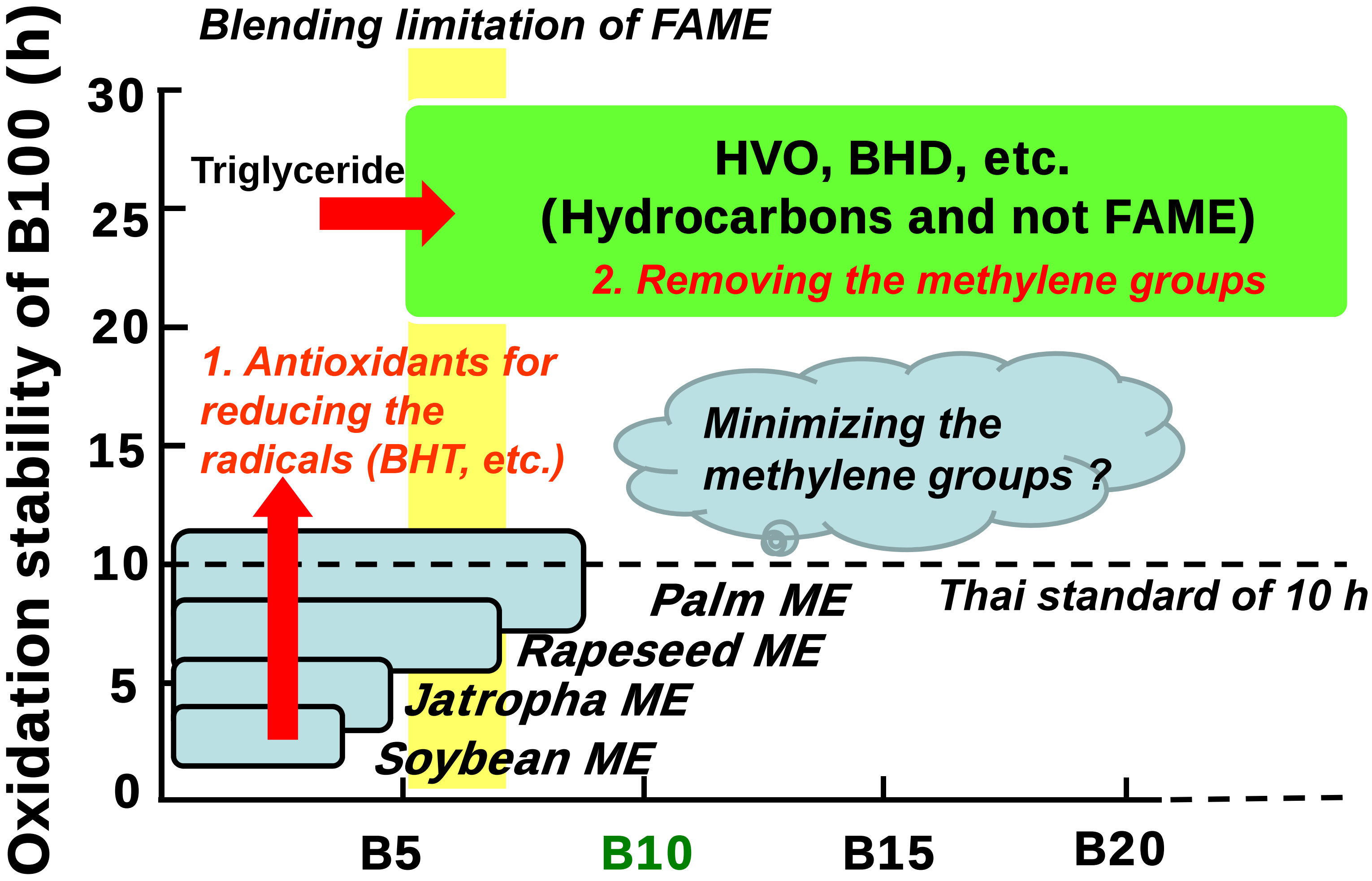
Recombination

Polymers

+Antioxidants (AH)

FOOH

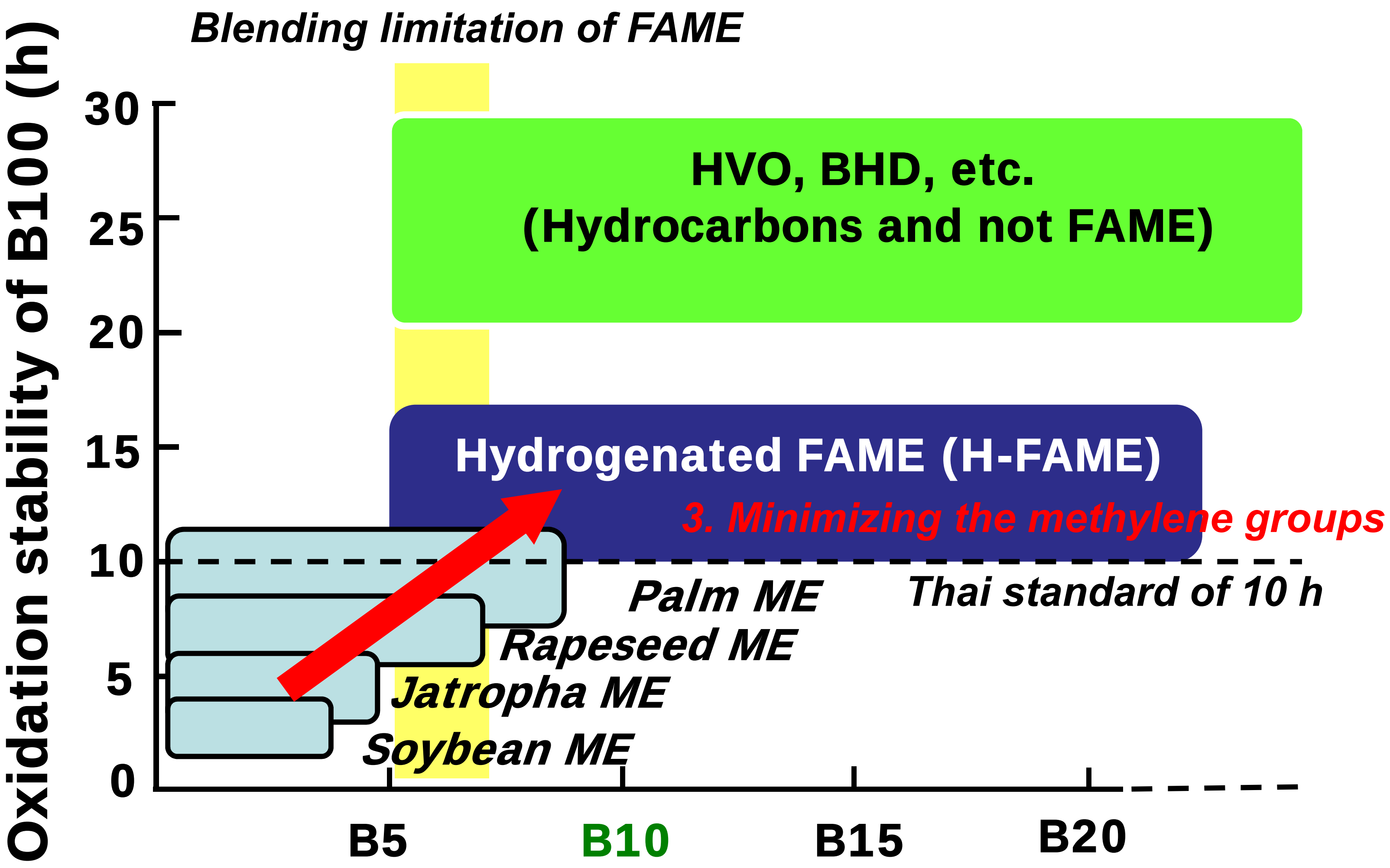
2-1. Two main ways to increase the oxidation stability



Biodiesel blended with petroleum diesel (Bx*)

**X vol% of biodiesel and (100-X) vol% of petroleum diesel*

Hydrogenation way to increase the oxidation stability

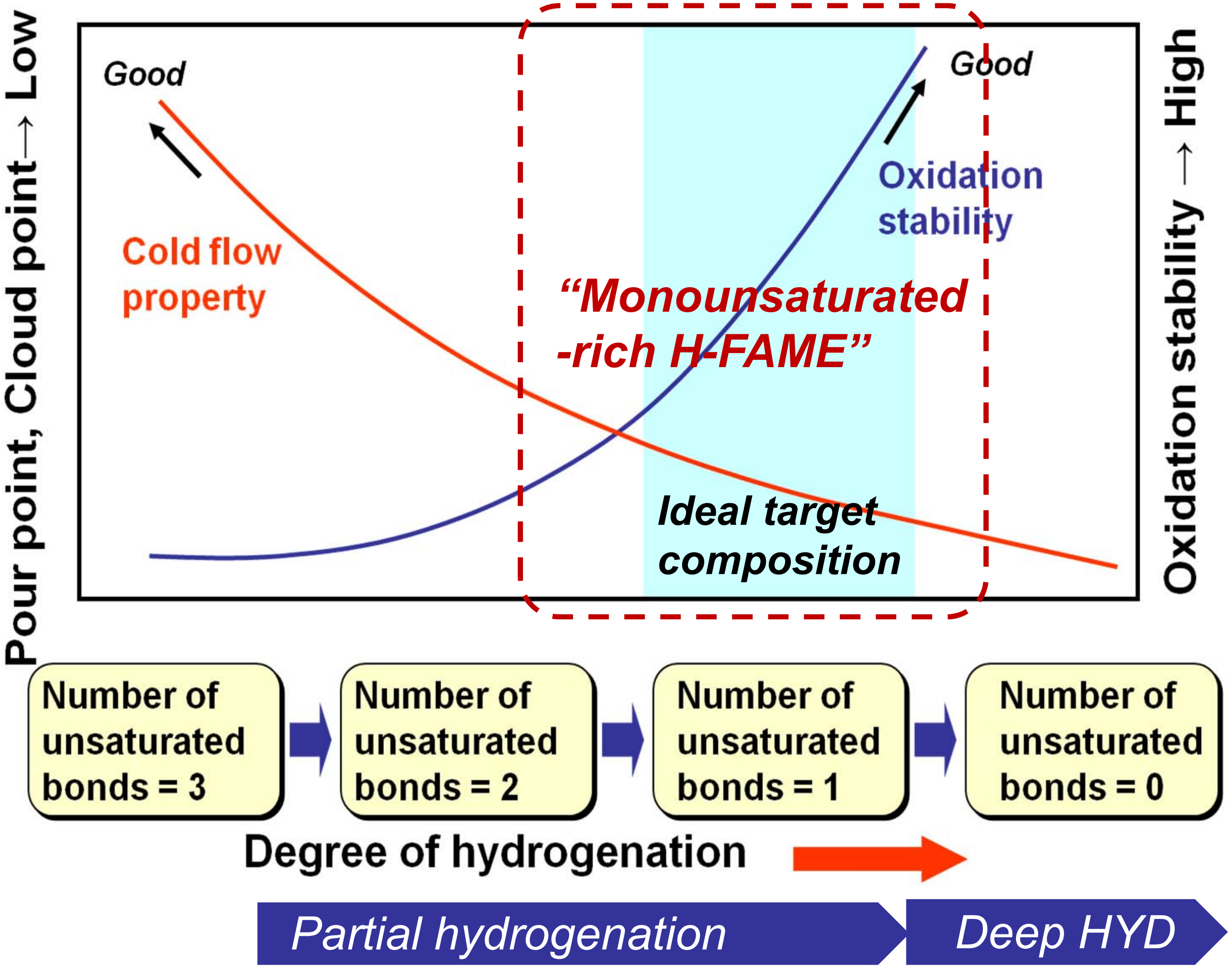


Biodiesel blended with petroleum diesel (Bx*)

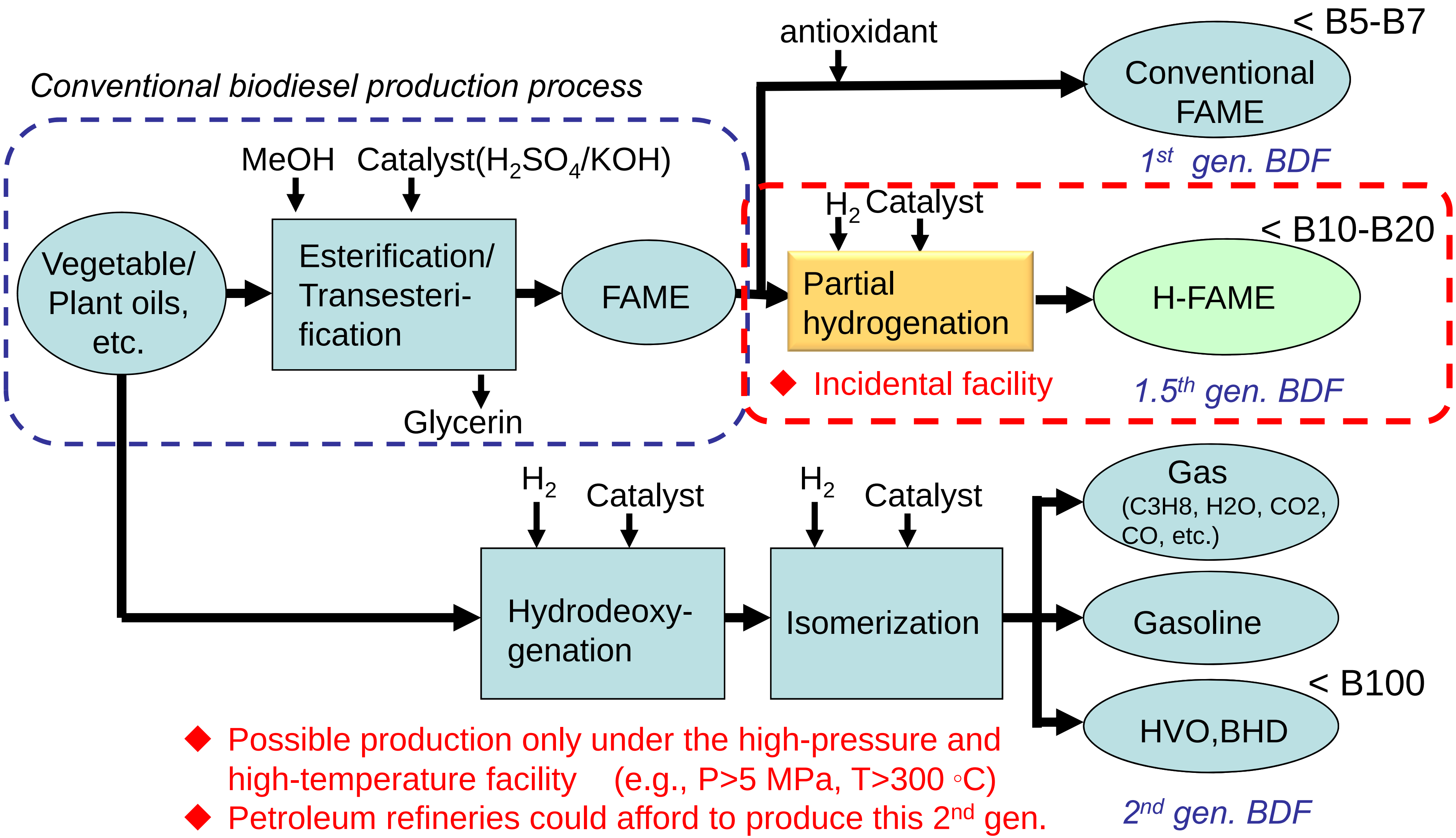
**X vol% of biodiesel and (100-X) vol% of petroleum diesel*

2-2. What is H-FAME ?

H-FAME: Partially hydrogenated FAME which contains maximal amounts of the monounsaturated FAME after decreasing the amounts of the polyunsaturated FAME with minimal increases in the saturated FAME amounts.

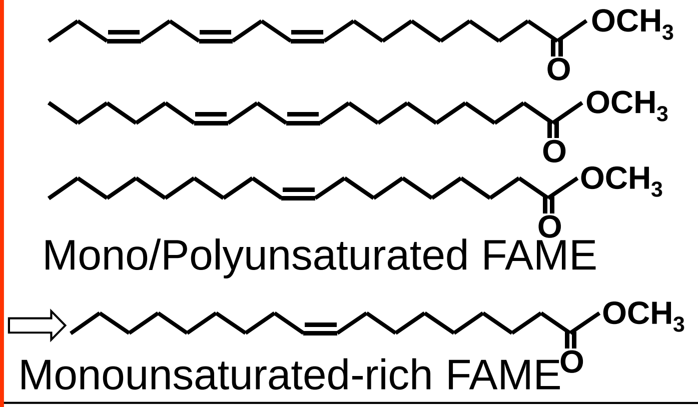
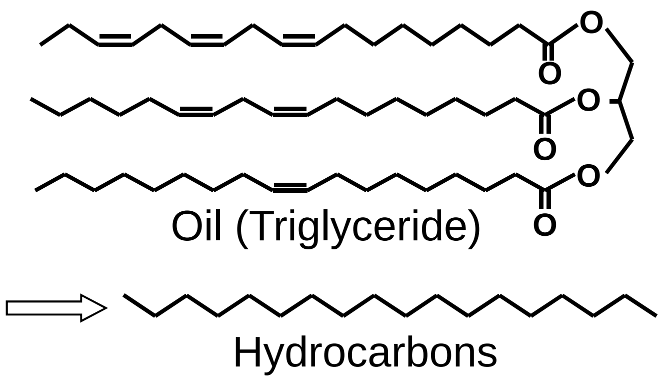


3. How to produce the H-FAME

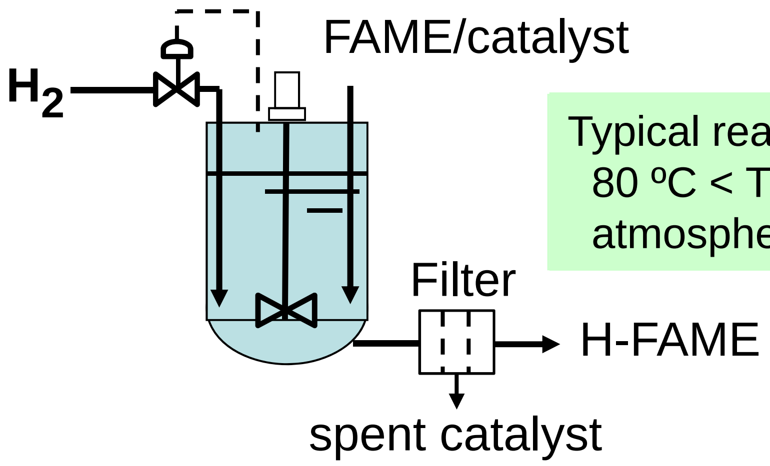


- Possible production only under the high-pressure and high-temperature facility (e.g., P>5 MPa, T>300 ◦C)
- Petroleum refineries could afford to produce this 2nd gen. biodiesel.

3-1. Comparison between the H-FAME and HVO (BHD)

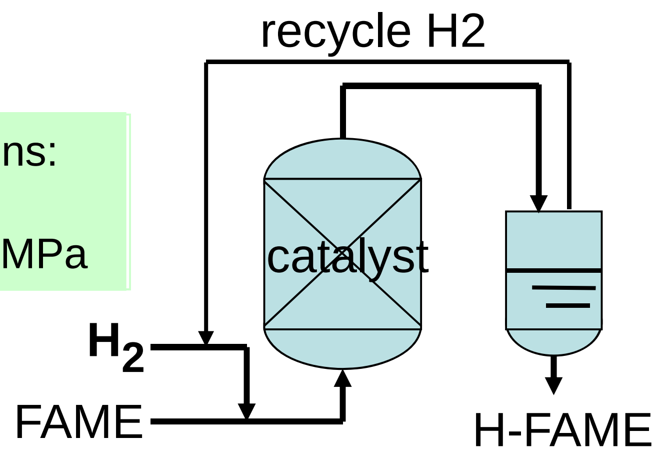
	H-FAME (1.5th gen. FAME)	**HVO (2nd gen. biofuel)**
Reaction	 Mono/Polyunsaturated FAME Monounsaturated-rich FAME	 Oil (Triglyceride) Hydrocarbons
Hydrogen consumption	Partial hydrogenation : $3H_2$	Hydrogenolysis/hydrogenation: $18H_2$ Decarboxylation: $9H_2$
Oxidation Stability	Relatively high	High
Reaction Conditions	Low pressure (atmospheric~0.5MPa) Low temperature (80~120ºC)	High pressure (>5MPa) High temperature (>300ºC)
Catalysts	Ni catalysts, Noble metal catalysts, etc.	Water (steam)-tolerant NiMo catalysts, CoMo catalysts, etc.
Further processing	None	Isomerization for conditioning cold flow property and cetane number
Location of processing facility	Local Community~ Refinery (small ~ large plants)	Petroleum refinery (Neat ~ Coprocessing)

3-2. Catalysts and process for partial hydrogenation



<Slurry reactor>

Typical reaction conditions:
80 ºC < T < 140 ºC
atmospheric < P < 1.0 MPa



<Fixed-bed reactor>

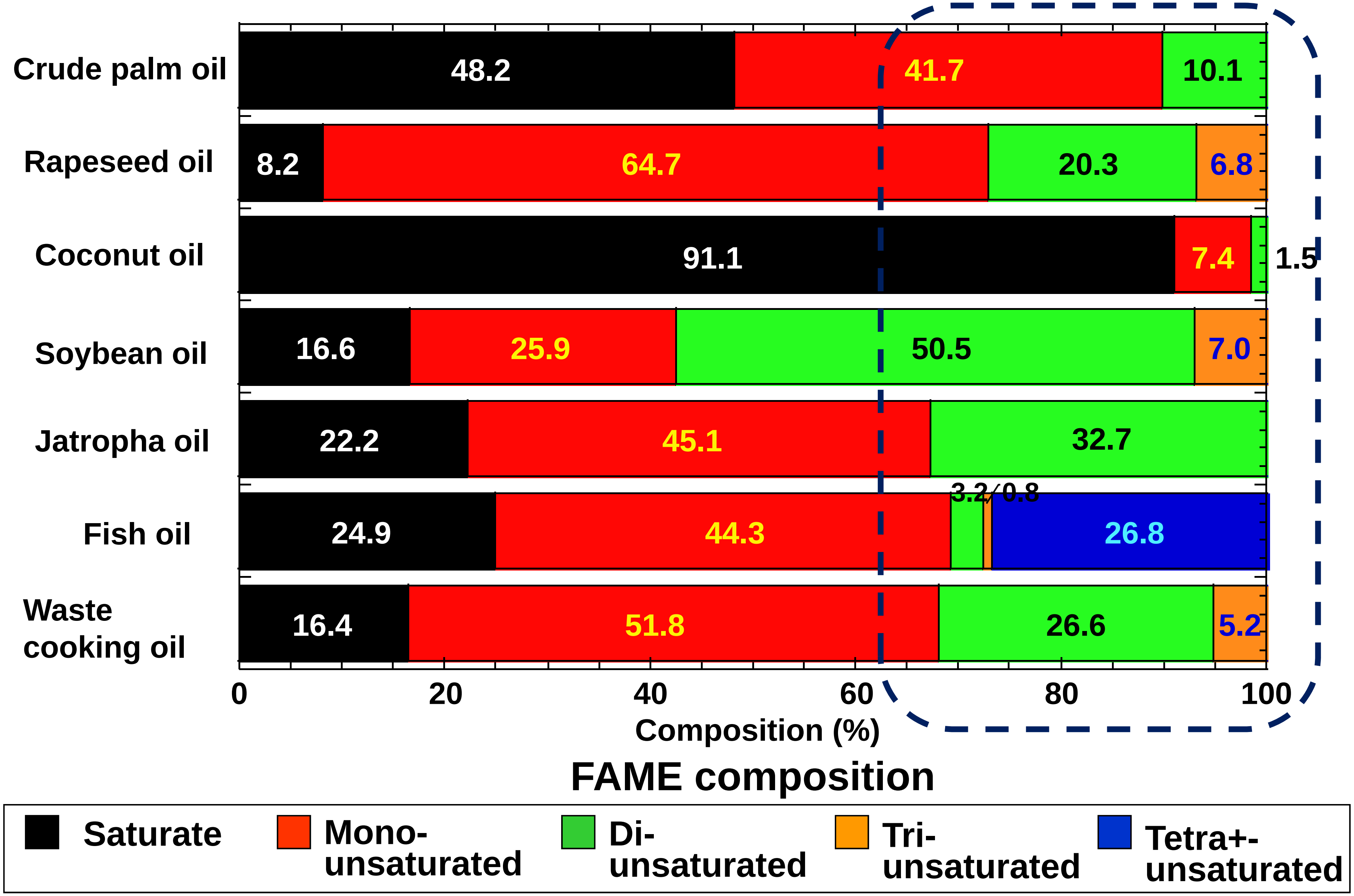
◆ Slurry reactors with the powder catalysts and fixed-bed reactors with the grain catalysts could be used.

◆ Mass transfer limitations are significant for the grain catalysts, e.g., egg-shell metal loadings over the grain support for minimizing them.

◆ Reaction conditions will be milder for Pd catalysts than Ni catalysts, i.e., lower temperature and H2 pressure, etc. Ni catalysts have been commonly used in the fats and VO hydrogenation.

◆ Reaction conditions will affect on the hydrogenation performances (lots of information on VO hydrogenation). Tans-isomers are also not preferable in FAME upgrading due to the higher pour point:
For increasing the monoene selectivity: increases in temperature and cat. amount;
For increasing the *cis*-isomers: increases in H2 pressure and mixing of 3-phases.

3-3. Possible production of H-FAM from all of the feedstock



FAME composition

3-4. Advantages of H-FAME

Advantages of H-FAME at low pressure hydrogenation

- No need to use the high-pressure facilities (P<0.5MPa)
- Low temperature hydrogenation conditions (T<100-120 ºC)
- Intrinsically stable BDF for oxidation; minimizing the sludge formation via. thermal degradation, safely use in long-term storage and transportation, etc.
- Decreasing the phorbol ester contents
- Increase in Cetane number, etc.
- Possible high concentration use up to 20-30 vol%, etc.

Disadvantages of hydrogenation upgrading

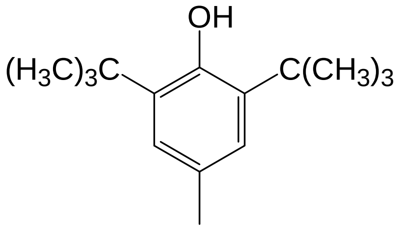
- Need of on-site hydrogenation production unit, or H2 delivery systems, but upgrading at the central refinery will overcome this point.
- Costly than the conventional antioxidant addition, but more advantages

Highly stable H-FAME for oxidation

Oxidation stability of B100 (neat BDF)

FAME	BHT (ppm)	Induction time via. Rancimat (h)
Rapeseed FAME	0	3.8
	100	4.5
	1,000	8.0
	5,000	14.9
	10,000	18.5
H-FAME* from Rapeseed oil	0	17.8

* T=80 °C, PH2=0.5 MPa, 1.5 h



BHT

◆

Partial hydrogenation of B100 will be quite effective to increase the oxidation stability, i.e., equivalent to ca. 1 wt% BHT addition.

◆

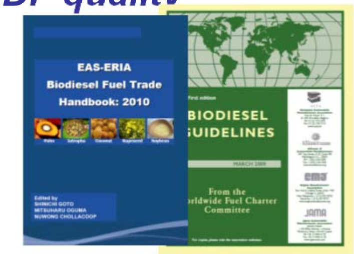
For preparing B7 in EU, 1,000 ppm of BHT will be added into B100.

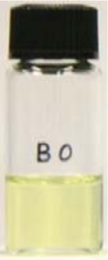
Possible use of H-FAME for higher blending

Possible use of H-FAME for its higher blending

◆*EAS-ERIA BDF standard, (EEBS):2008*

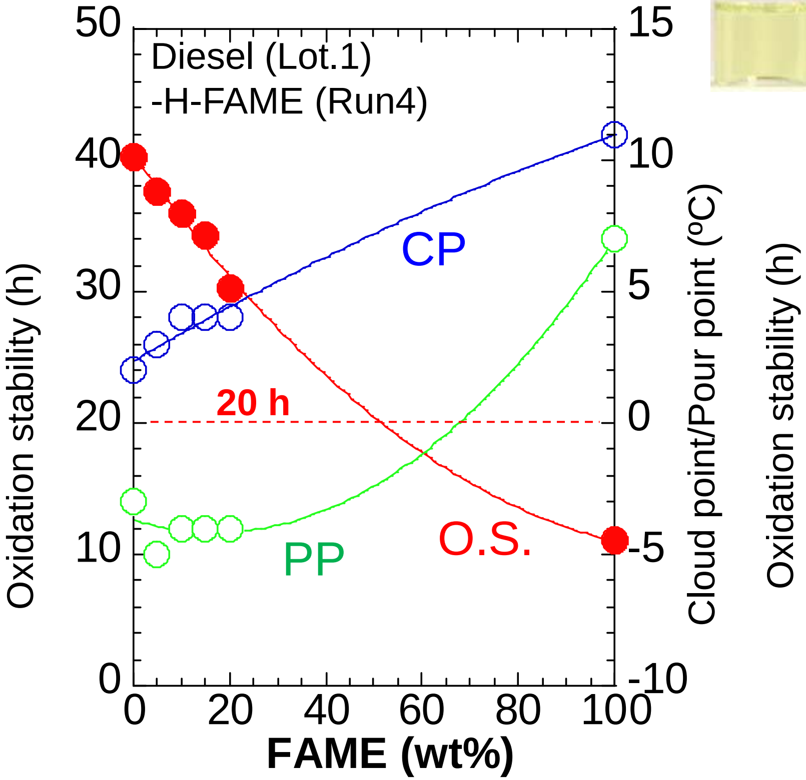
◆*WWFC Guideline BDF quality*





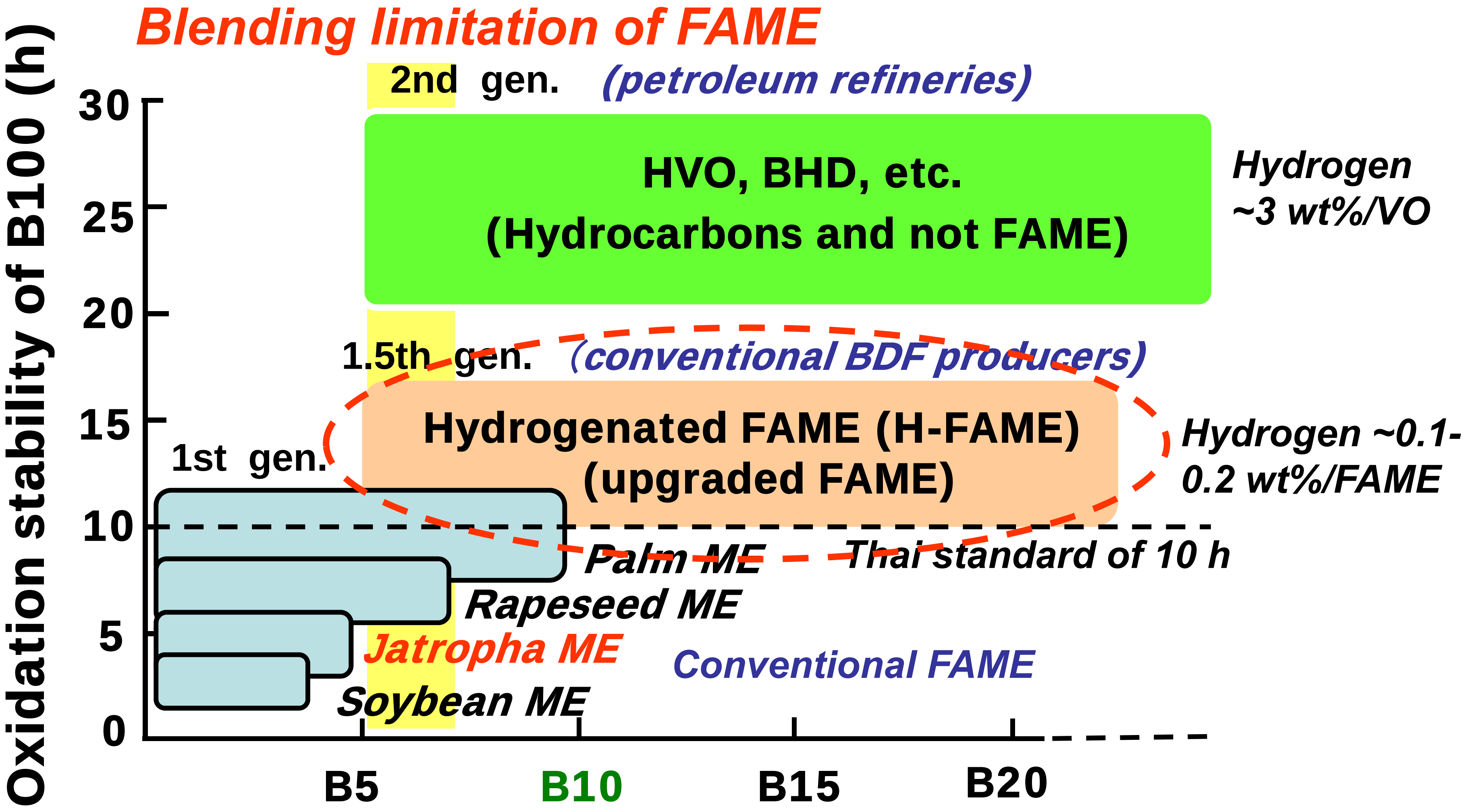
Thai petroleum diesel

Upgraded Jatropha FAME
(H-FAME)



- ◆ *Oxidation stability of mixed fuel (FAME≤40wt%) showed more than 20 h (EN590).*
- ◆ *Oxidation stability depended on not only FAME quality but also petroleum diesel quality.*
- ◆ *Cold flow property was not influenced by FAME content in the range of FAME≤20wt%.*

3-5. Positioning of H-FAME



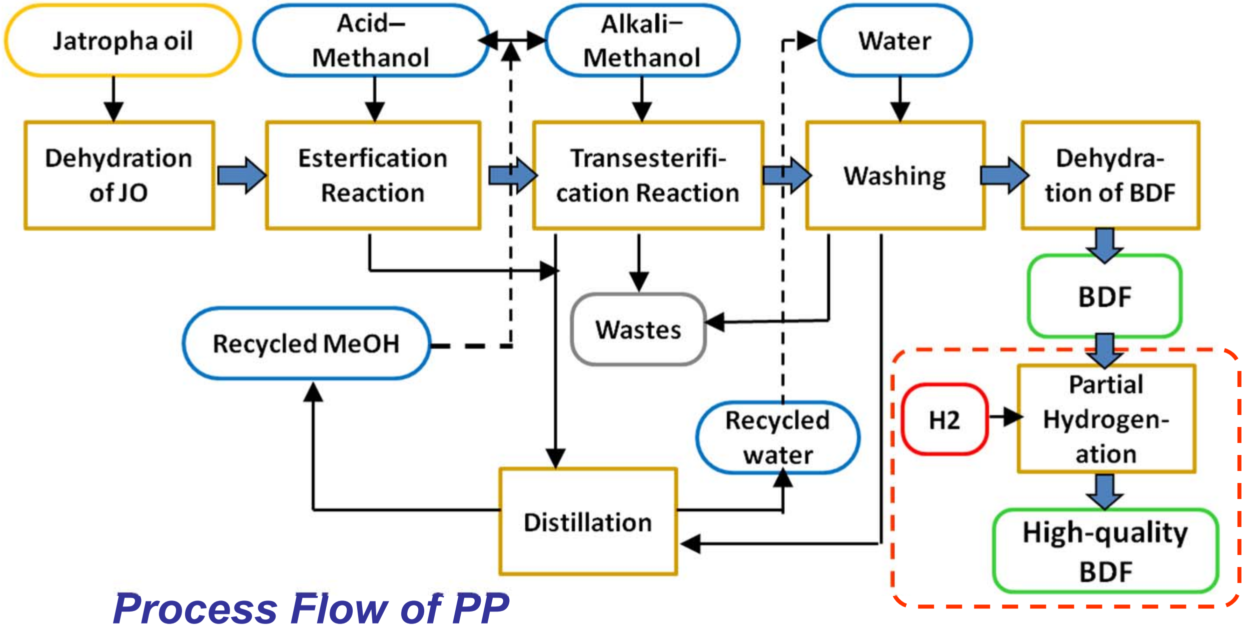
Biodiesel blended with petroleum diesel (Bx*)

**X vol% of biodiesel and (100-X) vol% of petroleum diesel*

3-6. High-Quality BDF Production PP (1.0 ton/day) @TISTR

BDF Production Unit (1.0 ton-BDF/day)

BDF Upgrading Unit (partial hydrogenation of polyunsaturated FAME)



Jatropha oil
Acid–Methanol
Alkali–Methanol
Water
Dehydration of JO
Esterfication Reaction
Transesterification Reaction
Washing
Dehydration of BDF
BDF
Recycled MeOH
Wastes
Recycled water
Distillation
H2
Partial Hydrogenation
High-quality BDF

Process Flow of PP

High-quality BDF

1st generation BDF
→1.5th generation BDF

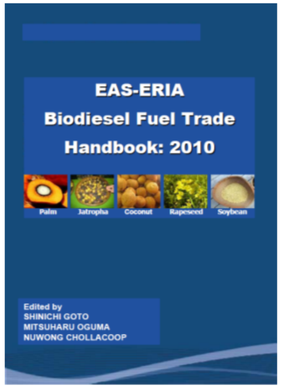
Quality of BDF produced by the pilot plant in TISTR

Items	Units	EU	Japan	EAS-ERIA BDF Standard	WWFC	TISR's PP
		EN14214:2003	JIS K2390:2008	(EEBS):2008	March, 2009	Product BDF
Ester content	mass%	**96.5 min.**	**96.5 min.**	**96.5 min.**	**96.5 min.**	**99.7**
Density	kg/m3	**860-900**	**860-900**	**860-900**	**Report**	**876**
Viscosity	mm2/s	**3.50-5.00**	**3.50-5.00**	**2.00-5.00**	**2.0-5.0**	**5.02**
Flashpoint	**deg. C**	**120 min.**	**120 min.**	**100 min.**	**100 min.**	**186**
Sulfur content	mass%	**0.0010 max.**	**0.0010 max.**	**0.0010 max.**	**0.0010 max.**	**0.00025**
Distillation, T90	**deg. C**	**-**	**-**	**-**	**-**	**-**
Carbon residue (100%) or **Carbon residue (10%)**	mass%	**-** **0.30 max.**	**-** **0.3 max.**	**0.05 max.** **0.3 max.**	**0.05 max.** **-**	**0.14**
Cetane number		**51.0 min.**	**51.0 min.**	**51.0 min.**	**51.0 min.**	**57**
Sulfated ash	mass%	**0.02 max.**	**0.02 max.**	**0.02 max.**	**0.005 max.**	**<0.001**
Ash content	mass%	**-**	**-**	**-**	**0.001 max.**	**-**
Water content	mg/kg	**500 max.**	**500 max.**	**500 max.**	**500 max.**	**385**
Water and sediment	vol%	**-**	**-**	**-**	**0.05 max.**	**-**
Total contamination	mg/kg	**24 max.**	**24 max.**	**24**	**24**	**8.3**
Copper corrosion		**Class-1**	**Class-1**	**Class-1**		**Class-1a**
Corrosion: Ferrous		**-**	**-**	**-**	light rusting. Max	**-**
Acid value	mgKOH/g	**0.50 max.**	**0.50 max.**	**0.50 max.**	**0.5 max.**	**0.16**
Oxidation stability	hrs.	**6.0 min.**	**(**)**	**10.0 min. (****)**	**10 min.**	**15.1**
Iodine value		**120 max.**	**120 max.**	**Reported (***)**	**130 max.**	**70.5**
Methyl Linolenate	mass%	**12.0 max.**	**12.0 max.**	**12.0 max.**	**12.0 max.**	**0**
Polyunsaturated FAME **(more than 4 double bonds)**	mass%	**1 max.**	**N.D.**	**N.D. (***)**	**1 max.**	**N.D.**
Methanol content	mass%	**0.20 max.**	**0.20 max.**	**0.20 max.**	**0.20 max.**	**<0.01**
Monoglyceride content	mass%	**0.80 max.**	**0.80 max.**	**0.80 max.**	**0.80 max.**	**0.54**
Diglyceride content	mass%	**0.20 max.**	**0.20 max.**	**0.20 max.**	**0.20 max.**	**0.20**
Triglyceride content	mass%	**0.20 max.**	**0.20 max.**	**0.20 max.**	**0.20 max.**	**0.06**
Free glycerol content	mass%	**0.02 max.**	**0.02 max.**	**0.02 max.**	**0.02 max.**	**0**
Total glycerol content	mass%	**0.25 max.**	**0.25 max.**	**0.25 max.**	**0.25 max.**	**0.17**
Na+K	mg/kg	**5.0 max.**	**5.0 max.**	**5.0 max.**	**5 max.**	**<3**
Ca+Mg	mg/kg	**5.0 max.**	**5.0 max.**	**5.0 max.**	**5 max.**	**<2**
Phosphorous content	mg/kg	**10.0 max.**	**10.0 max.**	**10.0 max.**	**4 max.**	**<1**
Trace metals		**-**	**-**	**-**	**no addition**	**-**

Demands for high quality BDF

(*) Equivalent to diesel oil
(**) Meet diesel oil specification
(***) Need data check and further discussion
(****) Need more data & discussion from 6 to 10 hrs.

Mid-term target

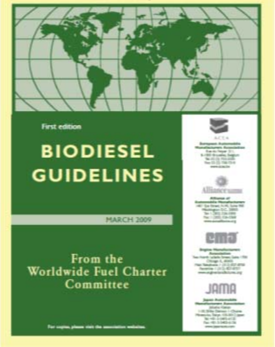


EAS-ERIA
Biodiesel Fuel Trade
Handbook: 2010

Edited by
SHINICHI GOTO
MITSUHARU OGUMA
NUWONG CHOLLACOOP

◆ ***EAS-ERIA BDF standard, (EEBS):2008***

Final target



First edition
BIODIESEL
GUIDELINES
MARCH 2009
From the
Worldwide Fuel Charter
Committee

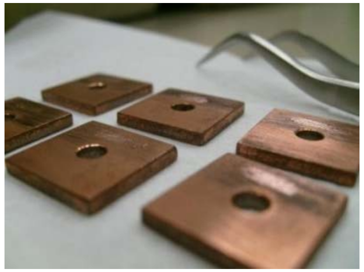
◆ ***WWFC Guideline BDF quality***

EAS: East Asia Summit ; ERIA: Economic Research Institute for ASEAN and East Asia ; WWFC: World Wide Fuel Charter

4. Materials compatibility and engine performances of H-FAME

Test temp.:
Room temp. to 90°C

Rubber Hose



Copper Plates

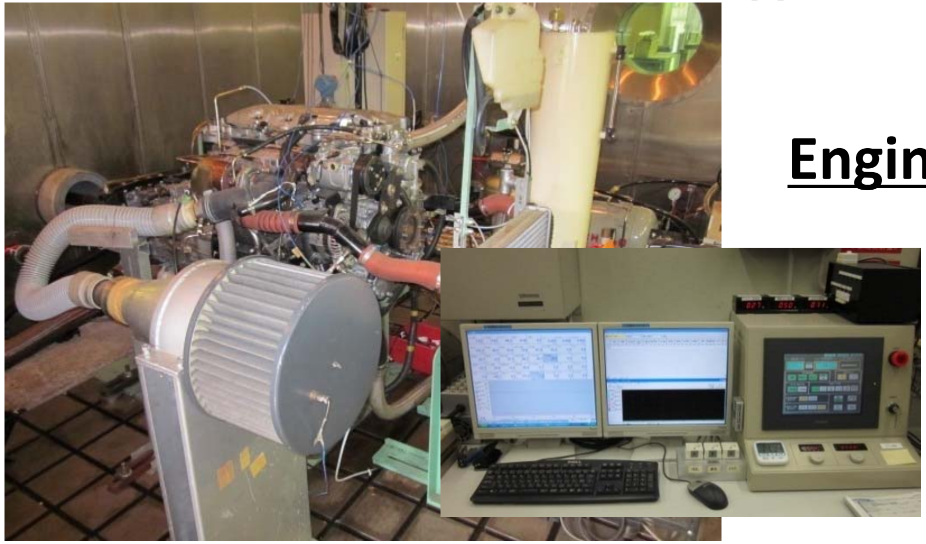
Material Immersion Test

<Tested Fuels>

- **Diesel Fuel**
- **FAME**
- **FAME + Additive (JME+A)**
- **H-FAME(HJME)**
- **H-FAME+ Additive (HJME+A)**

<Tested Materials>

- **Rubber: Fuel hose (9Z01) installed between a fuel tank and a fuel filter**
- **Metal: Copper (C1100) used in a diesel injection pump**



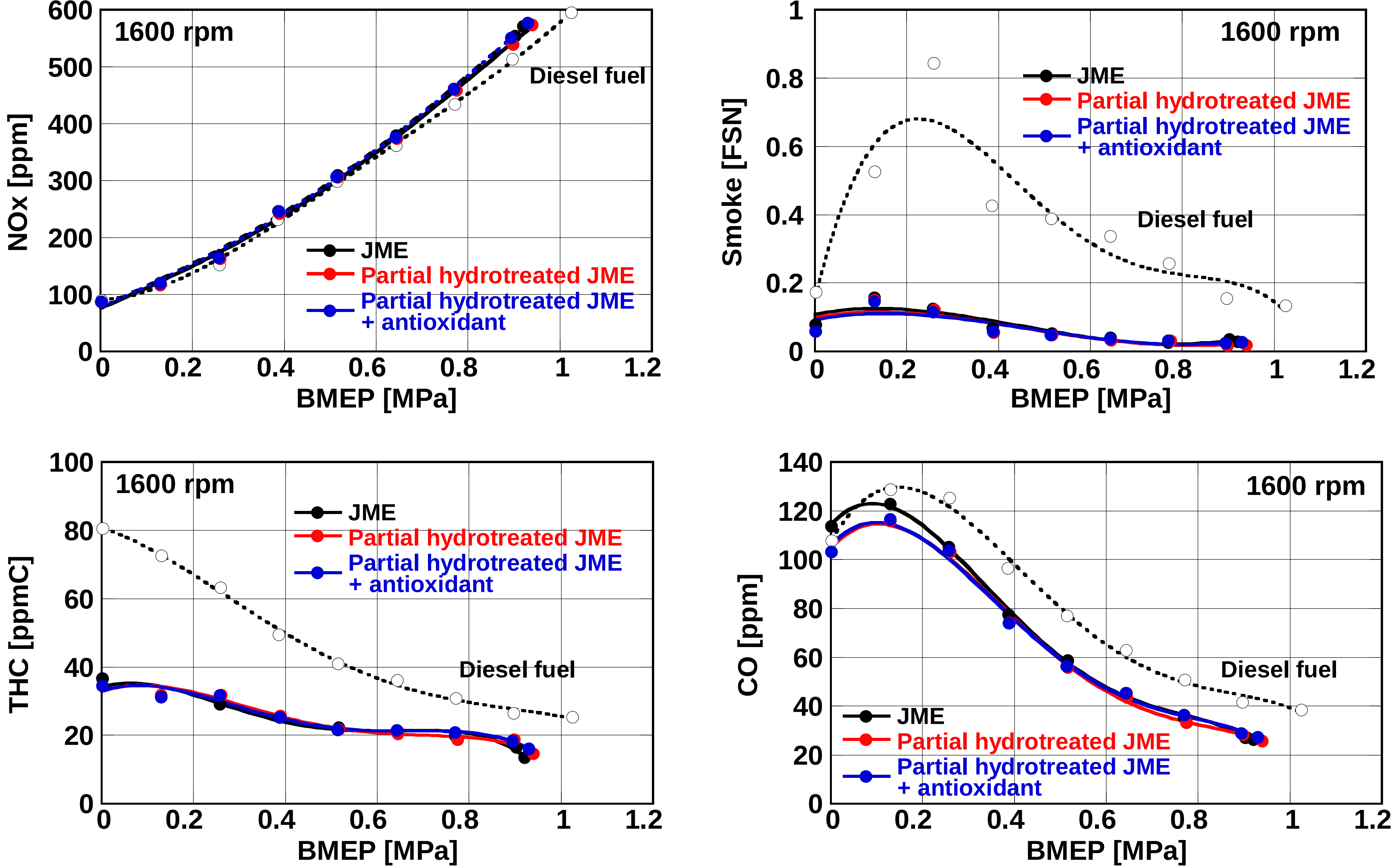
Engine Dynamometer (AIST)

Test fuels for engine performance

- Conventional diesel fuel
- FAME (JME): Oxidation stability = 1hr.
- H-FAME: " = 12hr.
- H-FAME + antioxidant " > 30hr.

Evaluation of engine and emission performances of H-FAME

Emission characteristics (Nox, smoke, THC and CO)



4-1. On-road durability test by using B10

B10: 10 vol% of Jatropha H-FAME blended with 90 vol% of Thai petro-diesel

Isuzu Spark-S
(M/T)

TRI PETCH ISUZU SALES CO.,LTD.

50,000 km distance
(about 5 months)

ITA

25th Anniversary
MTEC
a member of NSTDA

IEMT

ptt

Petroleum diesel
(S<50 ppm)

TISTR

H-FAME

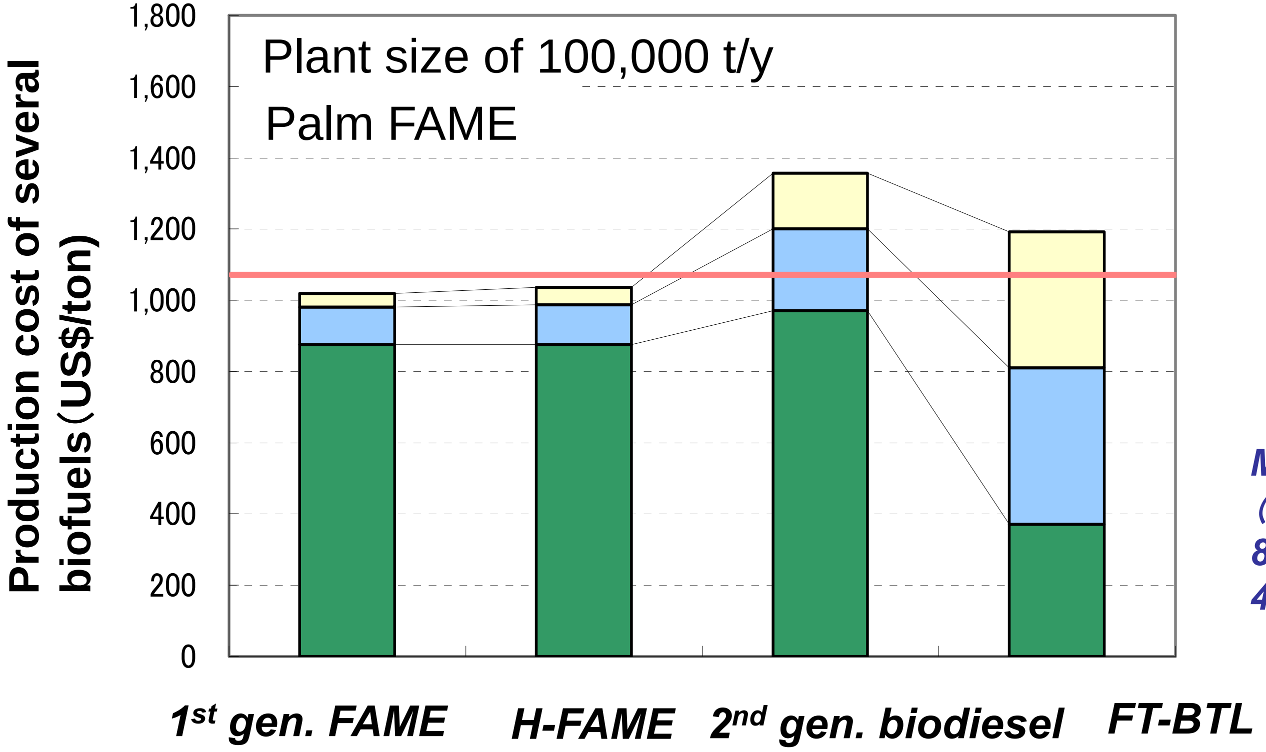
ISUZU

AIST

WASEDA University

MOU ceremony on “Innovation on New Non-Food Biodiesel Project”
(2012.7.30) @Bangkok

5. Feasibility study of H-FAME



Diesel price in Thailand（2011）

🟨 ROI 10%
🟦 Fixed costs
🟩 Variable costs

ROI: Return on investment

Market price of Palm oil （US-CIF)：
800 US$/ton（2010.Apr)
440 US$/ton (2008. Dec)

Mitsubishi Chemical Techno-Research Corporation (2011)

◆**Small cost up for 1.5th gen. FAME compared with 1st gen. FAME, but much less than 2nd generation biodiesel, even after newly installation of an on-site H2 production plant.**

◆**High proportion of variable costs for 1st, 1.5th and 2nd generation FAME production, i.e., fixed costs share about 70 % of the total production cost for 1st and 1.5th gen. FAME, so reduction of raw materials costs will be the key to increase its feasibility.**

◆**Lots of issues for Jatropha to be solved: improvement of tissue culture and species, improvements of cultivation techniques and oil extraction techniques, labor-intensive cultivation and harvesting, utilization of residues after oil extraction etc.**

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Thank you for your kind attention