Introduction of H-FAME* Technology for Thai B10 Program

** Partially Hydrogenated FAME*

Yuji Yoshimura[1] and Nuwong Chollacoop[2]

[1] Advance Industrial Science and Technology(AIST), Japan, Japan International Cooperation Agency (JICA) and [2] MTEC,
[2] National Metal and Materials Technology Center (MTEC), National Science and Technology Development Agency (NSTDA) ,Thailand,

The 1st APEC WS, December 14, 2017 @ NSTDA/Thailand

Issues for higher blending of Biodiesel

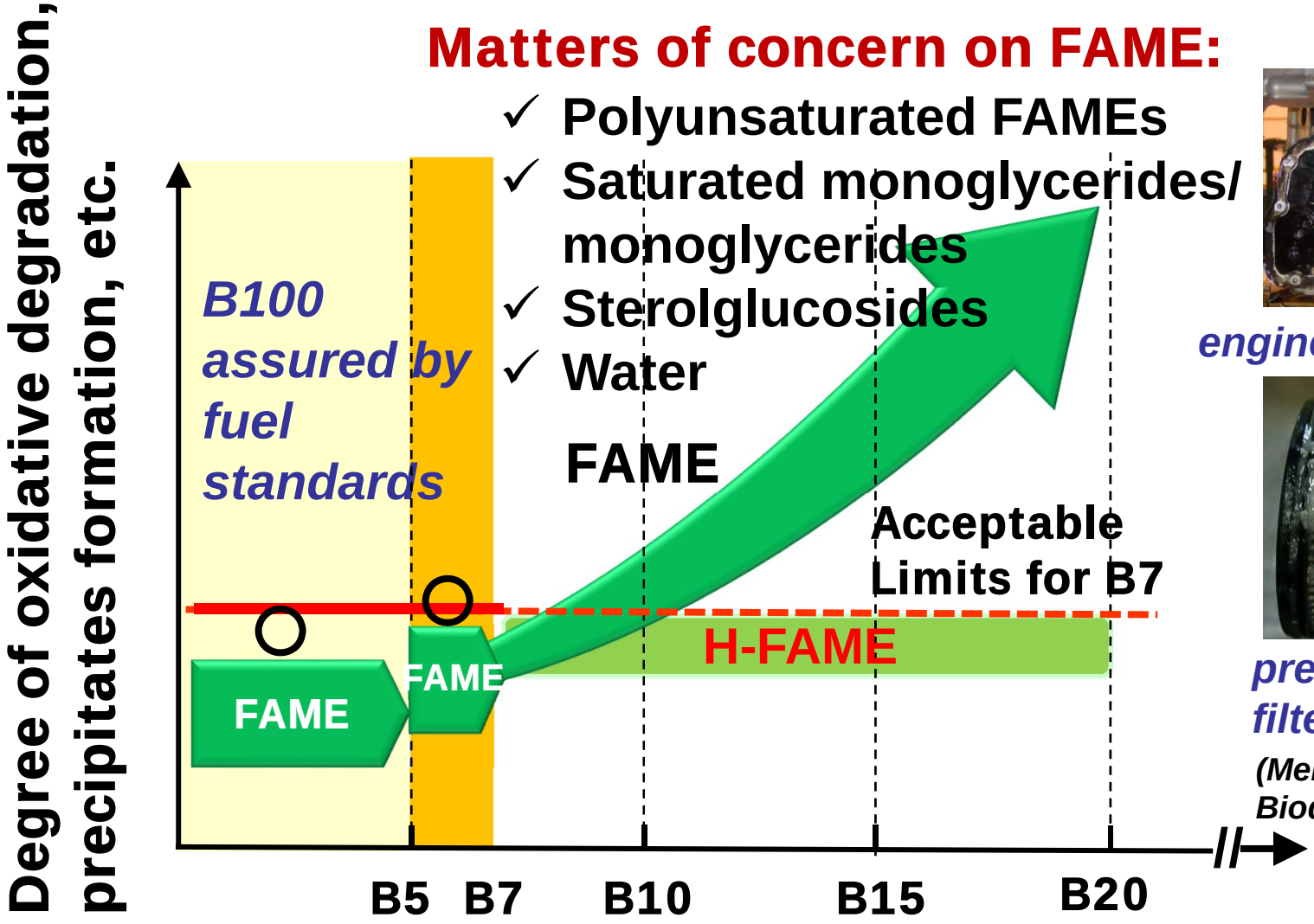
Matters of concern on FAME:

- ✓ Polyunsaturated FAMEs
- ✓ Saturated monoglycerides/ monoglycerides
- ✓ Sterolglucosides
- ✓ Water

engine oil sludging

precipitates/ filter plugging

(Mercedes-Benz Biodiesel Brochure)



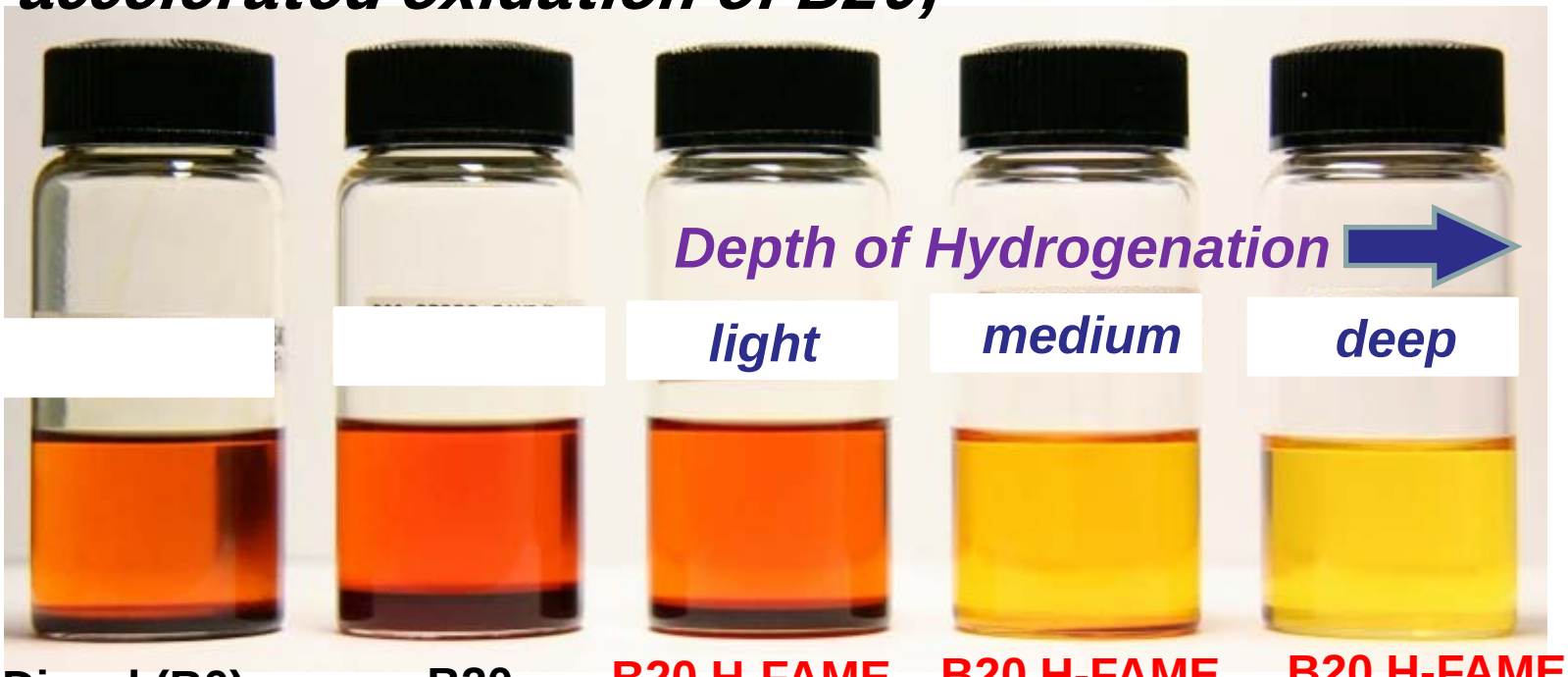
Biodiesel blended with petroleum diesel (Bx*)

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

H-FAME an Alternative Upgraded Biodiesel

Simulating the sludge formation after oxidation

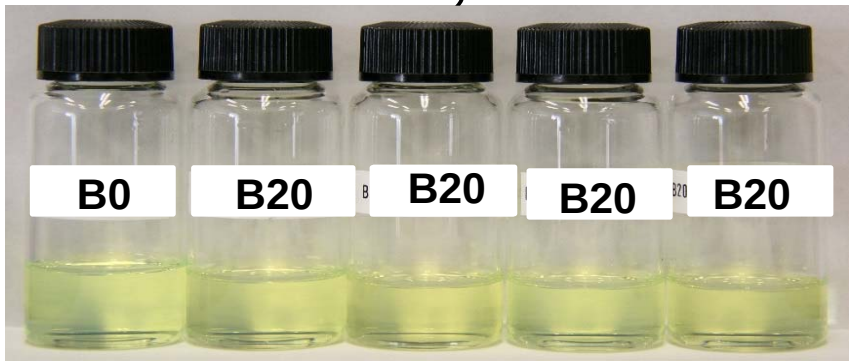
After accelerated oxidation of B20,



Diesel (B0) **B20** **B20 H-FAME** **B20 H-FAME** **B20 H-FAME**

EURO V diesel **Thai Palm FAME**

Before oxidation,



Accelerated oxidation condition:
Bx=20g, T=135 ºC (>115 ºC*),
O2 Flow=100 ml/min,
Oxidation period=16 h.

****Testing condition for oxidation stability in Japanese quality assurance law for B5 (former method).***

H-FAME
an Alternative Upgraded Biodiesel

H-FAME as a new alternative Biodiesel

H-FAME (Partially Hydrogenated FAME):

New alternative biodiesel superior in the oxidation and thermal stabilities, and produced after the partial hydrogenation of the current FAME.

H-FAME is a monoene-rich FAME within the limitation of cold flow property of B100.

H-FAME

an Alternative Upgraded Biodiesel

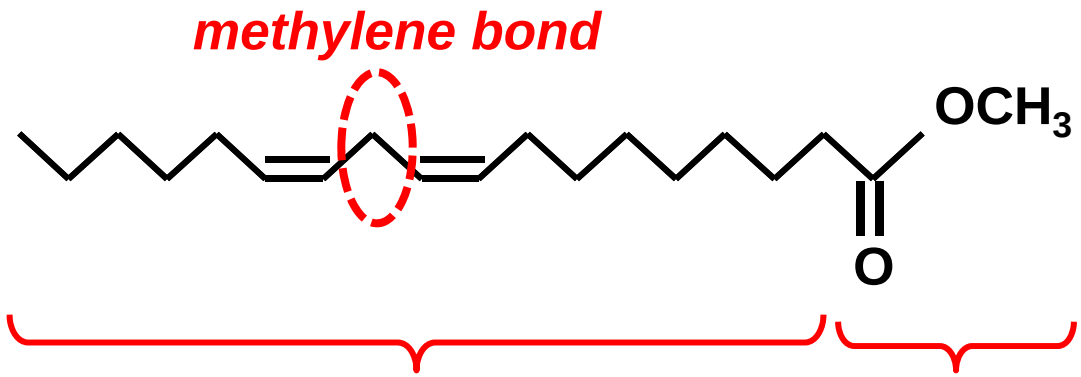
Contents

1. Concept of H-FAME
   Partially Hydrogenated FAME (H-FAME) as a new alternative biodiesel
2. Catalytic upgrading of biodiesel into H-FAME
3. Advantages of H-FAME
4. Automotive compatibility of H-FAME
5. Future perspective and conclusions

1. Concept of H-FAME

1-1. Molecular aspects of FAME

e.g., Methyl Linoleate (C18:2 FAME)



○*Comparable to diesel fractions (C12-C22)*

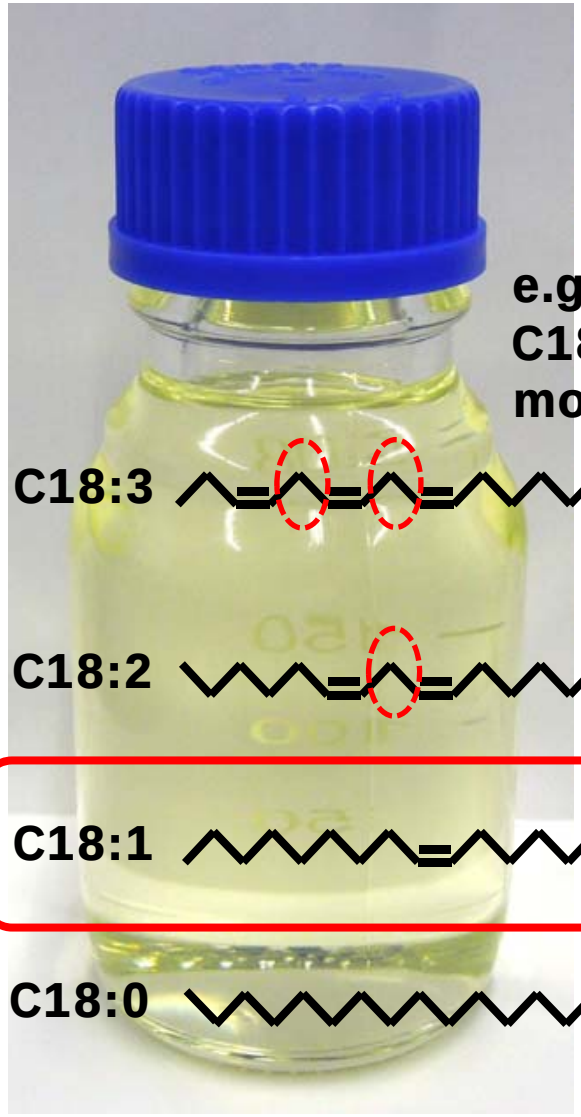
×*Tend to oxidize into peroxides, acids and polymers (deposits, corrosion, etc.)*

○*Solvency effect to minimize the carbon deposits, etc.*

×*Tend to hydrolyze into fatty acid and MeOH (water)*

H-FAME an Alternative Upgraded Biodiesel

1-2. Properties of FAME molecules



e.g.,
C18:n FAME molecule

C18:3

C18:2

C18:1

C18:0

Oxidation stability	Peroxide formation	Cold flow property	Solvency effect
Acid corrosion, polymers and sludge formation	Elastomer damage	filter plugging	cleaning effect
(98*) ××	××	◎◎	○
(41) ×	×	◎	○
(1) ○	○	○	○
(<1) ◎	◎	×	○

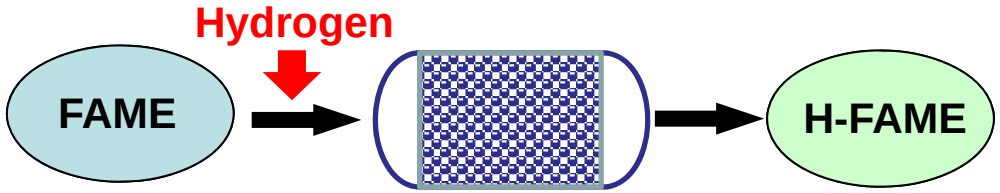
- *Ease of oxidation:*
  E.N. Frankel, Lipid Oxidation, 2005

Monoene (monounsaturated FAME) seems to be most preferable.

H-FAME an Alternative Upgraded Biodiesel

1-3. H-FAME as a monoene-rich FAME

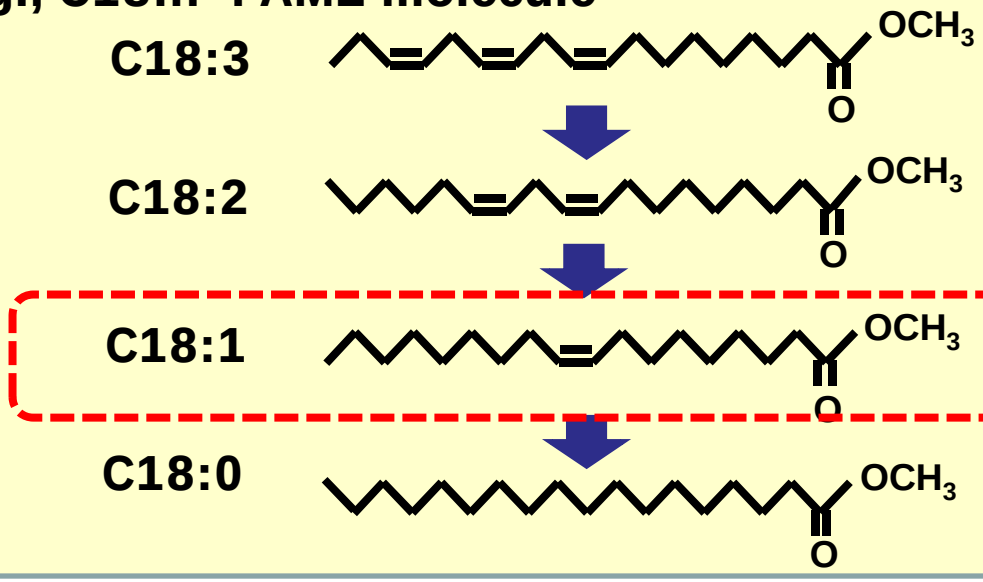
Partial hydrogenation technology, a proven technology for fat hardening, is applied to condition the double-bonds structure in FAME, and to upgrade into H-FAME.



T < 150 °C
P < 1 MPa

FAME + Hydrogen = H-FAME

e.g., C18:n FAME molecule



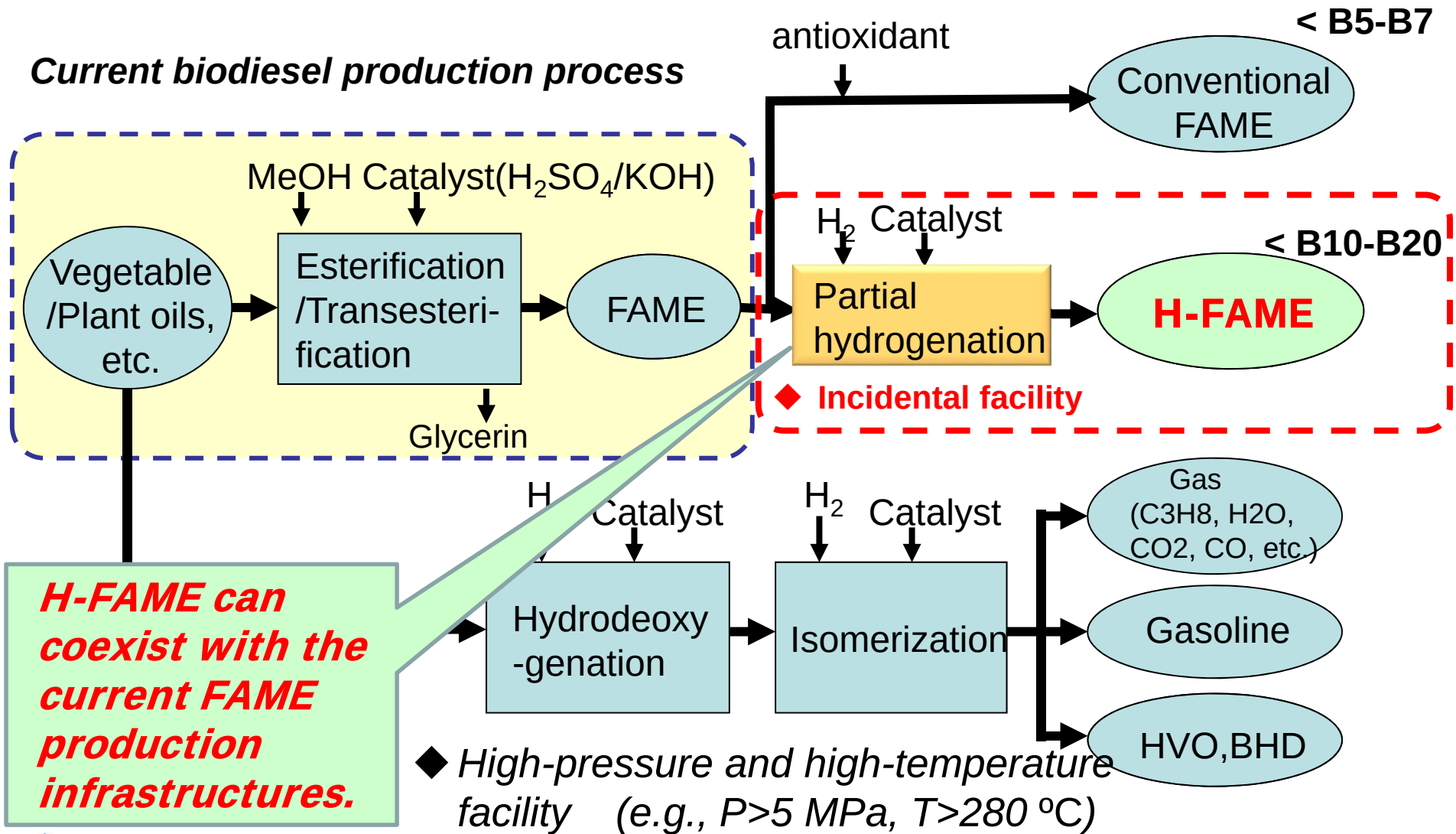
Degree of hydrogenation

Partial hydrogenation

Complete hydrogenation

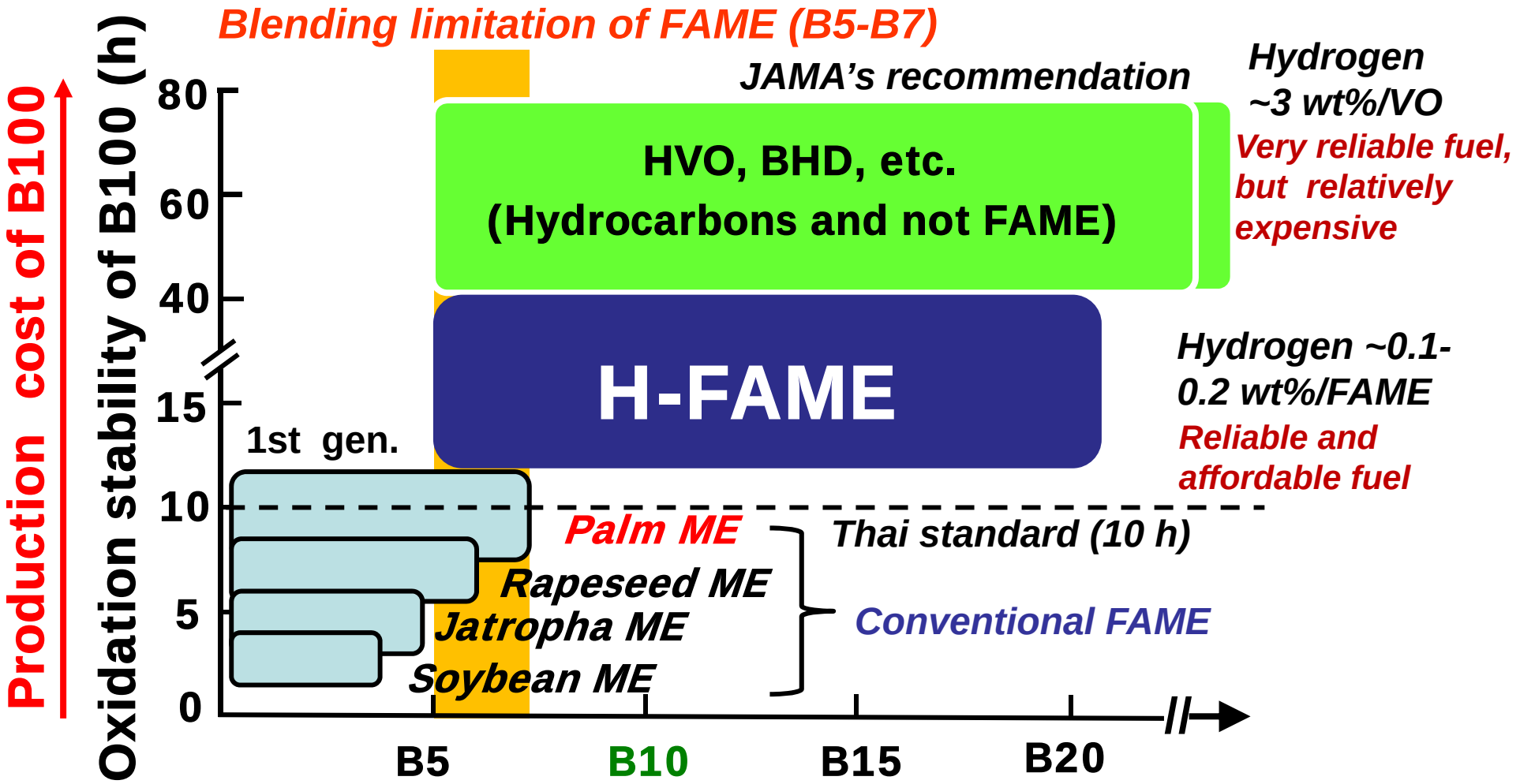
H-FAME an Alternative Upgraded Biodiesel

1-4. H-FAME production process



H-FAME an Alternative Upgraded Biodiesel

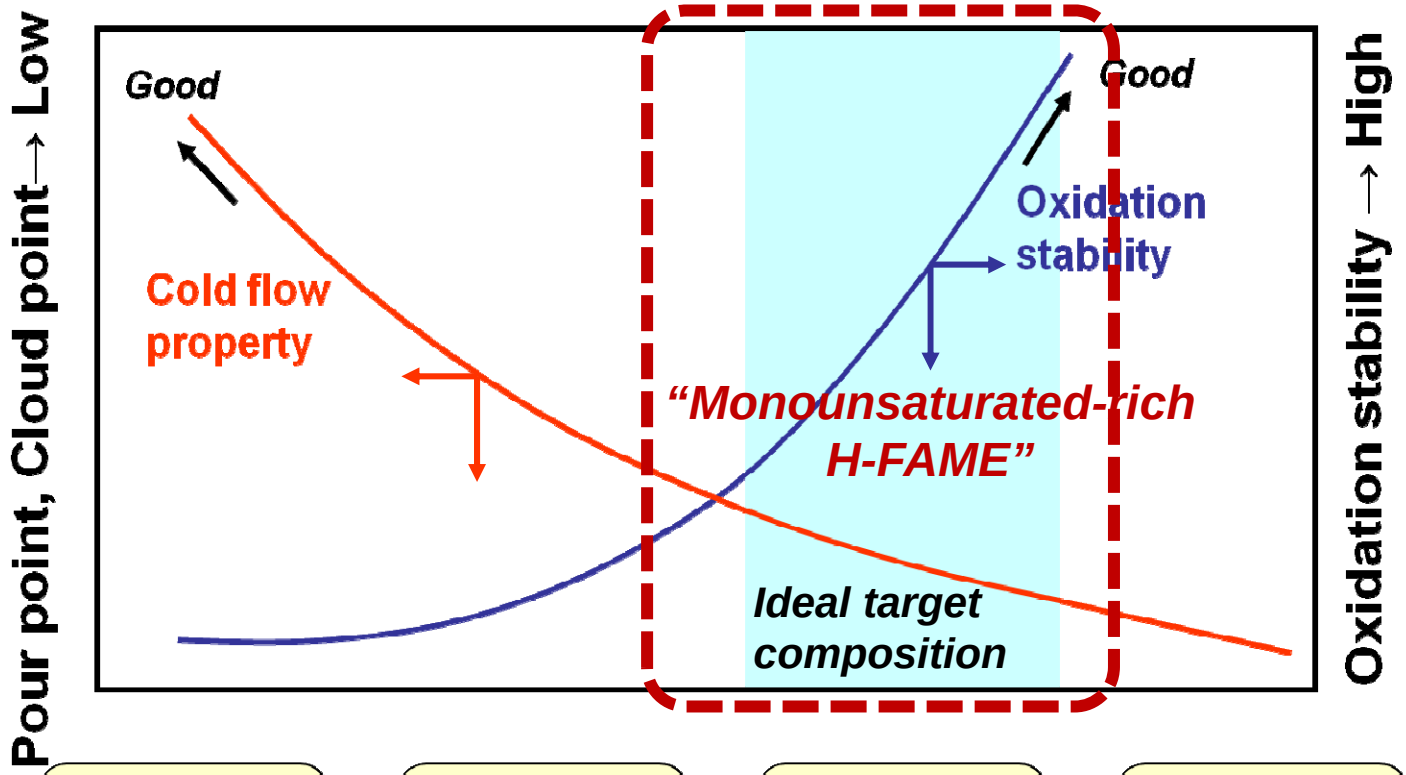
1-5. Positioning of H-FAME in biodiesels



H-FAME an Alternative Upgraded Biodiesel

2. Catalytic upgrading of biodiesel into H-FAME

2-1. Hydrogenation into monoenes-rich FAME



Structure of unsaturated FAME

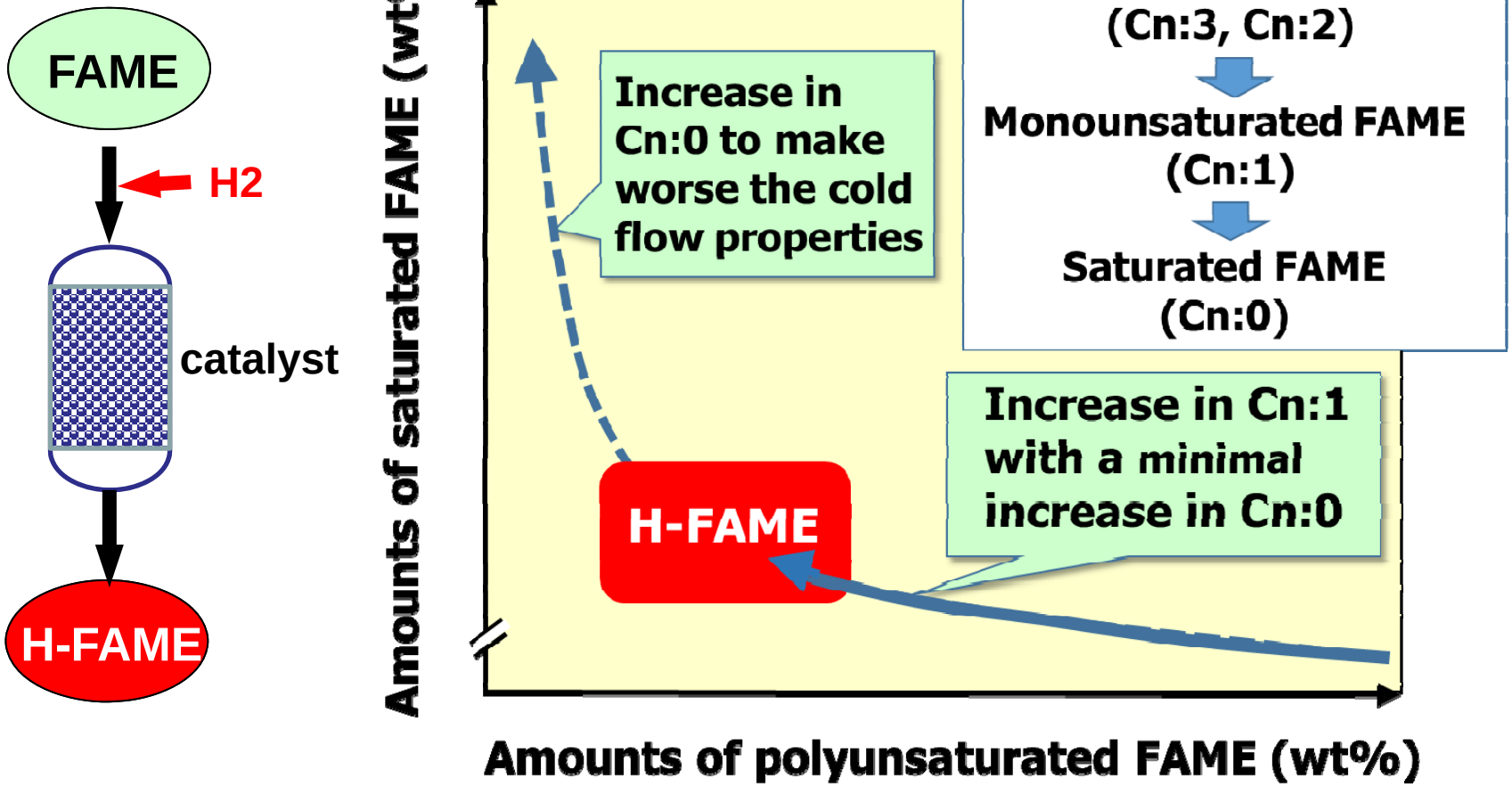
Number of unsaturated bonds = 3 → Number of unsaturated bonds = 2 → Number of unsaturated bonds = 1 → Number of unsaturated bonds = 0

Degree of hydrogenation →

Partial hydrogenation | *Deep HYD*

H-FAME an Alternative Upgraded Biodiesel

2-2. Optimization of H-FAME compositions



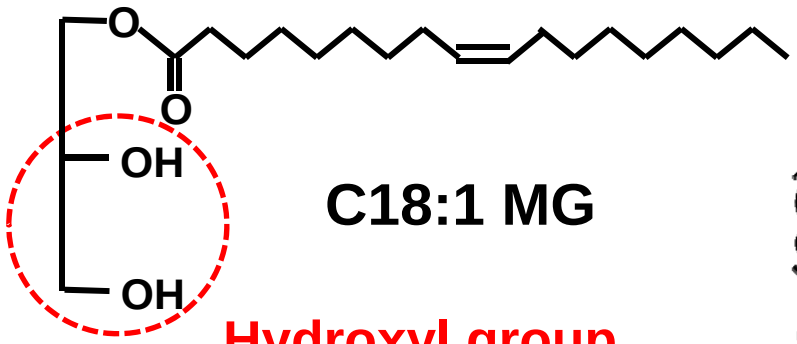
- Target composition of H-FAME will be optimized by: amounts of polyunsaturated FAME and saturated FAME
- Pd catalysts were most selective for partial hydrogenation under the mild reaction conditions

H-FAME an Alternative Upgraded Biodiesel

2-3. Other key components for FAME upgrading

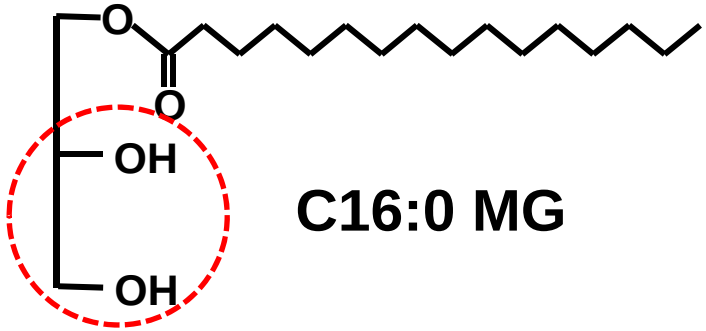
Typical Impurities in FAME

◆ **MG (Std. <0.7 mass %)**



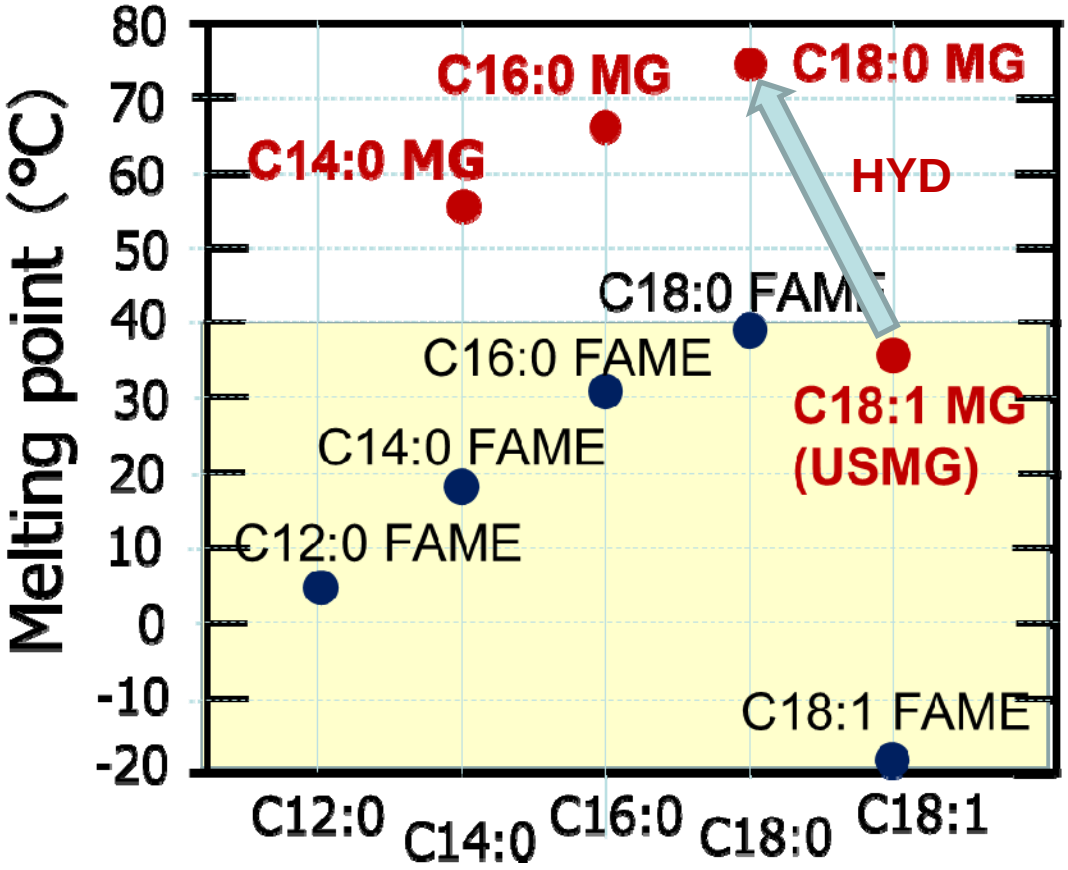
C18:1 MG

Hydroxyl group (hydrophilic)



C16:0 MG

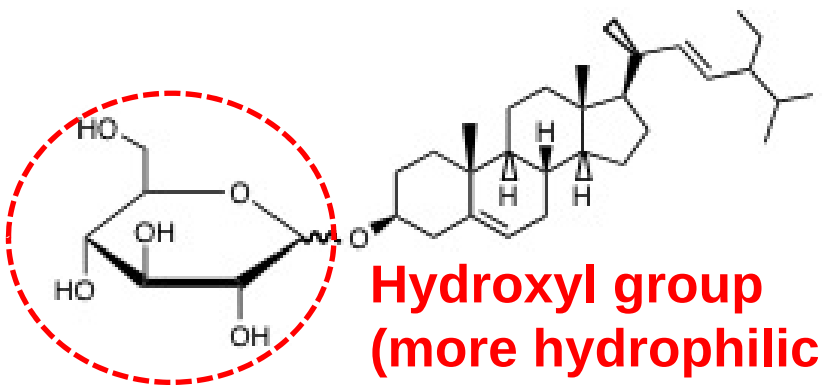
➢ ***Tend to precipitate under the cold weather, and more significant for saturated monoglycerides (SMG) (filter plugging, etc.)***



H-FAME
an Alternative Upgraded Biodiesel

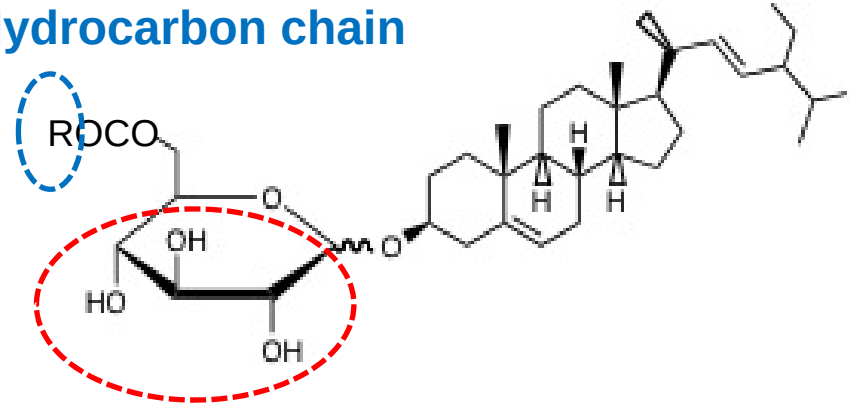
2-3. Other key components for FAME upgrading

◆**Sterol glucoside (SG)** **(Not standardized)**



Hydroxyl group (more hydrophilic than MG/SMG)

Hydrocarbon chain



Esterified sterol glucosides: less hydrophilic than SG

SG: 283-287 ºC (mp)

- ***Tends to precipitate during the FAME storage even under the room temp. (filter plugging, etc.)***
- ***Will take time to precipitate, but may work as a nuclei for SMG precipitation***

- ***Will cause less issues in the precipitates formation***

SG: Palm FAME (30-60 ppm);
Palm H-FAME (about 30-40 % reduction with adsorbents)

H-FAME an Alternative Upgraded Biodiesel

2-4. Removing impurities from crude H-FAME

- **Vacuum distillation:**
  (conventional or molecular ones)
  MG,SMG,SG,ESG, Saturated FAME, etc.
  -→ Need to add antioxidants into distillates

- **Adsorbents + Filtration:**
  MG, SMG, SG, FAME, etc.

Used in the TISTR's pilot plant

- **Wintering + Filtration:**
  SMG, SG, Saturated FAME, etc.

- **Wintering + Centrifuge:**
  SMG, SG, Saturated FAME, etc.

Impurity removing methods will be selected depending on the requirement level of MG and SG

H-FAME
an Alternative Upgraded Biodiesel

2-5. Typical properties of palm H-FAME (@TISTR)

Items	Units	Thailand DOEB 2014	EAS-ERIA BDF Std (EEBS):2008	WWFC March, 2009	TISR's PP H-FAME
Density	kg/m3	860-900	860-900	Report	872
Viscosity	mm2/s	3.50-5.00	2.00-5.00	2.0-5.0	4.5
Flashpoint	ºC	120 min.	100 min.	100 min.	168
Sulfated ash	mass%	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.	375
Total contamination	mg/kg	24 max.	24 max.	24 max.	1
Oxidation stability	hrs.	10 min	10.0 min. (**)	10 min.	86.3
Iodine value		120 max.	Reported (*)	130 max.	42
Monoglyceride content	mass%	0.70 max.	0.80 max.	0.80 max.	0.18
Trace metals		-	-	no addition	-
Cloud point	ºC	Report	-	-	16 ºC
CFPP	ºC	Report	-	-	16 ºC
Additive		Approval	-	-	-
Saturated monoglyceride in MG	mass%	-	-	-	0.08
Sterol glucoside	ppm	-	-	-	24

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

H-FAME an Alternative Upgraded Biodiesel

3. Advantages of H-FAME

3-1. Advantages of H-FAME and H-FAME process

1. Meets with all of FAME standards (EN, WWFC, EAS-ERIA, Thai, etc.)

2. High oxidation stability (>>10h) (less acids/corrosion)

6. Detoxification of Phorbol ester (PE)

H-FAME (1/2)

3. Less peroxides formation (more elastomer tolerance)

5. Increase in Cetane number
CN~65 for Palm H-FAME
CN~59 for Jatropha H-FAME

4. Decrease in heavier fraction (less poly-merization/ deposits)

H-FAME
an Alternative Upgraded Biodiesel

3-2. Advantages of H-FAME and H-FAME process

7. Less sludge formation during oxidative/thermal degradation (less deposits)

8. Eases of removal of saturated fatty acid monoglyceride (SMG)

12. No need of high pressure facilities and distillation units

H-FAME (2/2)

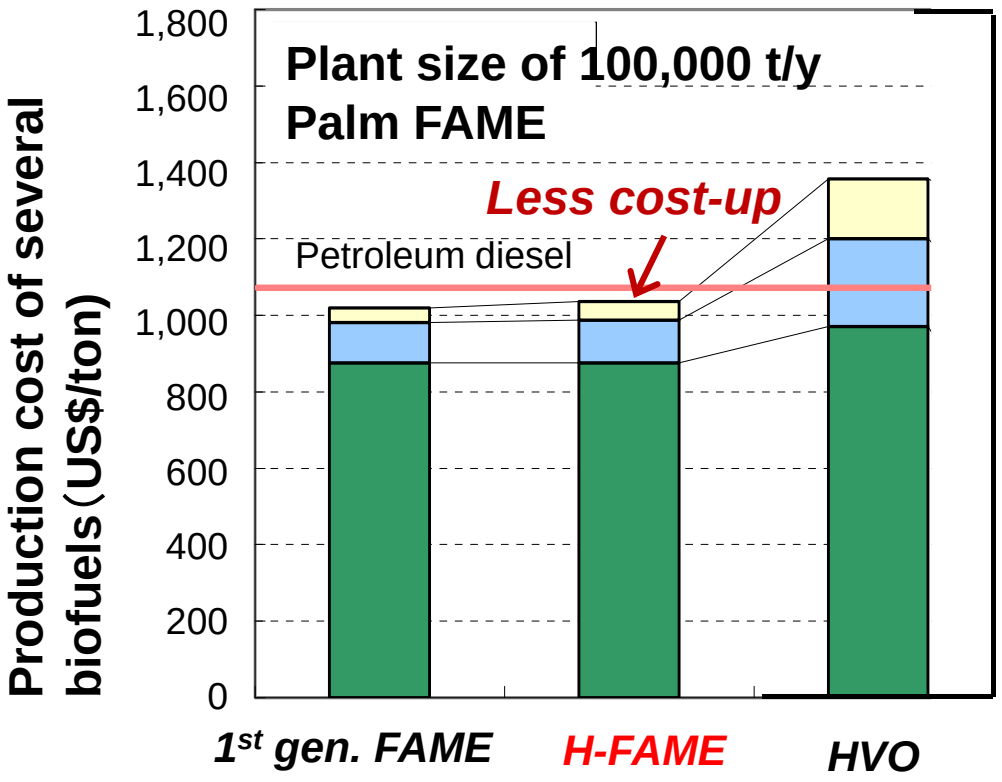
9. Eases of sterol glyceride (SG) removal

11. Volume-up reaction

10. Eases of metals removal

H-FAME an Alternative Upgraded Biodiesel

3-3. Feasibility of H-FAME (affordability)



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).

Environmental Research Institute, Waseda University (2011)

- **Small cost increase for H-FAME compared with 1st gen. FAME, but much less than HVO (BHD), even after newly installation of an on-site H2 package unit (steam reforming of methanol).**

H-FAME an Alternative Upgraded Biodiesel

4. Automotive compatibility of H-FAME

4-1. On-road test by using B20 (Palm H-FAME)

◆Verification of automotive compatibility of H-FAME, with the collaboration of Isuzu Thailand group and petroleum company .

◆Testing fuel of B20: 20 vol % of Palm H-FAME blended with 80 vol % of Thai petro-diesel.

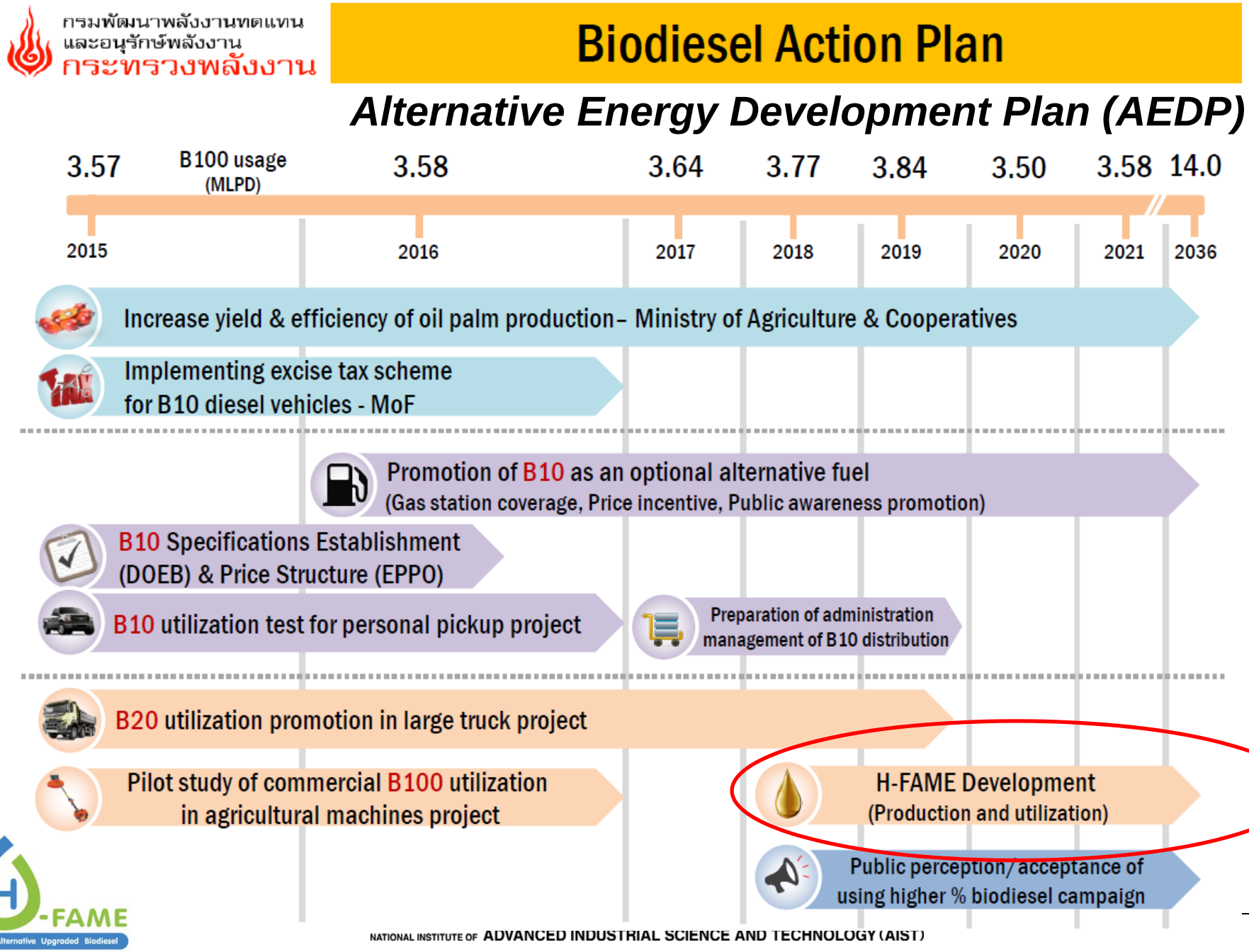
◆ Testing periods: Jan.5, 2015 ～ Mar. 2015 (50.000 km).

◆ Testing vehicle: ISUZU pick up truck, D-MAX Super Daylight (EUROIV)

H-FAME an Alternative Upgraded Biodiesel

5. Future Perspective and Conclusions

5-1. H-FAME adopted in Thai AEDP (2015-2036)



H-FAME
an Alternative Upgraded Biodiesel

5-2. Thailand-Japan collaboration on H-FAME

2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021

SATREPS

Thai-Japan JST-JICA PJ（2010-2015）

Jatropha H-FAME

◆*D&D of high-quality biodiesel*

Palm H-FAME

JST, JICA, AIST, NSTDA, MTEC a member of NSTDA, WASEDA University, TISTR

Jatropha H-FAME on-road test B10

Palm H-FAME on-road test B20

Follow-up work

Department of Alternative Energy Development and Efficiency, MINISTRY OF ENERGY

DEDE PJ Demonstration of B10

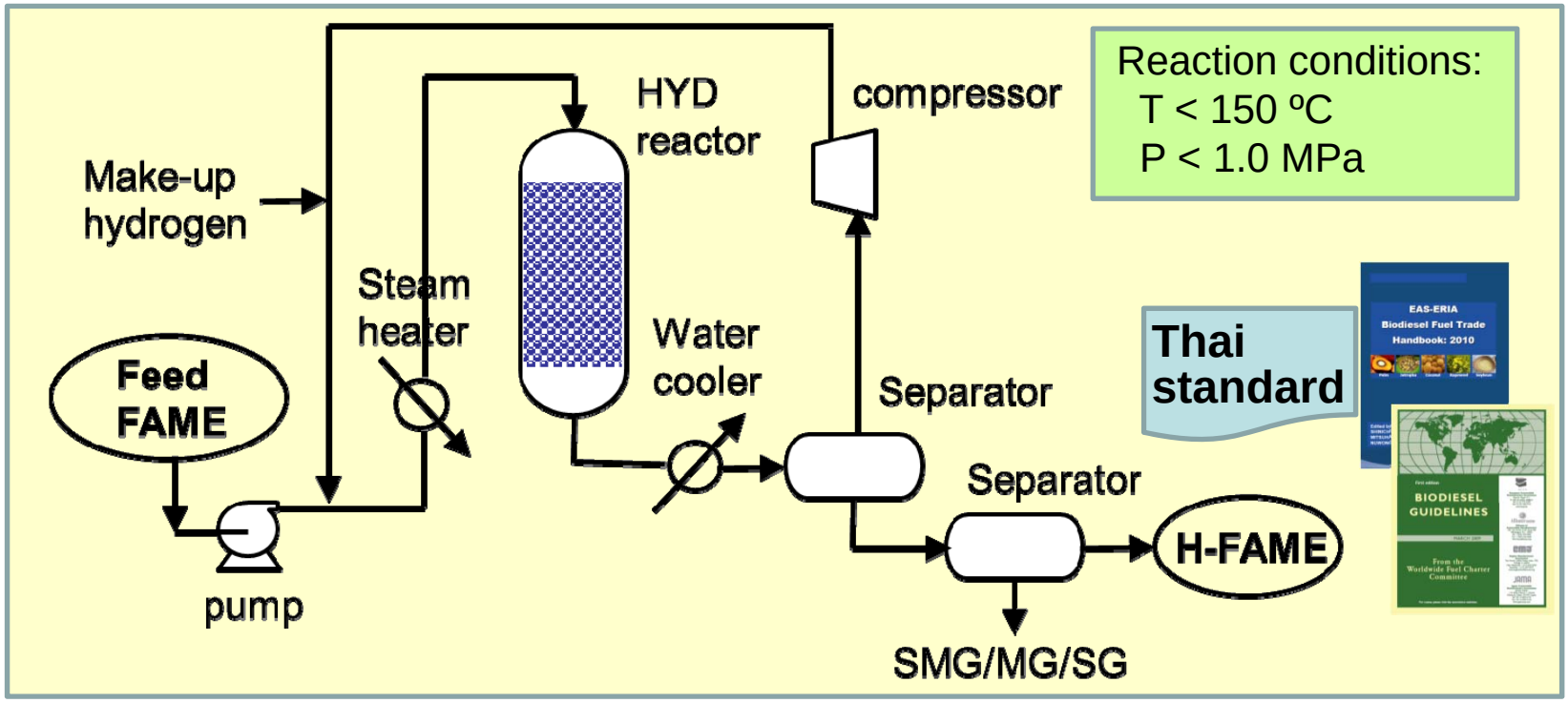
MTEC a member of NSTDA, TISTR, AIST

Thai and Japanese companies, etc.

H-FAME commercialization

H-FAME an Alternative Upgraded Biodiesel

5-3. H-FAME technology in DEDE B10 Project



1. **H-FAME production via. demonstration plant (around 20,000 L of H-FAME)**
2. **On-road durability tests to show the automotive compatibility of H-FAME blended diesel (B10) to the public, etc.**
3. **Quality assurance of FAME (B100) and B10**

H-FAME an Alternative Upgraded Biodiesel

8. Conclusions

1. Higher blending use of FAME (>7 vol%) promotes the oxidative degradation of FAME to result in the acids, polymers and sludge formation, etc.
2. Precipitation issues are getting more significant, e.g., C16:0 MG for Palm FAME under the cold weather and SG even under the room temperature
3. Partially hydrogenated FAME (H-FAME) is a new alternative biodiesel as well as a reliable and affordable biodiesel to solve these issues
4. H-FAME can be used as a nation-wide automotive biodiesel blend stock and can be safely used up to B20 for Palm H-FAME, i.e., sufficient safety side for B10
5. H-FAME can be applied to any kind of FAMEs

H-FAME an Alternative Upgraded Biodiesel

Acknowledgements

We deeply appreciate JST and JICA for their financial supports.

We also really thank all of the research participants of NSTDA/MTEC, TISTR. KMUTNB, WASEDA U. and AIST for their contributions to this Project.

We also express gratitude to the ISUZU Thailand group for their kind supports on the on-road tests, and PTT, Bangchak and Thai oil for supplying the FAME(B100) and petro diesel (B0) and for measuring the fuel quality.

Thank you for your kind attention

H-FAME
an Alternative Upgraded Biodiesel