Pyrolysis of woody and algal biomass into liquid fuels

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Technological Overview

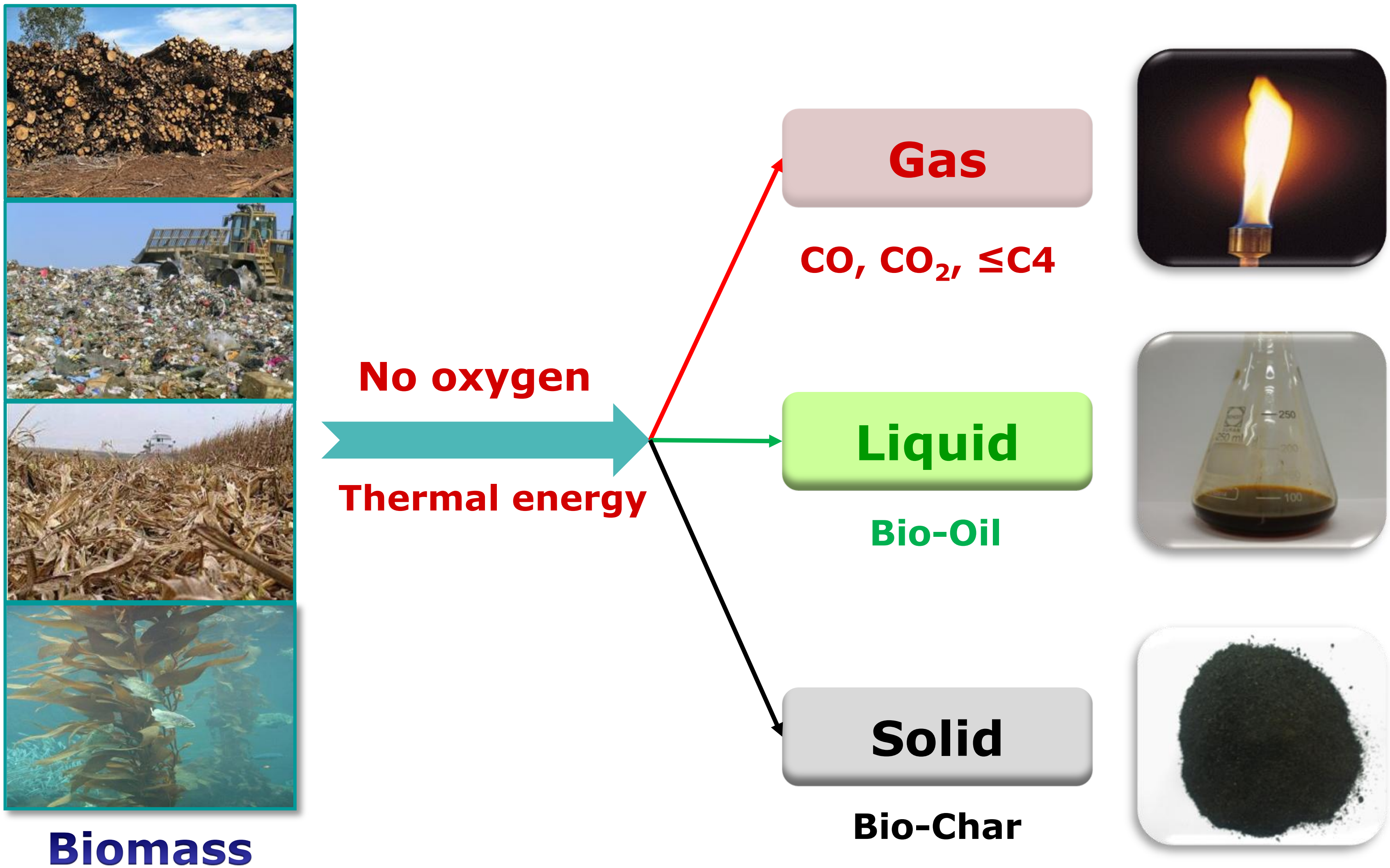
Research & Development Status

Results on Fluidized-bed Pyrolysis

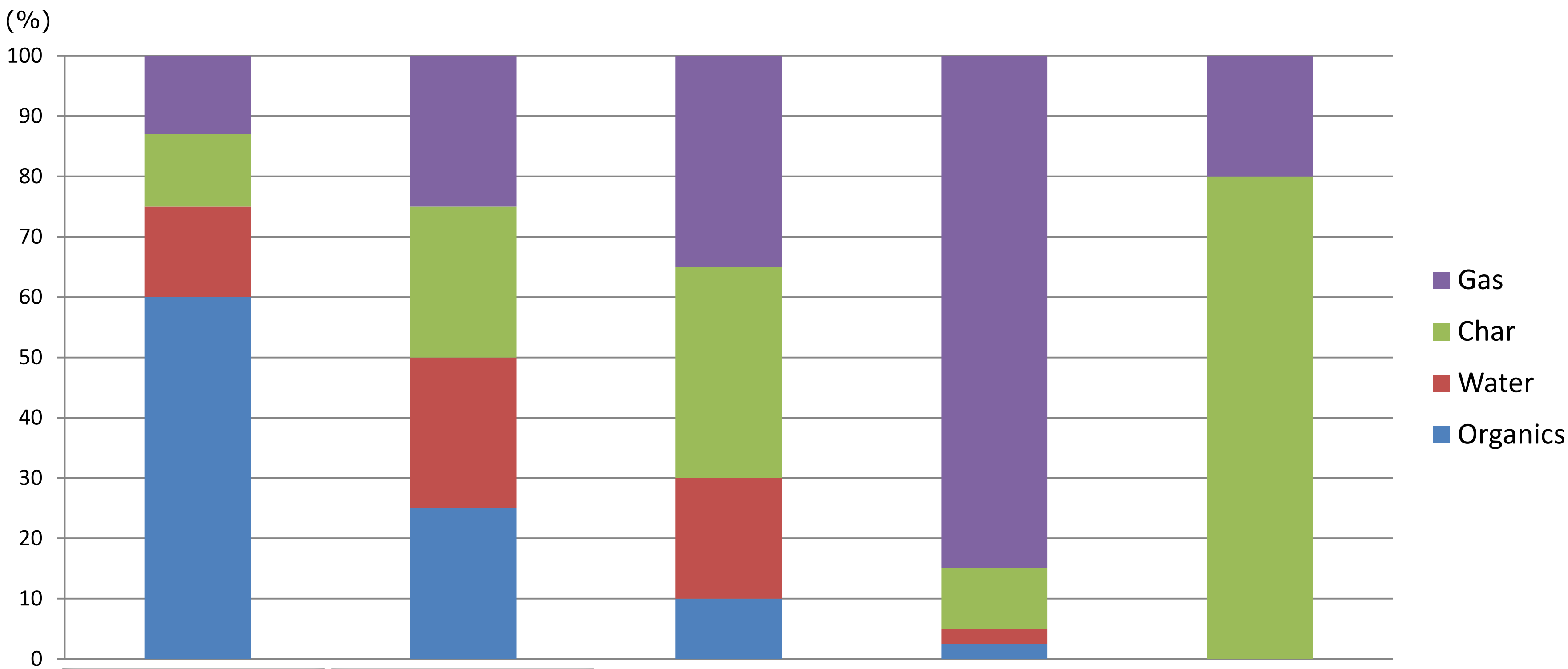
Results on Fixed-bed Pyrolysis

Conclusions

What is Pyrolysis?



Different Modes of Pyrolysis



Fast Pyrolysis

~ 500°C

short hot vapor residence time ~ 1 sec

Intermediate Pyrolysis

~ 500°C

hot vapor residence time ~ 10-30 sec

Slow Carbonization

~ 400°C

long vapor residence hours to days

Gasification

~ 750-900°C

Slow Torrefaction

~ 290°C

solids residence time ~ 30 min

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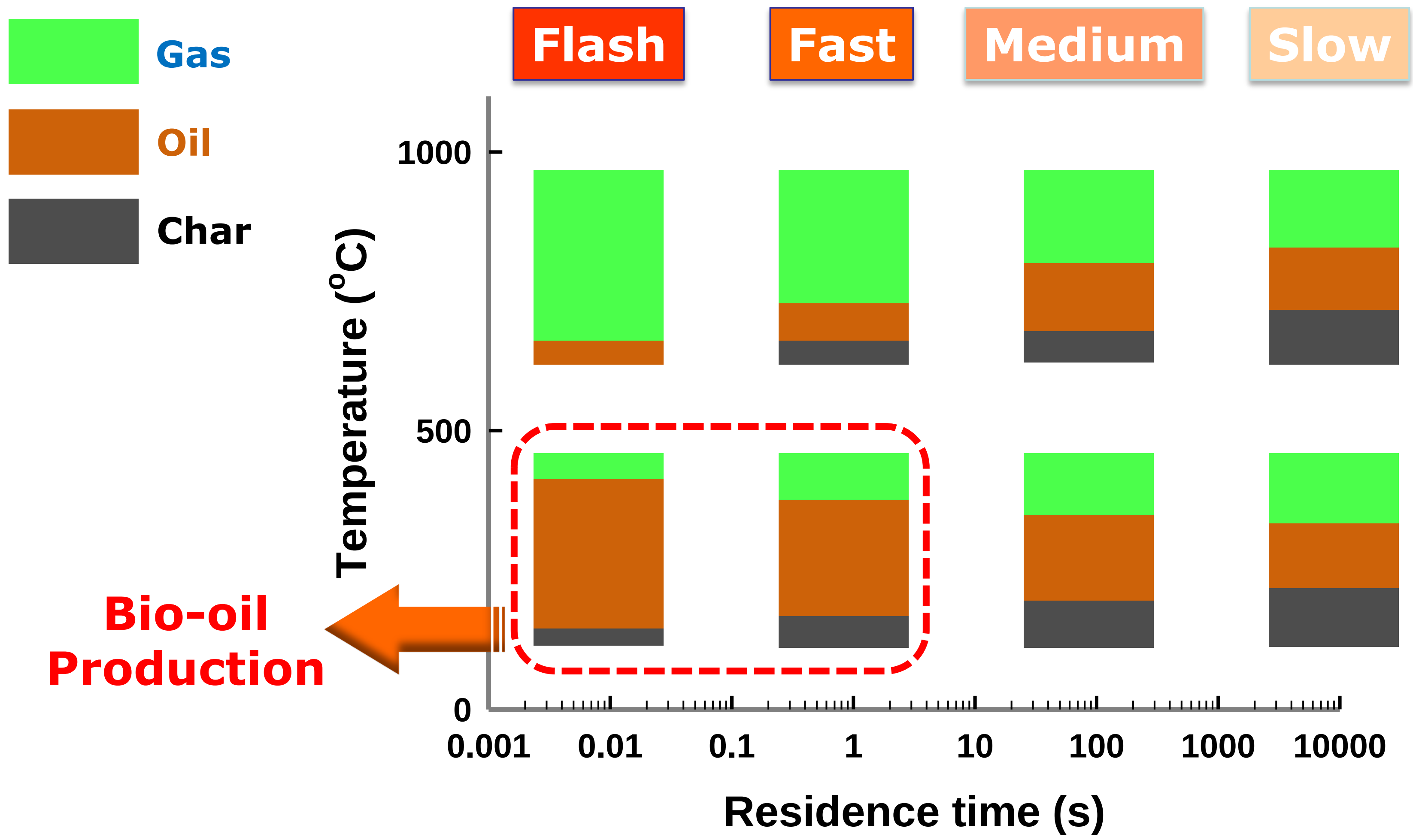
Product Distribution



Advantages and Disadvantages

Advantages

- Operates at atmospheric pressure and modest temperature
- Yields of bio-oil can exceed 70 wt-%
- Can use any type of biomass

Disadvantages

- High oxygen and water content of pyrolysis liquids makes them inferior to conventional hydrocarbon fuels
- Phase-separation and polymerization of the liquids and corrosion of containers make storage of these liquids difficult

Pyrolysis Reactors

Fluidized bed reactors

- Bubbling fluidized-bed reactor
- Circulating fluidized-beds/transport reactor

Non-fluidized bed reactors

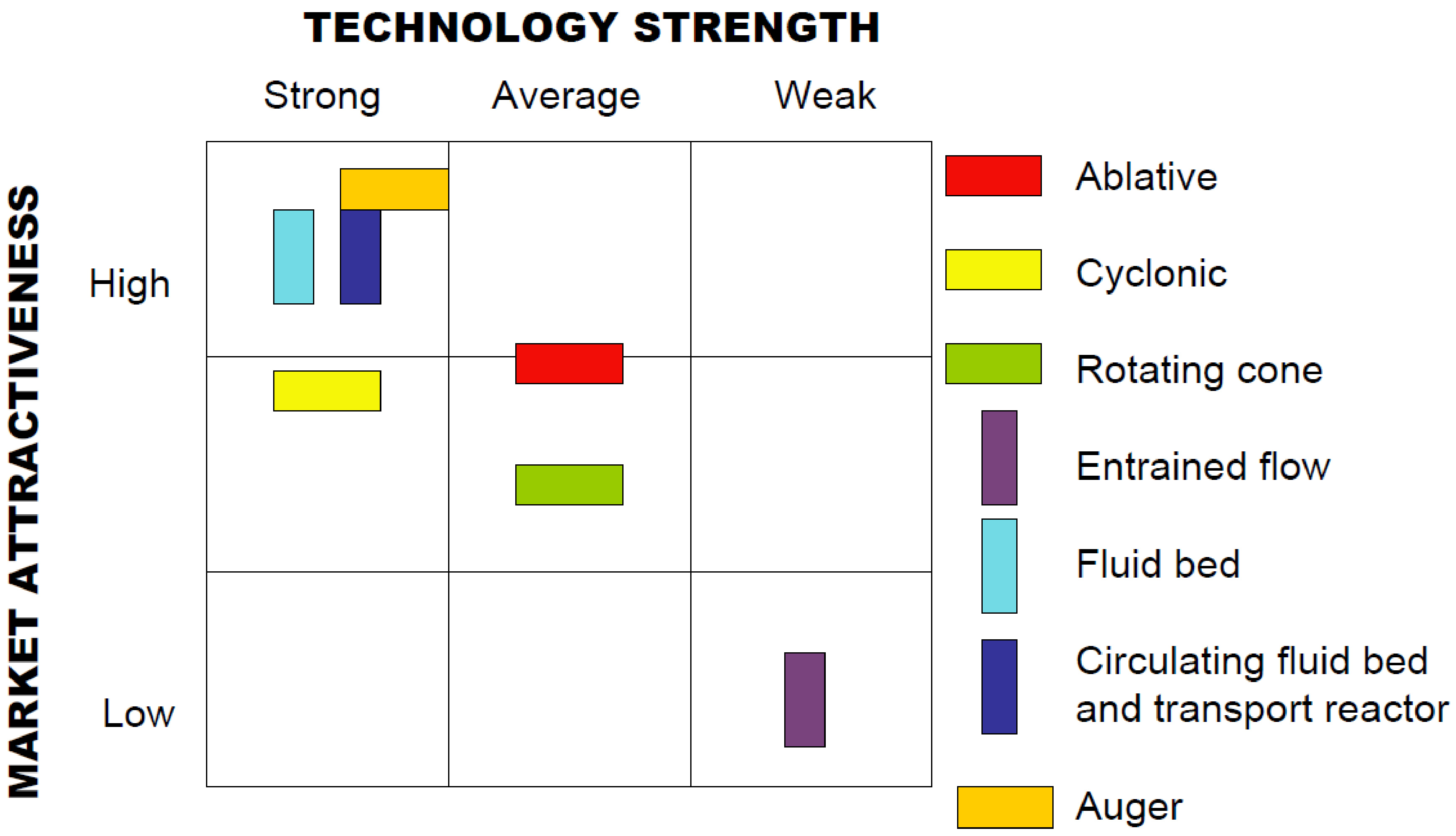
- Rotating cone pyrolyzer
- Ablative pyrolyzer
- Entrained flow reactor
- Vacuum pyrolyzer
- Auger pyrolyzer

Comparison of Various Reactors

Reactor	Status	Bio-oil wt%	Comp-lexity	Feed size	Inert gas need	Specific size	Scale up
BFB	Demo	75	Medium	Small	High	Medium	Easy
CFB	Pilot	75	High	Medium	High	Large	Easy
Entrained	None	65	High	Small	High	Large	Easy
Rotating cone	Pilot	65	High	V Small	Low	Small	hard
Ablative	Lab	75	High	Large	Low	Small	Hard
Auger	Lab	65	Low	Small	Low	Medium	Easy
Vacuum	Demo	60	High	Large	Low	Large	Hard
Lab: 1-20 kg/h		Pilot: 20-200 kg/h			Demo: 200-2000 kg/h		

Adapted from PYNE IEA Bioenergy htto://www.pyne.co.uk

Comparison of Various Reactors



Adapted from PYNE IEA Bioenergy htto://www.pyne.co.uk

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Bio-oil

Physical property		Typical value
Moisture content		25%
pH		2.5
Specific gravity		1.20
Elemental analysis	C	56%
	H	6%
	O	38%
	N	0-0.1%
HHV as produced		17 MJ/kg
Viscosity (40°C, and 25% water)		40-100 cp
Solids (char)		0.1%
Vacuum distillation residue		up to 50%

Characteristics
Liquid fuel; a dark brown, free-flowing liquid
An acrid smoky smell due to the low molecular weight aldehydes and acids
Ready substitution for conventional fuels in many stationary applications such as boilers, engine, turbines
Heating value of 17 MJ/kg at 25% water, is about 40% that of fuel oil diesel
Does not mix with hydrocarbon fuels
Not as stable as fossil fuels
Quality needs definition for each application

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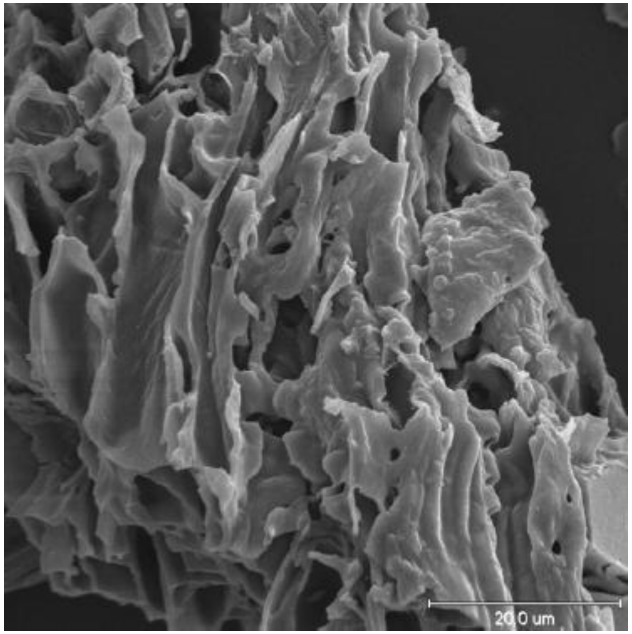
Byproducts

Gas (CO, H_2, light hydrocarbons)

- Can be used to heat pyrolysis reactor

Char: several potential applications

- Process heat
- Activated carbon
- Soil amendment



Bio-oil Upgrading

Physical Upgrading

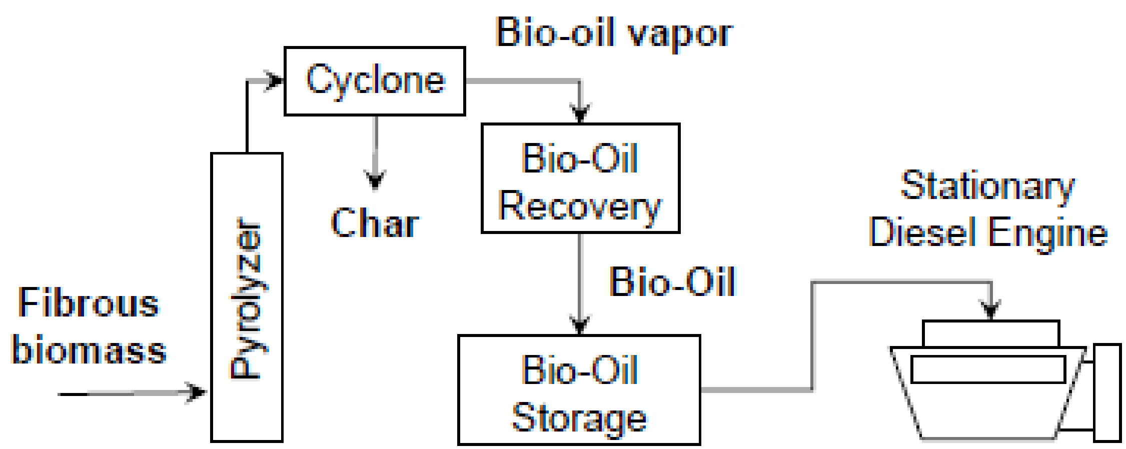
- Filtration
- Emulsions

Chemical and Catalytic Upgrading

- Hydrotreating
- Zeolite cracking
- Gasification to syngas

Applications of Bio-oil

- Energy Carrier
- Combustion
- Cofiring
- Engines and Turbines
- Chemicals
- Biorefinery



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Industrial Plants

Reactor	Industry	Country	Units built	Max size, kg/h
BFB	Agritherm Biomass Engineering Ltd Dynamotive RTI	Canada UK Canada Canada	2 1 4 5	200 200 8000 20
CFB	Ensyn Metso/UPM	Canada Finland	8 1	4000 400
Rotating cone	BTG	Netherlands	4	2000
Ablative	Py Tec	Germany	2	250
Auger	Abritech Lurgi LR Renewable Oil Intl	Canada Germany USA	4 1 4	2083 500 200
Vacuum	Pyrovac	Canada	1	3500
Moving bed and Fixed bed	Anhui Yineng Bio-energy Ltd	China	3	600

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Research Systems (>10 kg/h)

Reactor	Industry/Institute/University	Country	Max size, kg/h
BFB	Guangzhou Inst. Ener. Conv. NREL Texas A&M U. TNO U. Campinas U. of Science and Technology	China USA USA Netherlands Brazil China	10 10 42 10 100 650
CFB	VTT	Finland	20
Rotating cone	BTG	Netherlands	10
Ablative	Aston U. Inst. of Eng. Thermophysics	UK Ukraine	20 15
Auger	KIT (FZK) Texas A&M U.	Germany USA	500 30
Integral Catalytic Pyrolysis	TNO	Netherlands	30
Ceramic ball downflow	Shandong U. of Technology	China	110
Microwave	U. Minnesota	USA	10

Research and Development

- **Catalytic Pyrolysis (BFCC) & Hydrotreating (USA)**
  Company & Location: **KiOR** Inc., Columbus, Mississippi
  Capacity: 13 million gal cellulosic fuel per year (500 t/d biomass)
  Current yield 30 gal/t from 250-300 t/d (920,000 gal in 2013)
- **Fast Pyrolysis combined with CHP, Nov. 2013 (Finland)**
  Company & Location: **Fortum** Corp., Joensuu
  Capacity: 50,000 tons bio-oil per year (300,000-450,000 solid m^3/y)
- **RTP™ Technology since 1989 (Canada)**
  Company and Location: **Ensyn**, Renfrew, Ontario (150 t/d biomass)
  Capacity: >37 million gal for 5 commercial plants (>100 t/d biomass)
- **The world's leader in developing fluidized bed pyrolysis (Canada)**
  Company: **Dynamotive** Energy Systems (Bankrupted ?)
  130 t/d bio-oil at West Lorne (2005), 200 t/d bio-oil at Guelph (2007)
  BINGO (Biomass INto GasOil) : 2 stage upgrading
- **BTG's Rotating Cone Pyrolysis (Netherlands)**
  Company: **Biomass Technology Group (BTG)**, Enschede
  1st comm. plant in Malaysia: 2 t/h, Palm EFB (started in 2005, now closed)
  EMPYRO project: installed in Hengelo, the Netherlands
- **Integrated Hydropyrolysis and Hydroconversion (IH^2) (USA)**
  Company: **Gas Technology Institute (GTI)**, Des Plains, Illinois, USA
  Capacity: 50 kg/d biomass (2011)
  Combination of two catalytic processes at 100-500 psi with CRI catalysts

Bubbling Fluidized-bed Pyrolysis Reactor in Korea

- **Korea's 1st pilot plant for producing bio-oil (2012)**
  Company & Location: Daekyung ESCO Co., LTD, ., Goesan, Chungbuk, Korea
  Capacity: 1 kg/h Biomass (Lab), 2 t/d biomass (Pilot)
  Feedstock: Oil Palm EFB (Empty Fruit Bunch) obtained from Malaysia
  Developed with cold-bed and hot-bed experiments

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Biomass Properties

Property		Pine sawdust	Kelp
Physical property	Bulk density (g/cm^3)	0.19	0.57
	Heating value (MJ/kg)	17.3	12.7
Proximate analysis (wt.%)	Water	11.0	6.1
	Volatile	75.6	71.0
	Ash	13.5	22.9
Elemental analysis (wt.%)	C	47.3	35.2
	H	6.2	5.5
	O	44.0	40.5
	N	0.10	1.4
	S	-	0.5
Inorganic elements (wt.%)	K	0.065	6.1
	Ca	0.10	0.61
	Na	0.031	2.2

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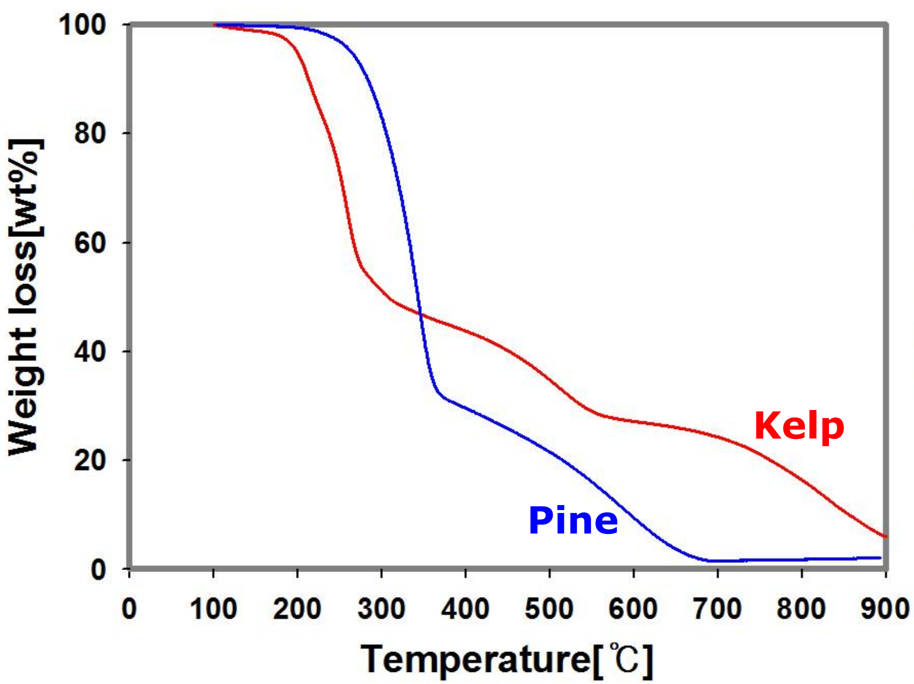
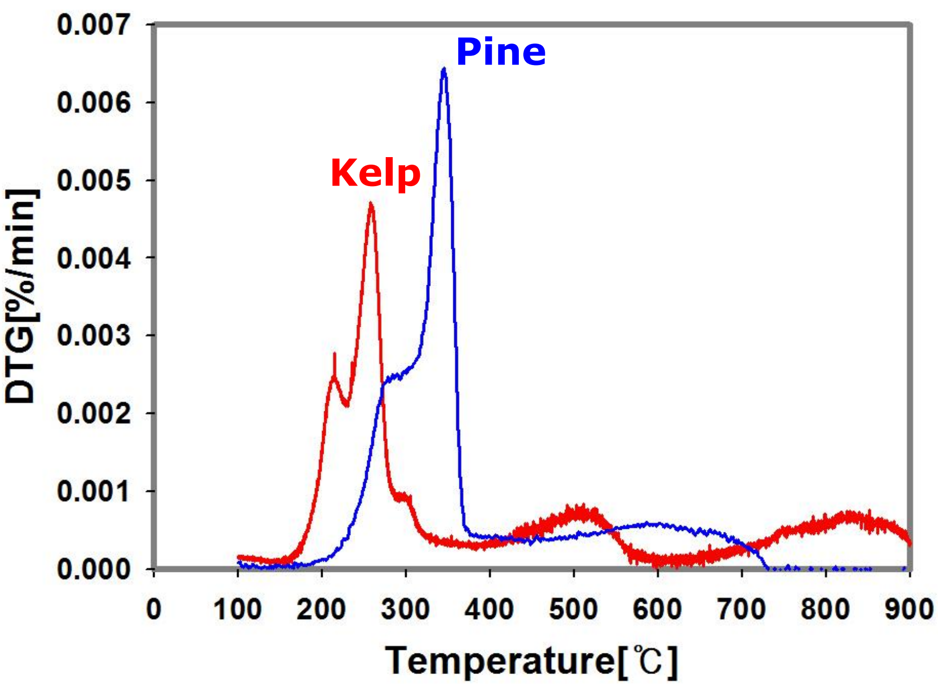
Thermogravimetric Analysis

TGA

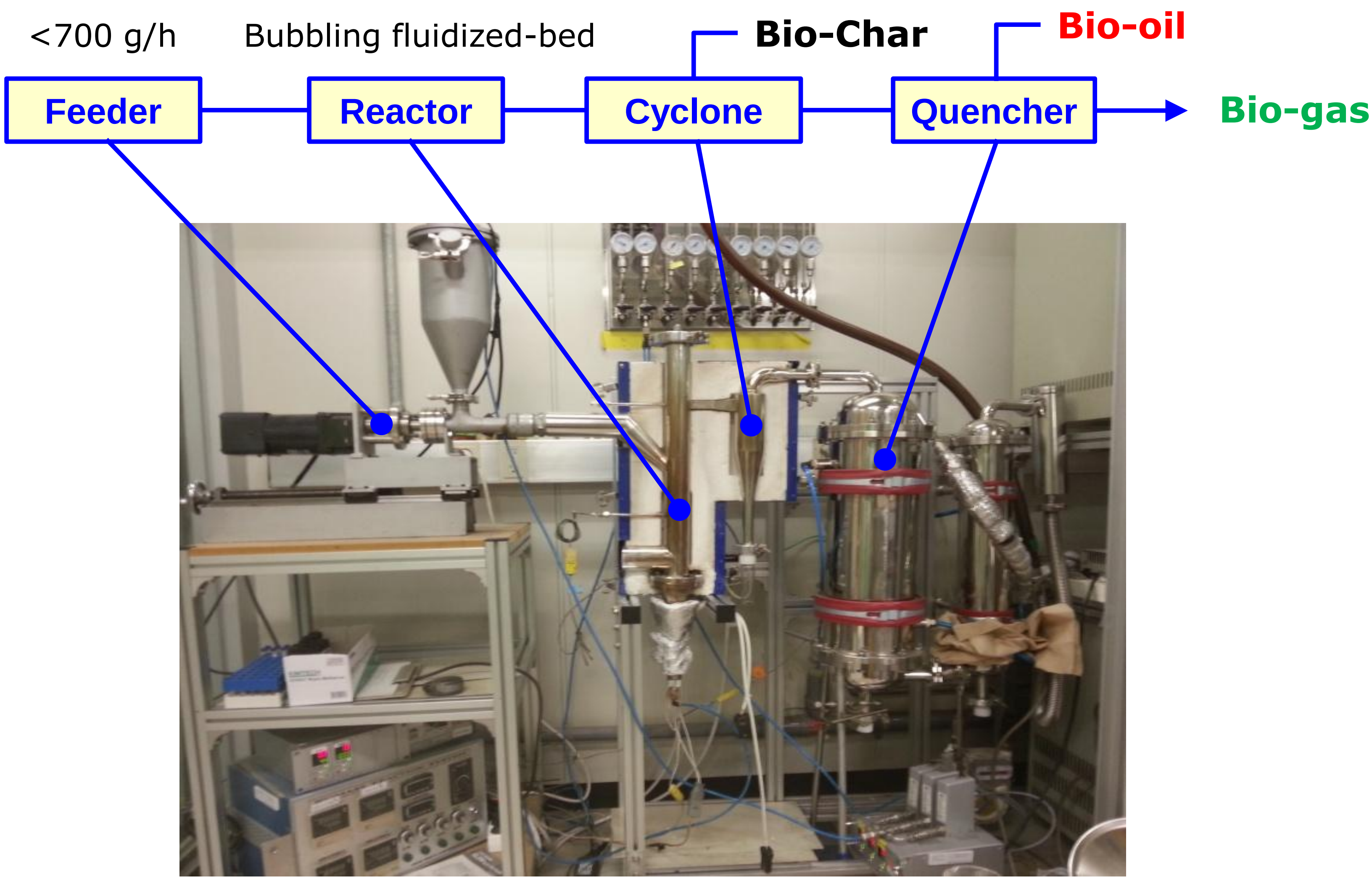


DTA

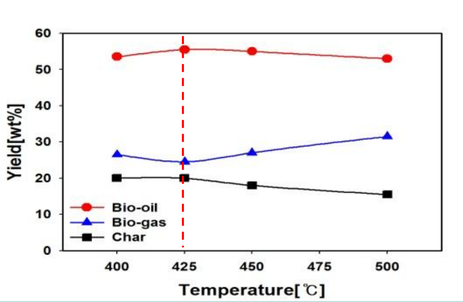
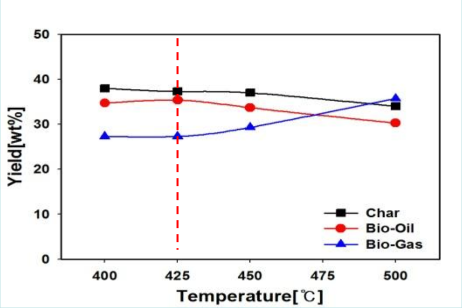
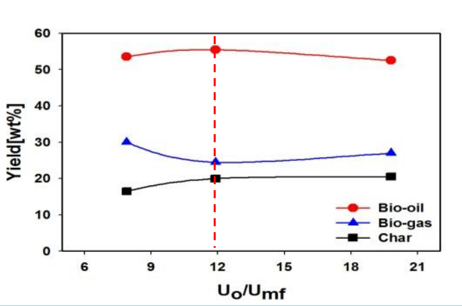
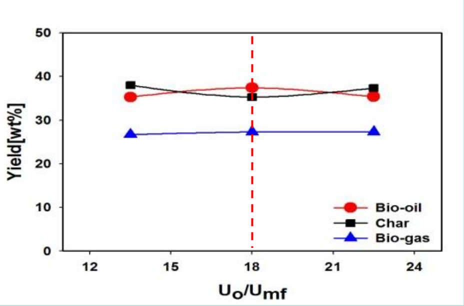


Major decomposition temperature range: 200-400°C

Fluidized-bed Fast Pyrolysis System



Effect of Operating Variables

<table>
<tr><th>Variable</th><th>Range</th><th>Pine sawdust</th><th>Kelp</th></tr>
<tr><td>Temperature (°C)</td><td>400-500
425</td><td>
</td><td>
</td></tr>
<tr><td>U_0/U_{mf}</td><td>8-22
12, 18</td><td>
</td><td>
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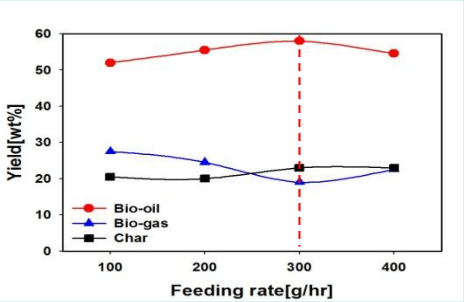
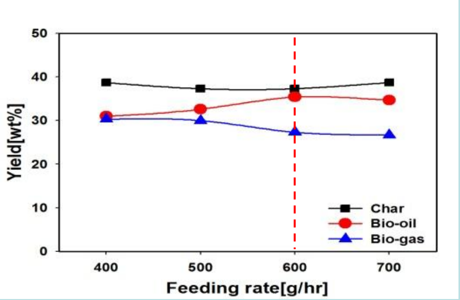
<tr><td>Feeding rate (g/h)</td><td>100-700
300, 600</td><td>
</td><td>
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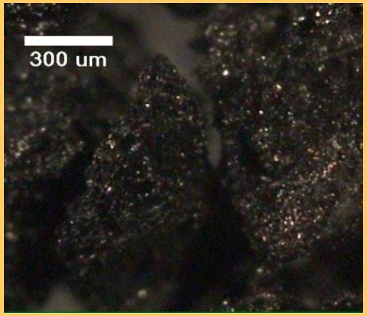
Bio-Oil Analysis

Property		Bio-oil from Pine	Bio-oil from Kelp	Fossil oil
Physical property	Water content (wt.%)	36.4	70.7	0.1
	Heating value (MJ/kg)	14.1	8.7	40.6
Elemental analysis (wt.%)	C	31.3	16.2	86.0
	H	8.2	10.2	13.6
	O	56.2	63.9	-
	N	<0.3	<0.3	0.2
	S	<0.3	<0.3	<0.18

Bio-char from Kelp

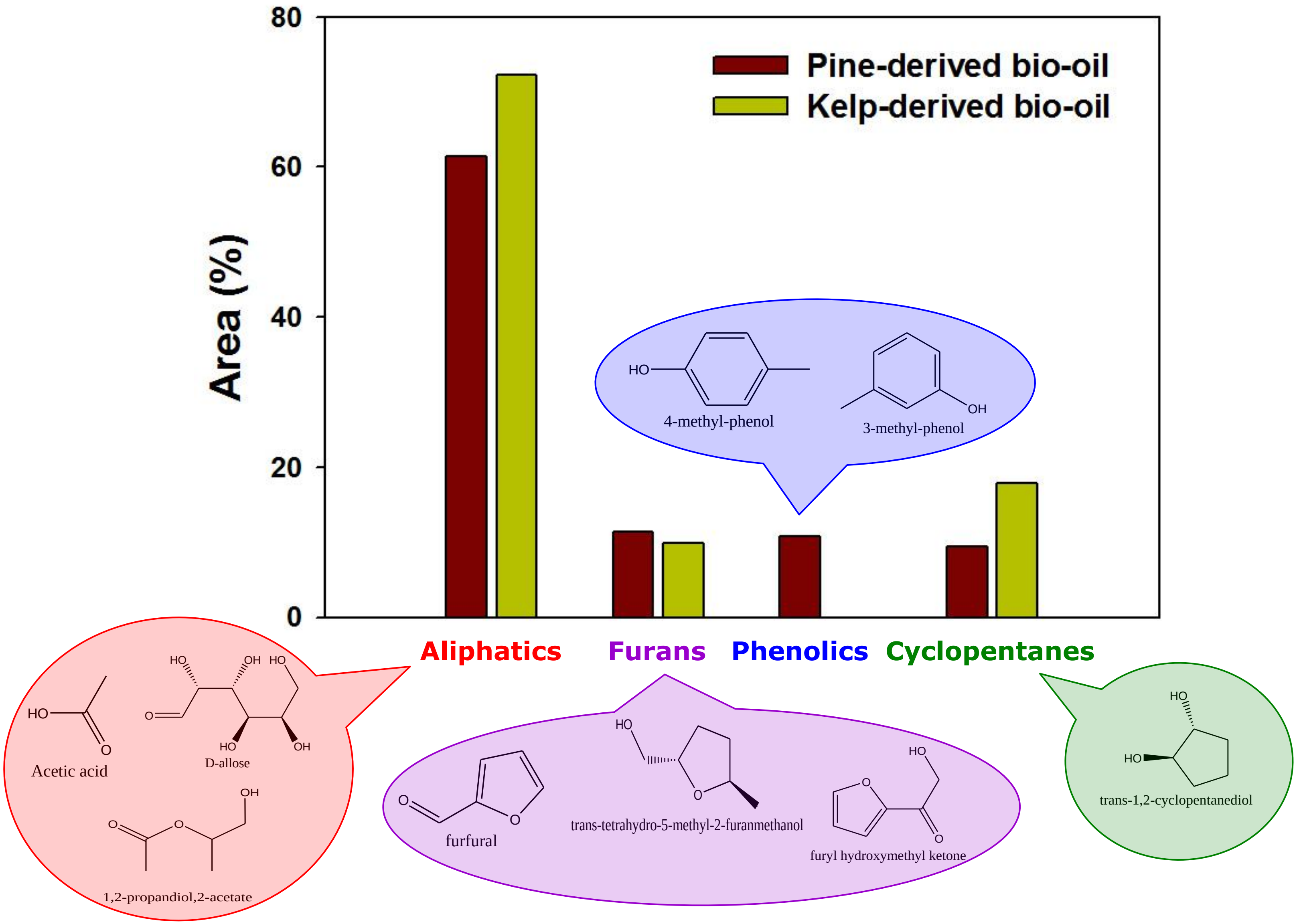


Severe agglomeration due to electrostatic force and secondary reactions

↓

raise problems in continuous operations

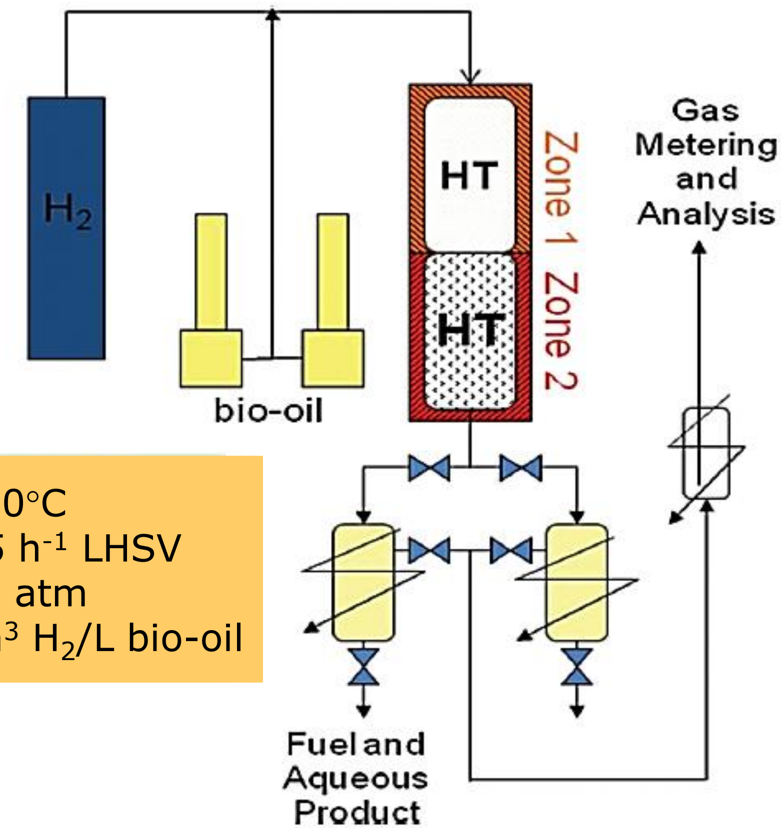
Bio-Oil Compositional Analysis



Catalytic Upgrading of Bio-Oil

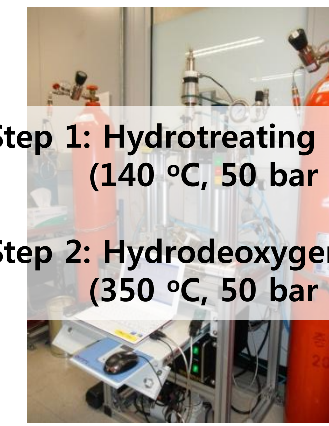
Two step catalytic reactions

Optimum catalyst ($Rh/SiO_2-Al_2O_3$) screened from model reactions (*Catal. Commun.* **2012**, *17*, 54) – guaiacol and eugenol



150-450°C
0.1-1.5 h^{-1} LHSV
75-150 atm
1-10 m^3 H_2/L bio-oil

Bio-oil
(oxygen 23%)

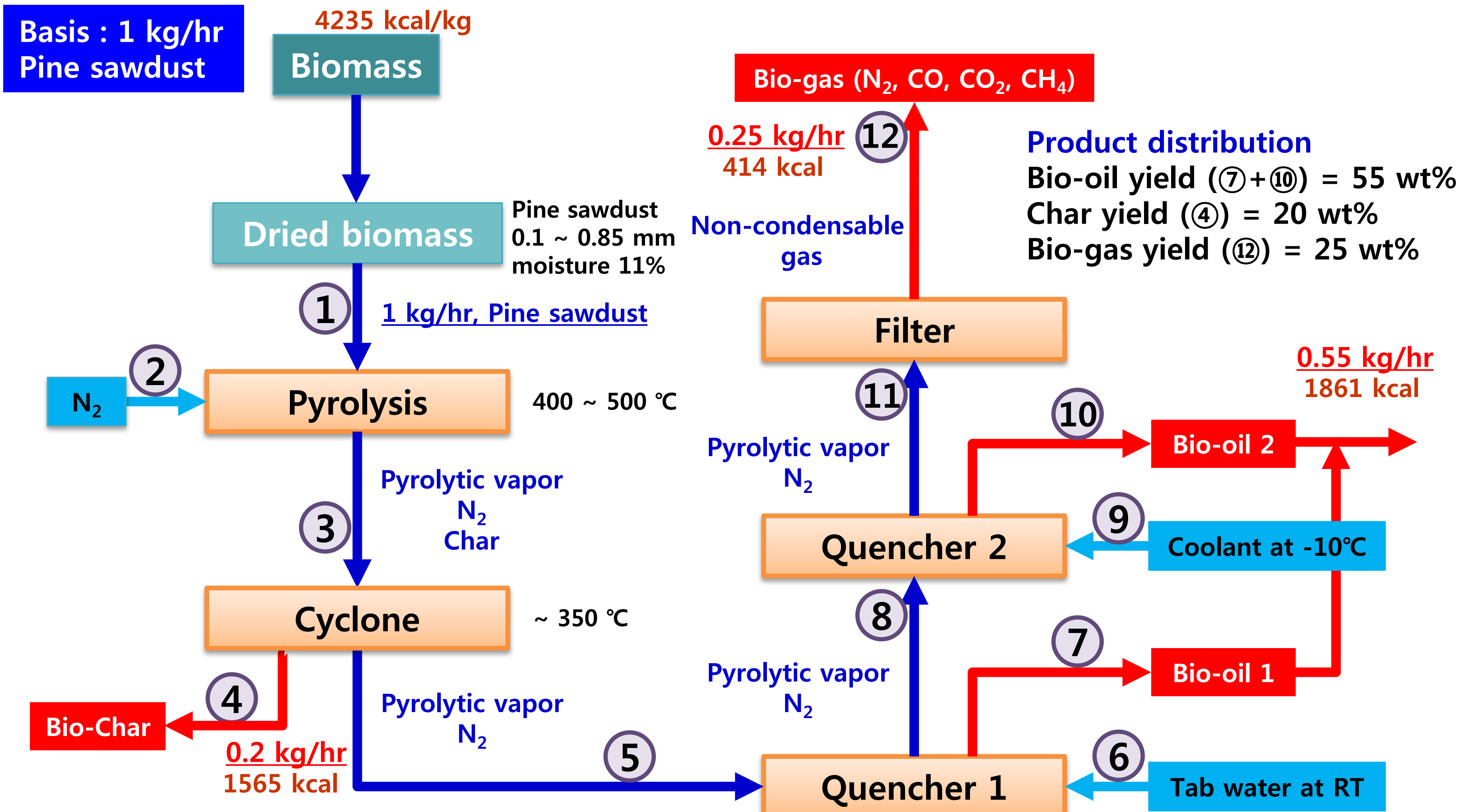


Step 1: Hydrotreating on $Rh/SiO_2-Al_2O_3$
(140 °C, 50 bar H_2 for 12 h)

Step 2: Hydrodeoxygenation on $Rh/SiO_2-Al_2O_3$
(350 °C, 50 bar H_2, 1 h)

Upgraded Bio-oil
(oxygen ~0%)

Process Flow Diagram



Heat requirement: 733 kcal → HHV of Bio-oil: 1861 kcal

Heat supply from bio-gas recycle (414 kcal) and char burning (1565 kcal)

Energy for biomass drying and crushing, cooling?

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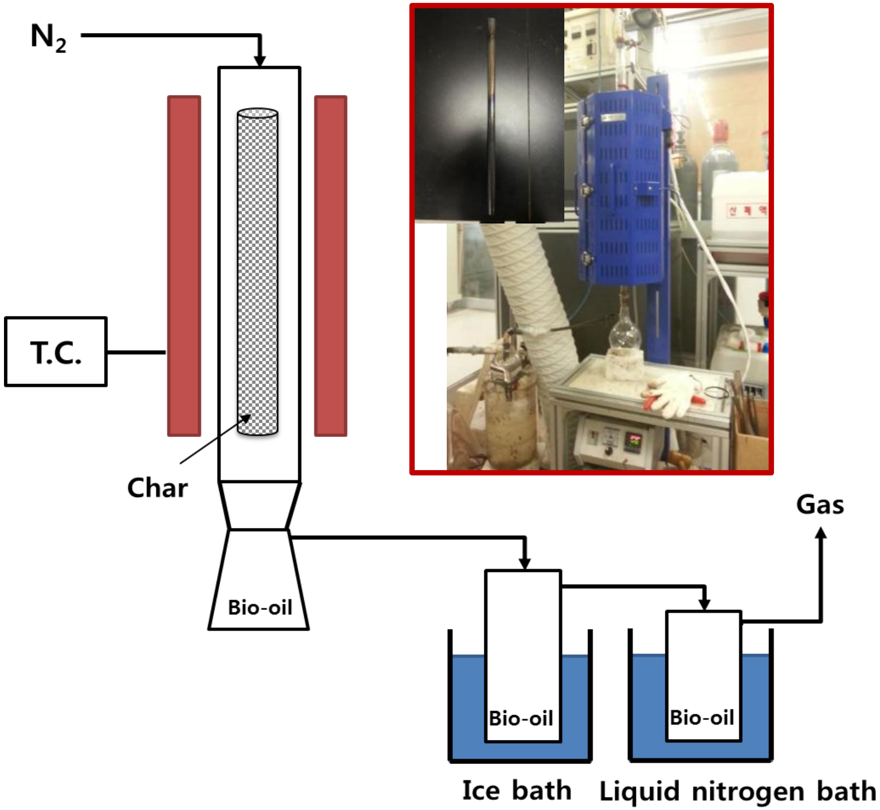
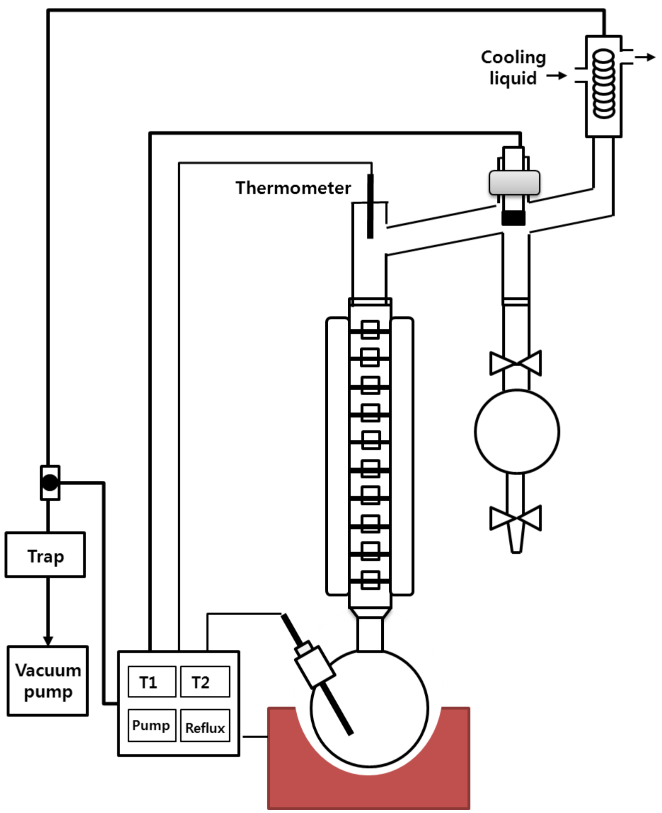
Conclusions

Fixed-bed Pyrolysis and Fractionation System

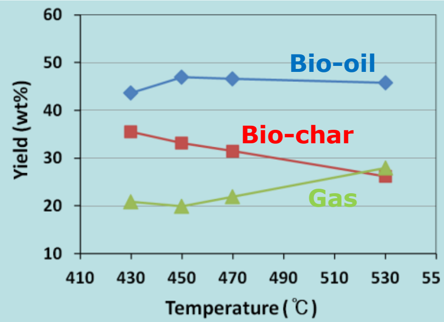
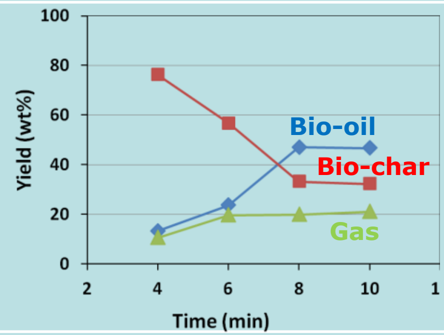
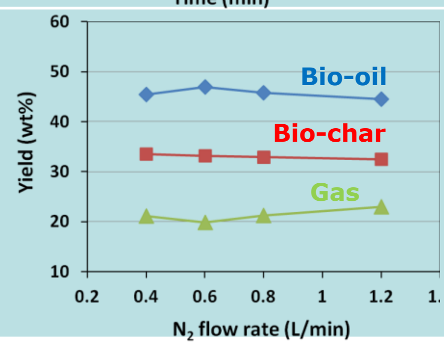
Fixed-bed Pyrolysis



Vacuum Distillation



Results of Fixed-bed Pyrolysis of Kelp

<table>
<tr><th>Variable</th><th>Range</th><th>Effect of Variables</th></tr>
<tr><td>Temperature (°C)</td><td>430-530
425</td><td>
</td></tr>
<tr><td>Retention time (min)</td><td>4-10
8</td><td>
</td></tr>
<tr><td>Carrier gas flow rate (L/min)</td><td>0.4-1.2
0.6</td><td>
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Results	
Product Yield (wt.%)	
Bio-oil	47.0
Bio-char	33.2
Gas	19.8
Proximate analysis (wt.%) of bio-char	
Water	1.90
Volatile	29.75
Fixed carbon	7.46
Ash	60.89
Elemental analysis (wt/%) of bio-char*	
C	47.57
H	2.35
O	46.01
N	1.75
S	2.32
HHV (MJ/kg)	13.54

*ash-free basis

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Fractionation of Crude Bio-oil

Vacuum distillation at 40 mmHg		Fraction I	Fraction II: Non-aqueous	Fraction II: Aqueous	Residue (solid coke)	Loss
Distillation temp. (°C)		<40	40-160		>160	
Yield (wt.%)		58.3	24.7		15.4	1.6
			5.9	18.8		
Water cont.(wt.%)		96.2	2.0	25.9	-	
Elemental Ratio	H/C		1.58	1.65	0.96	
	O/C		0.12	0.40	0.22	
Appearance		Bright yellow	Dark brown	Orange	Black	

Closer to the value
for aromatics
rather than for alkanes

Hydrodeoxygenation (HDO)

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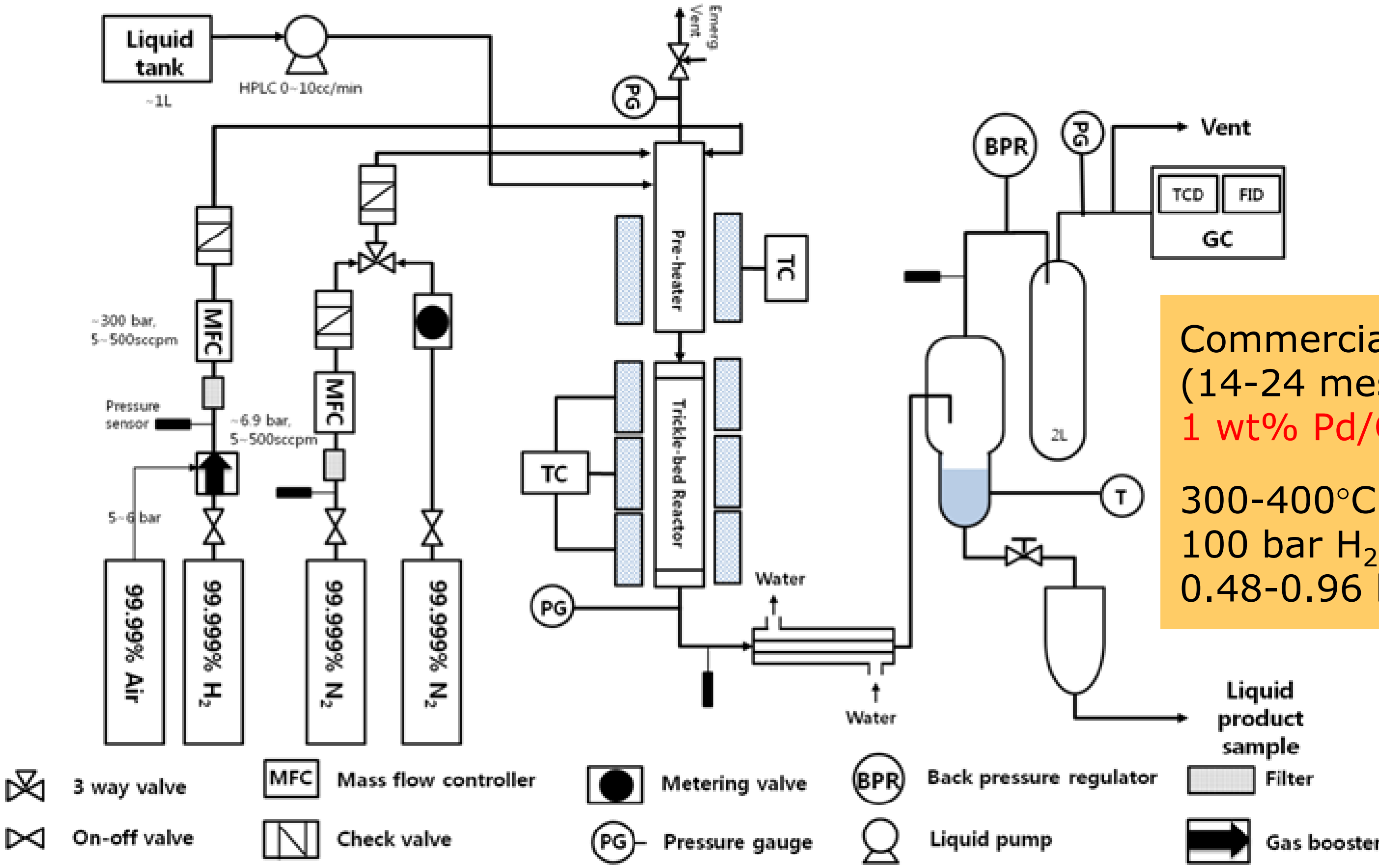
Hydrodeoxygenation (HDO) System

Down-flow Trickle-bed Reactor System

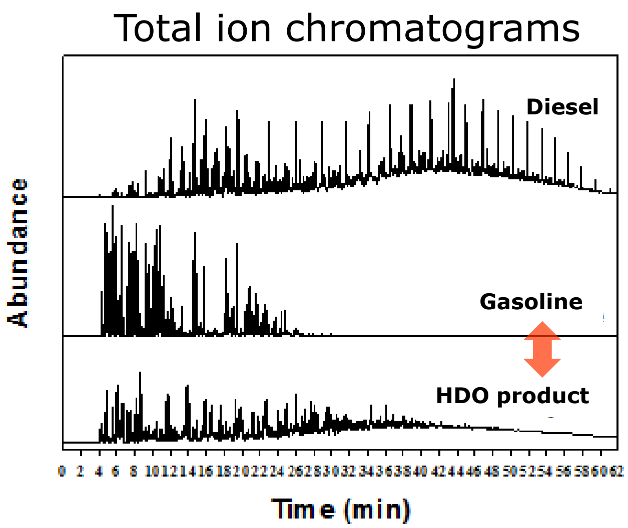


Commercial catalysts
(14-24 mesh pellet)
1 wt% Pd/C, 5 wt%Pd/Al_2O_3

300-400°C (400)
100 bar H_2
0.48-0.96 h^{-1} LHSV (0.48)

HDO Products

Property		HDO product	Gasoline	Diesel
Water content (wt.%)		1.23	0.0035	0.0042
Density @15°C (kg/m^3)		955.5	700.4	822.8
pH		5.4	-	-
Elemental analysis (wt.%)	C	75.10	82.68	86.58
	H	9.60	15.13	13.41
	O	8.68	2.09	0.01
	N	3.20	0.0016	0.0005
	S	0.11	0.0006	0.0005
HHV (MJ/kg)		37.54	45.80	45.96



1 kg of fractionated bio-oil

0.37 kg HDO product

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Summary

- Woody and algal biomass can be converted into liquid fuels for transportation by pyrolysis and catalytic upgrading. However, such fuel is not still economically feasible compared with successful bio-oil applications in heat and power generation.
- Two step catalytic upgrading process can readily remove oxygen from bio-oil under relatively mild conditions.
- Non-fluidized bed reactor system can be considered for algal biomass pyrolysis. Relatively inexpensive and compact pyrolysis and upgrading system needs to be developed.

Challenges

- The cost of the bio-oil, which is 10% to 100% more than fossil fuel
- Availability: there are limited supplies of bio-oil for testing and development of applications
- A lack of standards for use and distributions of bio-oil. Inconsistent quality inhibits wider usage.
- Bio-oil is incompatible with conventional fuels
- Users are unfamiliar with this material
- Dedicated fuel handling system are needed
- Pyrolysis as a technology does not enjoy a good image

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Dr. Jeong-Myeong Ha (Catalytic upgrading)

Prof. Hee Chul Woo & Mr. Jae Hyung Choi
(Fixed bed pyrolysis of algal biomass)