Catalytic Upgrading of Conventional Biodiesel into H-FAME by Partial Hydrogenation

• Yuji Yoshimura[1,*], Makoto Toba[1], Takehisa Mochizuki[1], Shih-Yuan Chen[1], Yoko Abe[1], Chanakan Puemchalad[2], Nattawee Teerananont[2], Piyanan Sreesiri[2],

• Nuwong Chollacoop[3], Paritud Bhandhubanyong[4]

[1] Advance Industrial Science and Technology(AIST), Japan, and Japan International Cooperation Agency (JICA) and MTEC,
[2] Thailand Institute of Scientific and Technological Research (TISTR), Thailand,
[3] National Metal and Materials Technology Center(MTEC), Thailand,
[4] Panyapiwat Institute of Management, Thailand

NAC 2017, March 30, 2017 @ NSTDA/Thailand

H-FAME as a new alternative Biodiesel

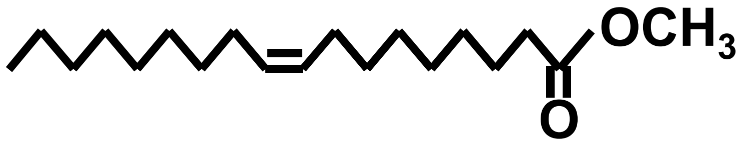
H-FAME (Partially Hydrogenated FAME):

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

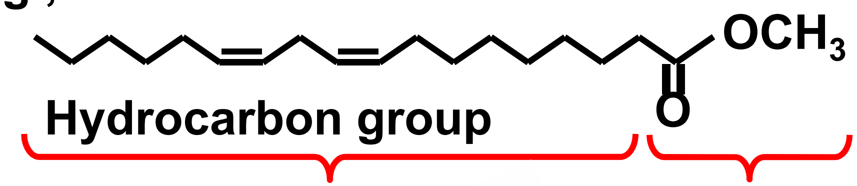
an Alternative Upgraded Biodiesel



Feature of typical compounds in Biodiesel

◆ **FAME as main components**

e.g., C18:2FAME



Methyl ester group

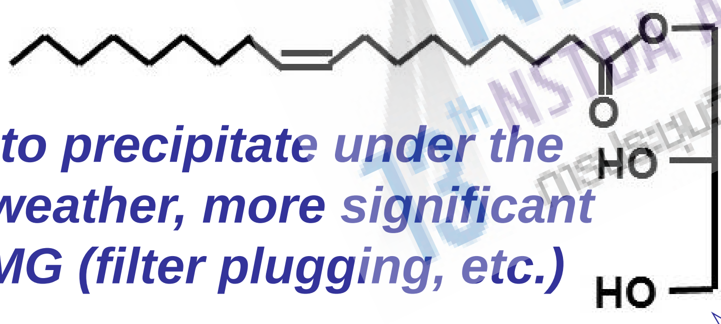
- *Comparable to diesel fractions*
- *Tend to be oxidized into peroxides, acids and polymers (deposits, corrosion, etc.)*

(Std. oxidation stability > 10h)

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

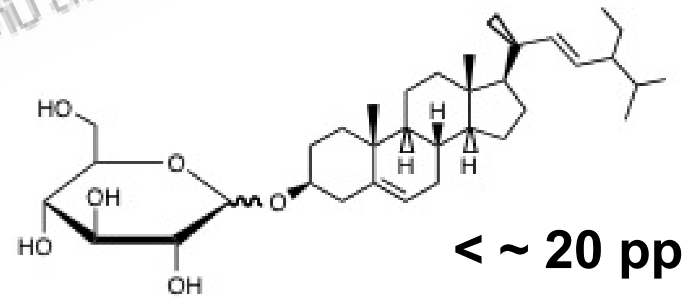
Impurities

◆ **MG (Std. <0.7 mass %)**



- *Tend to precipitate under the cold weather, more significant for SMG (filter plugging, etc.)*

◆ **Sterol glucoside (SG)**



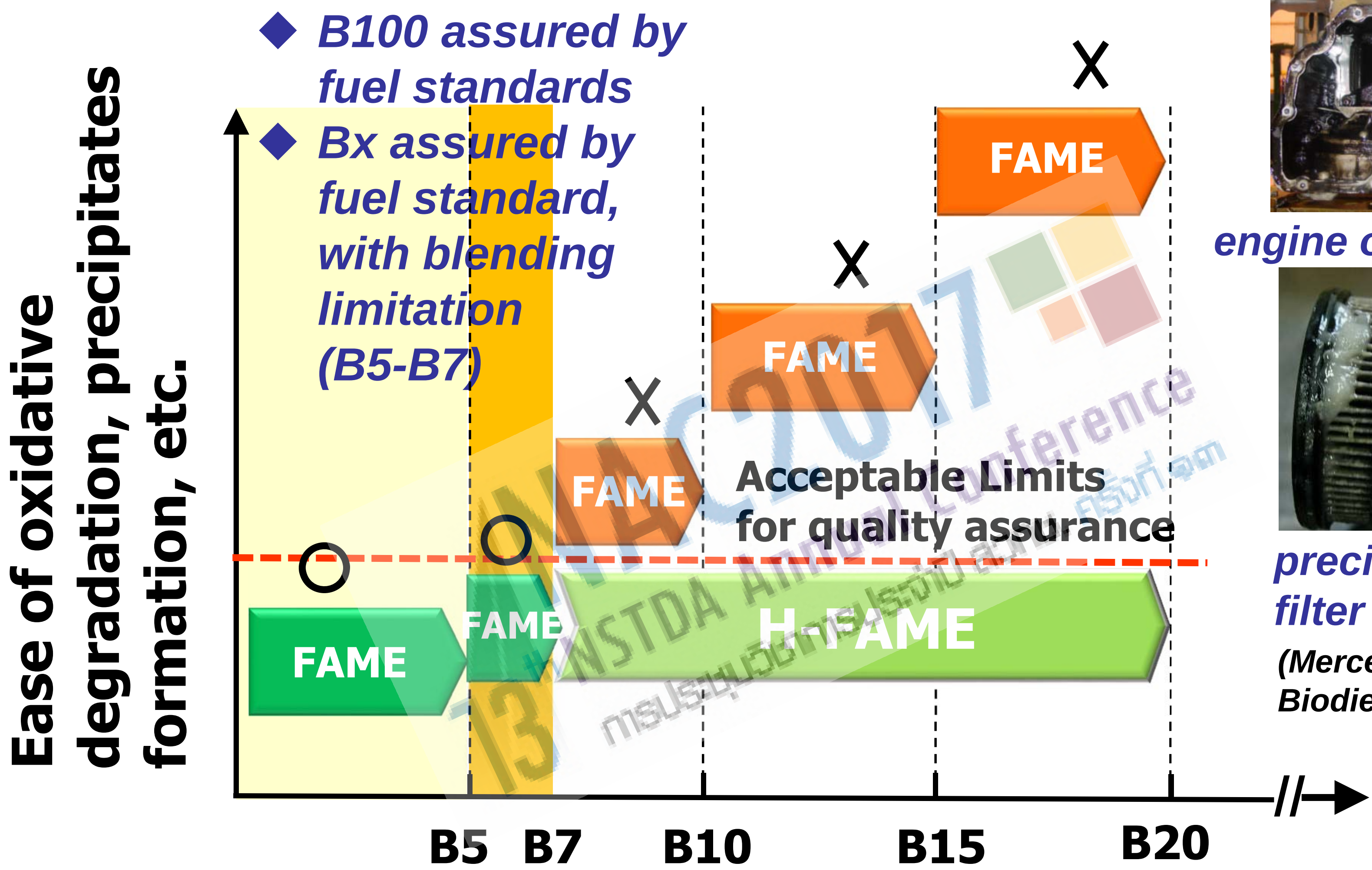
< ~ 20 ppm

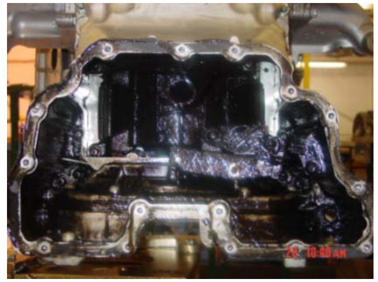
- *Tend to precipitate during storage even under the r.t. (filter plugging, etc.)*

◆ **Water (Std. <500 ppm)**

- *Tend to promote hydrolysis of FAME into fatty acids and MeOH. Acids promote oxidation and polymerization of FAME*

Issues for higher blending of Biodiesel





engine oil sludging

precipitates/ filter plugging

(Mercedes-Benz Biodiesel Brochure)

Biodiesel blended with petroleum diesel (Bx*)

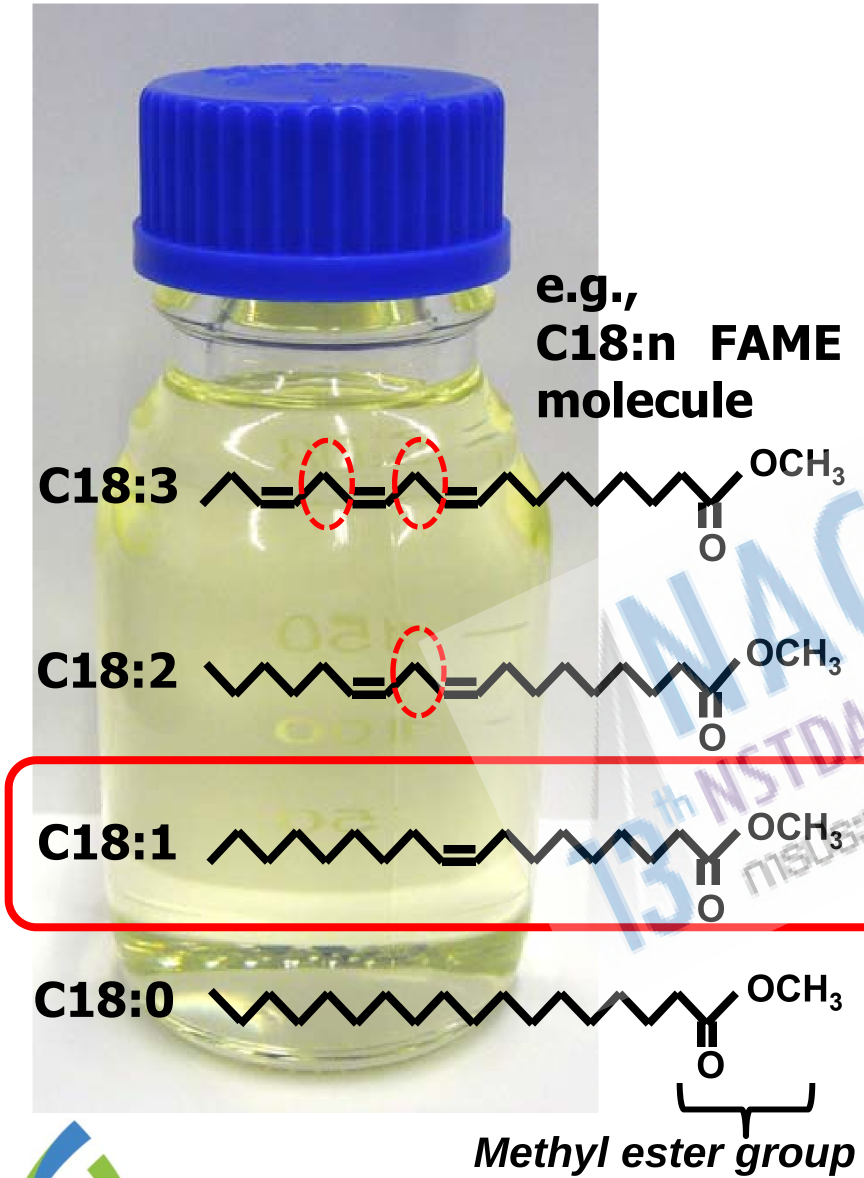
**X vol% of biodiesel and (100-X) vol% of petroleum diesel*

H-FAME an Alternative Upgraded Biodiesel

Contents

1. Concept of H-FAME

1-1. Properties of FAME molecules



	Oxidation stability	Peroxide formation	Cold flow property	Solvency effect
	Acid corrosion, polymers and sludge formation	Elastomer damage	filter plugging	cleaning effect
C18:3	(98*) ××	××	◎◎	○
C18:2	(41) ×	×	◎	○
C18:1	(1) ○	○	○	○
C18:0	(<1) ◎	◎	×	○

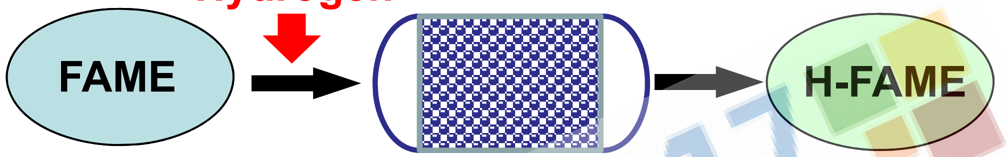
- *Ease of oxidation: E.N. Frankel, Lipid Oxidation, 2005*

Monoene (monounsaturated FAME) seems to be most preferable.

H-FAME an Alternative Upgraded Biodiesel

1-2. H-FAME as a monoene-rich FAME

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



Hydrogenation catalysts

T<140 ºC
P<0.5 MPa

FAME + Hydrogen = H-FAME

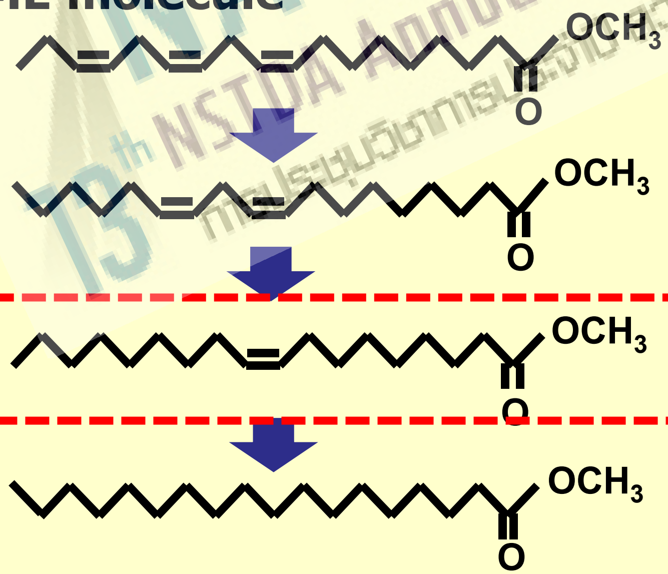
e.g., C18:n FAME molecule

C18:3

C18:2

C18:1

C18:0

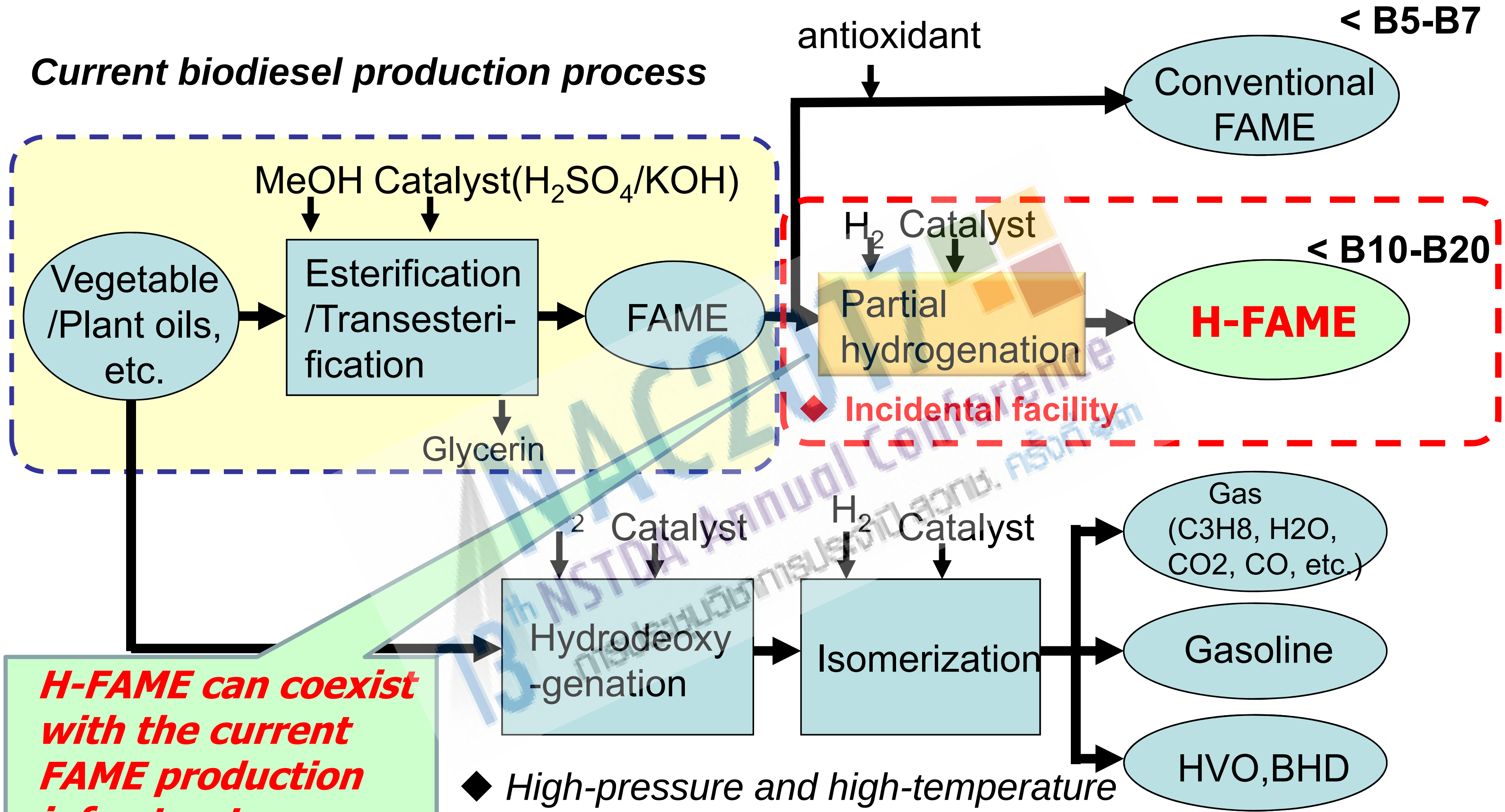


Degree of hydrogenation

Partial hydrogenation

Complete hydrogenation

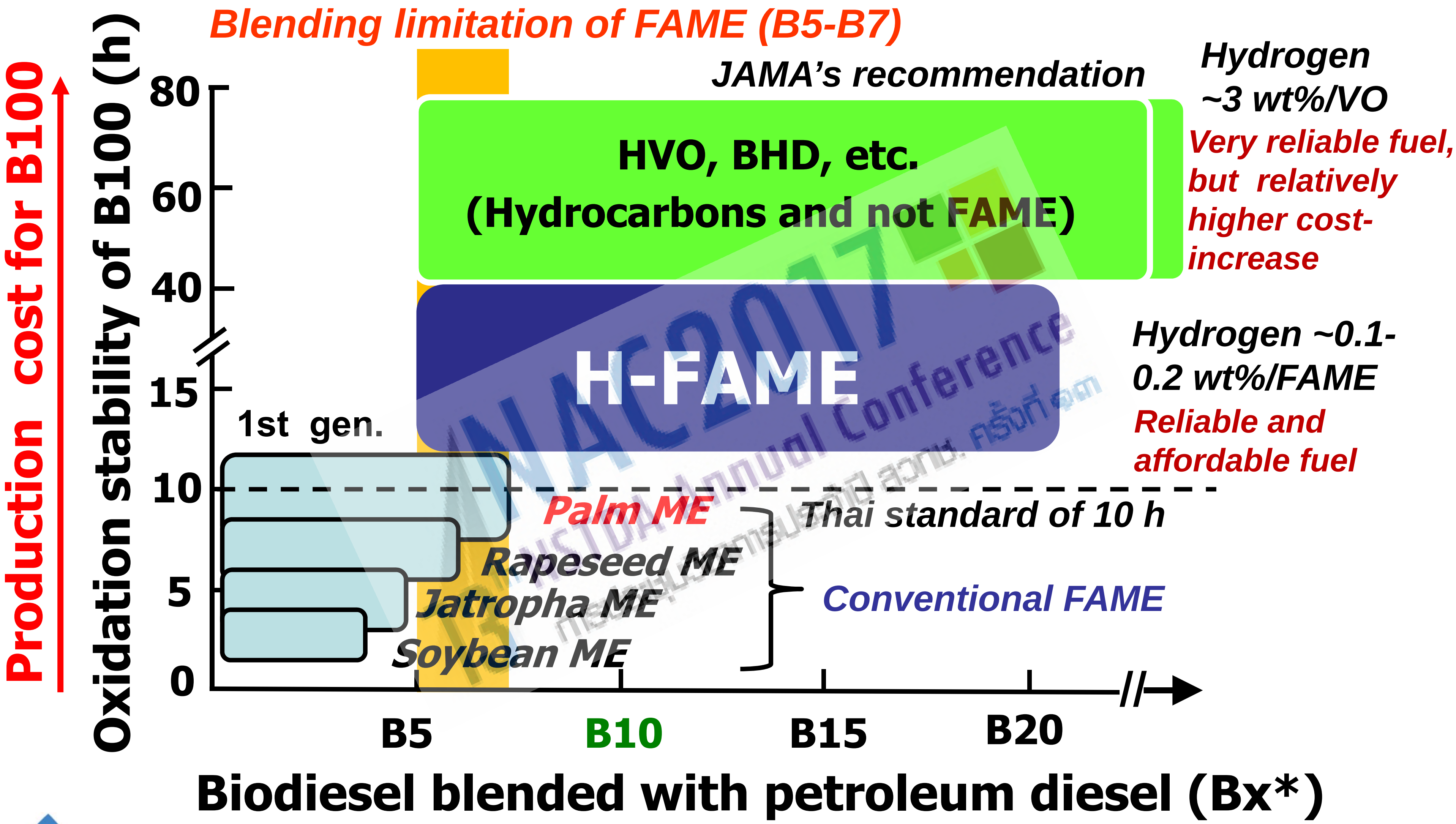
1-3. H-FAME production process



H-FAME can coexist with the current FAME production infrastructures.

- *High-pressure and high-temperature facility (e.g., P>5 MPa, T>280 ºC)*
- *Large plant size to get a scale merit*
- *Very high hydrogen consumption*

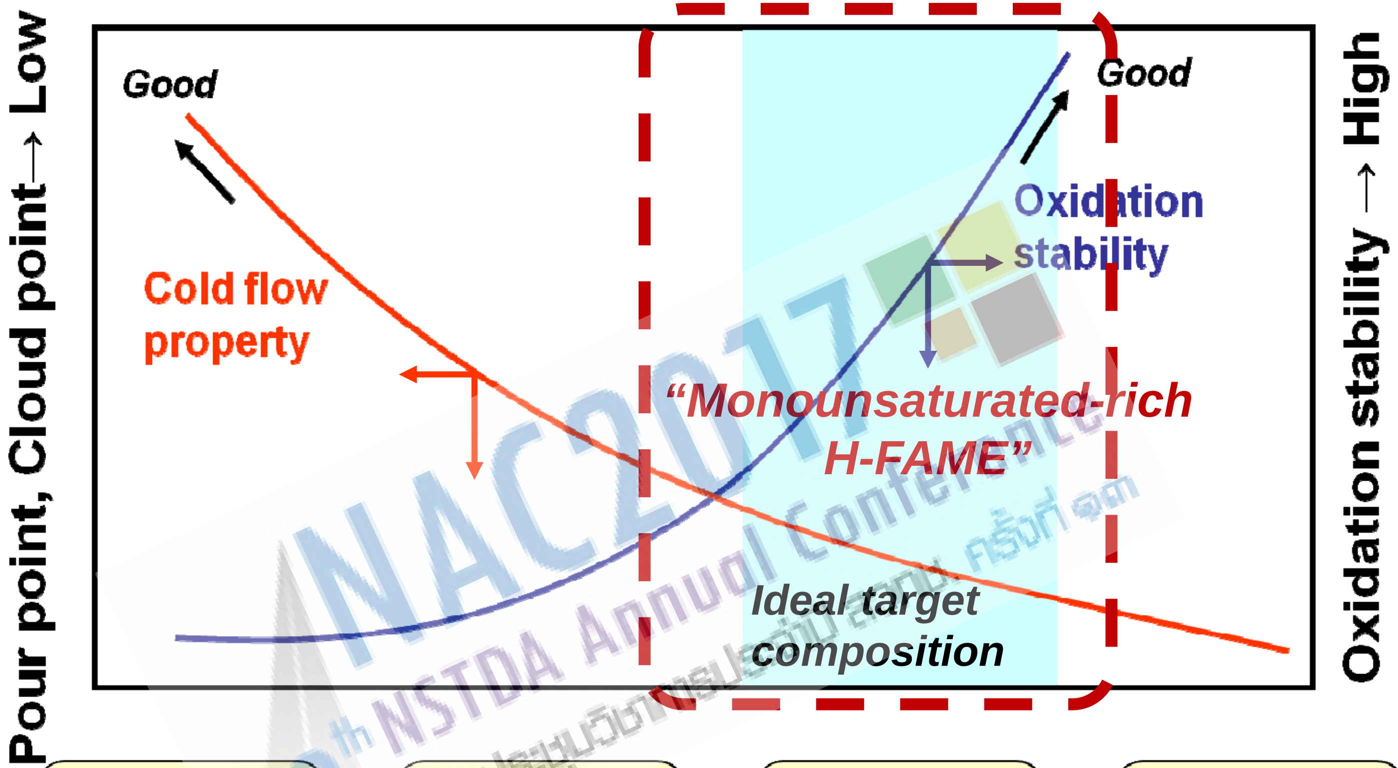
1-4. Positioning of H-FAME in biodiesels



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

2. Catalytic upgrading of biodiesel into H-FAME

2-1. Hydrogenation into monoenes-rich FAME



Structure of unsaturated FAME

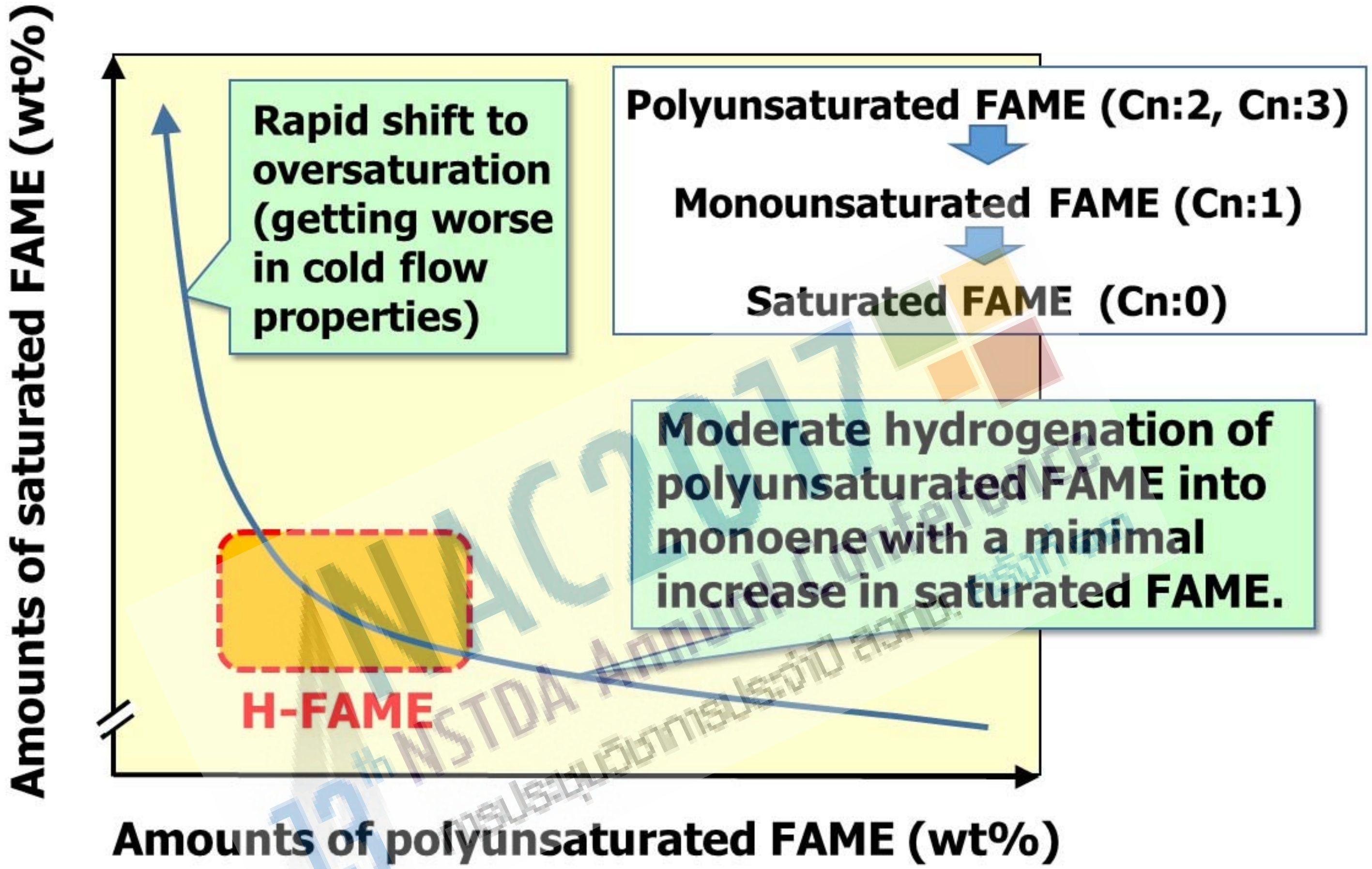
Number of unsaturated bonds = 3 → Number of unsaturated bonds = 2 → Number of unsaturated bonds = 1 → Number of unsaturated bonds = 0

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 related with;
- Residual amounts of polyunsaturated FAME (oxidation stability > 10h)
- Incremental amounts of saturated FAME (cloud point within standard/reported, <16 ºC in Thailand)

2-3. Importance of hydrogenation conditions

To produce a monoene-rich FAME within the limitation of cold flow property of B100.

<General understanding>

Partial hydrogenation under the lower surface hydrogen over the catalytic materials such as Pd particles

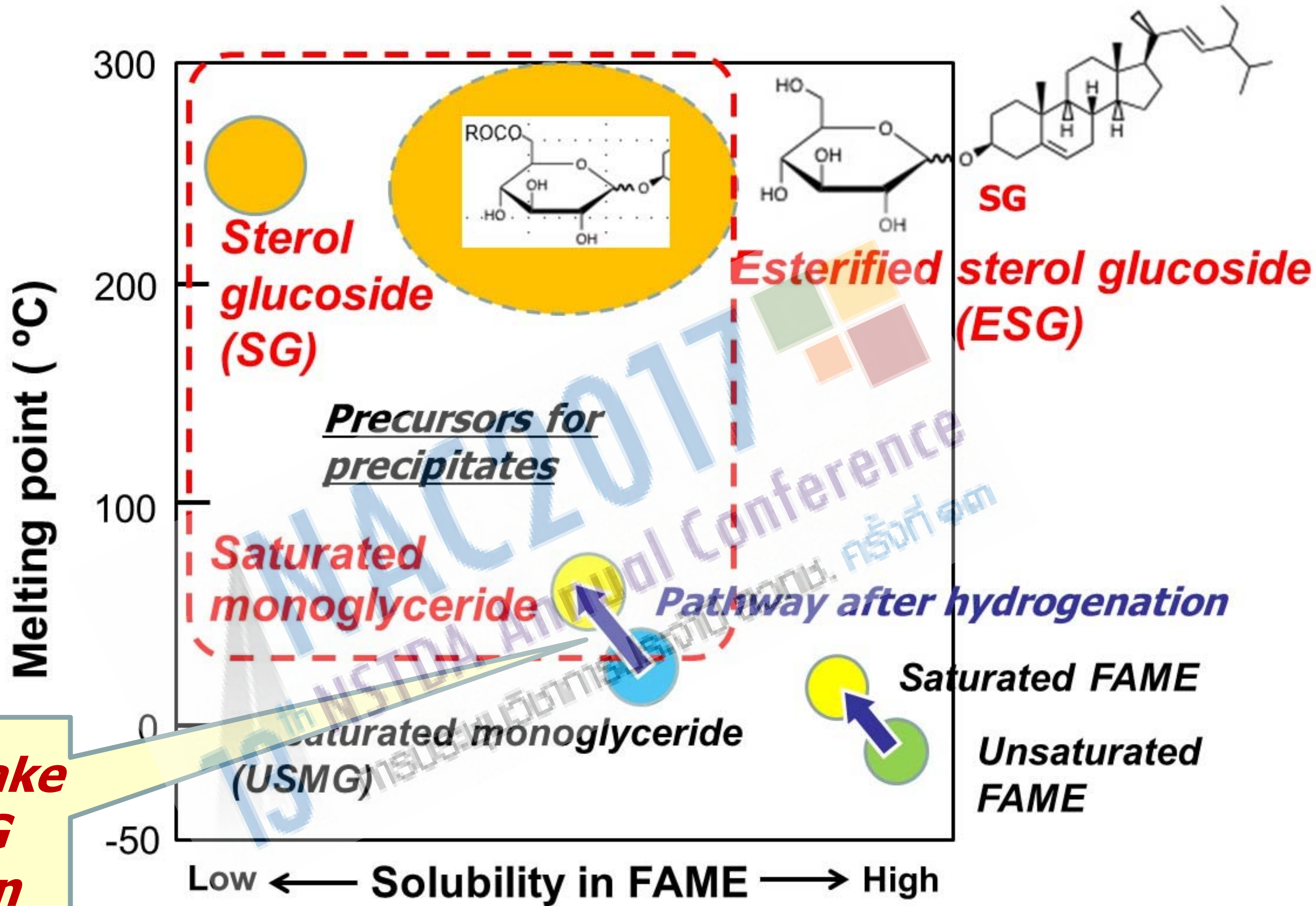
<Reaction conditions>

- **P: lower p(H2)**
- **T: higher temperature**
- **F/Wcat: higher space velocity (shorter contact time), less pore diffusion limitation in catalyst support from another viewpoint**

<Catalysts>

- **Increase in hydrogenation selectivity and stability**
- **Increase in sulfur tolerance even for several ppm of sulfur**

2-4. Simultaneous hydrogenation of MG



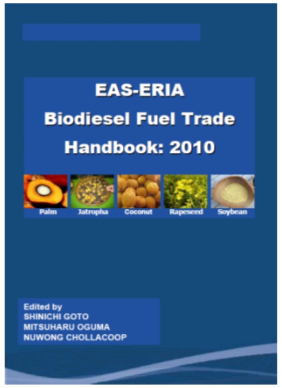
HYD will make ease of SMG precipitation

- **Saturated monoglyceride (SMG) for filter plugging under the cold weather**
- **Sterol glucoside (SG) for precipitate formation during storage even at room temperature**

2-5. Properties of Palm H-FAME (Pilot Plant @TISTR)

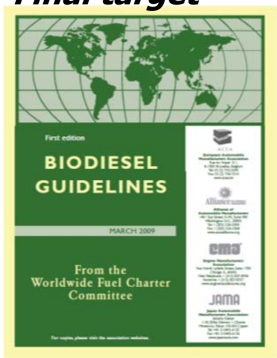
Items	Units	EU EN14214:2003	Thailand	EAS-ERIA BDF Standard (EEBS):2008	WWFC March, 2009	TISR's PP H-FAME
Ester content	mass%	96.5 min.	96.5 min.	96.5 min.	96.5 min.	98.9
Density	kg/m3	860-900	860-900	860-900	Report	872
Viscosity	mm2/s	3.50-5.00	3.5-5.0	2.00-5.00	2.0-5.0	4.5
Flashpoint	deg. C	120 min.	120 min.	100 min.	100 min.	168
Sulfur content	mass%	0.0010 max.	0.0010 max.	0.0010 max.	0.0010 max.	0.0002
Distillation, T90	deg. C	-	-	-	-	354.5
Carbon residue (100%) or	mass%	-	-	0.05 max.	0.05 max.	
Carbon residue (10%)		0.30 max.	0.30 max.	0.3 max.	-	0.15
Cetane number		51.0 min.	51 min.	51.0 min.	51.0 min.	> 64
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.	375
Water and sediment	vol%	-	-	-	0.05 max.	-
Total contamination	mg/kg	24 max.	24 max.	24 max.	24 max.	1
Copper corrosion		Class-1	Class-1	Class-1	-	Class-1a
Corrosion: Ferrous		-	-	-	light rusting. Max	-
Acid value	mgKOH/g	0.50 max.	0.5 max.	0.50 max.	0.5 max.	0.3
Oxidation stability	hrs.	6.0 min.	10 min.	10.0 min. (****)	10 min.	86.3
Iodine value		120 max.	120 max.	Reported (***)	130 max.	42
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.	0.70 max.	0.80 max.	0.80 max.	0.18
Diglyceride content	mass%	0.20 max.	0.20 max.	0.20 max.	0.20 max.	0.14
Triglyceride content	mass%	0.20 max.	0.20 max.	0.20 max.	0.20 max.	0.04
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.	0.1
Na+K	mg/kg	5.0 max.	5.0 max.	5.0 max.	5 max.	<2
Ca+Mg	mg/kg	5.0 max.	5.0 max.	5.0 max.	5 max.	<2
Phosphorous content	mg/kg	10.0 max.	10 max.	10.0 max.	4 max.	<1
Trace metals		-	-	-	no addition	-
Cloud point	deg. C	-	Report	-	-	16
CFPP	deg. C	-	Report	-	-	16
Additive		-	Report	-	-	-

Mid-term target



◆*EAS-ERIA BDF standard, (EEBS):2008*

Final target



◆*WWFC Guideline BDF quality*

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

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

2-5-1. 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

H-FAME (1/2)

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

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

3. **Less peroxides formation (more elastomer tolerance)**

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

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

6. **Detoxification of Phorbol ester (PE)**

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

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

8. Make ease of removal of saturated fatty acid monoglyceride (SMG)

H-FAME (2/2)

12. No need of high pressure facilities and distillation units

9. Make ease of sterol glyceride (SG) removal (but, slight)

11. Volume-up reaction

10. Make ease of metals removal

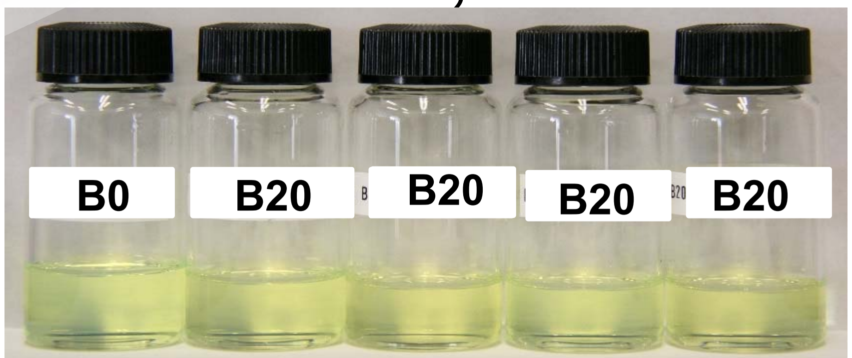
3-3. H-FAME to suppress the formation of sludge

After accelerated oxidation,

H-FAME is very effective to minimize the sludge formation !

Diesel (B0) (Japanese EURO V diesel) | **B20 Current FAME (Thai Palm FAME)** | **B20 H-FAME** | **B20 H-FAME** | **B20 H-FAME**

Before oxidation,

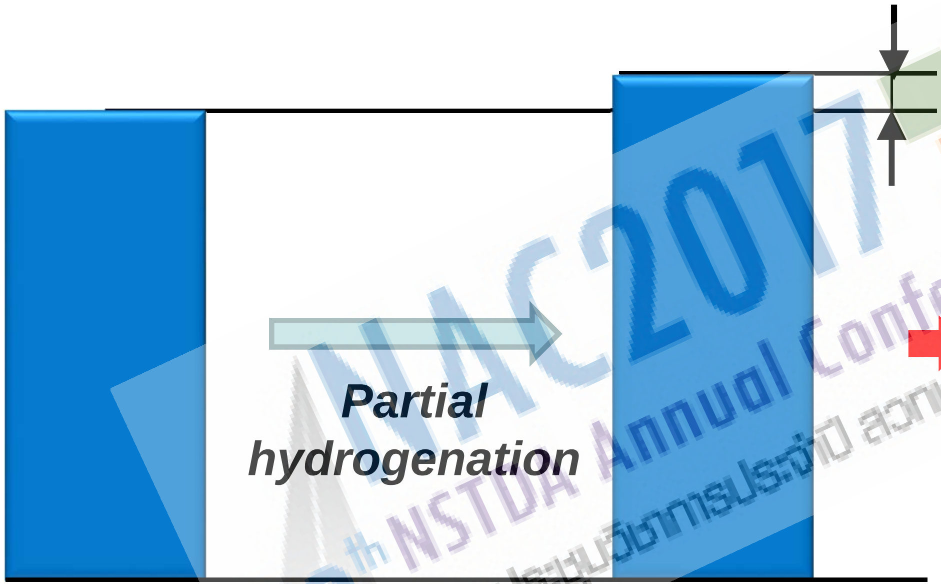


Accelerated oxidation condition:
Bx=20g, T=135 ºC (>115 ºC*),
O2 Flow=100 ml/min,
Oxidation period=16 h.

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

H-FAME an Alternative Upgraded Biodiesel

3-4. Volume-gain after partial hydrogenation



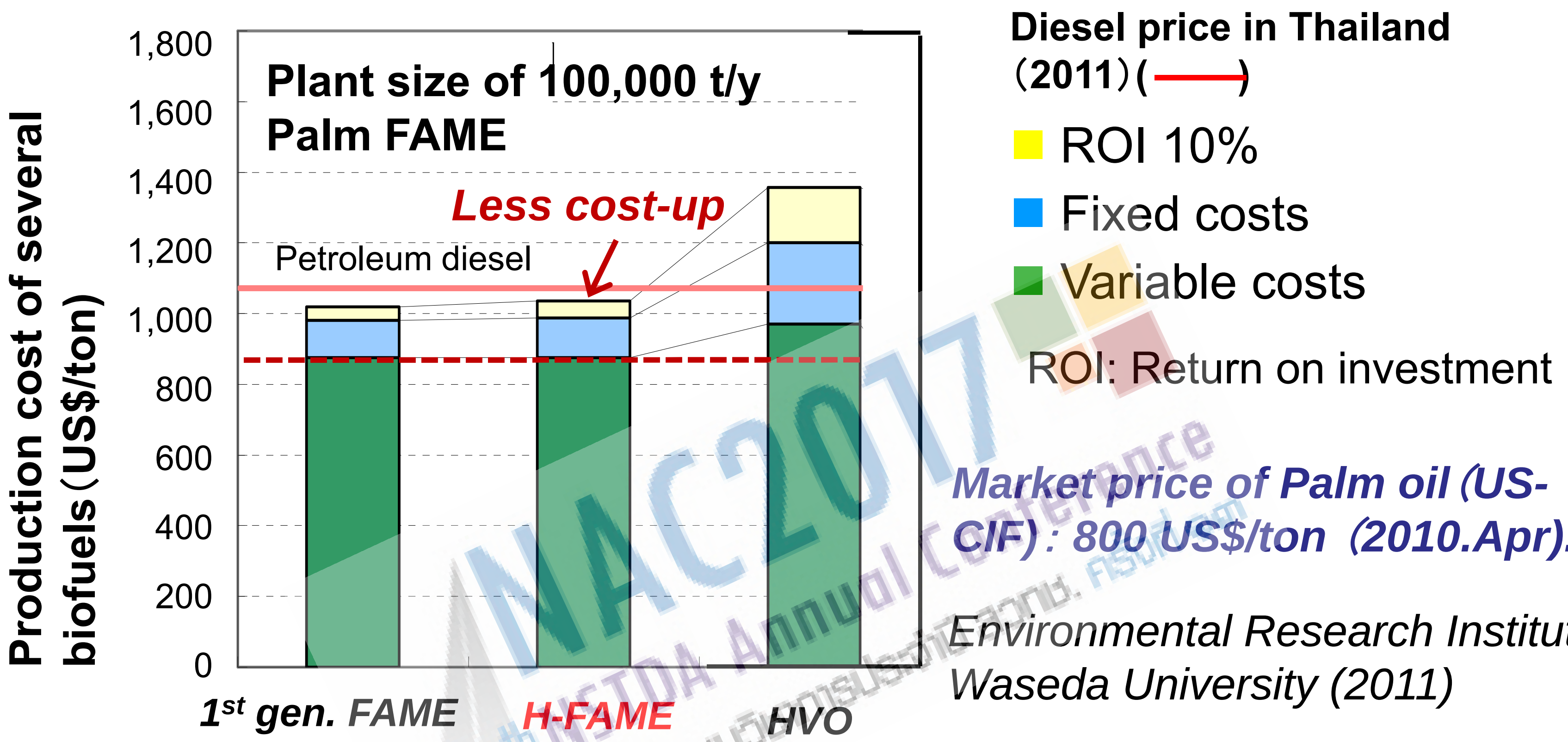
Palm FAME (B100)

Palm H-FAME (B100)

*About 1-2 %
increase in volume
at the same weights*

Biodiesel (B100) sales are based on the volume of biodiesel

3-5. Feasibility of H-FAME (affordability)



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

Environmental Research Institute, Waseda University (2011)

- **Small cost up 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.**
- **High proportion of variable costs for FAME, H-FAME and HVO. i.e., more than 80 % of the total production cost , so reduction of raw materials costs will be the key to increase its feasibility.**

4. Automotive compatibility of H-FAME

4-1. On-road test by using B10 (Jatropha H-FAME)

- ◆Verification of automotive compatibility of H-FAME, produced in JST-JICA PJ, with the collaboration of Isuzu Thailand group and PTT.
- ◆Testing fuel of B10: 10 vol% of Jatropha H-FAME blended with 90 vol% of Thai petro-diesel.
- ◆ Testing periods: November, 2012 – May, 2013 (50.000 km).
- ◆ resting vehicle: ISUZU pick up truck (EURO III).

Successfully finished !

"ISUZU can accept the Jatropha bio-diesel B10 using on ISUZU diesel engine same as general diesel used"

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

4-2. 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)

Successfully finished !

Fuel: B20 of Palm H-FAME

5. Future Perspective and Conclusions

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

กรมพัฒนาพลังงานทดแทนและอนุรักษ์พลังงาน
กระทรวงพลังงาน

Biodiesel Action Plan

B100 usage (MLPD)	2015	2016	2017	2018	2019	2020	2021	2036
	3.57	3.58	3.64	3.77	3.84	3.50	3.58	14.0

- Increase yield & efficiency of oil palm production – Ministry of Agriculture & Cooperatives
- Implementing excise tax scheme for B10 diesel vehicles - MoF

- Promotion of B10 as an optional alternative fuel (Gas station coverage, Price incentive, Public awareness promotion)
- B10 Specifications Establishment (DOEB) & Price Structure (EPPO)
- B10 utilization test for personal pickup project
- Preparation of administration management of B10 distribution

- B20 utilization promotion in large truck project
- Pilot study of commercial B100 utilization in agricultural machines project
- H-FAME Development (Production and utilization)
- Public perception/acceptance of using higher % biodiesel campaign

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, WASEDA University, NSTDA, MTEC (a member of NSTDA), TISTR

Jatropha H-FAME on-road test B10

Palm H-FAME on-road test B20

Isuzu's pick up trucks

Follow-up in-house work at MTEC, TISTR, AIST

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.

- ◆ *R&D of H-FAME technology*
- ◆ *Proof of automotive compatibility of H-FAME*

Main activities in DEDE PJ

.Production of 20,000L of H-FAME
.On-Roard tests by 8 pick-up trucks and several school buses by using B10 H-FAME
.Modified FAME standard (MG content, etc.)

H-FAME commercialization

H-FAME
an Alternative Upgraded Biodiesel

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

For supporting the Biodiesel Action Plan in Thai Alternative Development Plan (AEDP):

<Confirming of automotive compatibility>

- **Further on-road durability tests in Thailand to show the automotive compatibility of H-FAME blended diesel to the public etc.**

<Upscaling of H-FAME plant units>

- **Demonstration plant study of H-FAME technology in Thailand for leading to the commercial application.**

....will be confirmed through the DEDE B10 Project

5-4. Conclusions

1. **Partially hydrogenated FAME (H-FAME) is a new alternative biodiesel superior in oxidation and thermal stabilities compared with conventional FAME, and a reliable and affordable biodiesel**
2. **H-FAME can be produced from any kinds of FAME more selectively over the Pd based catalysts.**
3. **H-FAME can be used as a nation-wide automotive biodiesel blend stock even at the higher blending use, e.g., up to B20 for Palm H-FAME.**
4. **H-FAME will support the *Thai Alternative Energy Development Action Plan (AEDP)* as one of the new alternative biodiesels, and will support the safe use of Bx in automotive transportation.**

Acknowledgements

Japan

AIST WASEDA JST JICA

Kingdom of Thailand

สวทช NSTDA MTEC a member of NSTDA TISTR KMUTNB

We deeply appreciate JST and JICA for their financial supports.

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

We also deeply thank 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