TNChE Asia 2023

TIChE

ศูนย์เชื้อเพลิงและพลังงานจากชีวมวล
Center of Fuels and Energy from Biomass

Biomass to Biofuels: Technology & Challenges

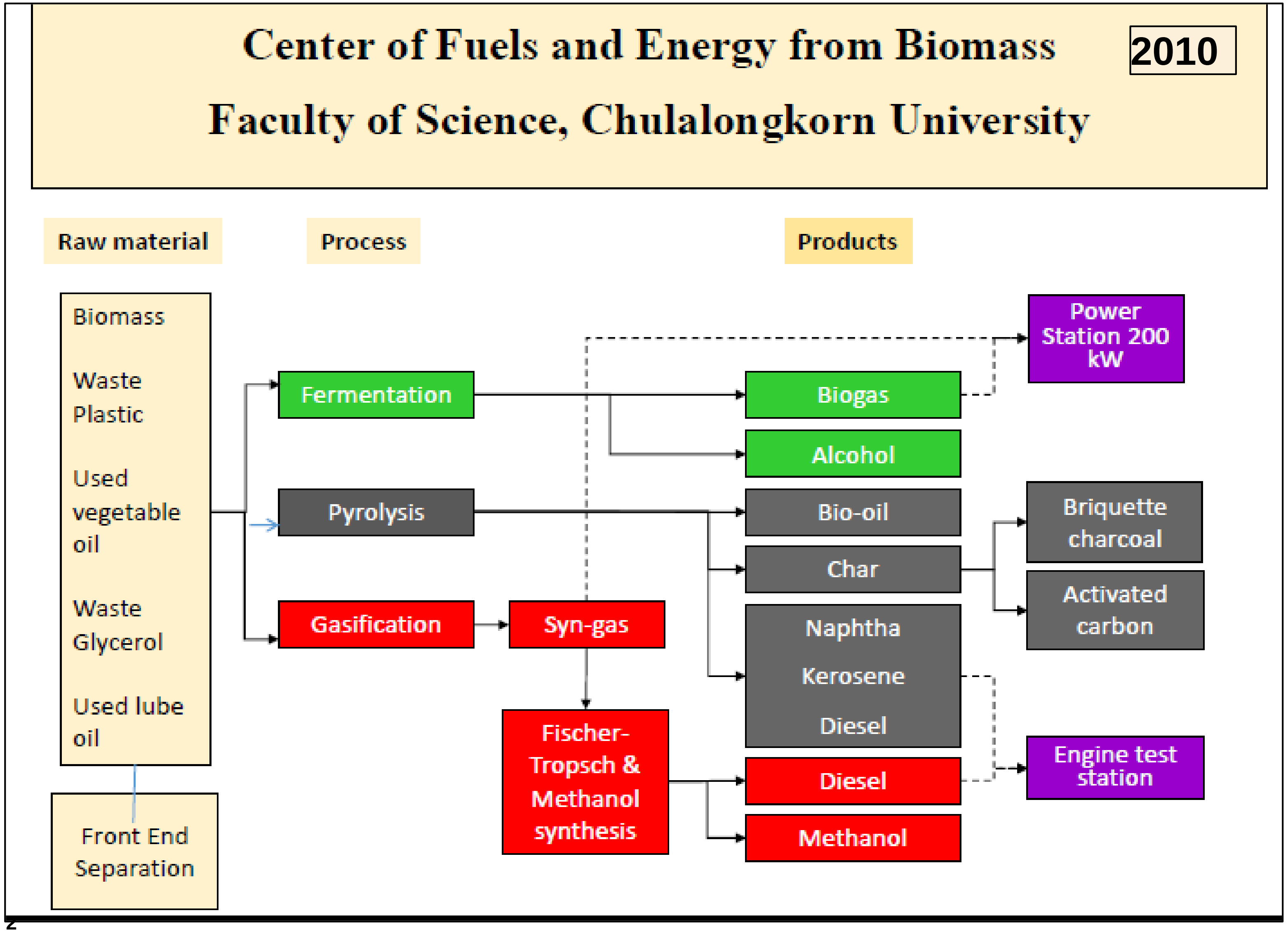
Prof. Dr. Tharapong Vitidsant

Director of Fuels and Energy from Biomass Center

Chulalongkorn University

June 22nd, 2023 Royal Criff Hotel Pattaya, Chonburi Province, Thailand

Introduction of Center of Fuels & Energy from Biomass



Center of Fuels and Energy from Biomass

Faculty of Science, Chulalongkorn University

2010

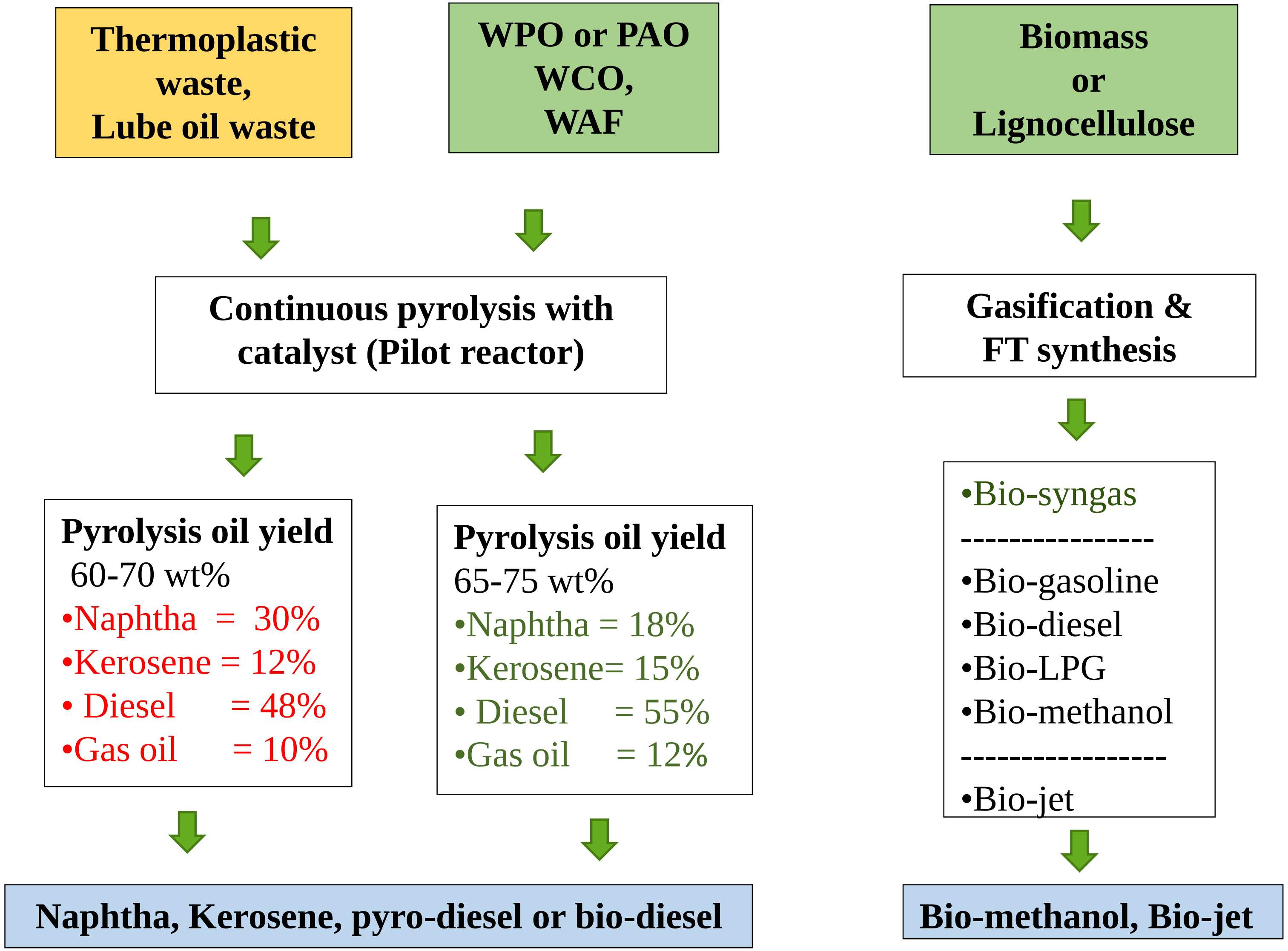
Focus recently on

- Waste plastics to Liquid fuels
- Biomass to Bio-oil + Char + combustible gas via pyrolysis
- Used vegetables oil to diesel by pyrolysis

- Biomass to Liquid Fuels (BTL) and Bio-jet (JICA and NEDO)

- Biomass to Briquette charcoal and Activated carbon

Project supporter: JICA, NEDO, NRCT, TRF, PEA, CU



Thermoplastic waste, Lube oil waste

WPO or PAO WCO, WAF

Continuous pyrolysis with catalyst (Pilot reactor)

Pyrolysis oil yield
60-70 wt%
- Naphtha = 30%
- Kerosene = 12%
- Diesel = 48%
- Gas oil = 10%

Pyrolysis oil yield
65-75 wt%
- Naphtha = 18%
- Kerosene= 15%
- Diesel = 55%
- Gas oil = 12%

Naphtha, Kerosene, pyro-diesel or bio-diesel

Biomass or Lignocellulose

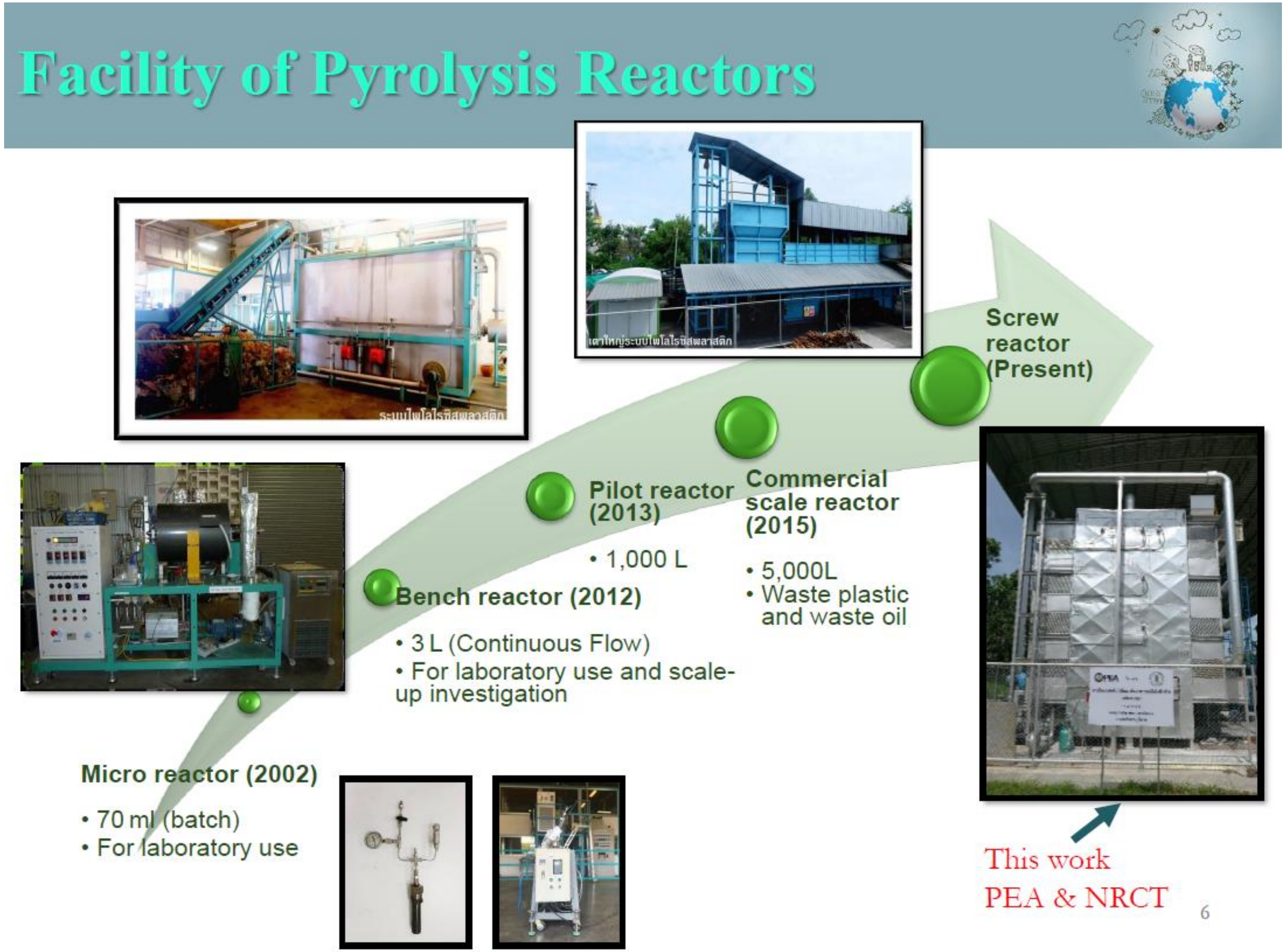
Gasification & FT synthesis

- Bio-syngas

- Bio-gasoline
- Bio-diesel
- Bio-LPG
- Bio-methanol

- Bio-jet

Bio-methanol, Bio-jet



Facility of Pyrolysis Reactors

Micro reactor (2002)

- 70 ml (batch)
- For laboratory use

Bench reactor (2012)

- 3 L (Continuous Flow)
- For laboratory use and scale-up investigation

Pilot reactor (2013)

- 1,000 L

Commercial scale reactor (2015)

- 5,000L
- Waste plastic and waste oil

Screw reactor (Present)

This work
PEA & NRCT

Production of Diesel from Waste Plastic and Waste Vegetable Oil by Pyrolysis from Screw Pilot Reactor

International Symposium on
Feedstock Recycling of Polymeric Materials (e-ISFR)
29-30 November, 2021 Online

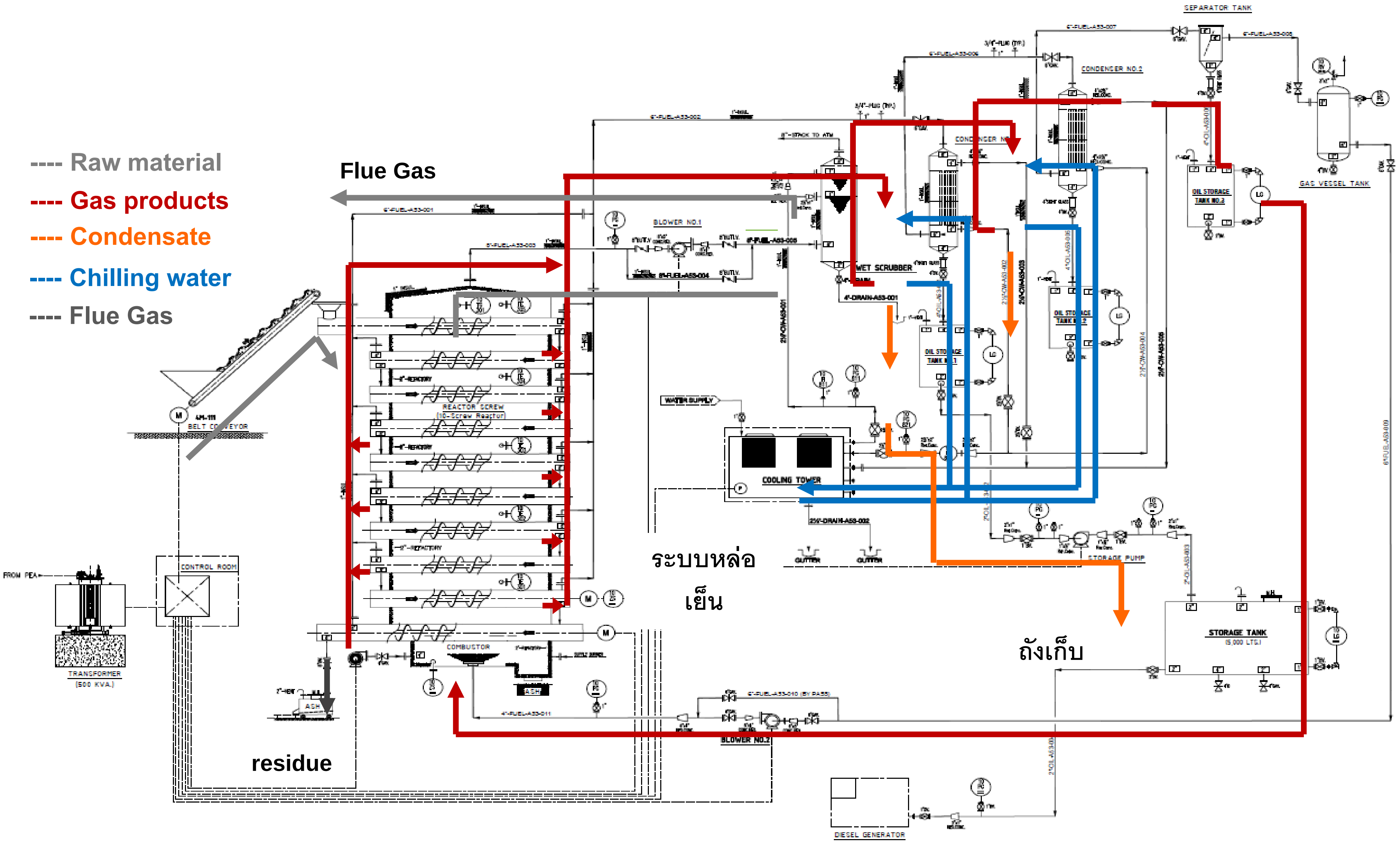
Presented by

Prof. Tharapong Vitidsant

Director of Fuel and Energy from Biomass Center
Faculty of Science, Chulalongkorn University
Bangkok, Thailand

Production of Diesel form Waste Plastic Plot reactor with 2000L/d Supported by PEA

Screw pilot reactor for pyrolysis reaction (4000 Kg feed /d)



---- Raw material

---- Gas products

---- Condensate

---- Chilling water

---- Flue Gas

Flue Gas

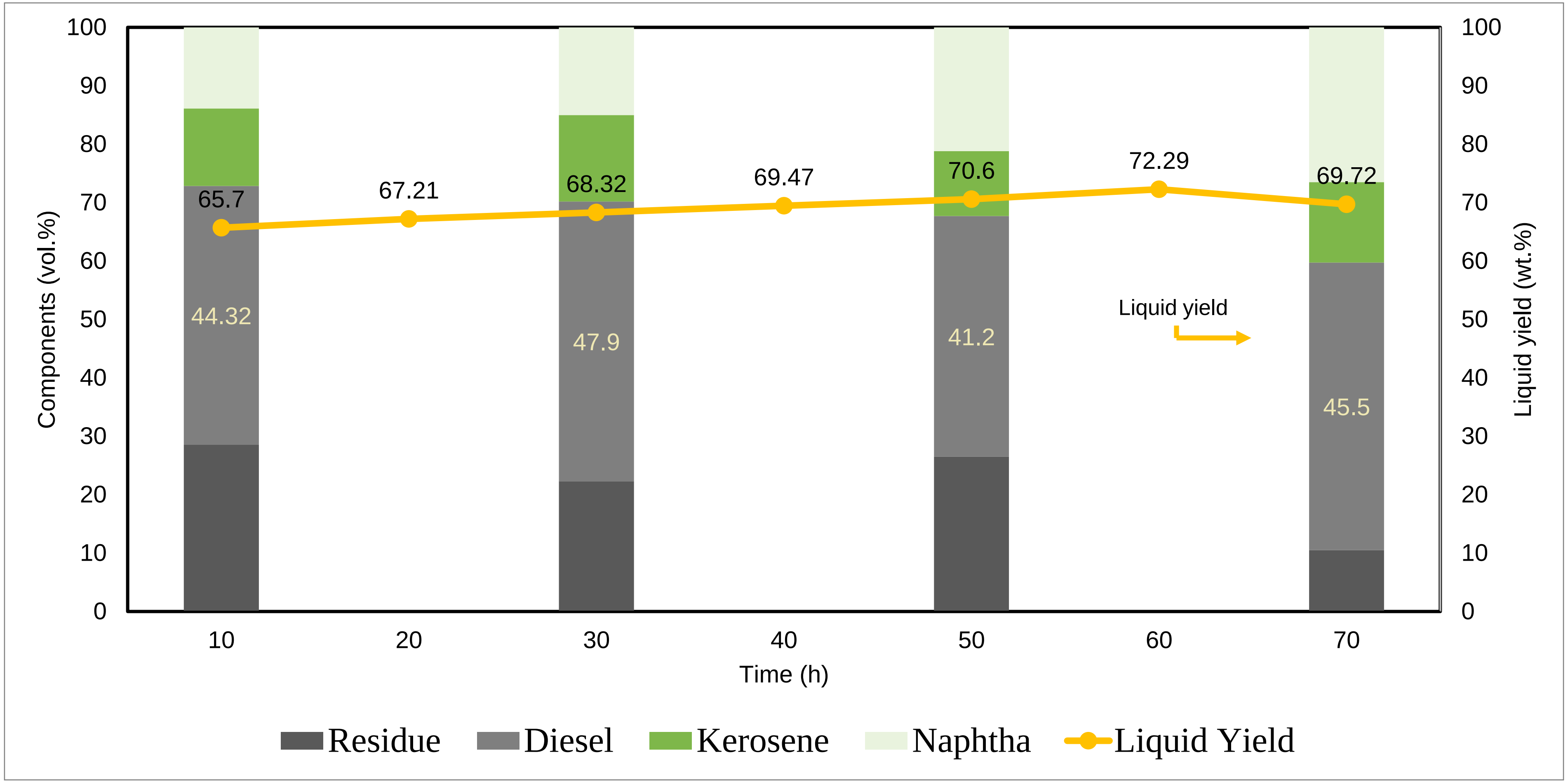
ระบบหล่อเย็น

ถังเก็บ

residue

Continuous operation results

Temperature	430 °C
Operation time	70 h
Total feed	6,100 kg (80 kg/h)
Total liquid product	4,212 kg (69.72 wt%)



Naphtha ~ -32 %
Kerosene ~ 15%
Diesel ~ 45%
Gas oil ~ 8%

First Plastic Waste pyrolysis Oil Shipment to Shell Singapore (PTE) LTD.
15/5/2023

Liquid Fuels for Electricity Generation from Waste Palm Oil and Animals Fat by Catalytic Pyrolysis in Continuous Screw Pilot Reactor

Prof. Dr.Tharapong Vitidsant

Fuels and Energy from Biomass Center, Chulalongkorn University
Bangkok, Thailand

11th INTERNATIONAL SYMPOSIUM ON FEEDSTOCK RECYCLINGOF POLYMERIC MATERIALS 2022
“INTO SUSTAINABILITY AND THE FUTURE OF RECYCLING”
29 November – 2 December 2022Nongnooch Garden Pattaya, Pattaya City, Chonburi, Thailand

Comparison between Transesterification and pyrolysis

	Transesterification	Pyrolysis
Products	FAME	Hydrocarbon, CO_2 ✓
By-product	Glycerol	Non ✓
Reaction time	Long	Shot ✓
Reaction temperature	Low	High X
Catalyst	Homogeneous	Heterogeneous ✓
Washing process	Necessary	Unnecessary ✓

3 Raw material with moisture less than 5%

WPO 20,000 l

UCO 1,000 l

AF 500 l

Screw pyrolysis reactor (800kg feed/d)

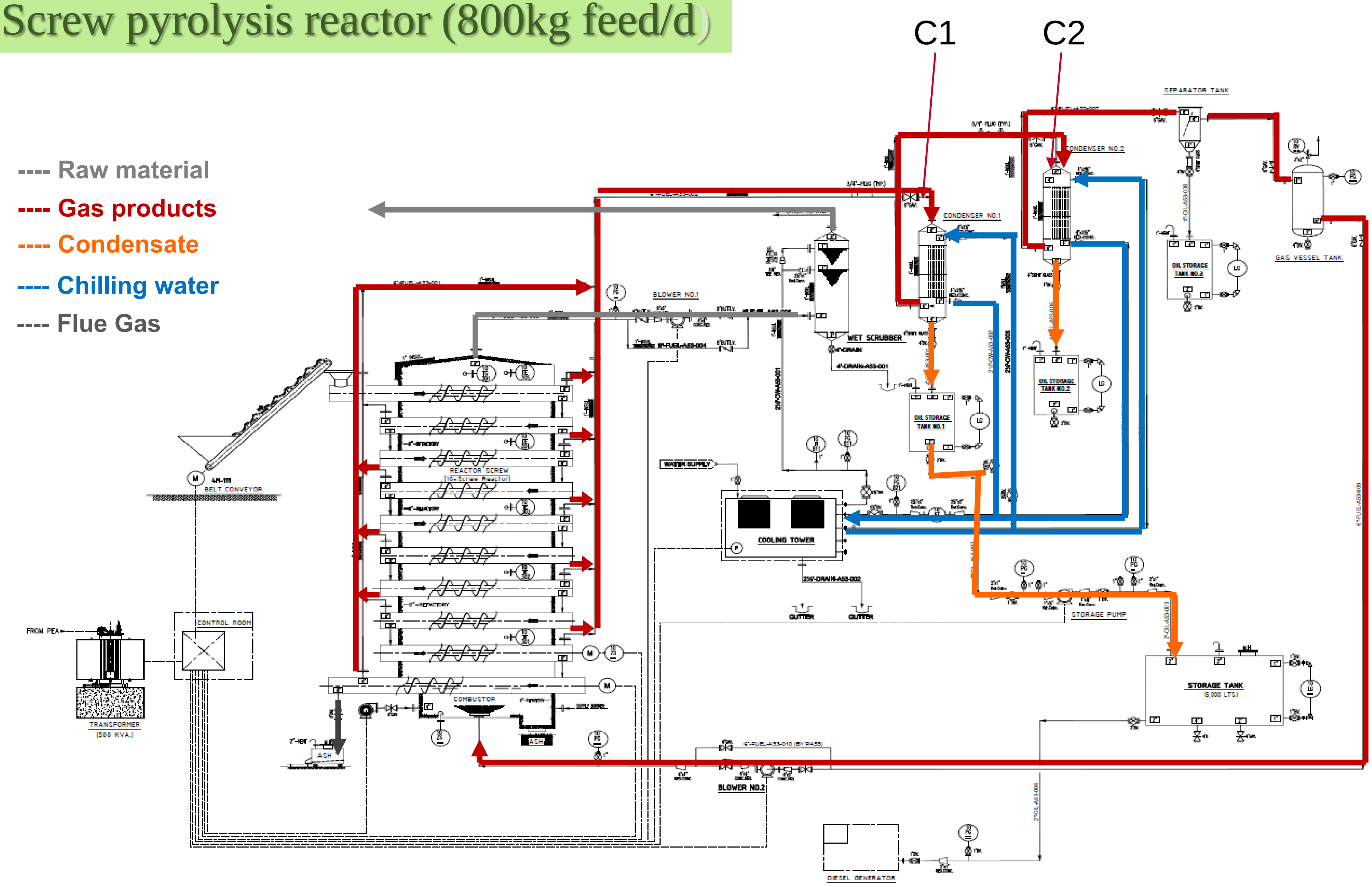
---- Raw material

---- Gas products

---- Condensate

---- Chilling water

---- Flue Gas



Continuous operation
a) daytime และ b) nighttime

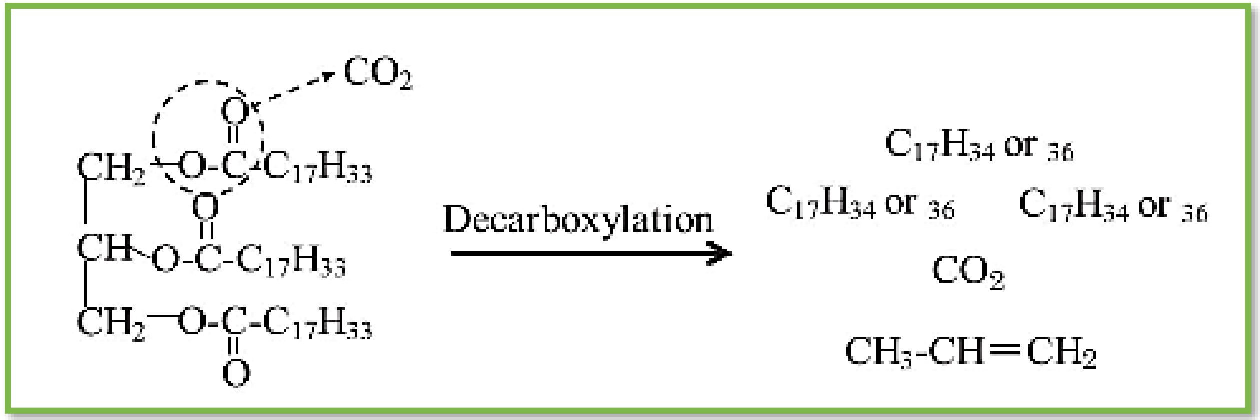
Pyrolysis of waste palm oil (Reactor)

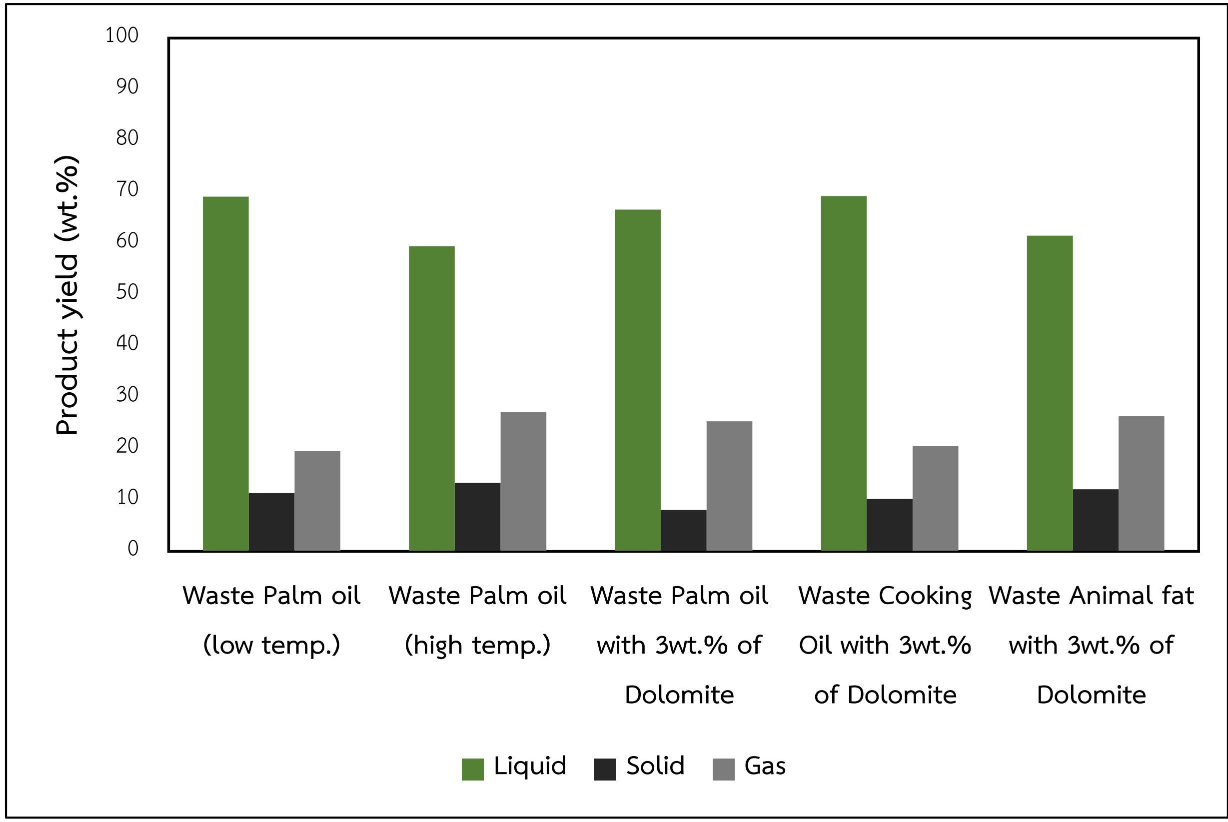
Results and discussion

Experiment in continuous screw reactor

Product yield of different raw material

Raw material	Product yield (wt.%)		
	Liquid	Solid	Gas
Waste Palm oil (425°C))	69.12	11.34	19.54
Waste Palm oil (450°C.)	59.47	13.38	27.15
Waste Palm oil with 3wt.% of Dolomite (425°C)	66.58	8.08	25.34
Waste Cooking Oil with 3wt.% of Dolomite (425°C)	69.25	10.23	20.52
Waste Animal fat with 3wt.% of Dolomite (425°C)	61.52	12.1	26.38

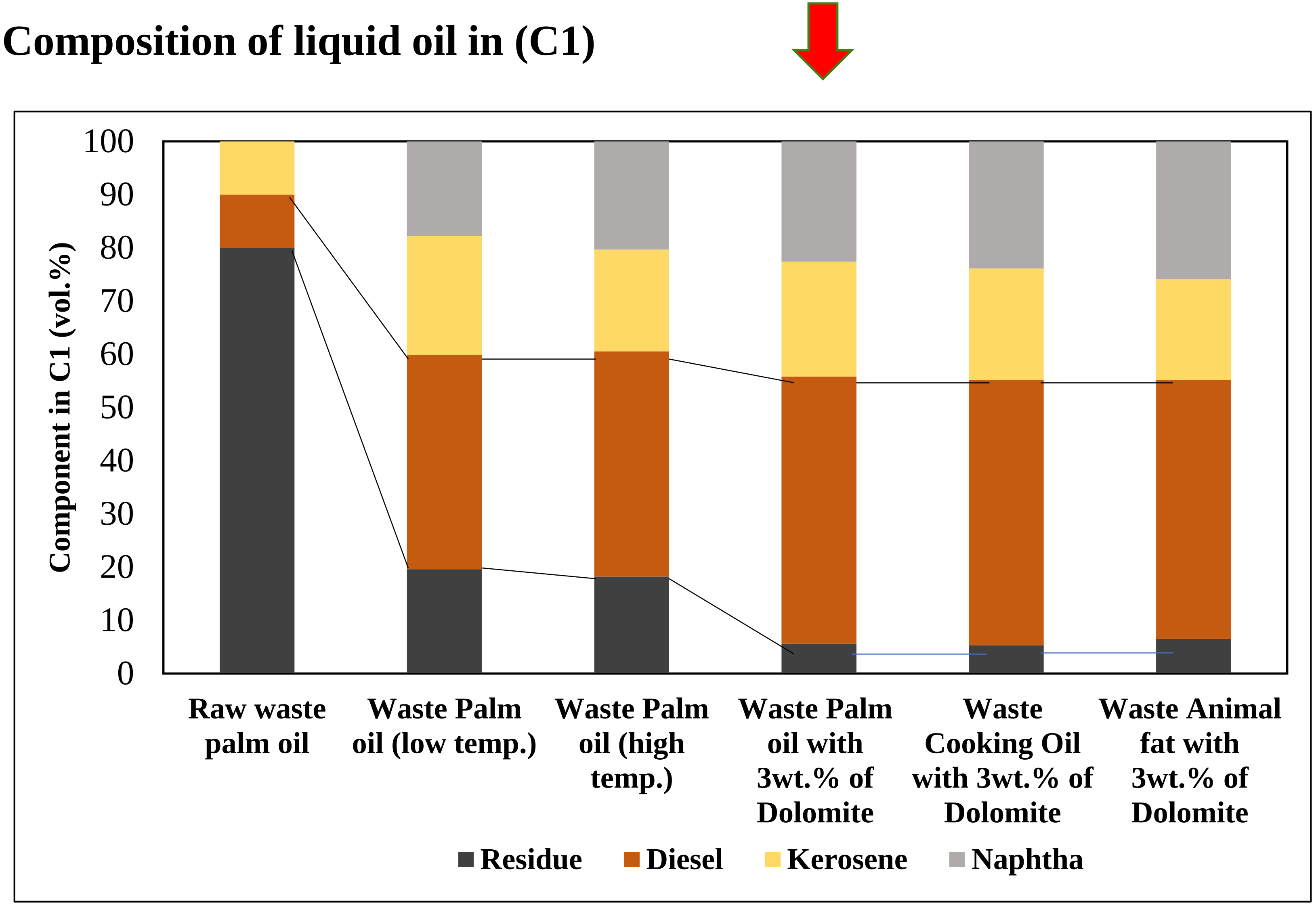




Results and discussion

Experiment in continuous screw reactor

Composition of liquid oil in (C1)



- Naphtha = 22.35%
- Kerosene = 21.12%
- Diesel = 50.90%
- Gas oil = 5.68%

Oil treatment for diesel

Composition (wt %)	**Plastic diesel**		**Palm diesel**		**Conventional Diesel**
	Condenser 1	After removal naphtha	Condenser 1	After removal naphtha	
Naphtha	21.60	**11.59**	22.35	**10.05**	**9.80**
Kerosene	17.92	**19.85**	21.12	**24.82**	**15.40**
Diesel	53.25	**59.55**	50.90	**58.70**	**61.10**
Residue	7.23	**9.01**	5.68	**6.43**	**9.70**

Property of treated pyrolysis oil by removing the excess of naphtha

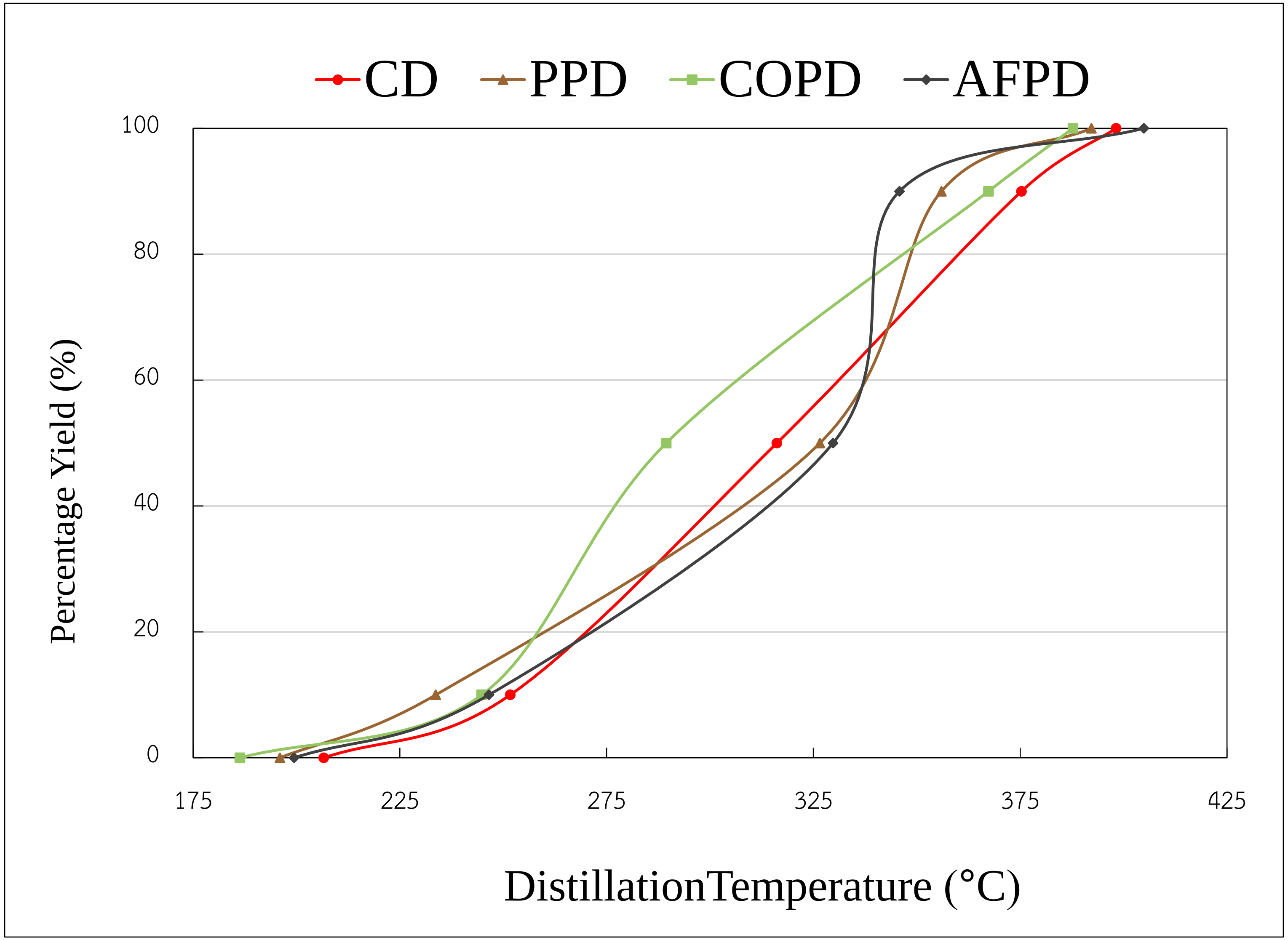
CD = Conventional diesel
PPD = Palm pyrolysis Diesel
COPD = Cooking oil pyrolysis diesel
AFPD = Animal fat pyrolysis diesel

Properties	Method	Diesel(CD)	PPD)	COPD)	AFPD
1.Density at 15 °C (kg/m^3)	ASTM D 1298	827.48	823.65	820.43	816.78
2.Kinematic Viscosity at 40 °C cSt	ASTM D 613	3.44	3.08	3.12	3.22
3.Heat Value (MJ/kg)	ASTM D 445	44.864± 0.295	41.300± 0.158	42.612± 0.203	44.160± 0.198
4.Carbon (%wt)		82.45 ± 0.66	79.23 ± 0.36	80.65 ± 0.53	81.21 ± 0.44
5.Hydrogen (%wt)		17.48± 0.02	17.68 ± 0.15	16.98 ± 0.25	15.42 ± 0.31
6.Nitrogen (%wt)		0.07 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00
7.Oxygen (by difference)		-	2.07 ± 0.02	3.02 ± 0.02	2.82 ± 0.06
7.API Gravity	ASTM D 1298	39.5	37.36	38.90	39.01
8.Distillation (°C)	ASTM D 86				
• **IBP**		206.59	196.00	1863.16	199.42
• **T10**		251.70	233.69	244.81	246.56.
• **T50**		316.18	326.58	289.42	329.76.
• **T90**		375.34	355.96	367.33	345.83
• **FBP**		398.21	392.23	387.77	404.93
9.Cetane Index	ASTM D 4737	55.85	52.15	51.32	48.41
10.Flash Point (°C)	ASTM D 92	81.50 ± 0.70	75.0 ± 0.48	79.0 ± 0.48	71.0 ± 0.84
11. Acid value (mg KOH/g)		0.30	0.98	0.43	0.55

Results and discussion

Experiment in continuous screw reactor

Distillation curve received from DGC (Simdist)



Technical Cooperation Project for “Comprehensive Conversion of Biomass and Waste to Super Clean Fuels by New Solid Catalysts

Thai Research Leader (Project Director)

Prof. Tharapong Vitidsant, Ph.D.

Department of Chemical Technology
Faculty of Science
Chulalongkorn University, Thailand

Funded by
Japan International Cooperation Agency (JICA)
Japan Science and Technology Agency (JST)

April 2017 – August 2023

Japanese Research Leader

Prof. Noritatsu Tsubaki, Ph.D.

Department of Environmental Applied Chemistry
Faculty of Engineering
University of Toyama, Japan

Development of catalyst technologies

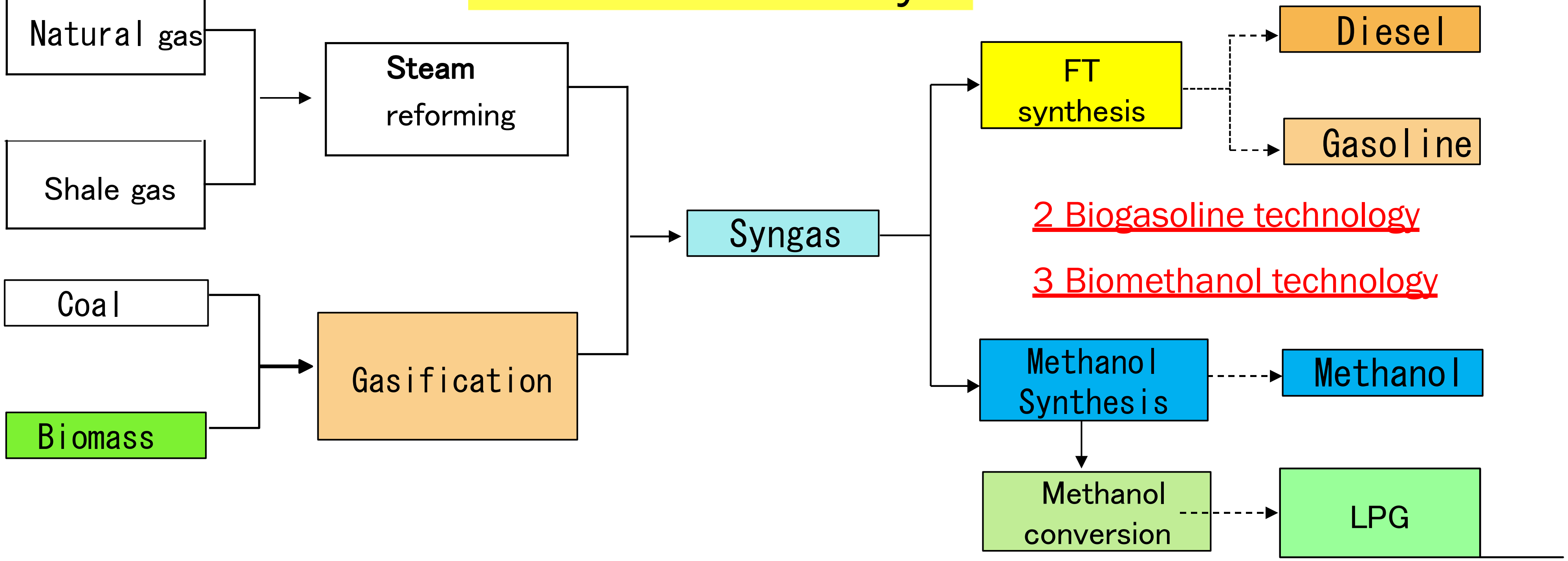
【Objectiv】

- Development of high active catalyst
- Development of active catalyst having high practical use properties
- Demonstration of biofuel production by connection driving with synthesis gas production

【Achievements】

- **Bio diesel, Bio gasoline, Bio LPG production**
- **Methanol synthesis operation and production**
- **Development of each elemental technology**

C1 chemistry



1 Biodiesel technology

Natural gas

Shale gas

Steam reforming

Coal

Biomass

Gasification

Syngas

FT synthesis

Diesel

Gasoline

2 Biogasoline technology

3 Biomethanol technology

Methanol Synthesis

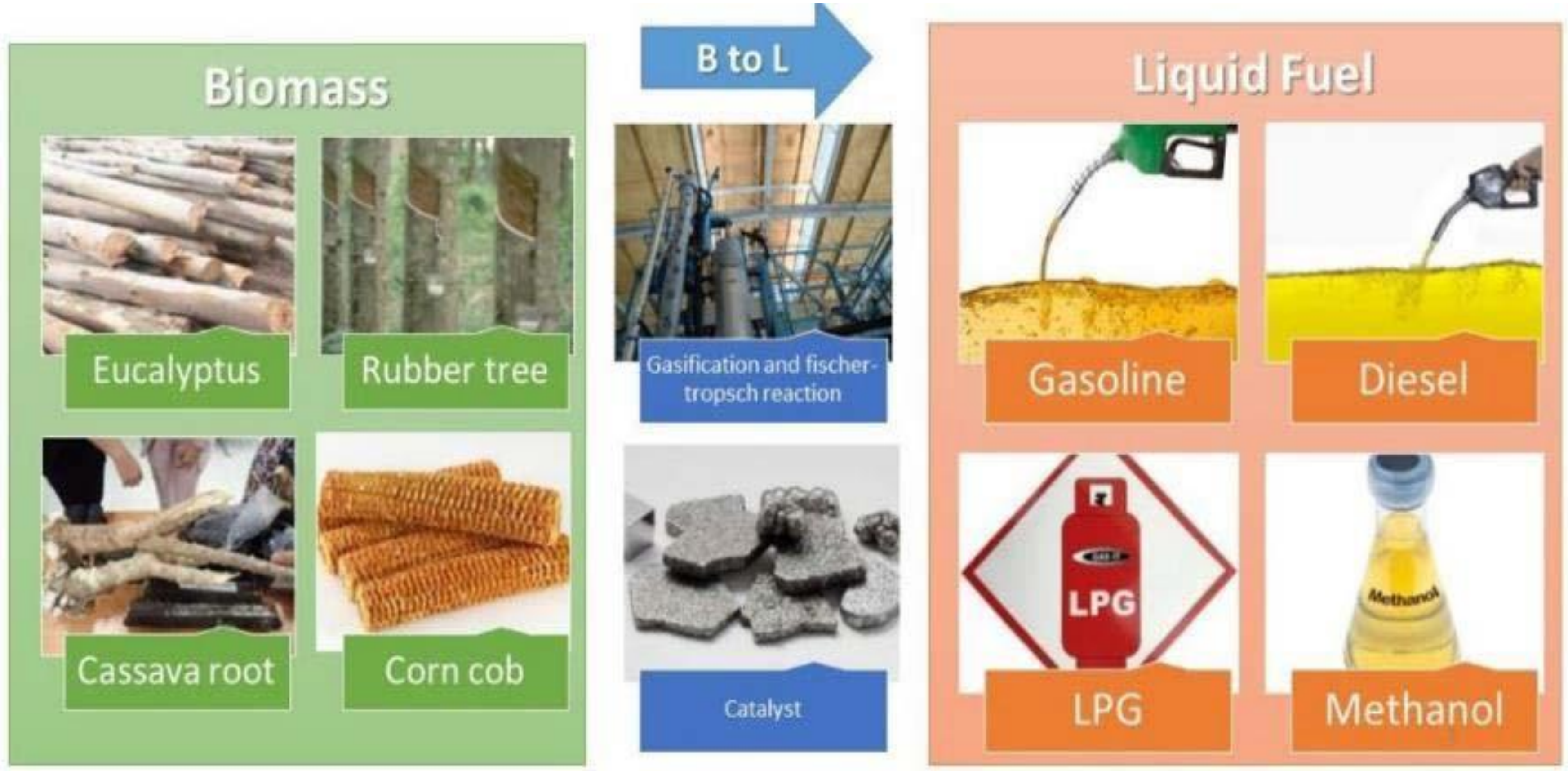
Methanol

Methanol conversion

LPG

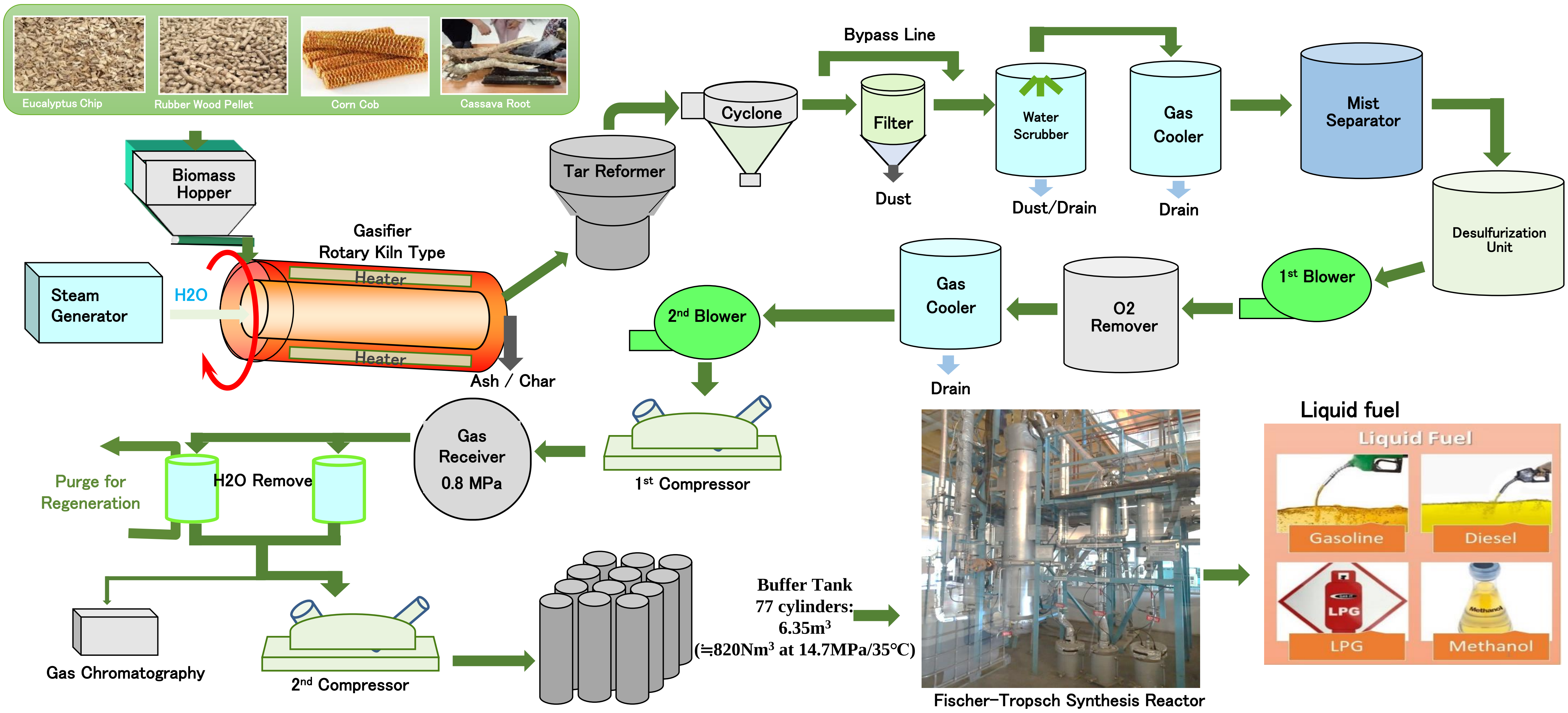
4 Bio-LPG technology

Gasification and catalyst Technologies



Biomass Gasification & Conversion Process

Nonedible biomass resources



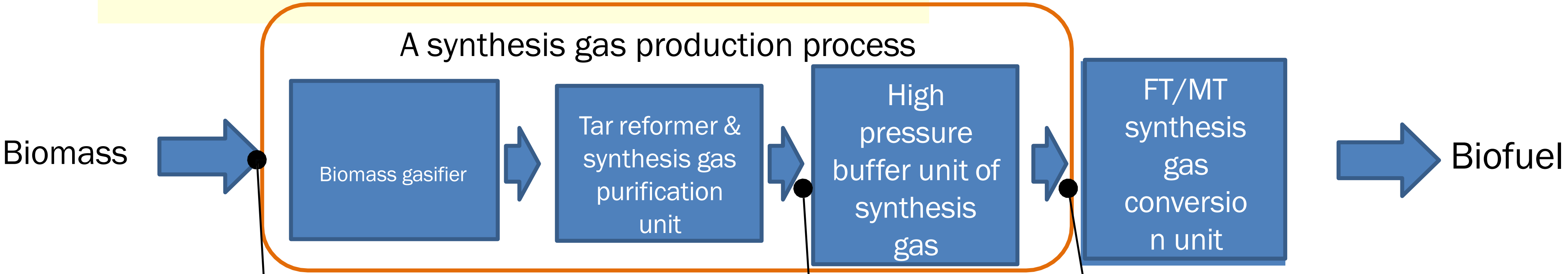
- Develop technology for controlling gas compositions
- Develop technology of gas purification
- Conduct trial operation in connection with catalytic conversion, and develop driving technology

★Perrformance for Gasification pilot reactor

$[H_2]/[CO]$: 1.75-2.25

$[H_2]+[CO]$: approx. 80%

Carbon conversion ratio : 60% or more



A synthesis gas production process

Biomass → Biomass gasifier → Tar reformer & synthesis gas purification unit → High pressure buffer unit of synthesis gas → FT/MT synthesis gas conversion unit → Biofuel

Biomass feed rate

max. 8kg/h

Typical property

C : 50 wt%dry
O : 6 wt%dry
H : 44 wt%dry
(Ash : 1 wt%dry)
H_2O : 20 wt%wet

Ash property

Ca : 60-70 wt%
K : 10-20 wt%
Mg : 2-5 wt%
Na : 2-5 wt%
Si : 1-2 wt%

Condition of synthesis gas

Flow rate : 6.0 Nm^3/h
Pressure : 0.1 MPa
Temperature : 50 degC

Property of synthesis gas

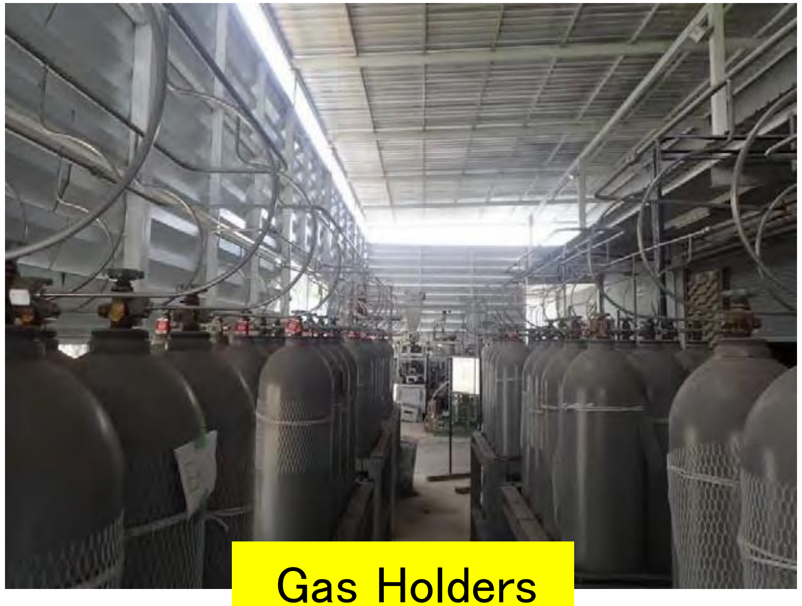
H_2 : 50-60 vol%
CO : 25-30 vol%
CO_2 : 10-20 vol%
CH_4 : 0.1-5 vol%
N_2 : Balance
H_2O : 100 ppmv or less
H_2S : 1 ppmv or less
NH_3 : 1 ppmv or less
O_2 : 20 ppmv or less
Tar : 20 ppmv or less

Supply condition to FT/MT

(Case 1: for FT)
Total volume : 488 Nm^3
Flow rate : 24 Nm^3/h
Pressure : 3 MPa or more
Temperature : 50 degC or less

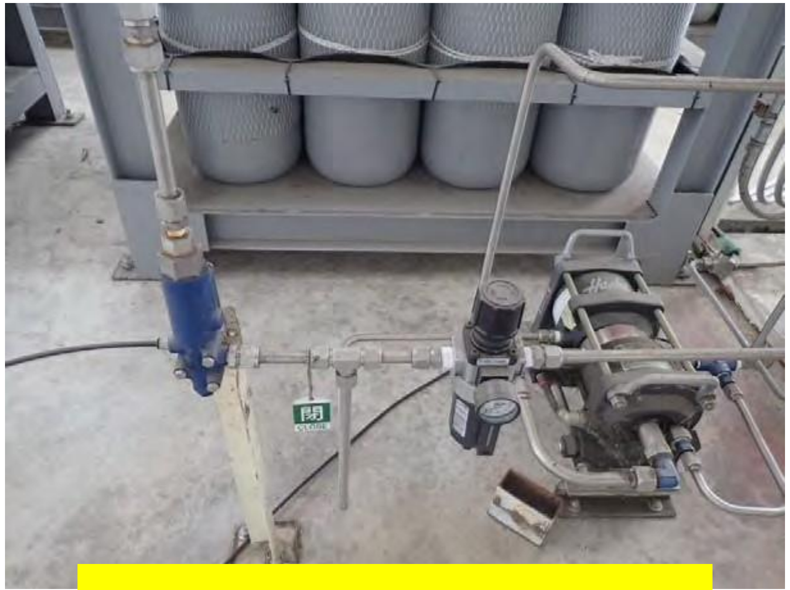
(Case 2: for MT)
Total volume : 244 Nm^3
Flow rate : 12 Nm^3/h
Pressure : 6 MPa or more
Temperature : 50 degC or less

Gasifier

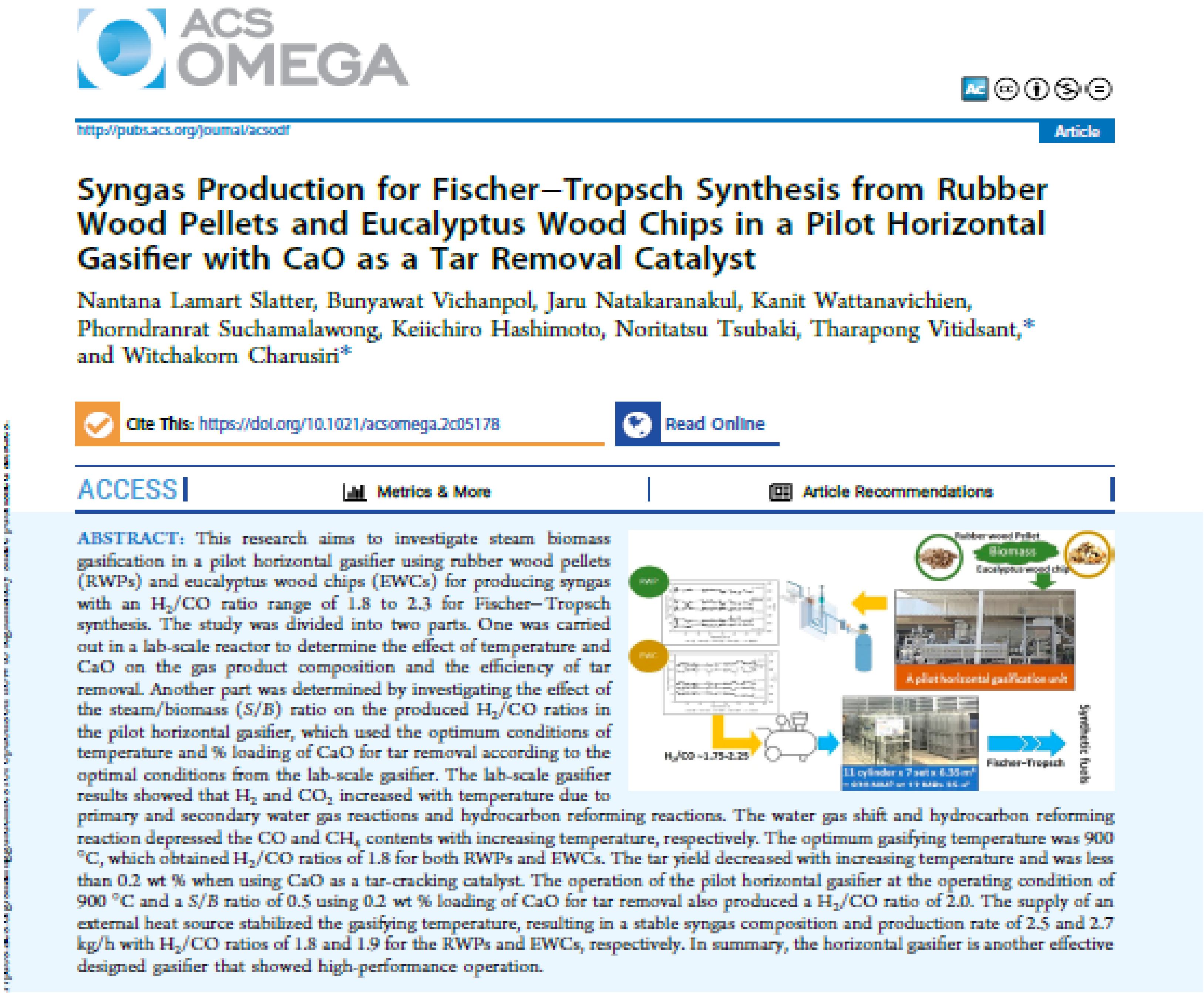


Gas Holders

Gas purification



High Pressure Compressor



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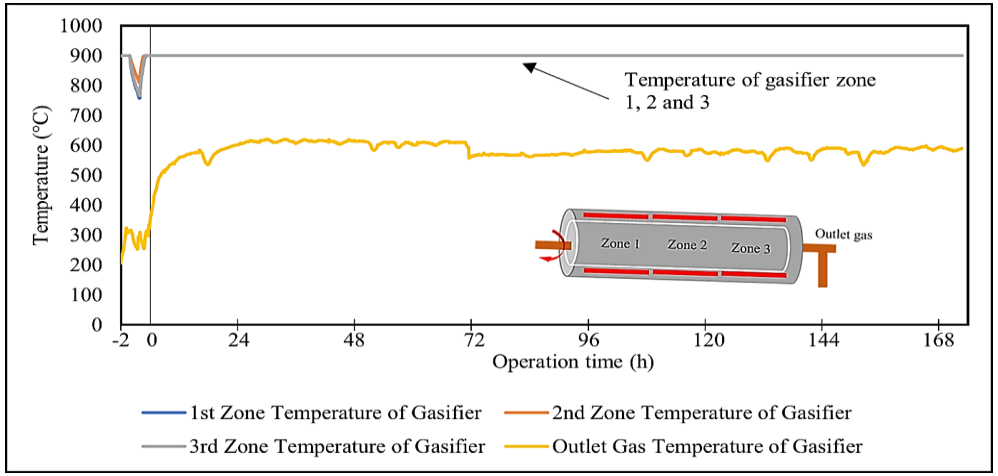
Article

Syngas Production for Fischer–Tropsch Synthesis from Rubber Wood Pellets and Eucalyptus Wood Chips in a Pilot Horizontal Gasifier with CaO as a Tar Removal Catalyst

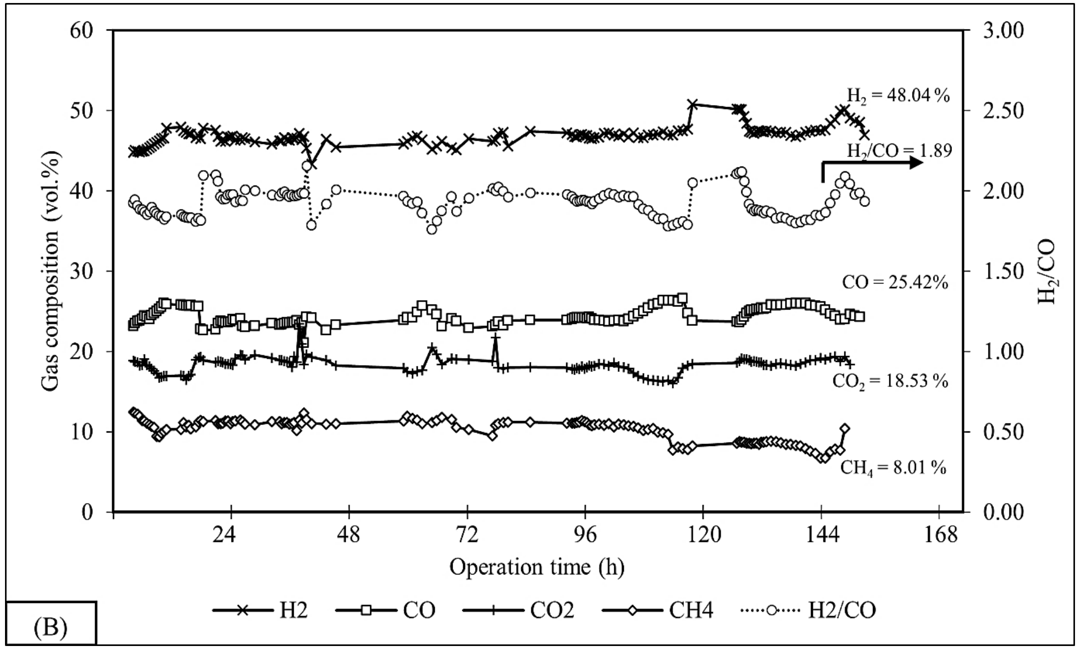
Nantana Lamart Slatter, Bunyawat Vichanpol, Jaru Natakaranakul, Kanit Wattanavichien, Phorndranrat Suchamalawong, Keiichiro Hashimoto, Noritatsu Tsubaki, Tharapong Vitidsant,* and Witchakorn Charusiri*

Cite This: https://doi.org/10.1021/acsomega.2c05178

ABSTRACT: This research aims to investigate steam biomass gasification in a pilot horizontal gasifier using rubber wood pellets (RWPs) and eucalyptus wood chips (EWCs) for producing syngas with an H_2/CO ratio range of 1.8 to 2.3 for Fischer–Tropsch synthesis. The study was divided into two parts. One was carried out in a lab-scale reactor to determine the effect of temperature and CaO on the gas product composition and the efficiency of tar removal. Another part was determined by investigating the effect of the steam/biomass (*S*/*B*) ratio on the produced H_2/CO ratios in the pilot horizontal gasifier, which used the optimum conditions of temperature and % loading of CaO for tar removal according to the optimal conditions from the lab-scale gasifier. The lab-scale gasifier results showed that H_2 and CO_2 increased with temperature due to primary and secondary water gas reactions and hydrocarbon reforming reactions. The water gas shift and hydrocarbon reforming reaction depressed the CO and CH_4 contents with increasing temperature, respectively. The optimum gasifying temperature was 900 °C, which obtained H_2/CO ratios of 1.8 for both RWPs and EWCs. The tar yield decreased with increasing temperature and was less than 0.2 wt % when using CaO as a tar-cracking catalyst. The operation of the pilot horizontal gasifier at the operating condition of 900 °C and a *S*/*B* ratio of 0.5 using 0.2 wt % loading of CaO for tar removal also produced a H_2/CO ratio of 2.0. The supply of an external heat source stabilized the gasifying temperature, resulting in a stable syngas composition and production rate of 2.5 and 2.7 kg/h with H_2/CO ratios of 1.8 and 1.9 for the RWPs and EWCs, respectively. In summary, the horizontal gasifier is another effective designed gasifier that showed high-performance operation.



Temperature profile at the gasifier zone during EWC gasification



Gas composition and H_2/CO ratio of the EWC gasification for 7 d.

Summary of the gasification conditions and results for the two different biomasses (RWP and EWC).

	RWP	EWC
Operating parameters:		
Operating time (h)	30.5	27.77
Biomass feed rate (kg/h)	4.34	3.90
Steam feed rate (kg/h)	2.02	2.32
S/B ratio (kg/kg)	0.47	0.59
Gas yield at constant volume of 0.9071 m^3:		
Produced gas rate (kg/h)	2.48	2.67
Gas/Biomass (kg/kg)	0.57	0.68
H_2/CO (mole/mole)	1.75	1.89
Gas compositions:		
H_2	48.44	48.04
CO	27.68	25.42
CO_2	15.22	18.53
CH_4	8.66	8.01
Low Heating value (LHV):		
MJ/Nm^3	12.88	11.66
Carbon balance (kg):		
Feed stock	47.66	55.30
Produced gas	23.61	24.89
Char (solid)	24.05	30.41
Cold gas efficiency (η_{cold}):	47.77	48.05
Carbon conversion in gas product (wt.%, η_{carbon}):	49.53	45.00

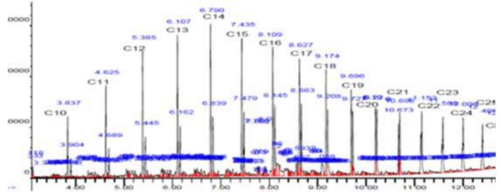
- Long-time operation for synthesis gas storage
- Operation for Biodiesel production

Supply condition to FT/MT (Case 1: for FT)
Total volume : 488 Nm³ Flow rate: 24 Nm³/h
Pressure : 3 MPa or more Temperature : 50 C or less

Synthesis gas supply to FT reactor

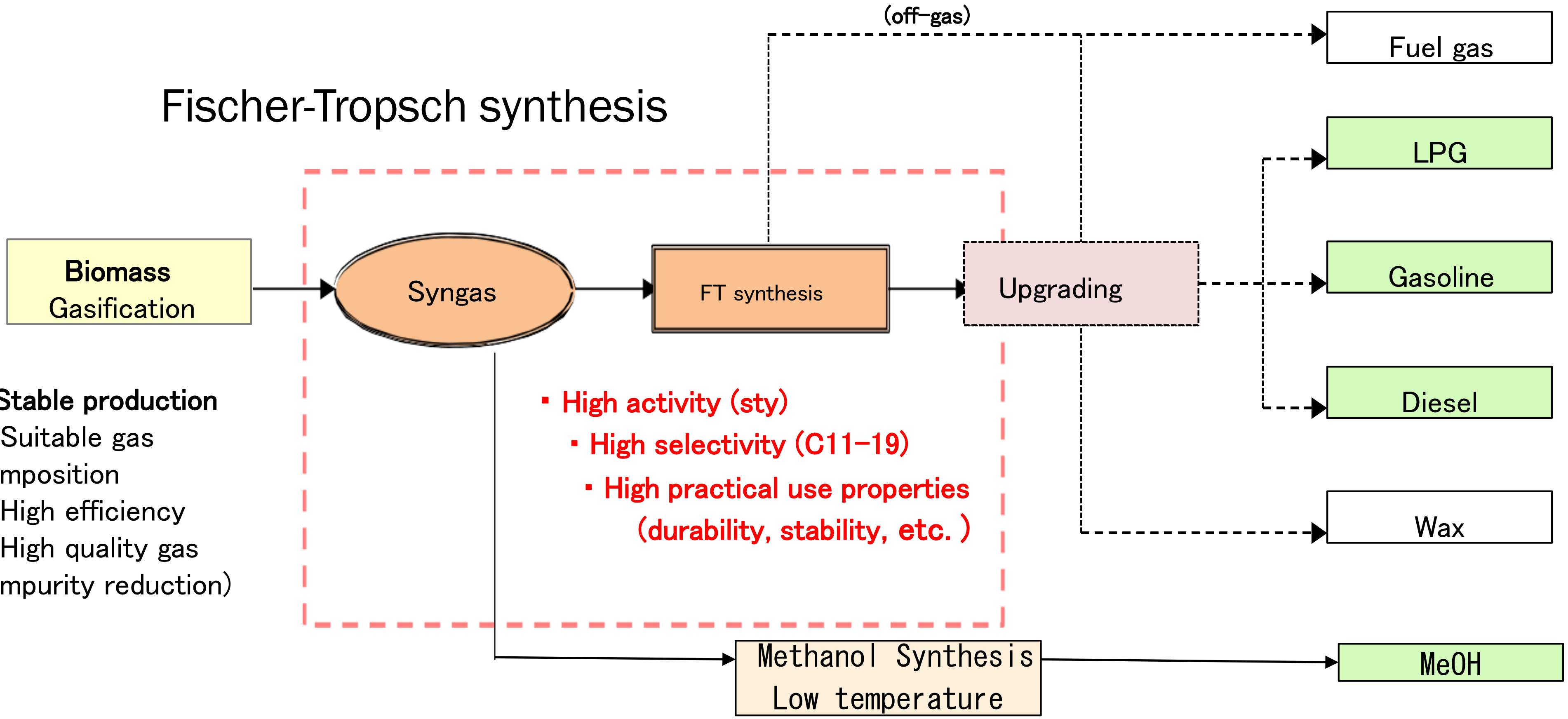
Biodiesel production

Analysis and evaluation



Biofuels technology

Fischer-Tropsch synthesis



Biomass
Gasification

- **Stable production**
- Suitable gas composition
- High efficiency
- High quality gas (impurity reduction)

Syngas

FT synthesis

- **High activity (sty)**
- **High selectivity (C11-19)**
- **High practical use properties (durability, stability, etc.)**

(off-gas)

Upgrading

Fuel gas

LPG — Capsule catalyst CuZnO/HZSM5

Gasoline — Capsule catalyst Co/SiO2@HZSM5

Diesel — Fe-K catalyst

Wax

Methanol Synthesis
Low temperature

MeOH — CuZnO plus MeOH

Operating condition and results

Product	Operating condition	CO conversion, %	Selectivity, %	Catalyst
Bio-diesel	280◦C, 2MPa	95.5	C_{11+} = 64.0%	Fe—K catalyst
Bio-gasoline	260◦C, 2MPa	63.7	$C_{5\text{-}11}$ = 70.5%	Capsule catalyst Co/SiO2@HZSM5
Bio-methanol	200◦C, 5MPa	50.7	85-90%	CuZnO plus MeOH
Bio-LPG	250◦C, 5MPa	63.6	C_3 = 16.1, C_4=59.4 total 75.5%	Capsule catalyst CuZnO/HZSM5

Seminar on Comprehensive Conversion of Biomass and Waste to Super Clean Fuels by New Solid Catalysts at The Center of Fuels and Energy from Biomass, Saraburi

On7 July 2023 at 09:30 – 12:20 hrs.

09:30-10:00	Registration
10:00-10:10	Opening remarks
10:10-10:30	“Overview of the Project, Comprehensive Conversion of Biomass and Waste to Super Clean Fuels by New Solid Catalysts”, Prof.Tharapong Vitidsant, Chulalongkorn University
10:30-11:00	“Development of catalyst technologies”, Prof. Noritatsu Tsubaki, University of Toyama
11:00-11:30	“Development of Synthetic gas production technology from various biomass resources and Social implementation proposal”, Dr. Keiichiro Hashimoto and Mr. Shinjiro Teuchi, JCOAL
11:30-11:50	Q&A, Discussions
11:50-12:00	Closing remarks
12:00-12:20	Observation tour of the SATPRES Pilot plant
12:20-13:45	-Lunch-

Waste plastic pyrolysis

Separation & Colorization

Bio-oil from Biomass pyrolysis

Diesel from used cooking oil pyrolysis

PE pyrolysis

BTL from FT synthesis

NEDO New Energy and Industrial Technology Development Organization JAPAN

北九州市立大学
THE UNIVERSITY OF KITAKYUSHU

JCOAL Japan Coal Energy Center

International joint R&D of CO_2 direct utilization jet fuel synthesis for carbon recycle

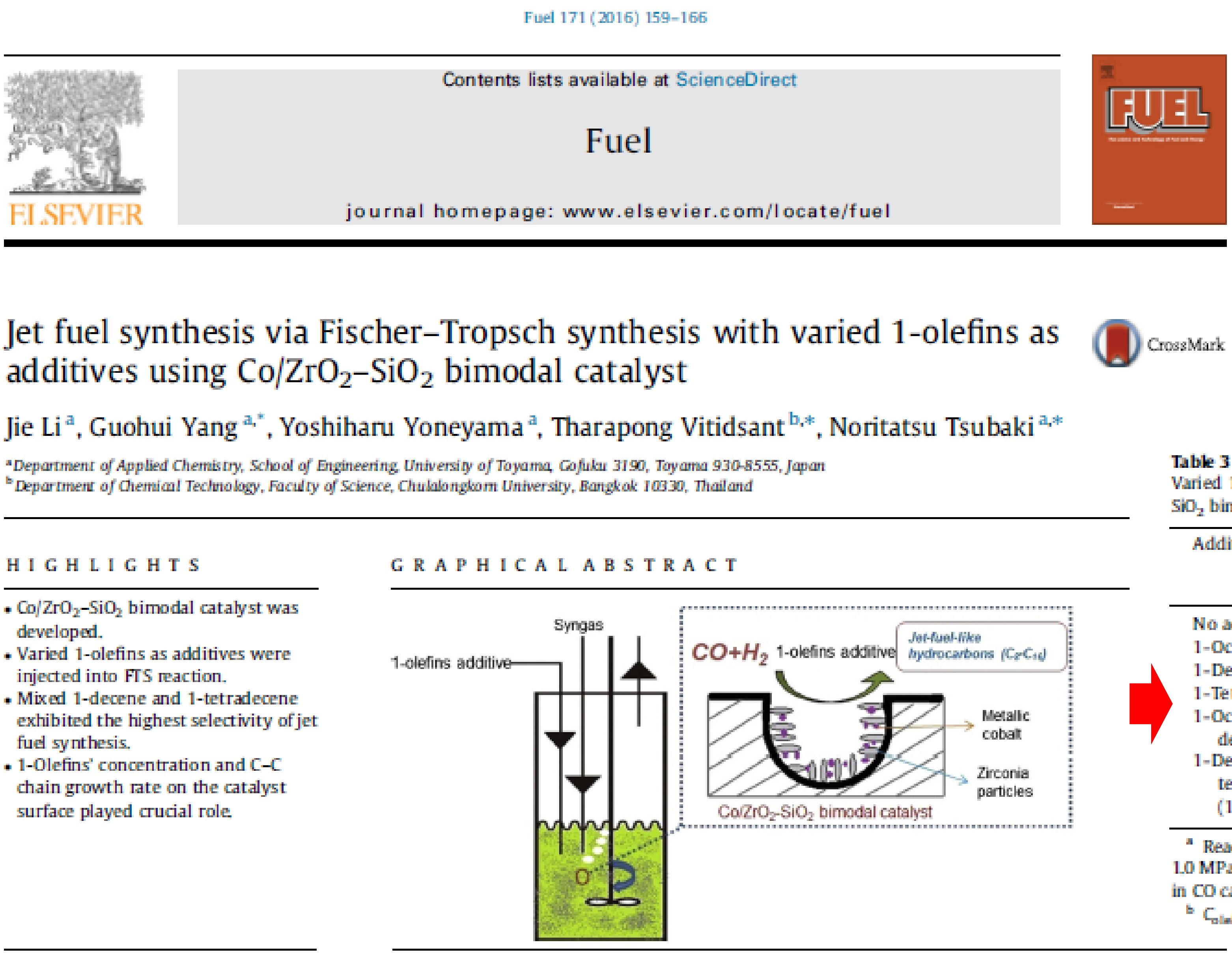
Supported by **NEDO**

Cooperation between

Chulalongkorn University and University of Toyama

Research area: Fuels and Energy from Biomass Center, CU Saraburi

November 2021 – December 2024
Phase 1



Fuel 171 (2016) 159–166

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Jet fuel synthesis via Fischer–Tropsch synthesis with varied 1-olefins as additives using $Co/ZrO_2–SiO_2$ bimodal catalyst

Jie Li[a], Guohui Yang[a,*], Yoshiharu Yoneyama[a], Tharapong Vitidsant[b,*], Noritatsu Tsubaki[a,*]

[a] Department of Applied Chemistry, School of Engineering, University of Toyama, Gofuku 3190, Toyama 930-8555, Japan
[b] Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

HIGHLIGHTS

- $Co/ZrO_2–SiO_2$ bimodal catalyst was developed.
- Varied 1-olefins as additives were injected into FTS reaction.
- Mixed 1-decene and 1-tetradecene exhibited the highest selectivity of jet fuel synthesis.
- 1-Olefins' concentration and C–C chain growth rate on the catalyst surface played crucial role.

GRAPHICAL ABSTRACT

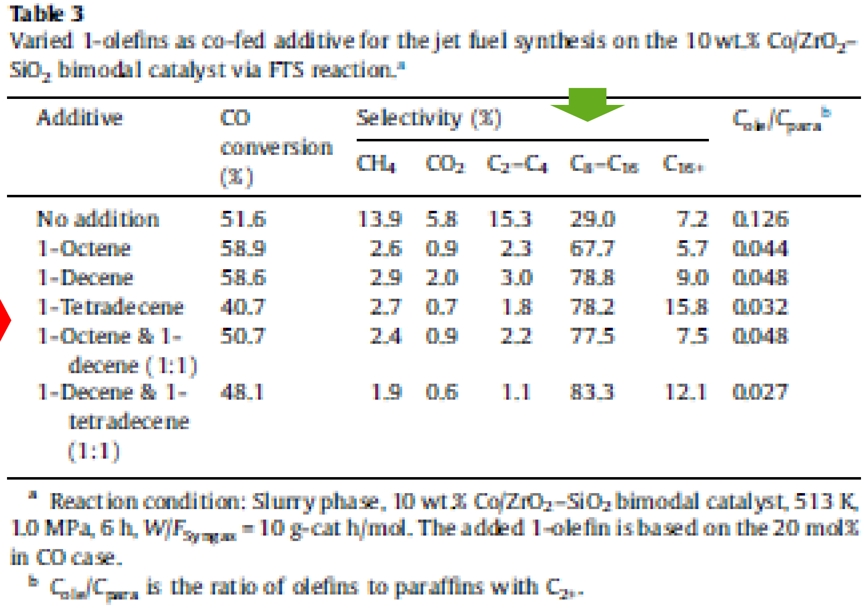


Table 3
Varied 1-olefins as co-fed additive for the jet fuel synthesis on the 10 wt.% $Co/ZrO_2–SiO_2$ bimodal catalyst via FTS reaction.[a]

Additive	CO conversion (%)	Selectivity (%)					C_{ole}/C_{para}[b]
		CH_4	CO_2	$C_2–C_4$	$C_8–C_{16}$	C_{16+}	
No addition	51.6	13.9	5.8	15.3	29.0	7.2	0.126
1-Octene	58.9	2.6	0.9	2.3	67.7	5.7	0.044
1-Decene	58.6	2.9	2.0	3.0	78.8	9.0	0.048
1-Tetradecene	40.7	2.7	0.7	1.8	78.2	15.8	0.032
1-Octene & 1-decene (1:1)	50.7	2.4	0.9	2.2	77.5	7.5	0.048
1-Decene & 1-tetradecene (1:1)	48.1	1.9	0.6	1.1	83.3	12.1	0.027

[a] Reaction condition: Slurry phase, 10 wt.% $Co/ZrO_2–SiO_2$ bimodal catalyst, 513 K, 1.0 MPa, 6 h, W/F_{Syngas} = 10 g-cat h/mol. The added 1-olefin is based on the 20 mol% in CO case.

[b] C_{ole}/C_{para} is the ratio of olefins to paraffins with C_{2+}.

Potential biomass as raw material for BTL


Eucarlyptus


Leucaena


Acacia


Nepier or Raja

Farming or Contact farming


Empty fruit bunch


Palm fiber


Palm shell


Palm trunk


Bagasse


Sugar cane leaves

By products

Commercial Development Process of Bagasse and Sugarcane Leaves to Dense Biomass for High Quality Briquette Charcoal and Activated Carbon Production

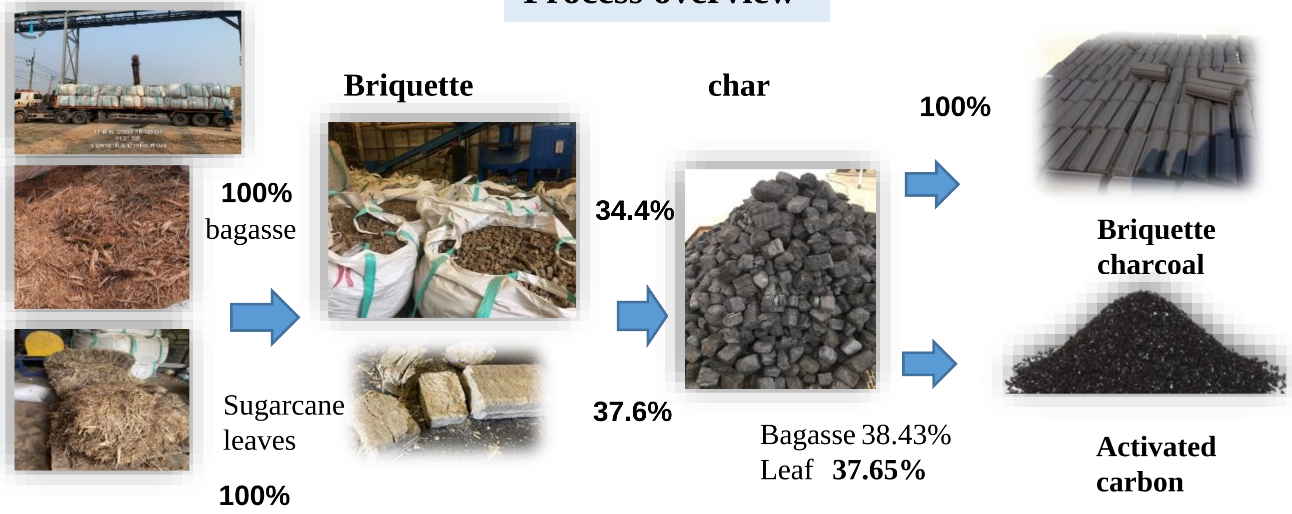
Prof. Tharapong Vitidsant

CU Unisearch and Center of Fuels and Energy from Biomass
Under BCG in Action
Thailand Research Fun
Program Management Unit for Competitiveness (PMUC)

Objectives

- To convert bulky biomass to briquette
- To convert dense biomass briquette to char by carbonization
- To produce briquette charcoal and activated carbon
- Cost estimation of each process

Process overview



100%
bagasse

Sugarcane
leaves

100%

Briquette

34.4%

37.6%

char

Bagasse 38.43%
Leaf **37.65%**

100%

Briquette charcoal

Activated carbon

Conversion machines

Briquetting machine

Carbonizer

Charcoal briquetting machine and Activator

Bagasse

Sugarcane
leaves

Overview conversion

Pyrolysis

- Waste plastic pyrolysis (From lab to commercial scale)
  - Spent FCC catalyst, 430 degree C
  - Liquid yield, 60-75%wt depend on purity
    Gas, 20-30% and solid 5-10%
- \- liquid product like as light crude

+ Naphtha	32%
+ Kerosene	15%
+ Diesel	45%
+ Fuel oil	8%

- Biomass pyrolysis

\- Used cooking oil pyrolysis (SATREPS under JICA) (From lab to pilot scale)
  + Liquid yield, 60-70 % wt

  + 18% of gasoline, 15% kerosene, 55% of diesel and 12% of gas oil

FT synthesis (From lab to pilot scale)

- Biomass to Liquid fuels via Gasification and FT synthesis
  + 5 kg. of biomass produces 1 liter of liquid fuel and 1.2 liter for bio-methanol

Summary of fuel from pyrolysis and FT process

- Pyrolysis of waste plastic and waste palm oil was successfully conducted at pilot scale.
- Yield and selectivity of both products as same as the reaction condition were almost the same.
- Pyrolysis oil were treated by separation of excess of naphtha in order that the remainder had the fraction close to conventional diesel.
- About 15% of naphtha was removed to produce diesel oil. The removes naphtha could be used as raw material loop to produce plastic.
- Diesel and Naphtha are aimed to produced by pyrolysis from PAO larger scale competing hydrocracking process.
- Next results of BTL process (JICA) will be shared to public in July 7, 2023 at Center of Fuels and Energy from biomass, Saraburi.
- Several biomass waste from agricultural and industrial activities could be converted to value-added products.

THANK YOU
FOR
YOUR ATTENTION