

The 4th Korea-Vietnam Green Chemistry conference 2013

BIODIESEL PRODUCTION TECHNOLOGY IN THAILAND

By

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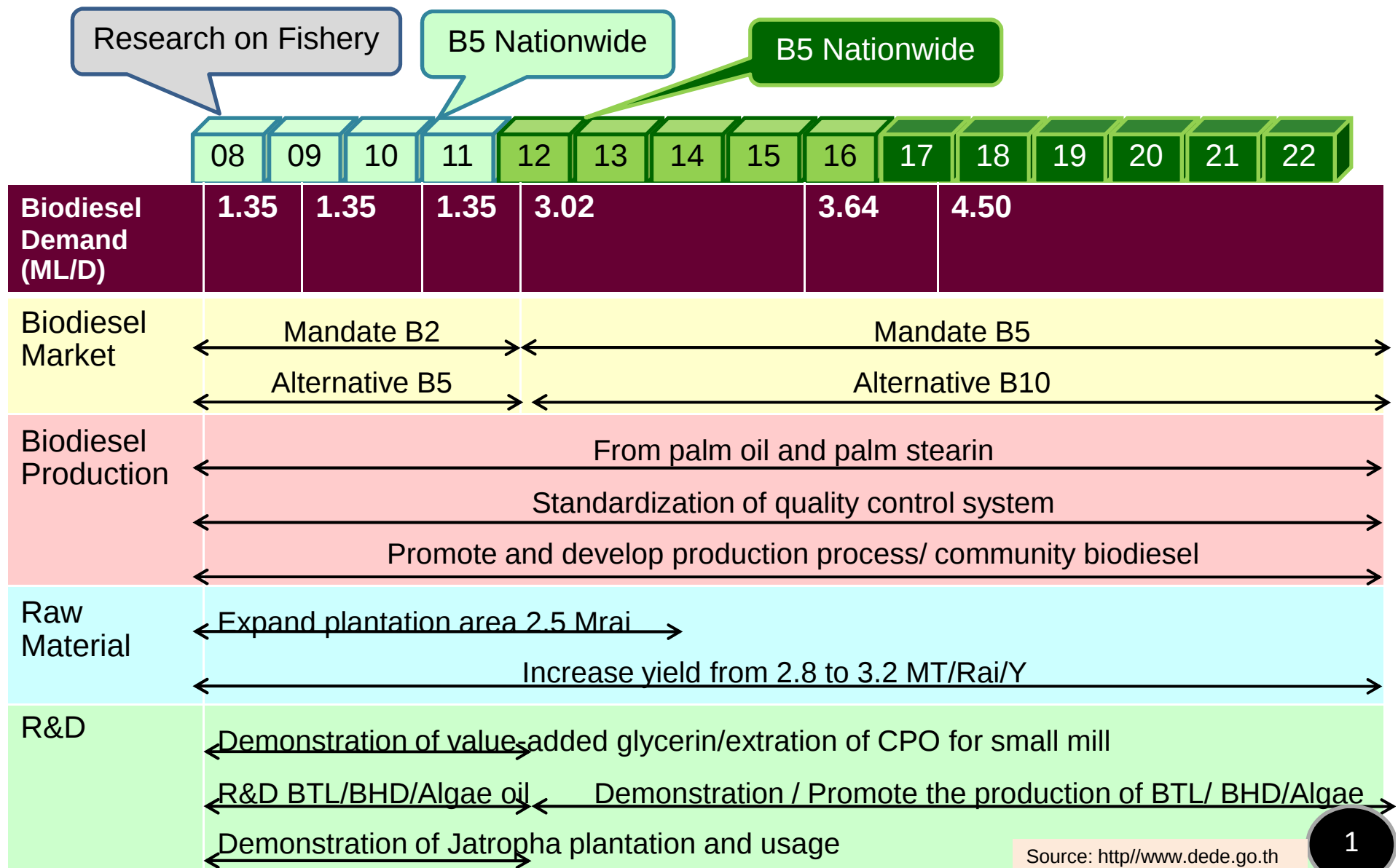
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Biodiesel Thailand– Thai Policy

REDP Master Plan 2008-2022: Biodiesel Roadmap



Market Situation – Installed Capacity



	Company name	Capacity (L/D)	Province
●	Patum Vegetable Oil Co., Ltd	1,400,000	Patumthani
●	Siam Gulf Petrochemical Co., Ltd	1,200,000	Petchburi
○	Enwegy Absolute Plc	800,000	Prajeenburi
○	Thai Oleochemical Co., Ltd	685,800	Rayong
●	Bioenergy Plus Co., Ltd	350,000	Ayutthaya
●	Bangchak Biofuel Co., Ltd	300,000	Ayutthaya
○	Pure Biodiesel Co., Ltd	300,000	Rayong
●	AI Energy Co., Ltd	250,000	Samutsakhon
○	New Biodiesel Co., Ltd	220,000	Suratthani
○	Verasuwan Co., Ltd	200,000	Samutsakhon
●	B. Grimm Green Power Limited	200,000	Chumphon
○	E-Ester Co., Ltd	50,000	Chiangrai
●	Bangchak Petroleum Plc	50,000	Bangkok
●	Bangkok Produce Plc	4,000	Saraburi
	Total	6,009,800	

Source: DEDE (updated) Jan, 2011

Current Feedstock for biodiesel production in Thailand

1. Crude palm oil (CPO)
(FFA $\approx$ 10%)



2. Refined bleach and deodorized palm oil (RBDPO)
(FFA $\approx$ 0.1%)



Current Feedstock for biodiesel production in Thailand (Continue)

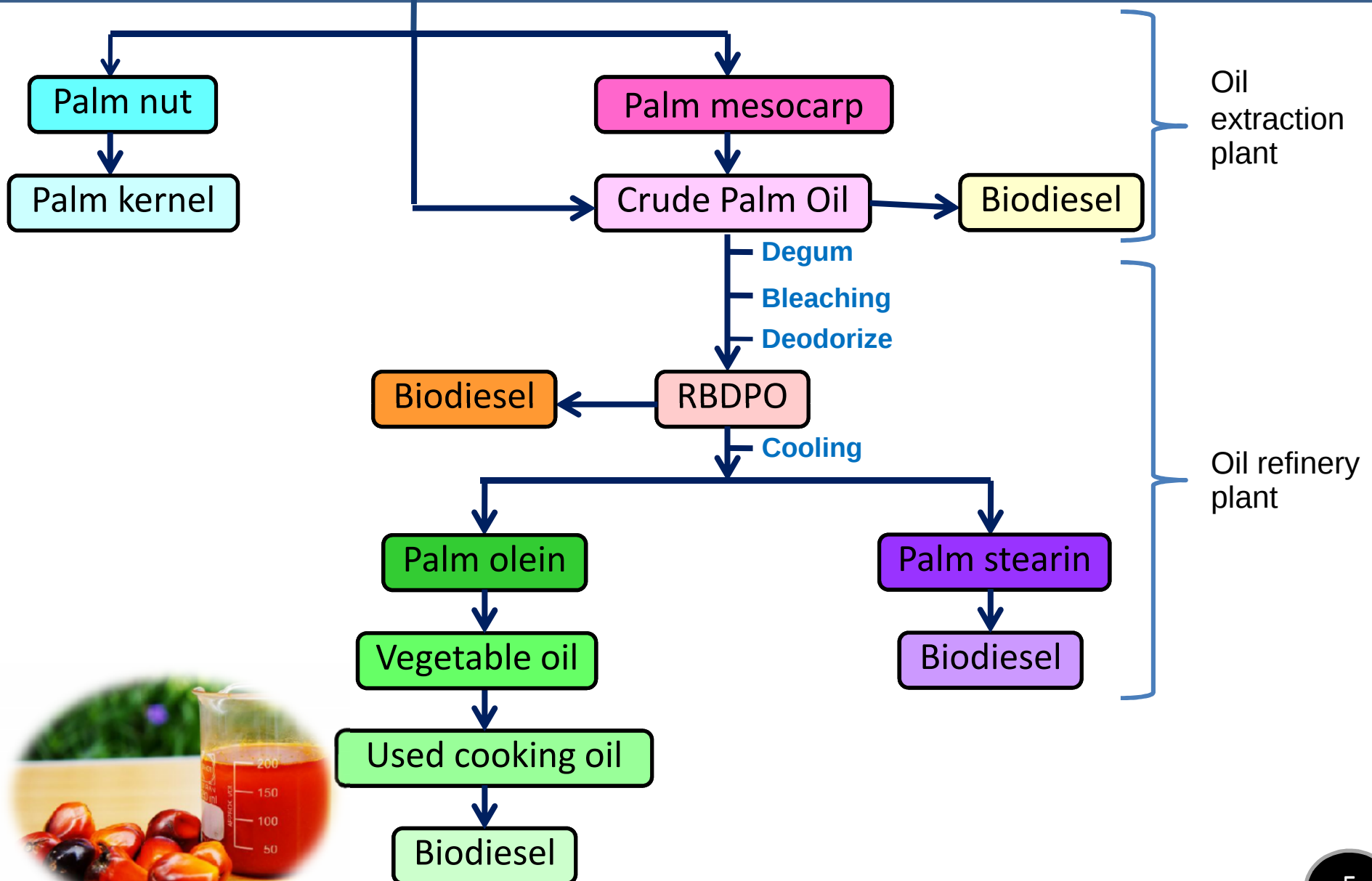
3. Palm stearin
(FFA $\approx$ 0.1%)



4. Used cooking oil
(FFA $\approx$ 0.5–2%)



Palm Fruits



Fatty acid composition of feedstocks

Fatty acid	CPO	Palm stearin	RBDPO	Used Cooking Oil
Lauric (C ₁₂)	0.35	0.25	0.32	1.02
Myristic (C ₁₄)	0.92	1.27	0.94	1.43
Palmitic (C ₁₆)	44.11	59.19	42.83	31.37
Palmitoleic (C _{16:1})	-	-	0.14	1.74
Stearic (C ₁₈)	4.36	4.43	4.43	4.89
Oleic (C _{18:1})	38.97	28.61	39.59	40.14
Linoleic (C _{18:2})	11.21	5.86	9.40	16.99
Arachidic (C ₂₀)	-	-	0.35	1.46
Lignoceric (C ₂₄)	-	-	1.69	-
Sum of saturated FA	49.74	65.14	50.56	40.17
Sum of unsaturated FA	50.18	34.47	49.13	58.87
FFA	8-10	0.1	0.1	0.5-2

Another feedstock : Jatropha oil and mixed crude palm oil

Fatty acid composition

Fatty acid	Lauric (C ₁₂)	Myristic (C ₁₄)	Palmitic C ₁₆	Stearic (C ₁₈)	Oleic (C _{18:1})	Linoleic (C _{18:2})	Linoleic (C _{18:3})	Sum of saturated FA	Sum of unsaturated FA	FFA (%)
Jatropha oil	-	-	14.85	7.43	47.65	29.80	0.19	22.28	77.64	5-15



Jatropha seed and oil



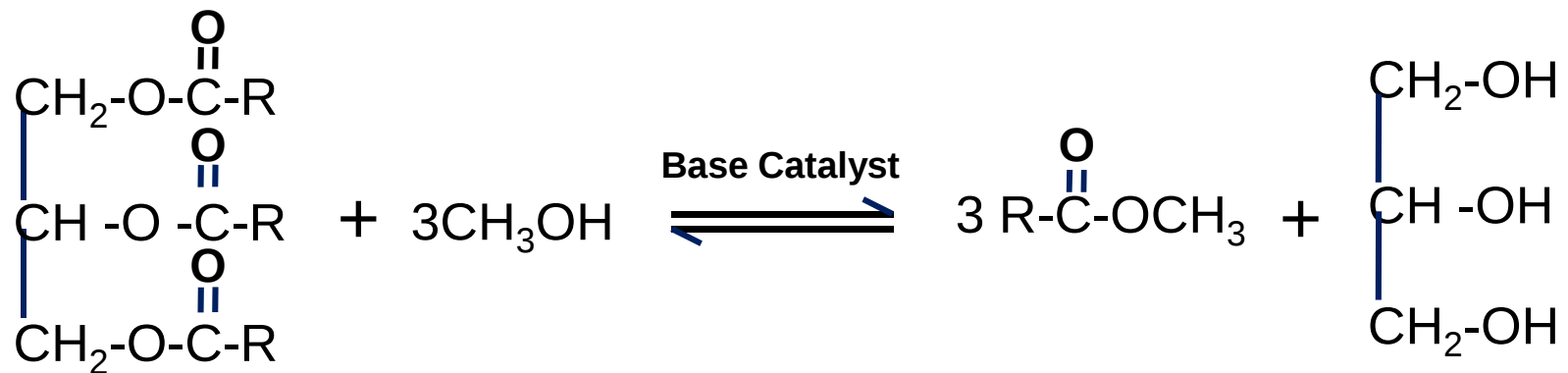
Palm fruit and mixed CPO
(FFA 8-10%)

Small oil extraction plant (300 kg/h)



Chemical Reaction for biodiesel production

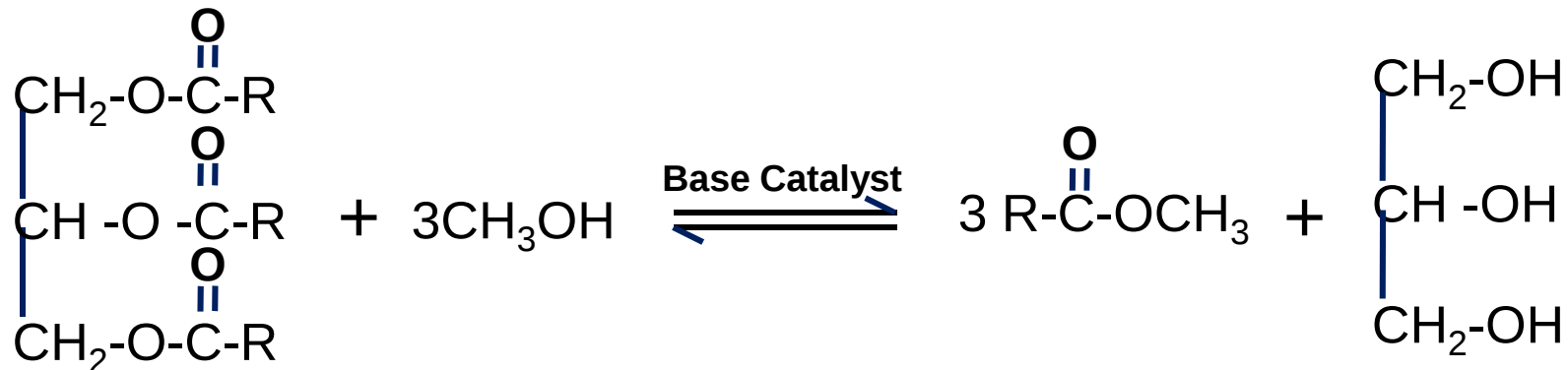
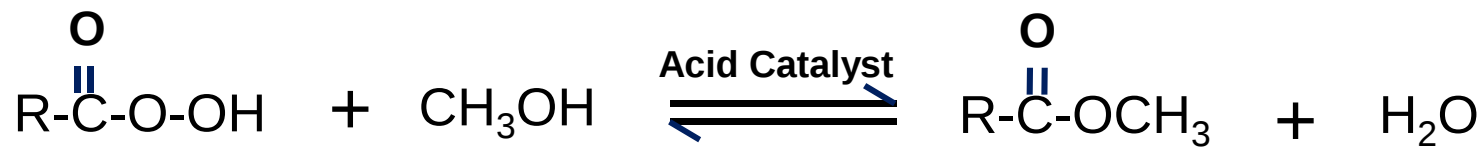
1. Transesterification reaction



➤ This reaction used with RBDPO, Palm stearin, Used cooking oil (FFA < 2%)

Chemical Reaction for biodiesel production (Continue)

2. Esterification reaction + Transesterification reaction



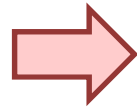
➤ These reactions used with CPO, mixed CPO, Jatropha curcas oil (FFA > 2%)

Biodiesel production process



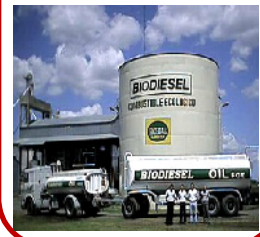
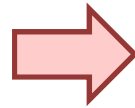
Plantation

Palm Fruit



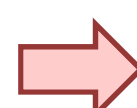
Crushing Mill

CPO



Biodiesel Plant

B 100



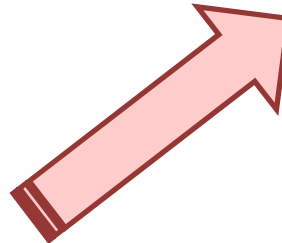
Oil Company



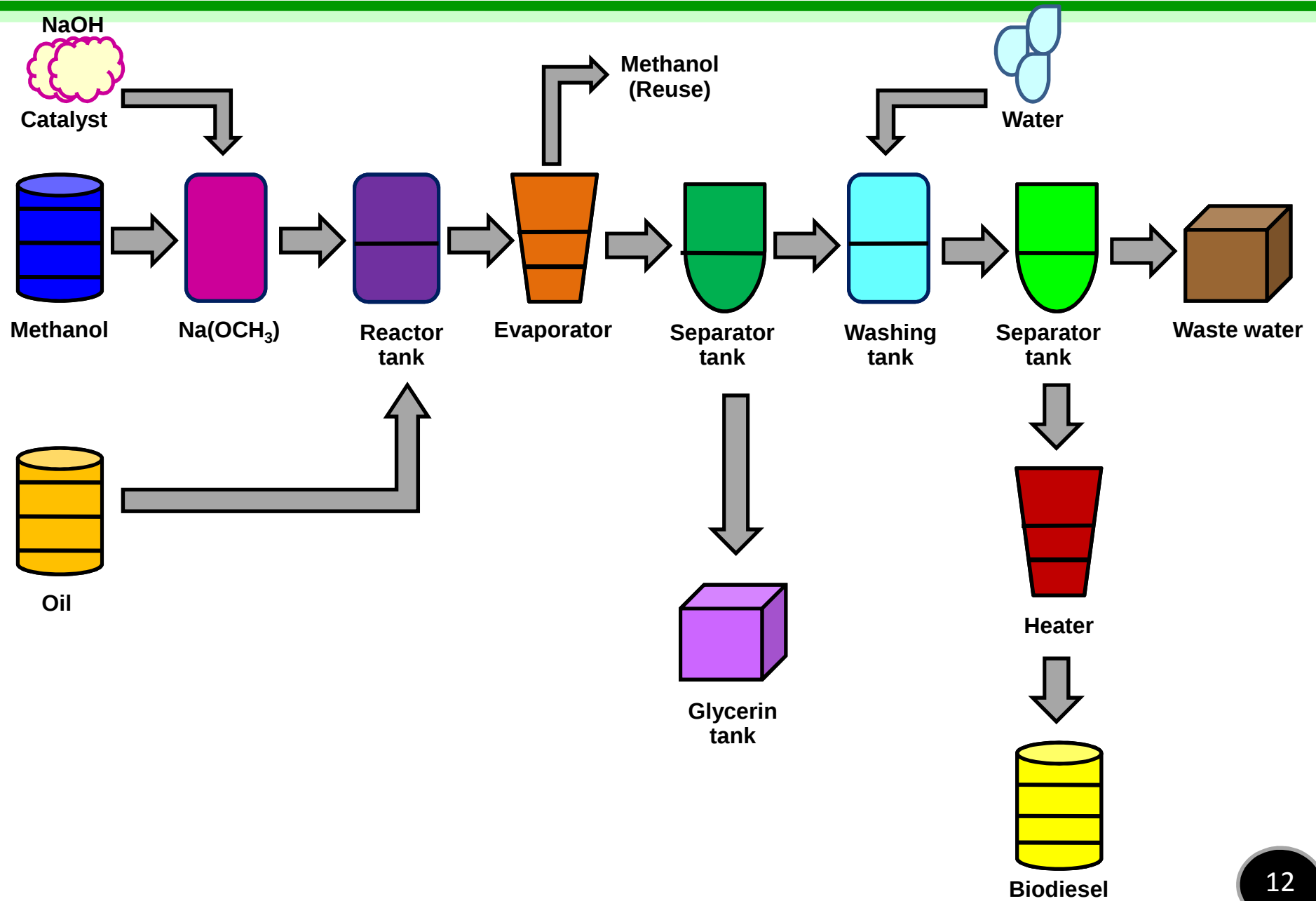
Car



Used cooking oil



Biodiesel Plant Diagram



Catalyst for biodiesel production

1. Homogeneous catalyst

- ☐ For transesterification : NaOH, KOH and NaOCH₃
- ☐ For esterification : H₂SO₄, HCl

2. Heterogeneous catalyst

- ☐ For transesterification : CaO from egg shell, Ca(OCH₃)₂ from quick lime
- ☐ For esterification : No research study

➤ Right now biodiesel production in Thailand only used homogenous catalyst



Biodiesel Purification

❑ To remove glycerol, soap, methanol and catalyst

1. Washing with water
2. Washing with ion exchange resin (IOWATIT GF 202)

➤ For washing with water, water can be reused by water treatment with microfiltration and reverse osmosis

Value-added glycerol

- ✓ Refined glycerol with purity > 95% and 99.7%
- ✓ Diglycerol and Triglycerol

Biodiesel Thailand – B100 Spec.

	Parameter	Unit	Standard limit	
1	Methyl Ester	% wt.	min	96.5
2	Density @15 °C	Kg/m ³	min	860
		-	max	900
3	Kinematic Viscosity @ 40 °C	Cst	min	3.5
		-	max	5.0
4	Flash Point	°C	min	120
5	Sulphur Content	mg/kg	max	0.0010
6	Carbon Residue on 10% distillation residue	% wt.	max	0.30
7	Cetane Number	-	min	51
8	Sulphated Ash	% wt .	max	0.02
9	Water Content	% wt .	max	0.05 max
10	Total Contaminate	% wt .	max	0.0024
11	Copper Strip Corrosion	-	max	No.1
12	Oxidation stability @ 110 °C	Hours	10 min	6 min

Biodiesel Thailand – B100 Spec. (Cont.)

	Parameter	Unit	Standard limit	
13	Acid Value	mg KOH/g	max	0.5
14	Iodine Value	g I ₂ /100g	max	120
15	Linolenic Acid Methyl Ester	% wt .	max	12.0
16	Methanol	% wt .	max	0.2
17	Monoglyceride	% wt .	max	0.80
18	Diglyceride	% wt .	max	0.20
19	Triglyceride	% wt .	max	0.20
20	Free glycerin	% wt .	max	0.02
21	Total glycerin	% wt .	max	0.25
22	Phosphorus	% wt .	max	0.0010
23	Sodium plus Potassium	mg/kg	max	5.0
24	Calcium plus Maganesium	Mg/kg	max	5.0
25	Additive	°C	Approved by DG of DOEB	

* DOEB : Department of energy business



Improvement of BD quality to meet Thai biodiesel standard

1. Increasing of oxidation stability

- Add antioxidant (TBHQ, BHA)

2. Decreasing of calcium and magnesium content

- Use soft water for water washing

3. Decreasing of water content

- Increase the duration of heating time

4. Decreasing of carbon residue on 10% distillation residue

- Add antioxidant (TBHQ)

Research on heterogeneous catalyst



Quick Lime

- Calcinations
- React with CH_3OH



$\text{Ca}(\text{OCH}_3)_2$



Calcium methoxide as highly effective catalyst for biodiesel production

Synthesis of catalyst



Quick lime was ground manually using mortar and pestle



60 Mesh screen



quick lime powder

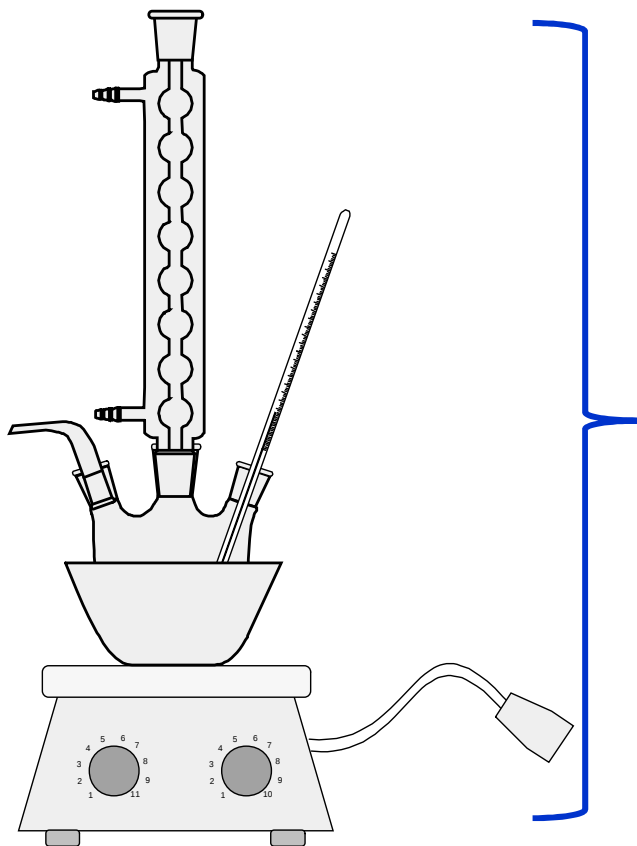
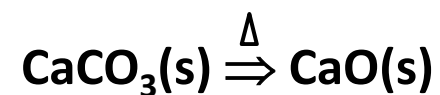
Synthesis of catalyst



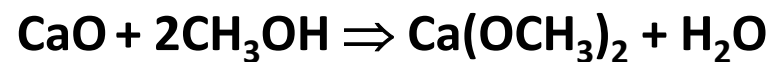
Quick lime powder



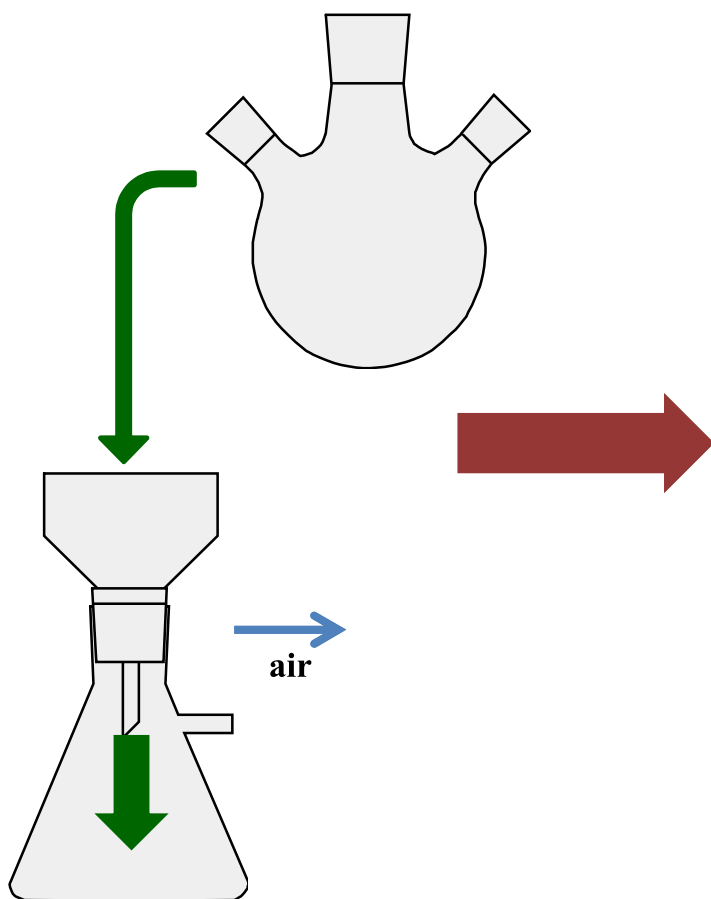
**Calcine at 700 °C for
3.0 h**



**5g calcined product was reacted
with 150 mL methanol under reflux
at 65 °C for 2 h and continuous
stirring 1500 rpm**



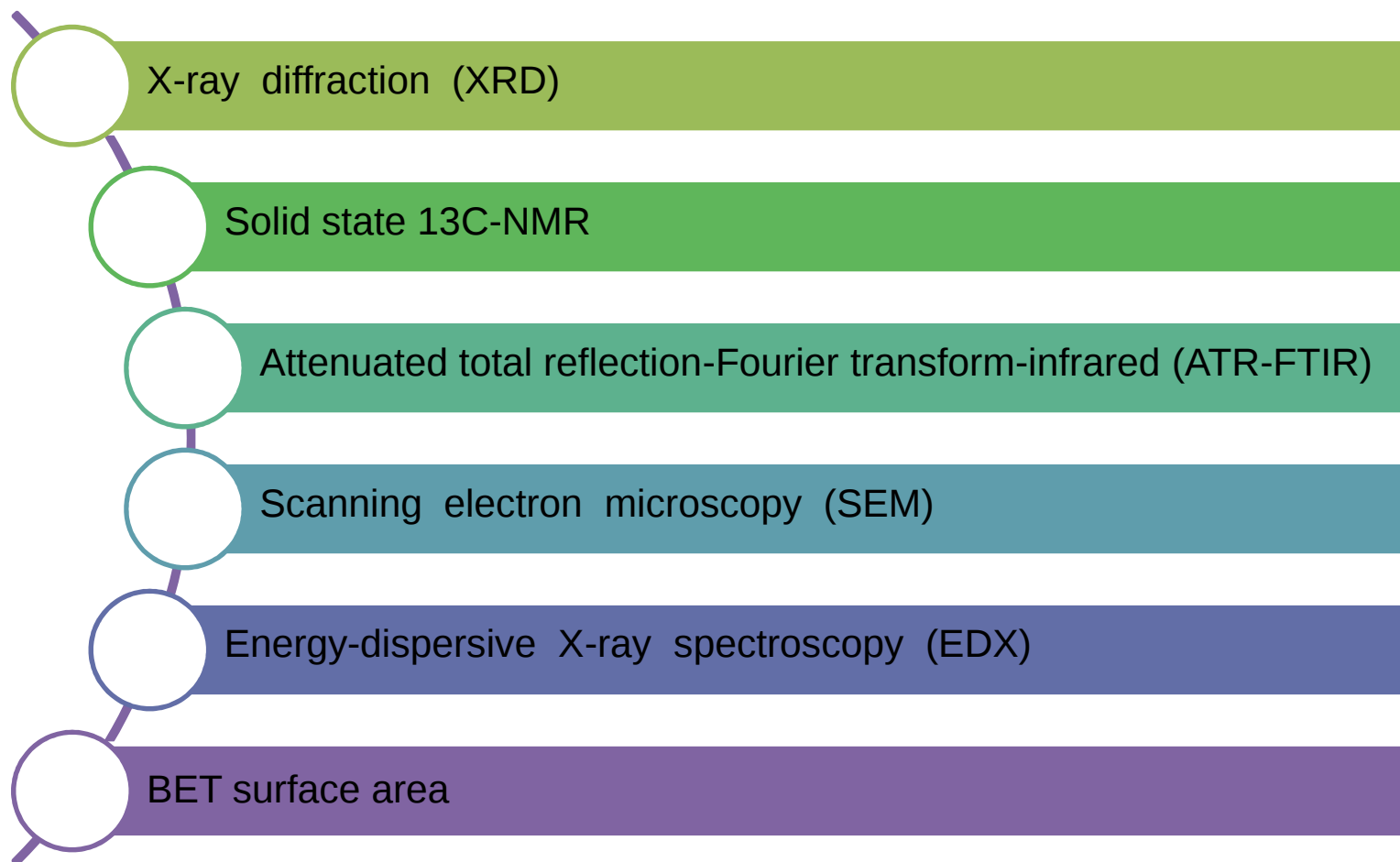
Synthesis of catalyst



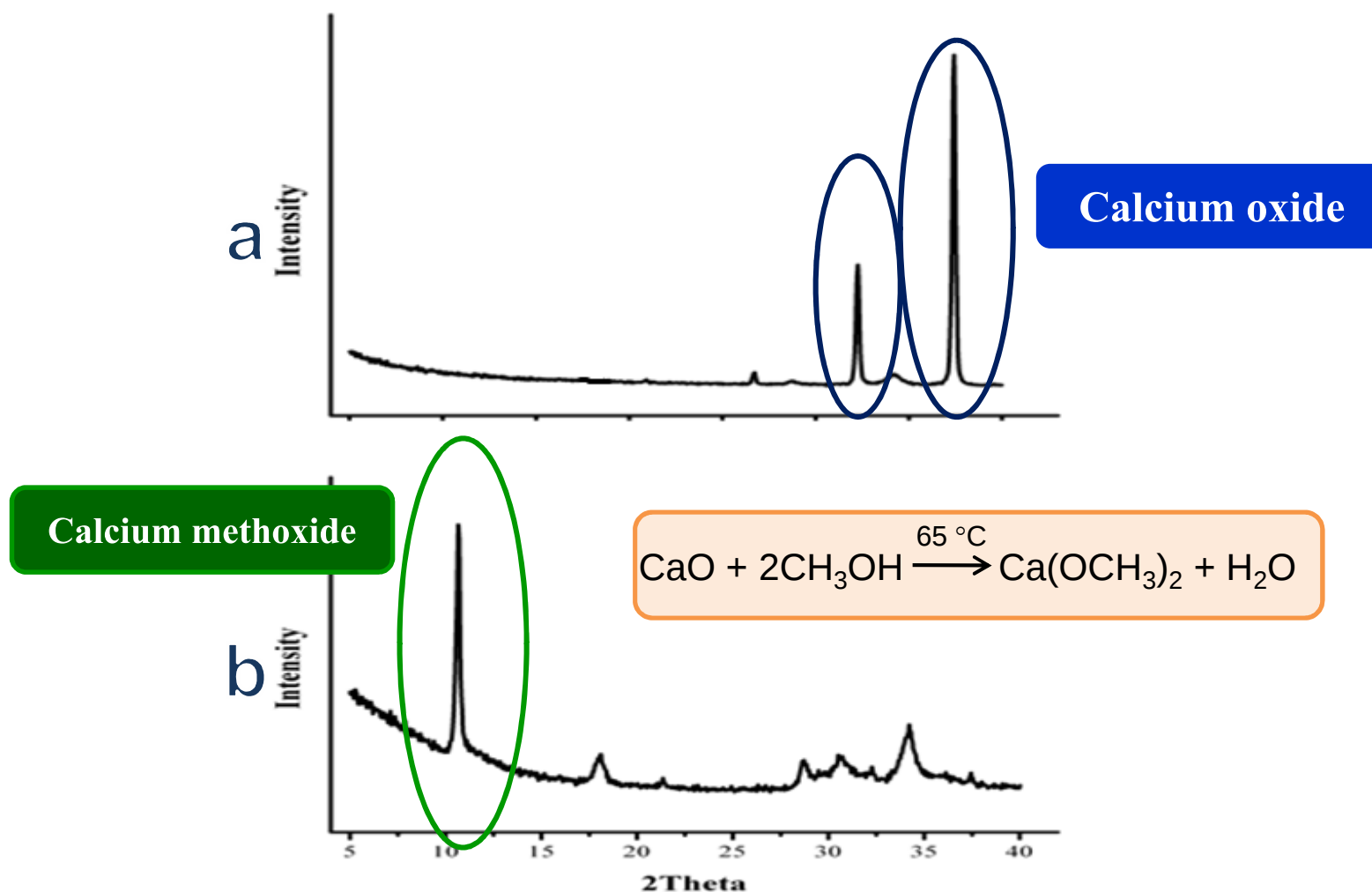
**Dried in the oven at
105 °C for 1 h**



Catalyst characterization

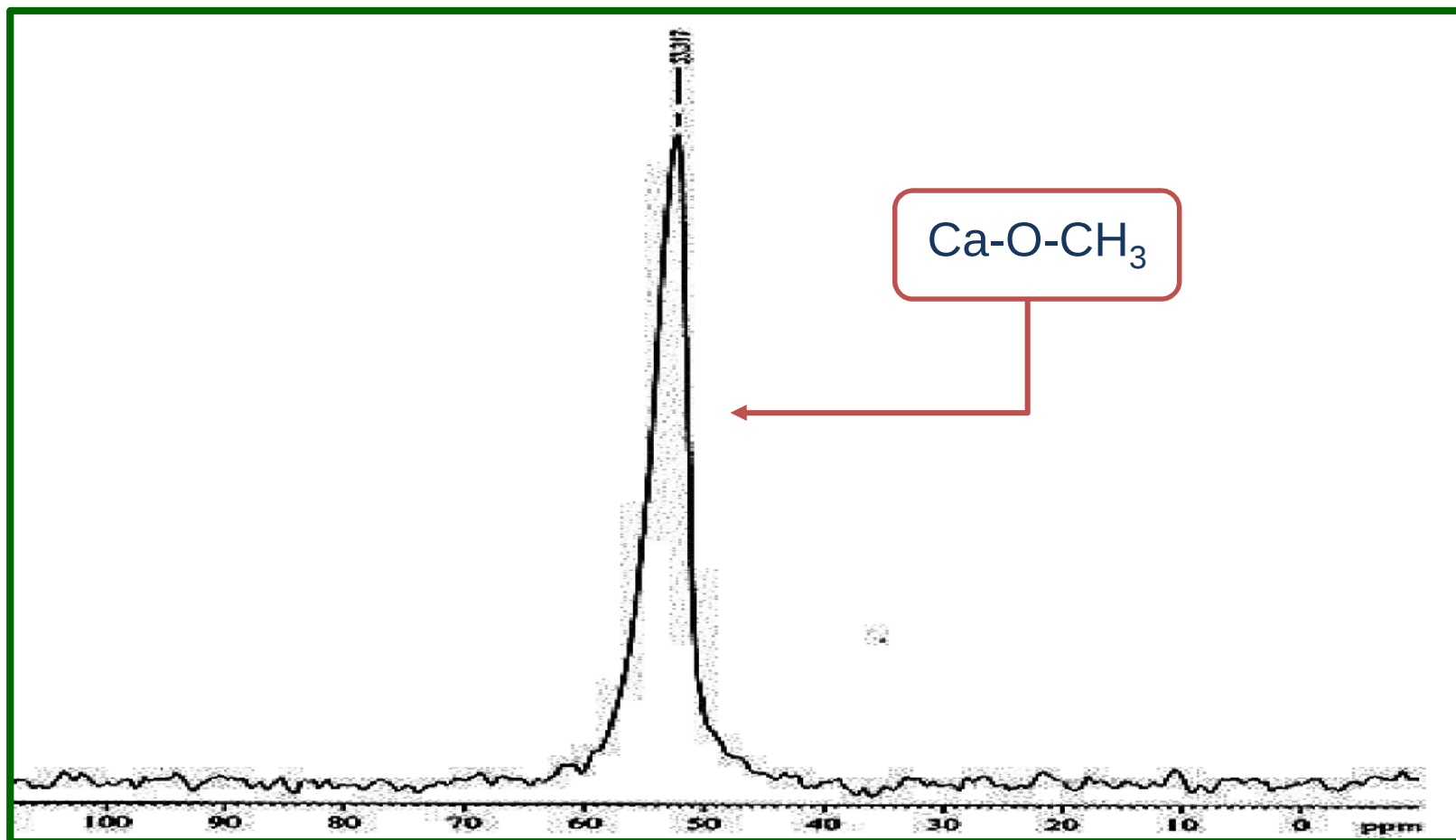


Characterizations of the synthesized catalyst



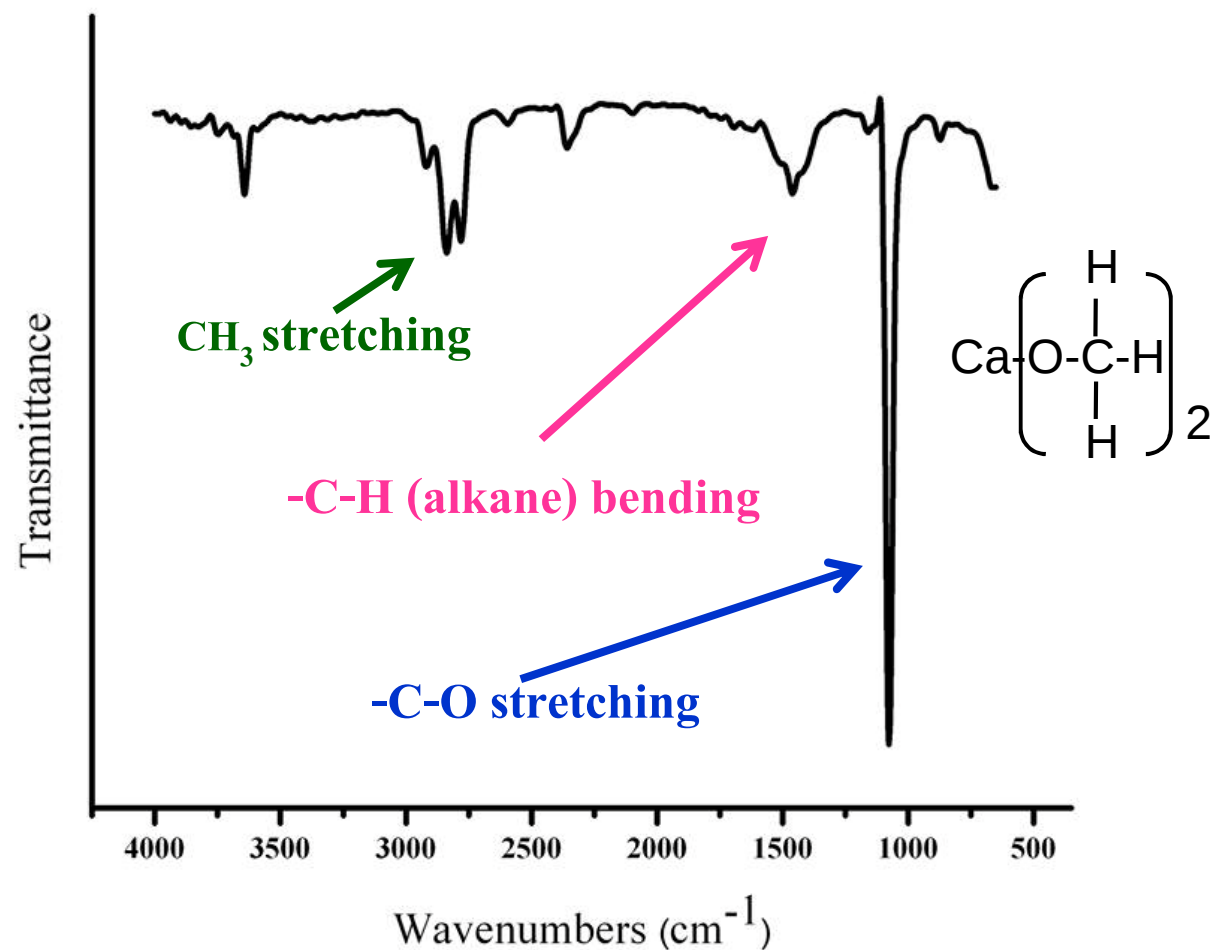
1. XRD patterns of (a) calcined quick lime; (b) calcium methoxide product.

Characterizations of the synthesized catalyst



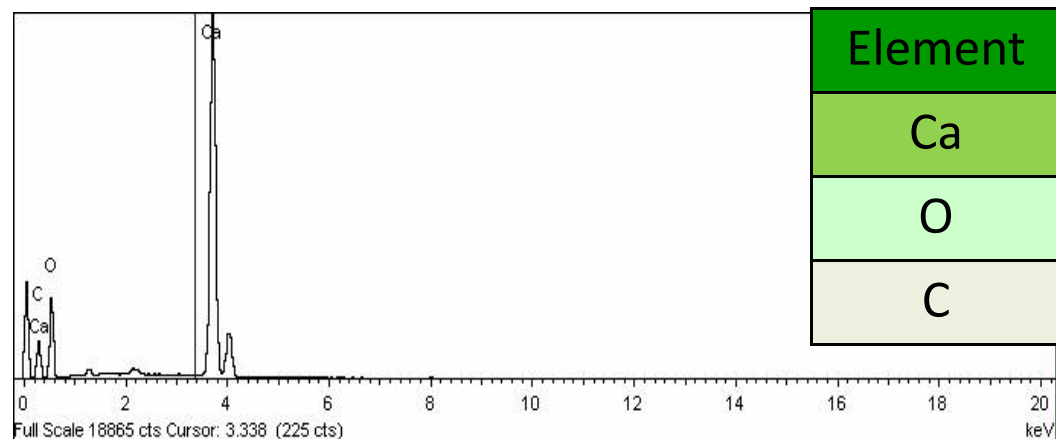
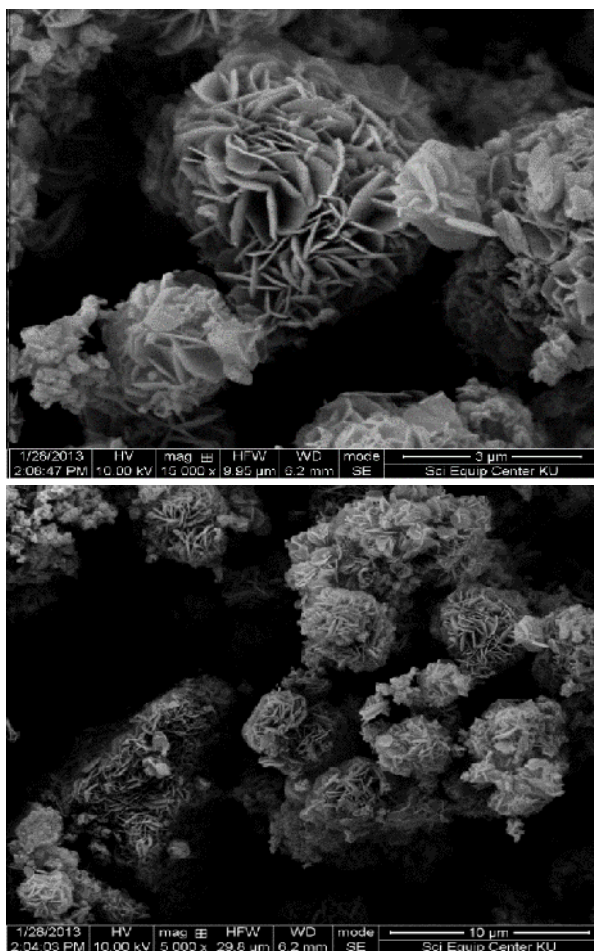
2. Spectra of solid state ^{13}C -NMR of calcium methoxide.

Characterizations of the synthesized catalyst



3. FTIR spectrum of calcium methoxide.

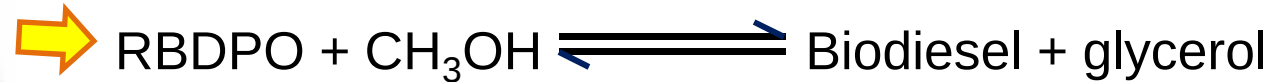
Characterizations of the synthesized catalyst



Properties	results
BET surface area (m ² /g)	38.46
Total pore volume (cm ³ /g)	0.33
Average pore diameter (nm)	34.39

4. SEM images, EDX spectrum and BET of calcium methoxide.

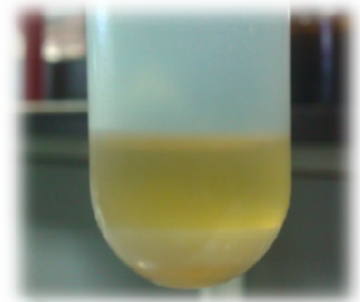
Biodiesel production



The reaction mixture was centrifuged



Biodiesel separation from glycerol and catalyst



The FAME (%) in biodiesel was analyzed by gas chromatography (GC)

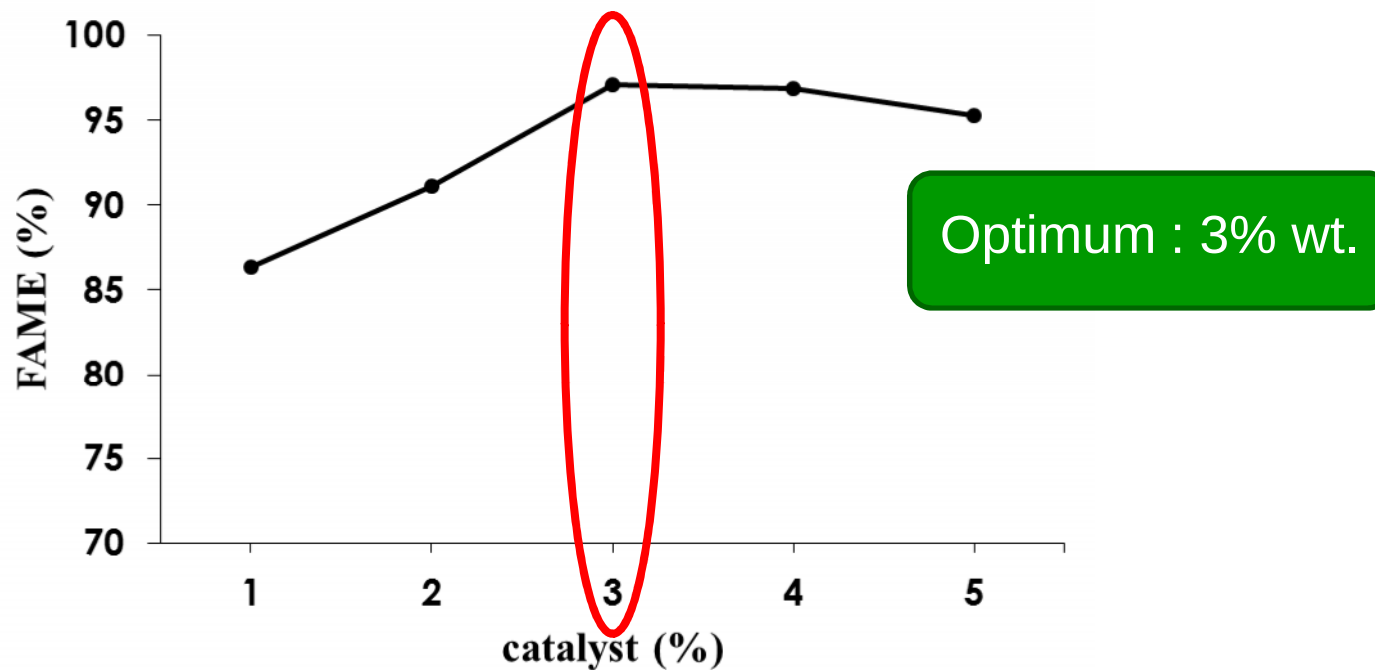




Variation effects on Transesterification

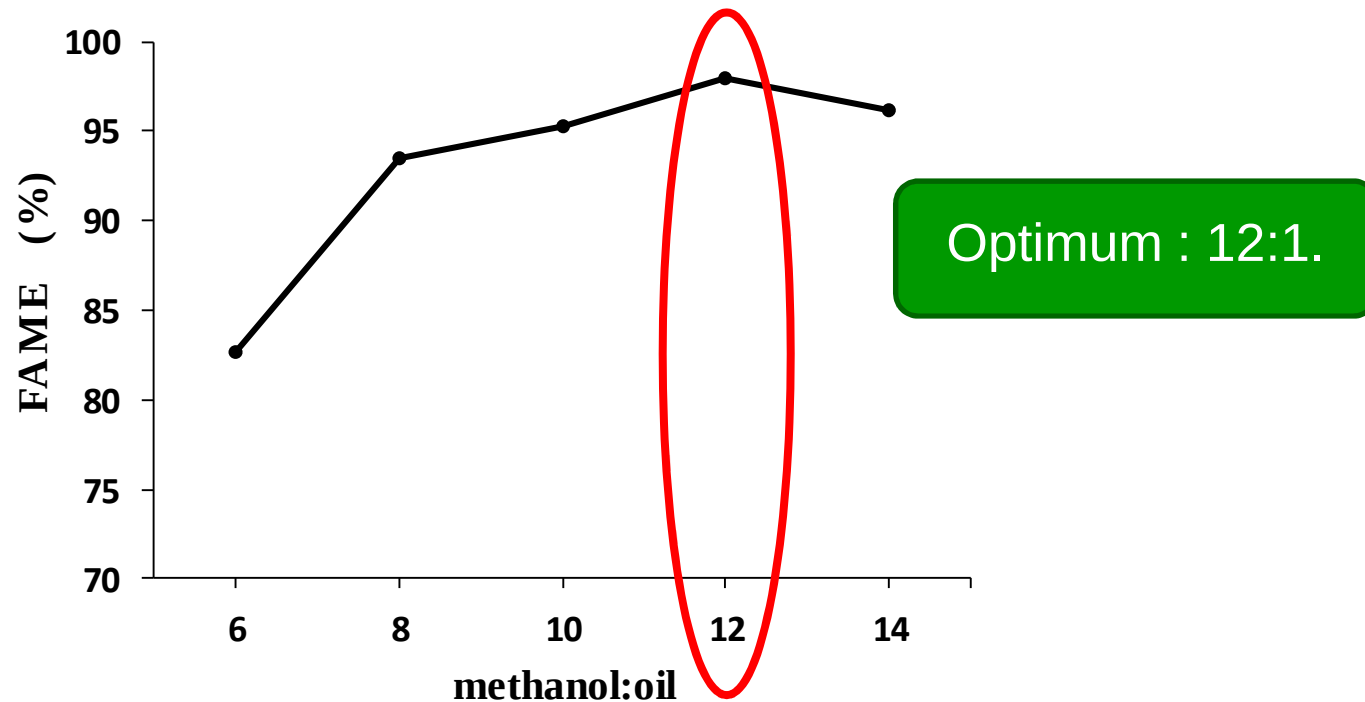
1. Catalyst concentration (1 to 3%wt.)
2. Methanol to oil molar ratio (6:1 to 12:1)
3. Reaction time (1 to 5 h)
 - ❖ Constant temperature at 65 °C
 - ❖ Constant stirring rate at 750 rpm

Catalyst concentration



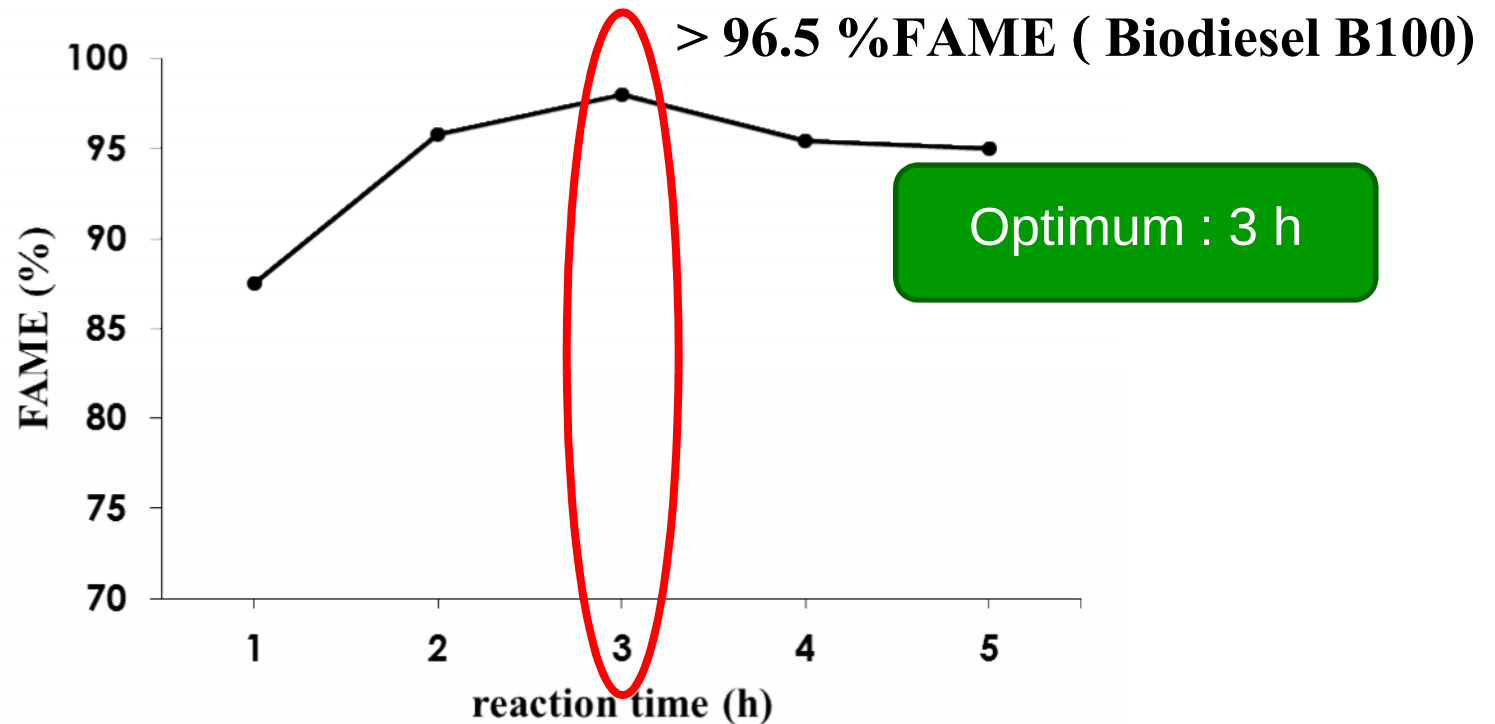
Effect of catalyst concentration on FAME(%), reaction time, 3h ;
methanol:oil molar ratio, 12:1 ; reaction temperature, 65 °C.

Methanol to oil molar ratio



Effect of methanol to oil molar ratio on FAME(%), catalyst concentration, 3% ; reaction time, 3h ; reaction temperature, 65 °C.

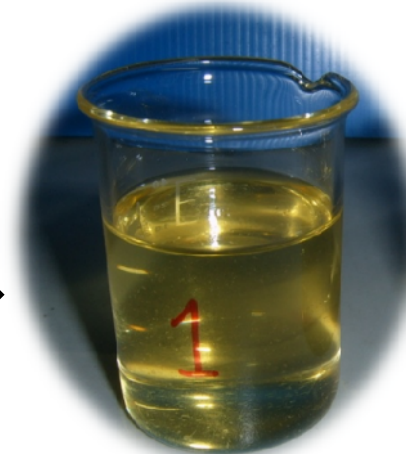
Reaction Time



Effect of reaction time on FAME(%), catalyst concentration, 3% ;
methanol:oil molar ratio, 12:1; reaction temperature, 65 °C.

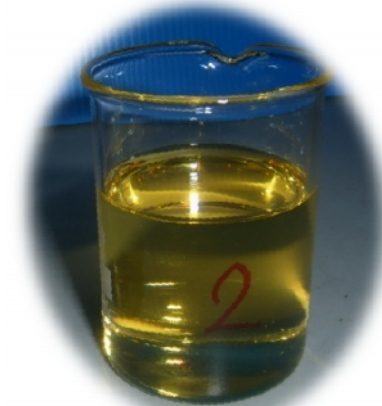
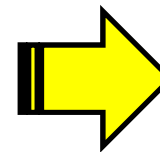
Optimum condition

65 °C, 12:1 methanol to oil
molar ratio, 3% wt. catalyst, 3 h
reaction time FAME = 97%



BD from solid catalyst

60 °C, 6:1 methanol to oil
molar ratio, 1% wt. catalyst, 1
h reaction time FAME = 98%



BD from liquid catalyst

Conclusion

1. Biodiesel in Thailand is mainly up to government 's policy
2. Palm oils (CPO, mixed CPO, RBDPO, Palm stearin) are the main raw materials in Thailand
3. Biodiesel must meet 24 parameter of Thai biodiesel standard
4. Green chemistry is one of the key of sustainability
 - ❑ Solid catalyst
 - ❑ Value added (glycerin, Vit A, Vit E)





For more information, please contact
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THANK YOU VERY MUCH

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