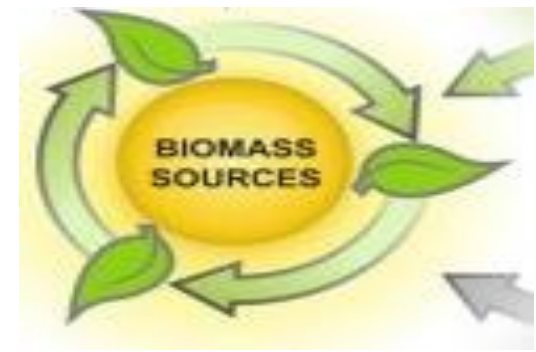


# Hydrothermal Liquefaction for Bio-oil and Chemicals : An Overview

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University of Agder, Norway.



**Biorefinery  
&  
Biochemical**  
6th - 7th March, 2019  
Amsterdam, The Netherlands

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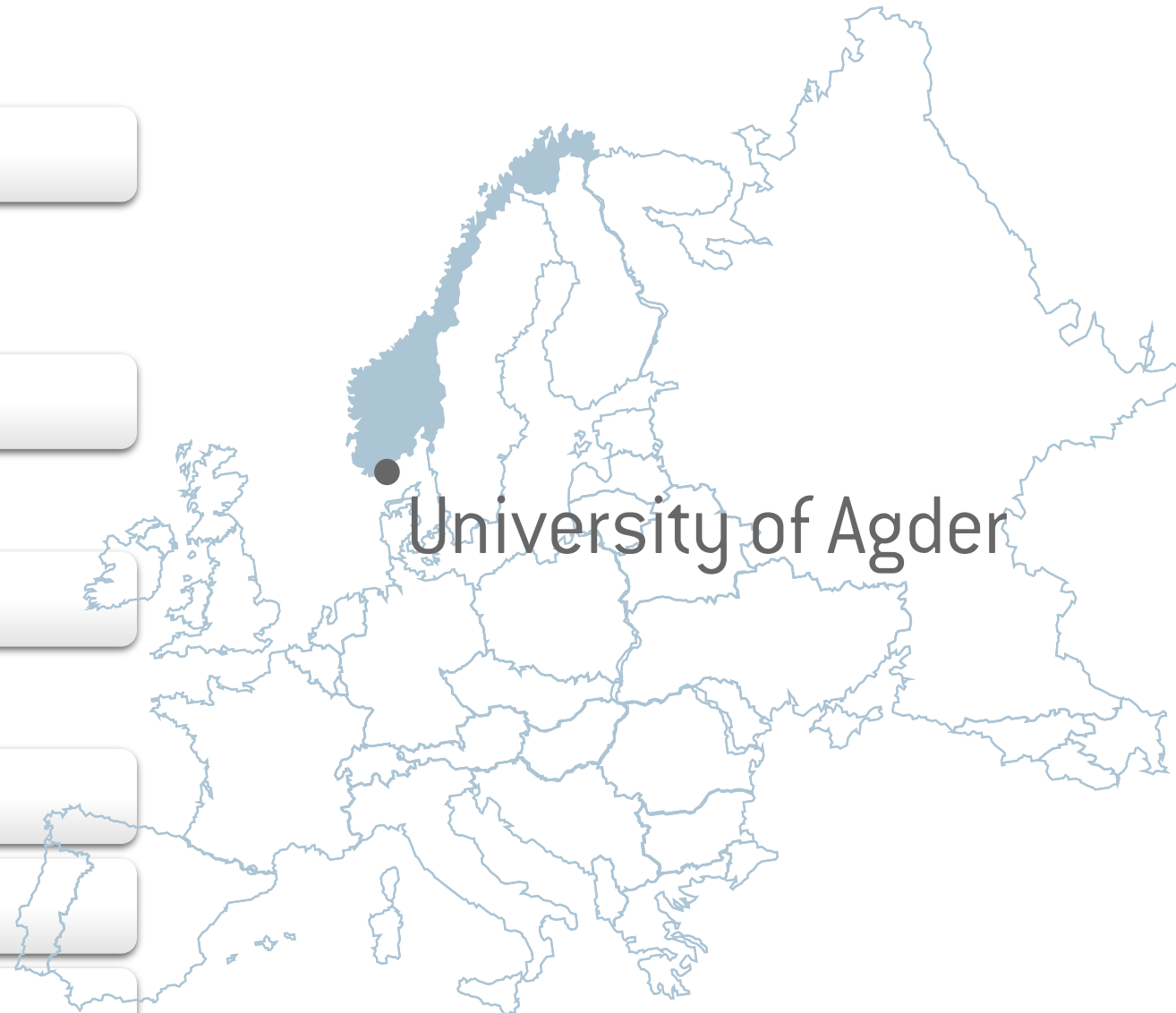
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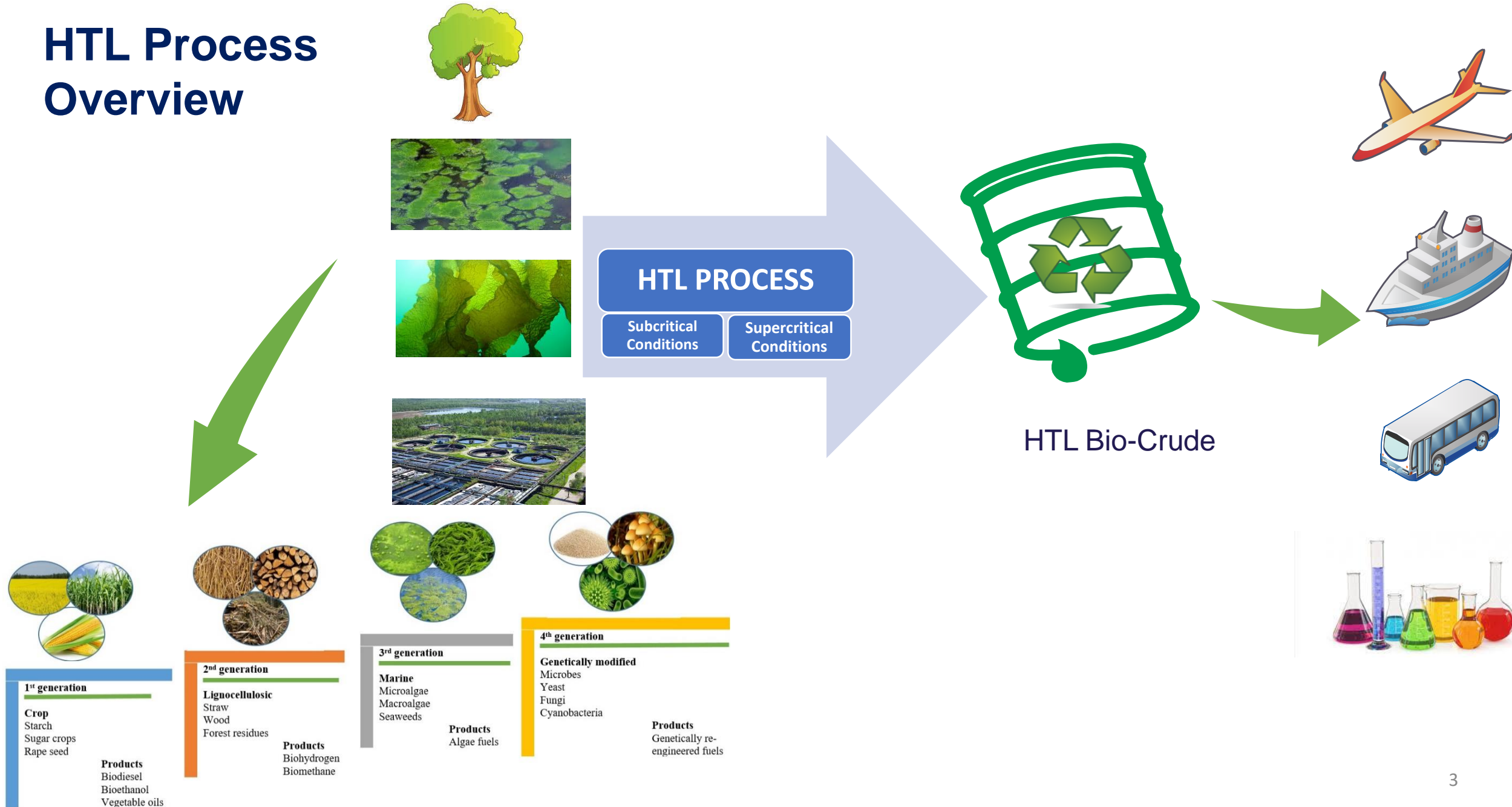
## HTL Vs Pyrolysis

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## Summery



# HTL Process Overview

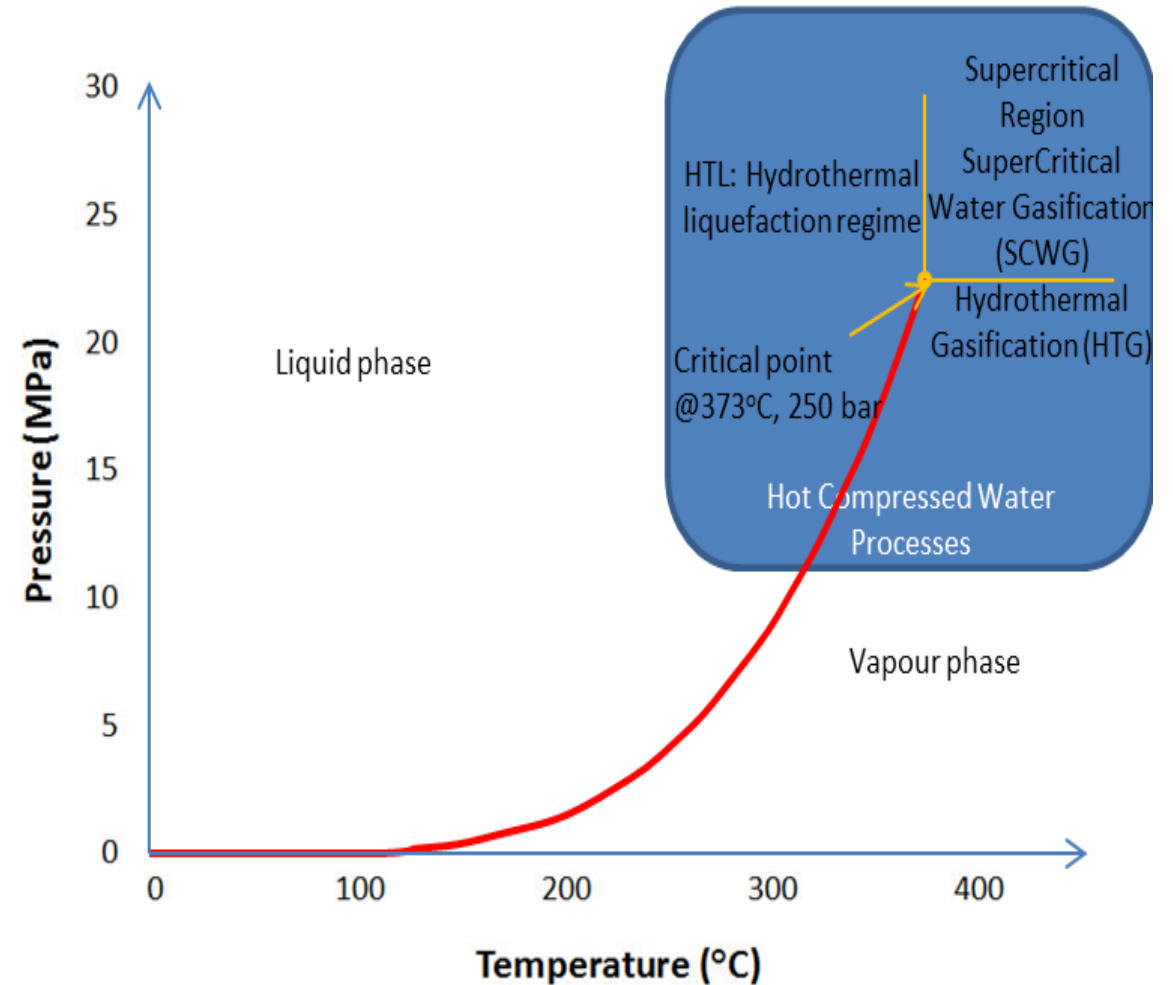


# HTL Process Overview

- High temperature, high pressure thermochemical process (280-420°C, 10-25MPa)
- Feedstock can be directly converted without an energy consuming drying step
- With or without catalyst
- The main products are a bio-crude, solid residue, water-soluble fraction and gases

## Why Hydrothermal Conversion ?

- water properties change drastically - from polar → a polar solvent - dissociation constant ↑↑
- many biomass streams are “wet”
- seen as robust technology

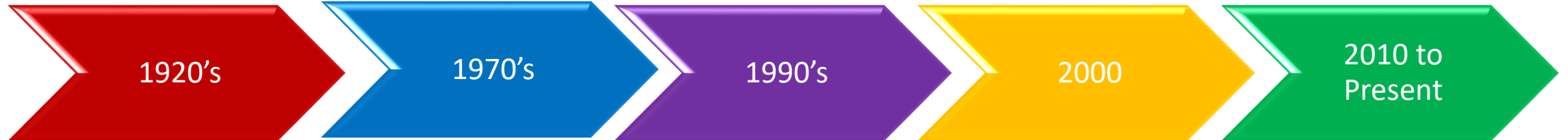


# History of Hydrothermal Liquefaction

- The concept of using hot water and alkali catalysts
- Concept of HTL proposed.
- First patent in 1925

- Focus dry, lignocellulosic biomass.
- Yutaka's group at "National Institute for Resources and Environment" in Japan.
- PNNL picks up the baton. Developed complementary Catalytic HTL

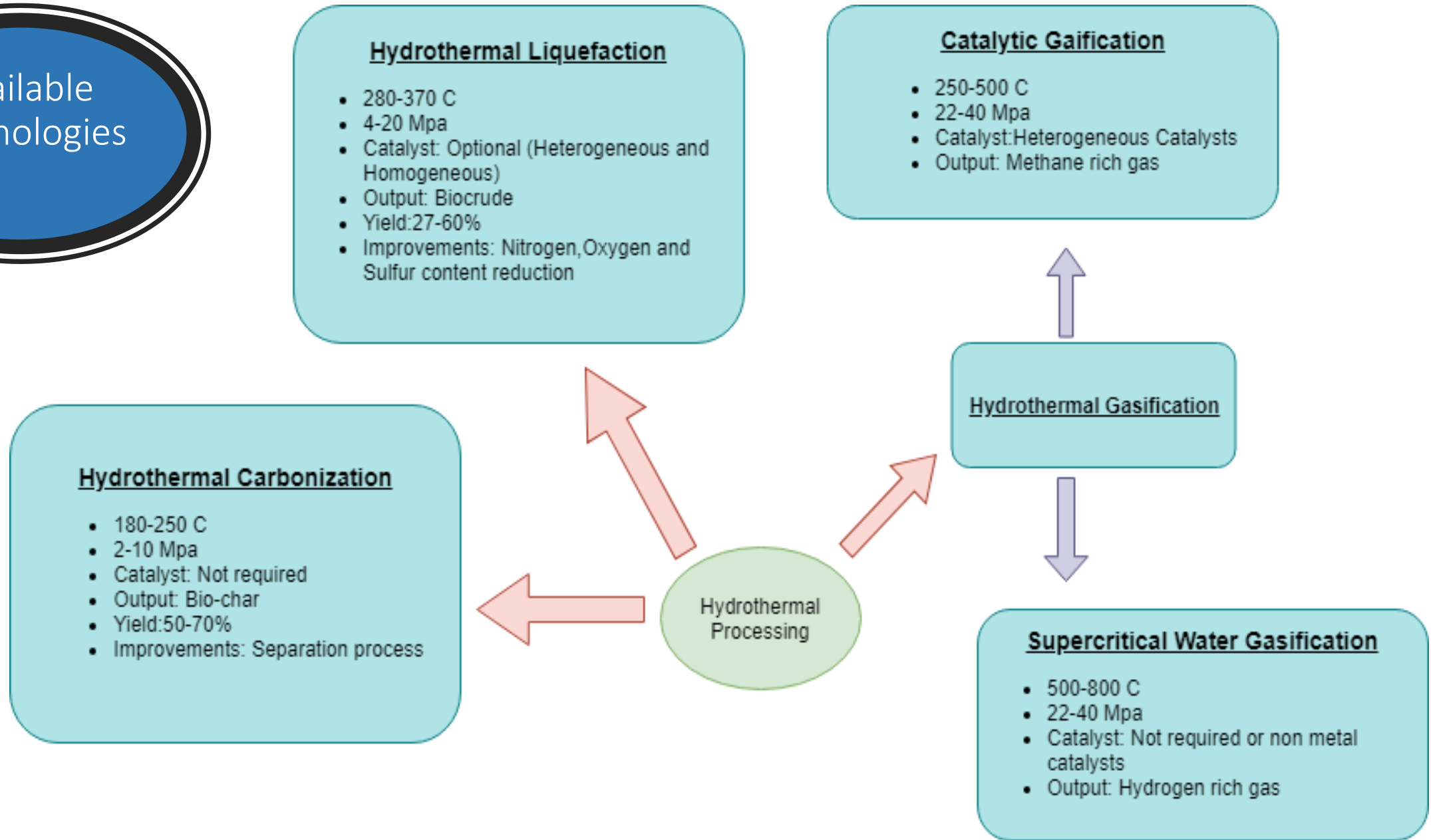
- Explosion of interest in HTL development and commercialization.
- Lignite Energy Resources , Altaca Energy , Steeper Energy, Nabros Energy.



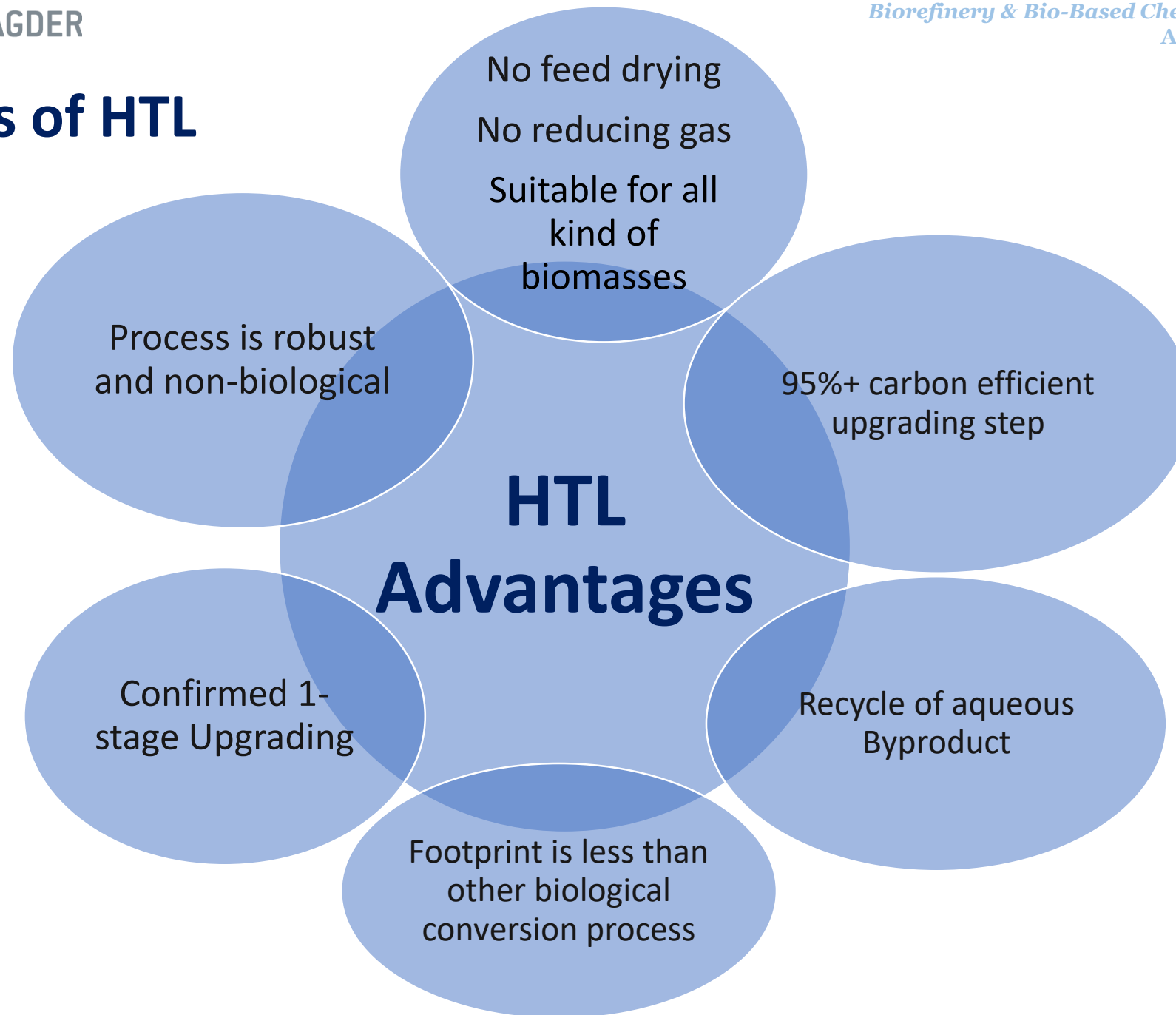
- Appell and co-worker at **Pittsburgh Energy Research Center.**
- Albany Biomass Liquefaction Experimental Facility at Albany, Oregon, US.
- Multiple R&D projects, including Shell Oil

- "Stranded in pilot scale phase"

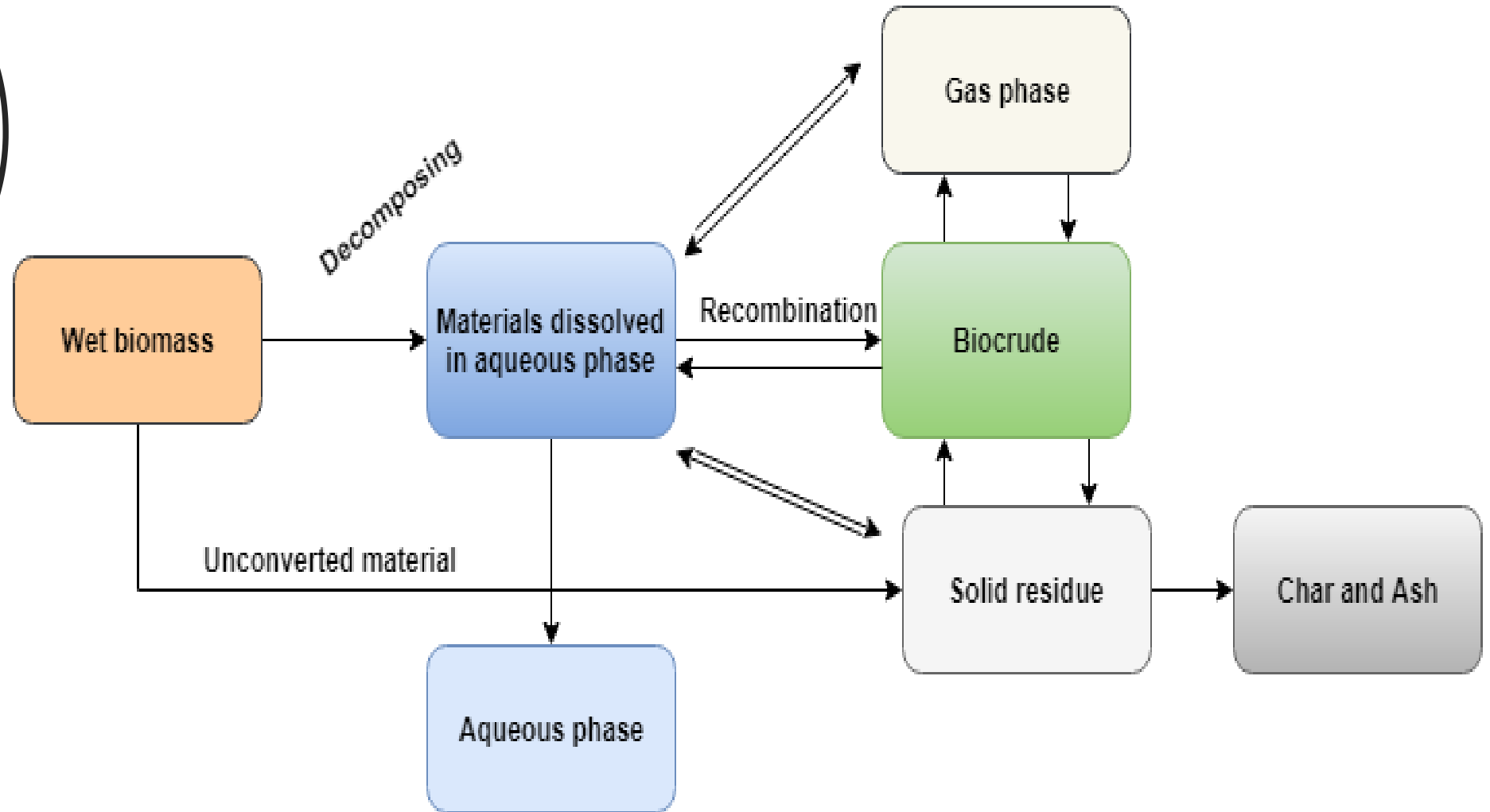
Available Technologies



# Advantages of HTL



Chemistry,  
conditions, and  
products of the  
HTL process



# HTL Pathway

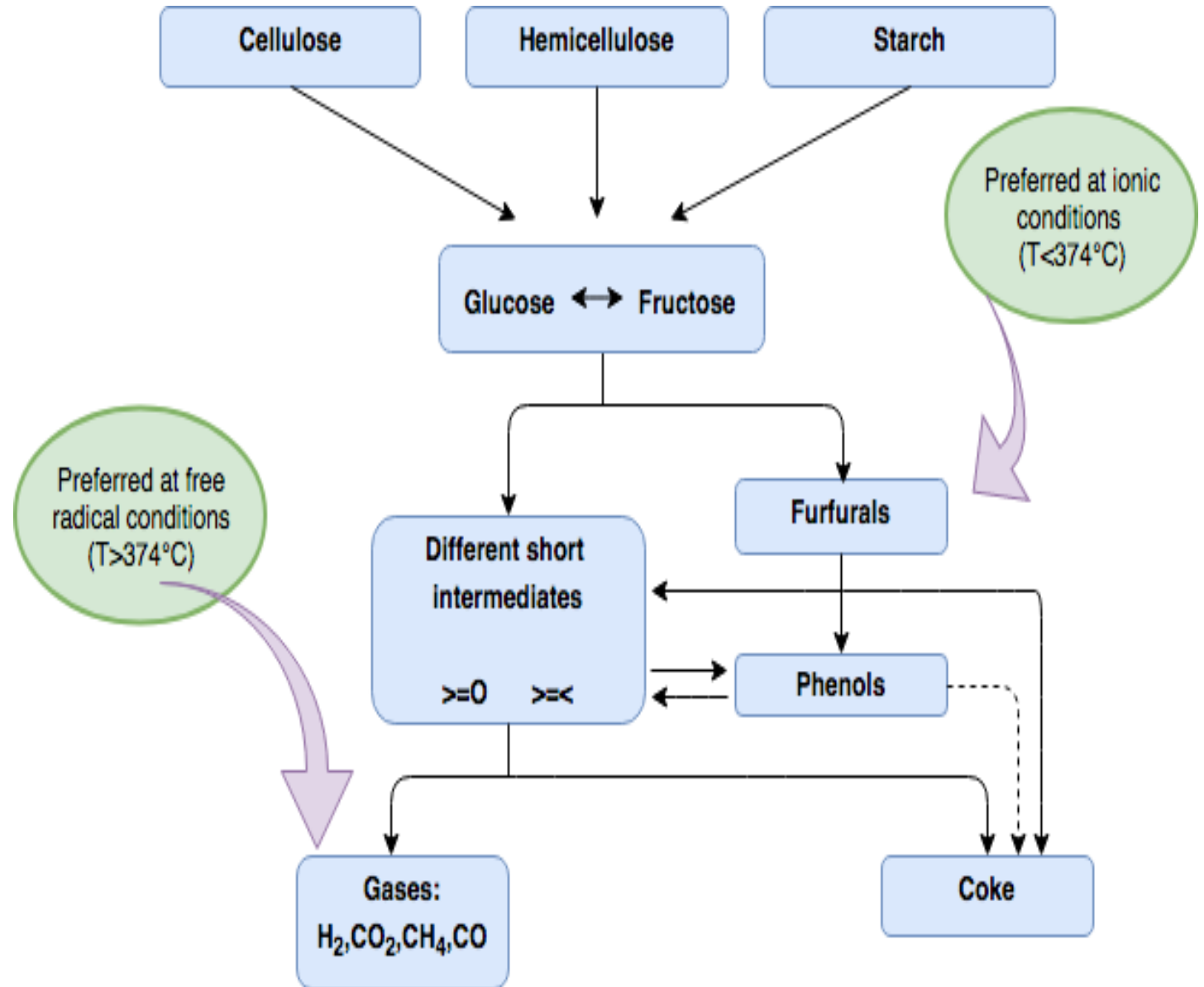
“Short intermediates” are formed by aldol splitting

a lower molecular weight than glucose and often with carbonyl groups and C-C double bonds

The degradation of cellulose to glucose is hydrolysis.

Formation of furfurals from fructose is multiple water elimination

free radical degradation, which is formed by decarboxylation of organic acids



Simplified Reaction Mechanism for Biomass Degradation

# HTL Pathway

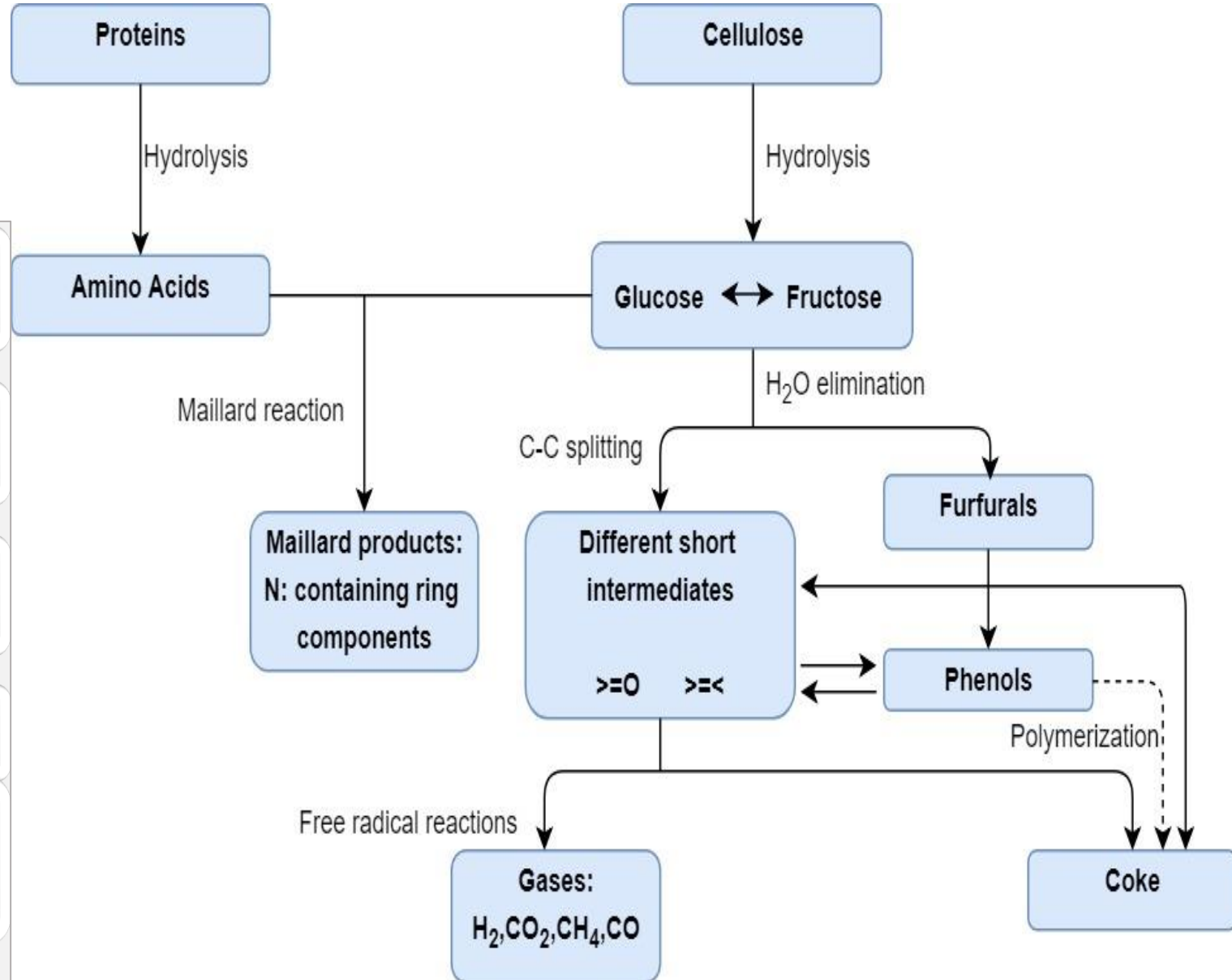
Carbohydrate degradation and protein degradation of biomass in supercritical water.

Via the Maillard reaction glucose or its consecutive products could react with amino acids or its consecutive products

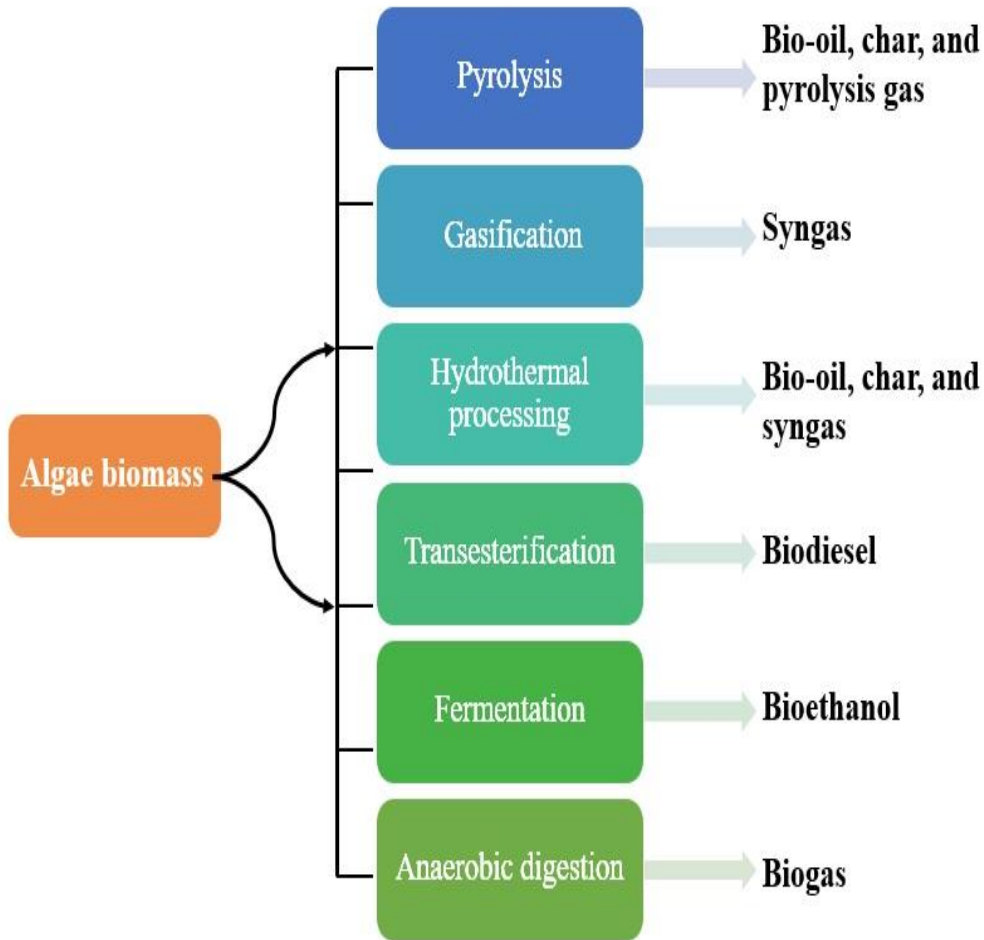
These types of reactions lead to nitrogen containing cyclic organic compounds.

Increase in the DOC

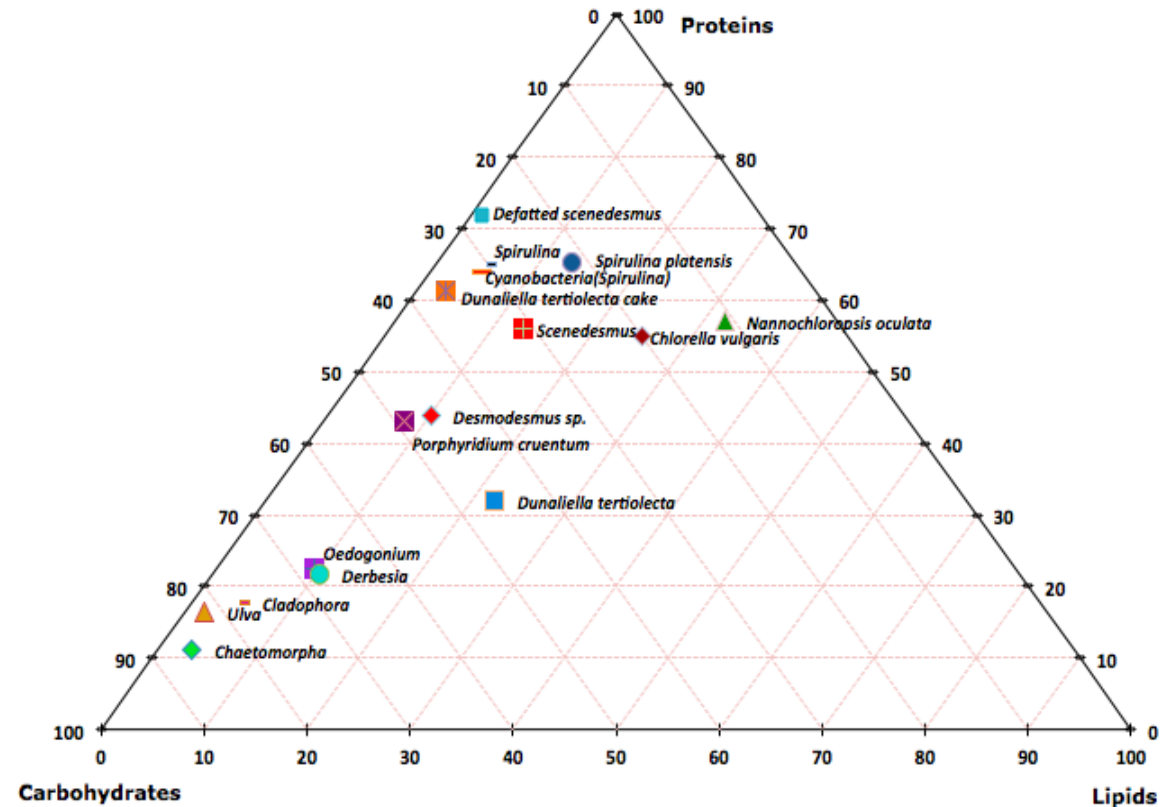
Higher nitrogen compound content in the products of HTL, which support the above fact.



# Algae for HTL



## Characteristics for algae used for hydrothermal liquefaction process



- **Lipid** is one of the major class of bio-macromolecules in algae
- Most algae proteins consist of **polymers of the amino acid** with  $C_1H_{1.56}O_{0.3}N_{0.26}S_{0.006}$ , which has calculated calorific value of 24 MJ kg<sup>-1</sup> (d.b.)
- Algae carbohydrates are monosaccharide polymers with elemental composition  $C_1H_{1.67}O_{0.83}$ , which has calculated calorific value of 17 MJ kg<sup>-1</sup> (d.b.),

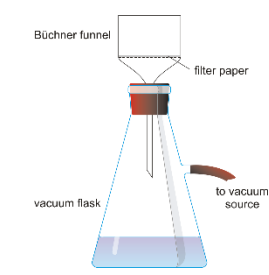
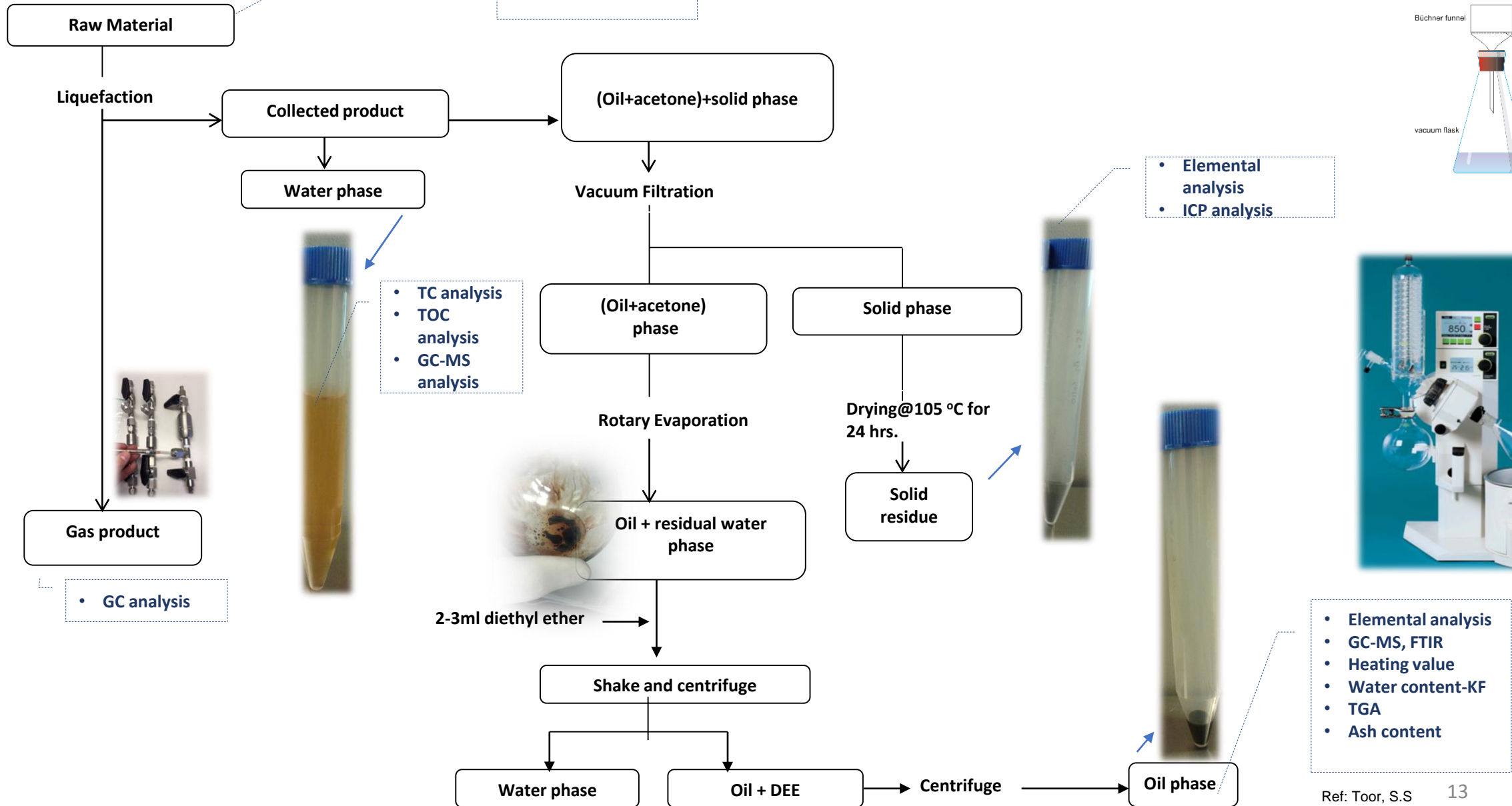
## Refining Technologies for HTL biocrude

- ❑ To address utilization of petroleum refining technologies for upgrading biomass-derived feedstocks from fast pyrolysis and hydrothermal liquefaction.
- ❑ For example:
  - Hydrotreating
  - Hydrocracking
  - Catalytic cracking
- ❑ Fuel products are the focus, but chemical or chemical feedstock products will also be considered.

### Fuels or Products from HTL

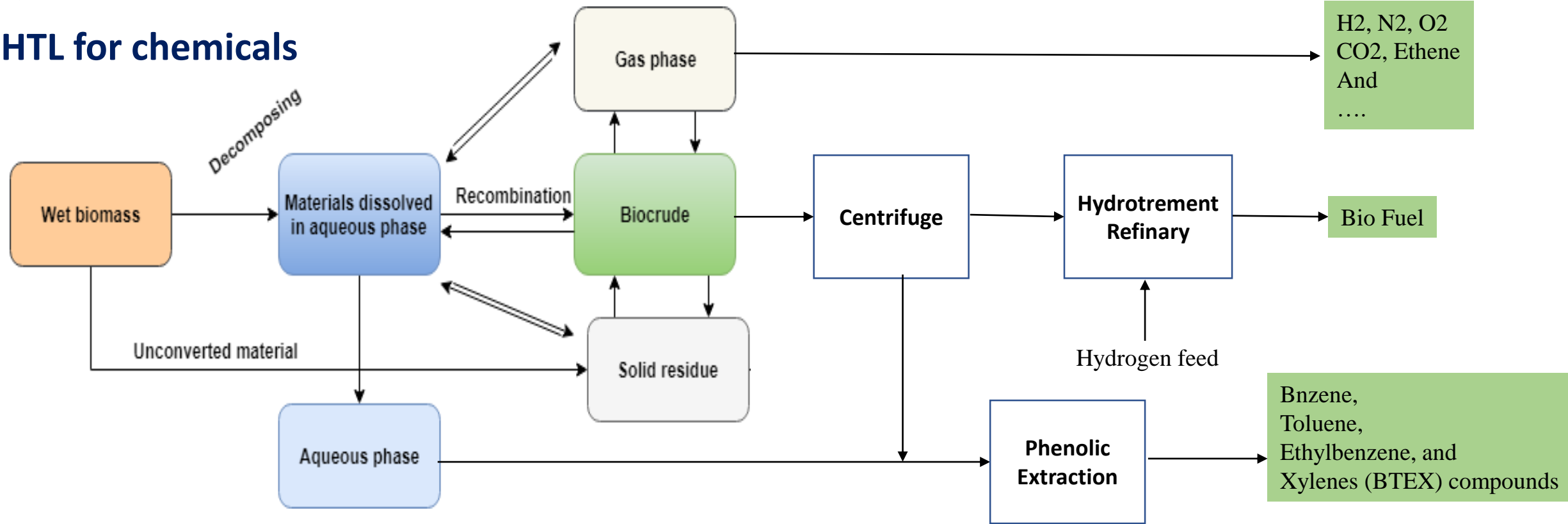
- ❖ Clean liquid biofuels for transportation
  - Gasoline
  - Diesel
  - Jet fuel
  - TBD
- ❖ Organic chemical products
  - Hydrocarbons
  - Oxygenates

# Separation procedure



- Elemental analysis
- GC-MS, FTIR
- Heating value
- Water content-KF
- TGA
- Ash content

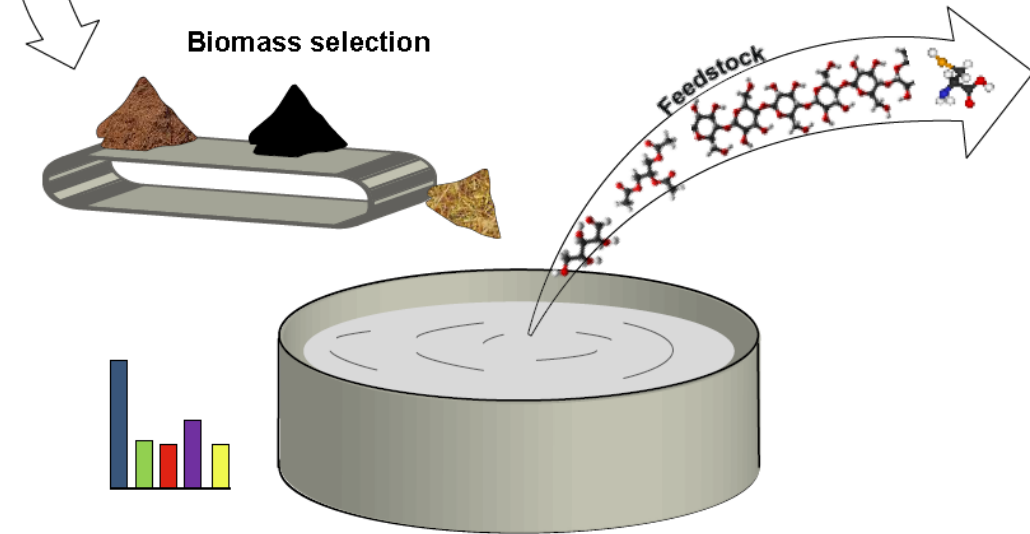
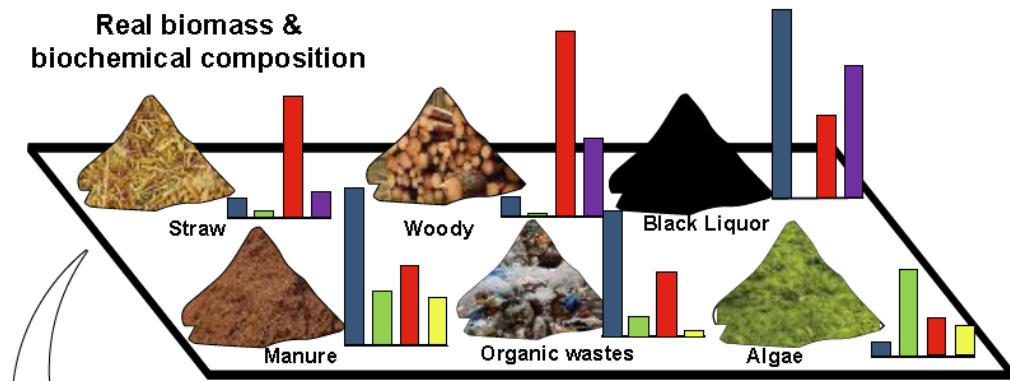
# HTL for chemicals



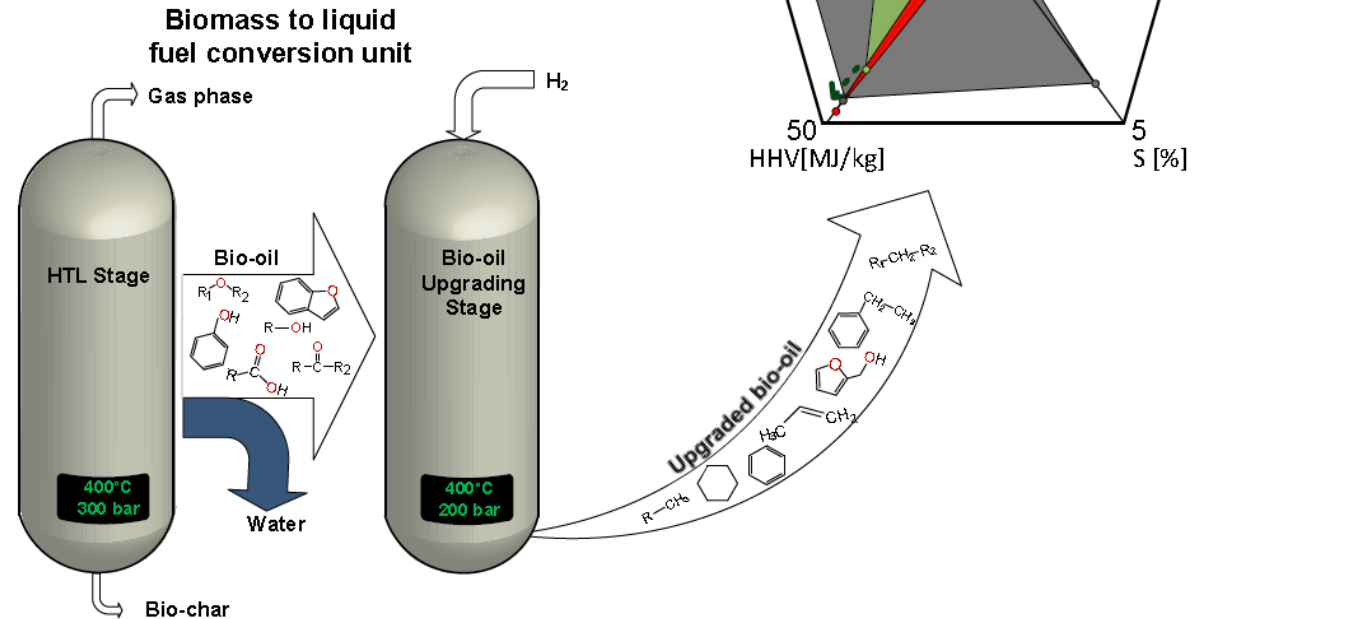
Top 10 chemicals in liquid products from the HTL assisted with various chemicals (area %). [Ref: Junying Chen ]

Water-Only		NH <sub>3</sub> ·H <sub>2</sub> O		H <sub>3</sub> PO <sub>4</sub>		Glycerol	
Hydrazinecarbothioamide	10.74	1,3-Dimethyl-benzene	12.41	2-Methyl-2-cyclopenten-1-one	9.80	Toluene	7.92
Methyl-pyrazine	10.00	Toluene	11.43	2,3-Dimethyl-2-cyclopenten-1-one	8.10	Ethylbenzene	4.81
3-Hexene	9.17	3-(Butylthio)-propanoic acid	7.26	3-Methyl-2-cyclopenten-1-one	7.90	o-Cymene	3.96
4-methyl-3-hexanol	6.93	4-Methyl-3-hexanol	3.33	Acetic acid	7.45	2,3-Dimethyl-1H-indole	2.32
2-Methyl-2-cyclopenten-1-one	3.79	o-Cymene	2.40	Methyl-pyrazine	6.95	1,3-Dimethyl-benzene	2.04
Pyrazine	3.29	3-Methyl-thiophene	2.22	2-Methoxy-phenol	6.63	2,6,10-Dodecatrien-1-ol, 3,7,11-trimethyl-, (Z,E)-	1.89
n-Hexane	2.88	6-Methyl-2-[(4-morpholinyl)methyl]-phenol	2.21	Butanoic acid	4.29	2-Methoxy-phenol	1.60
3-(Butylthio)-propanoic acid	2.67	2-Methyl-indolizine	2.08	Phenol	3.79	1-Pentadecene	1.57
Ethyl-pyrazine	2.46	Butanoic acid methyl ester	1.78	2-Methyl-pyridine	3.60	3-Hexyne	1.56
2,2-Dimethoxy-propane	2.38	1,3-Dimethyl-benzene	1.72	3-Ethyl-2-cyclopenten-1-one	3.41	2-Butenyl-benzene	1.56

# HTL biocrude upgradation



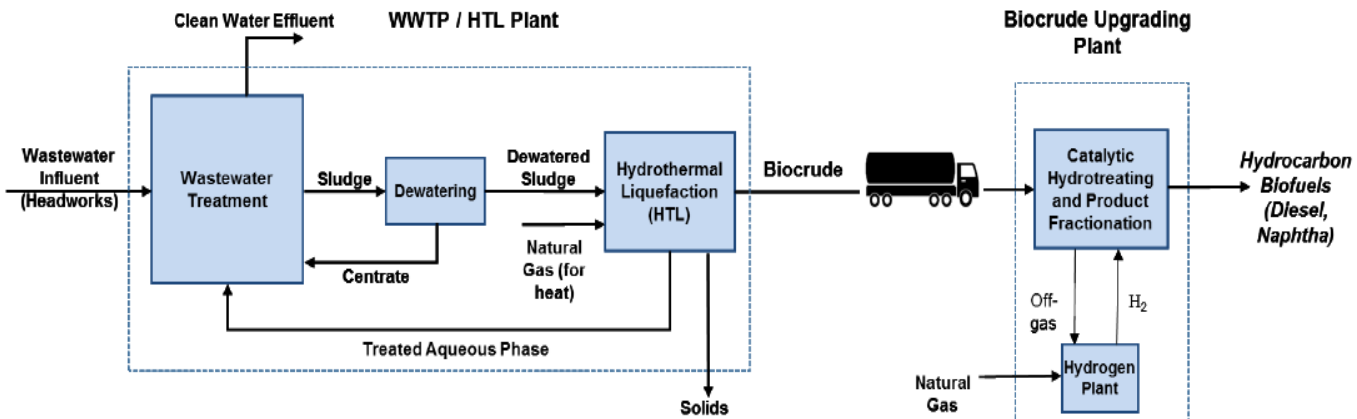
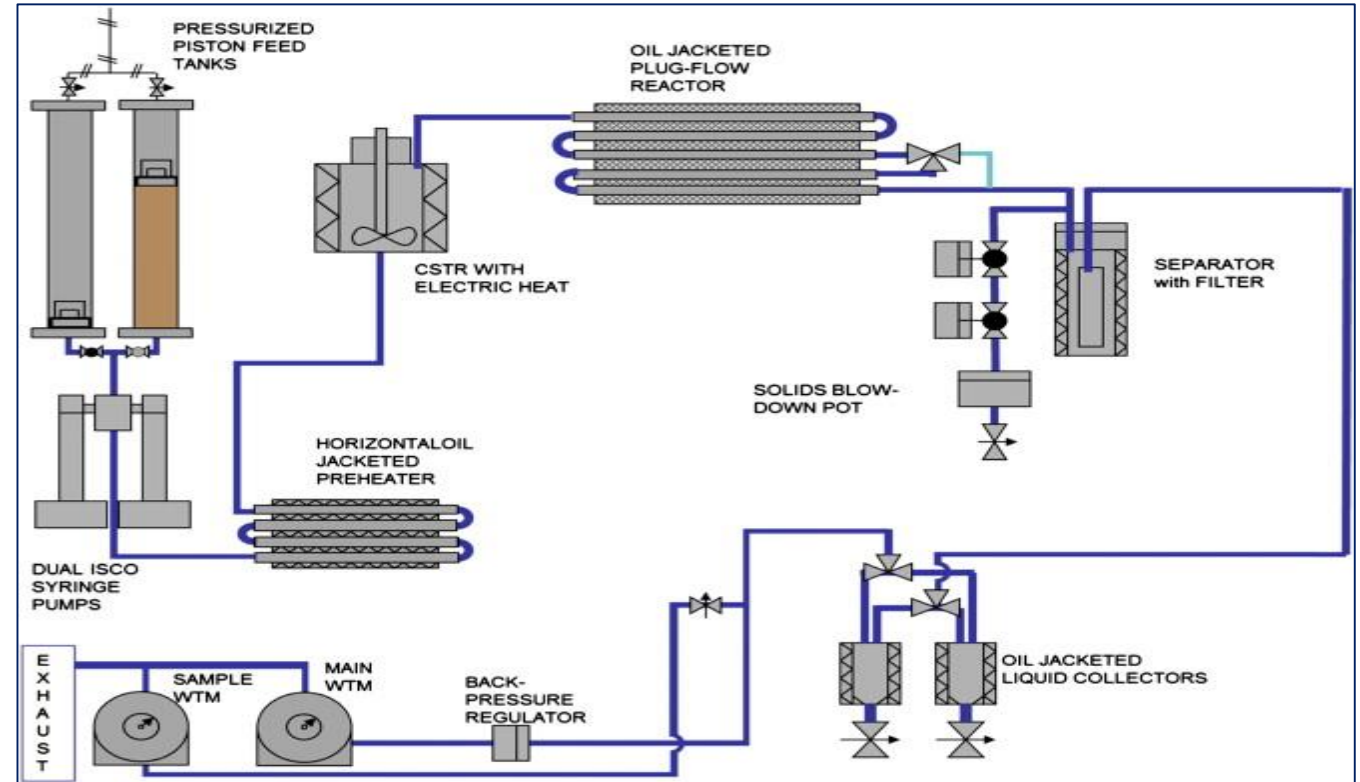
**Ideal composition of the HTL reactor feed**



# Continuous HTL Systems

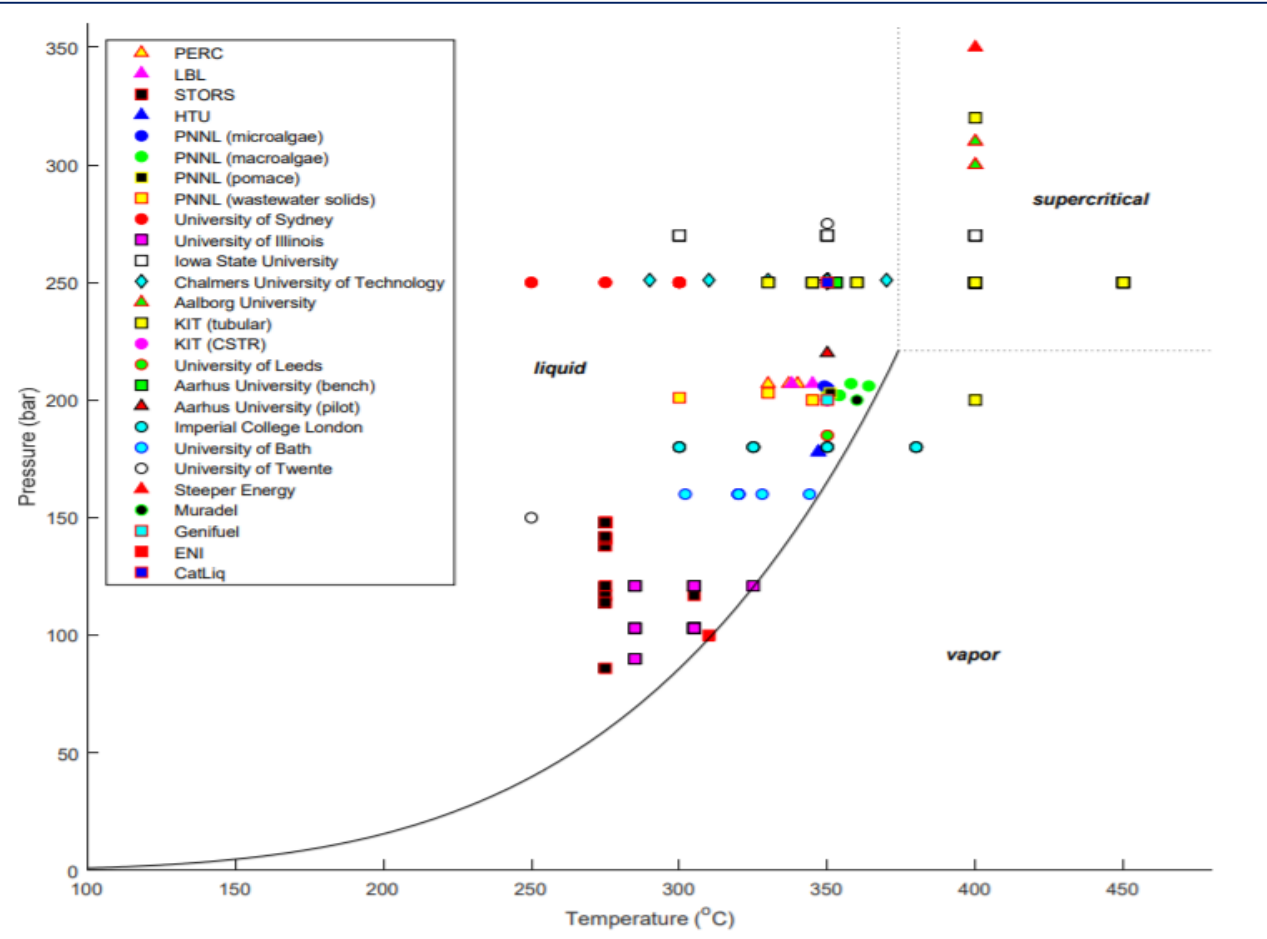
## Why Continuous?

1. Thermal Transience
2. Difficulty in decoupling temperature and pressure
3. Different contact pattern
4. Significant distance towards actual industrial implementation.

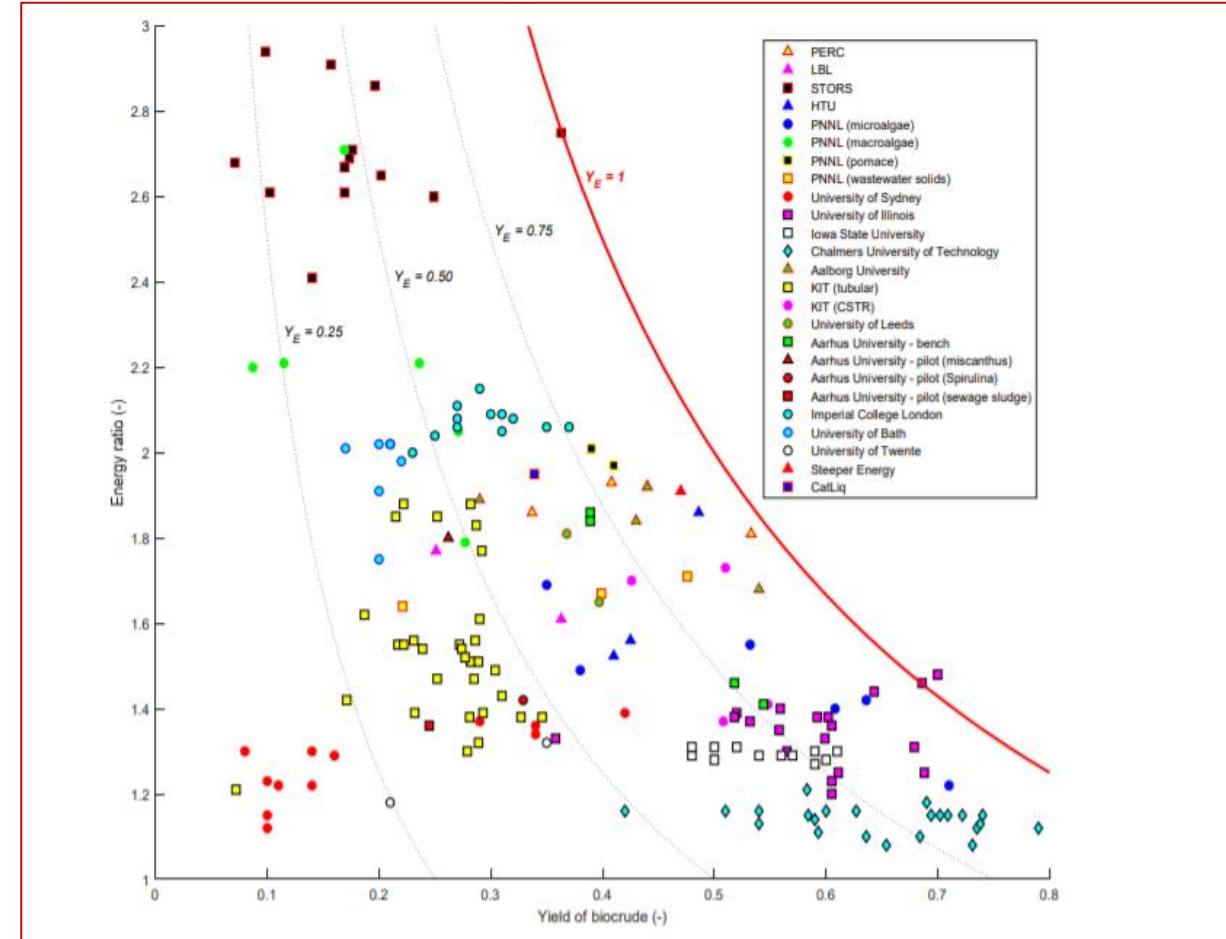


Douglas C. Elliott

# Continuous HTL Systems



State diagram of water reporting temperature and pressure of the continuous HTL



Energy ratio vs. bio-crude yields for the continuous HTL studies

## Continuous HTL Systems



Designed, built, and commissioned by Merrick



Steeper Energy, Aalborg University

# Co-liquefaction HTL Systems

## 1. Micro-macro algae ratio condition: 50/50 mass ratio

Temperature [°C]	Time [min]	Weight of slurry [gram]	Reactor Pressure [bar]	Gas pressure [bar]	Weight of solids [grams]	Weight of biocrude [grams]	Weight of water [grams]	Solids yield [wt.%, d.b.]	Aqueous yield [wt.%, d.b.]	Biocrude yield [wt.%, d.b.]	Gas <sup>a</sup> yield [wt.%, d.b.]
330	10	7.01	140	8.5	0.4075	0.2811	3.8529	31.66	26.54	21.84	19.96
	20	7.01	149	8.8	0.4104	0.2274	4.1877	31.89	21.75	17.67	28.69
	30	7.01	156	9.2	0.4269	0.2116	4.481	33.17	17.57	16.44	32.82
350	10	7.05	171	8.2	0.3337	0.2322	3.447	25.93	32.14	18.04	23.89
	20*	7.04	177	7.9	0.3966	0.3408	4.4767	30.81	17.56	26.48	25.15
	30	7.05	201	9.2	0.4668	0.2951	4.797	36.27	12.99	22.93	27.81
375	10	7.04	152	9.5	0.4168	0.2639	2.9015	32.39	22.89	20.51	24.21
	20*	7.01	191	10.1	0.4505	0.1906	4.353	35.01	19.40	14.81	30.78
	30	7.04	232	11.9	0.5024	0.1065	4.9885	39.04	10.29	8.28	42.39

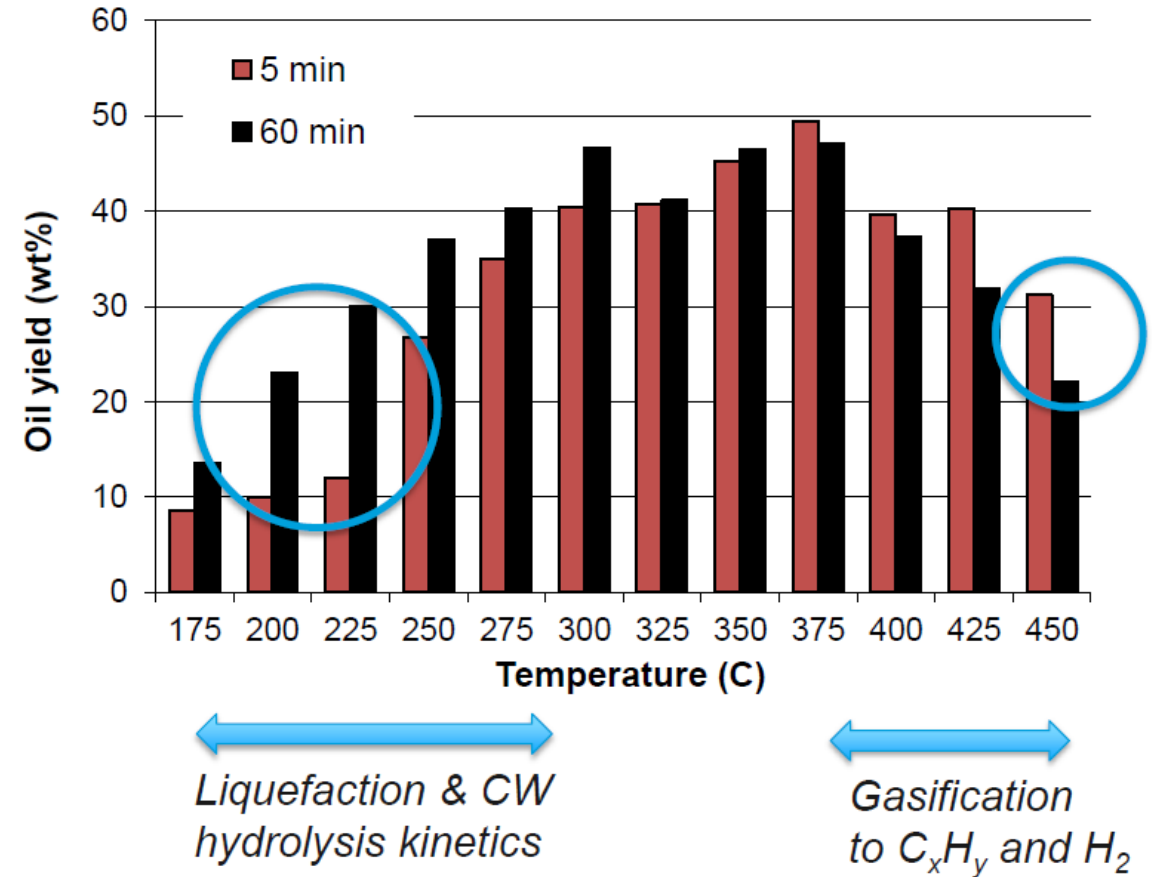
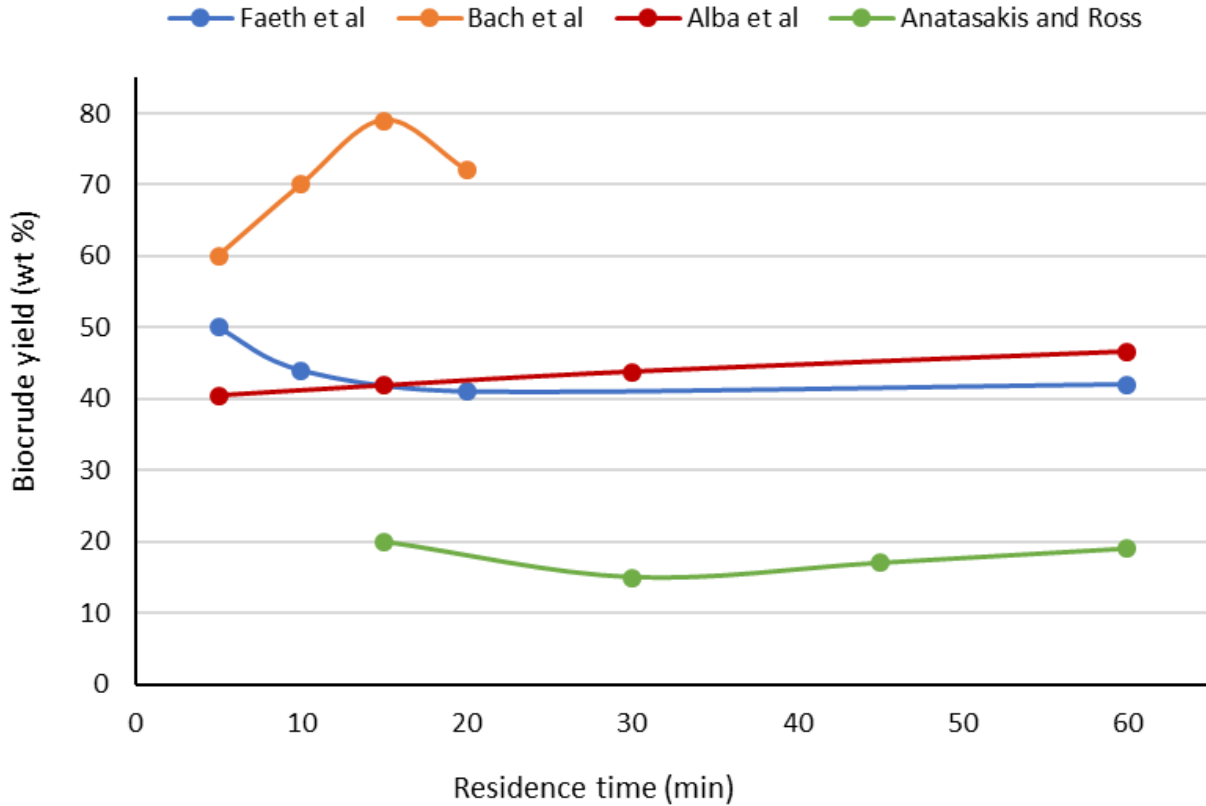
## 2. Micro-macro algae ratio condition: 70/30 mass ratio

350	10	7.01	157	3.1	0.1684	0.2041	1.8258	13.06	54.25	15.83	16.85
	30	7.02	166	3.7	0.3875	0.2694	3.7035	30.06	27.43	20.90	21.60
375	10	7.02	229	5.0	0.3745	0.2019	2.151	29.05	49.54	15.66	5.74
	30	7.01	185	0.2	0.3436	0.1758	3.1724	26.65	35.04	13.64	24.66

## 3. Micro-macro algae ratio condition: 30/70 mass ratio

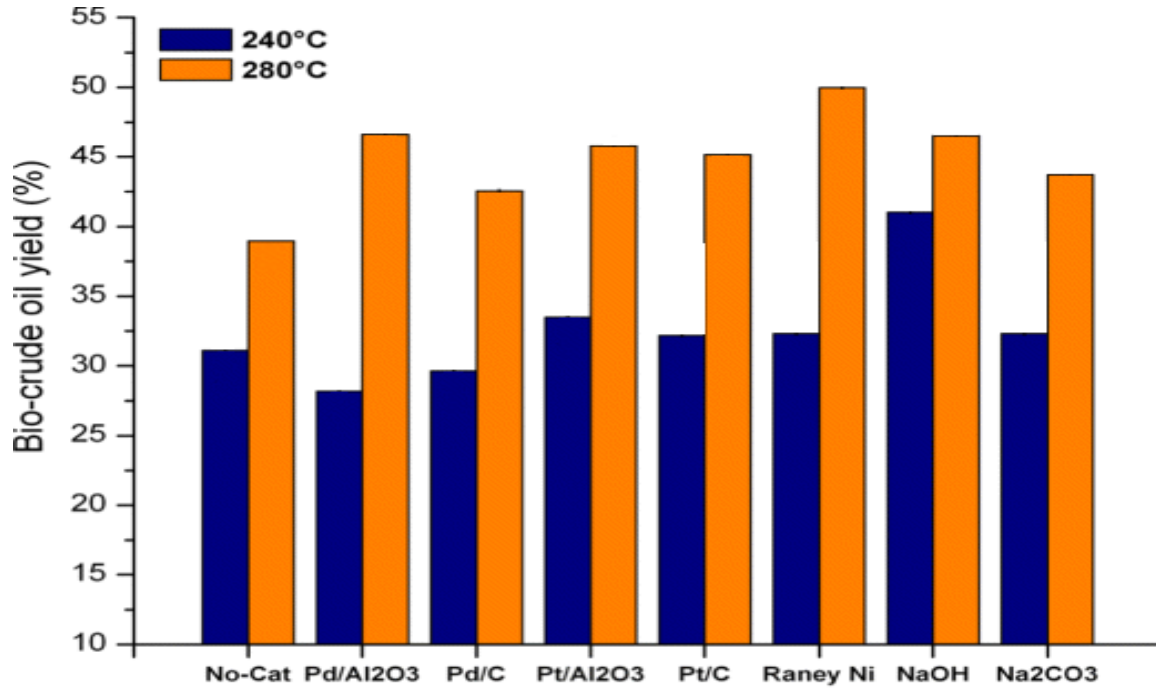
350	10	7.03	169	9.3	0.34723	0.2566	4.0313	27.03	22.66	19.98	30.32
	30	7.03	164	2.2	0.37048	0.1896	5.0685	28.84	7.91	14.76	48.48
375	10	7.04	226	1.1	0.3453	0.2777	4.9537	26.88	9.52	21.62	41.97
	30	7.01	232	1.2	0.4652	0.2945	5.1783	36.27	6.36	22.93	34.43

## Impact of resident time on biocrude yield

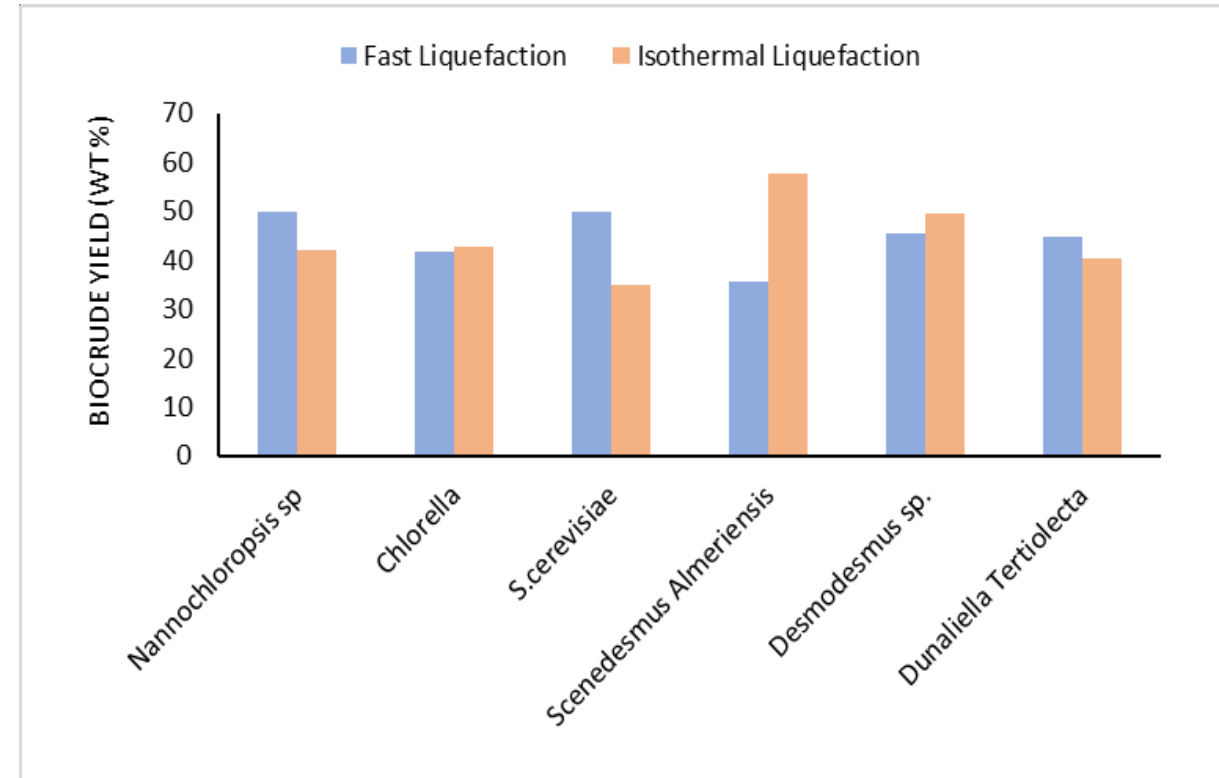


Ref: Wim Brillman

## Biocrude yields Analysis

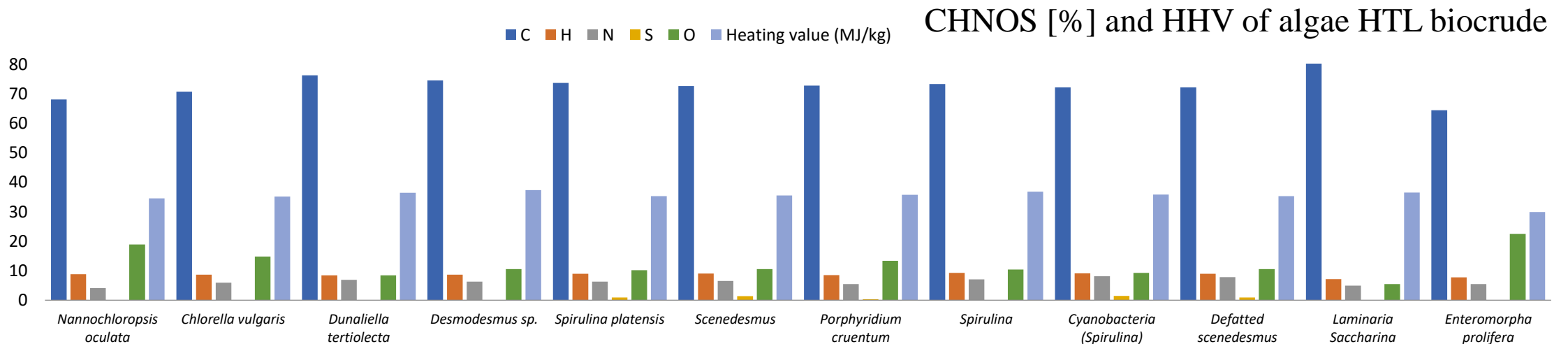
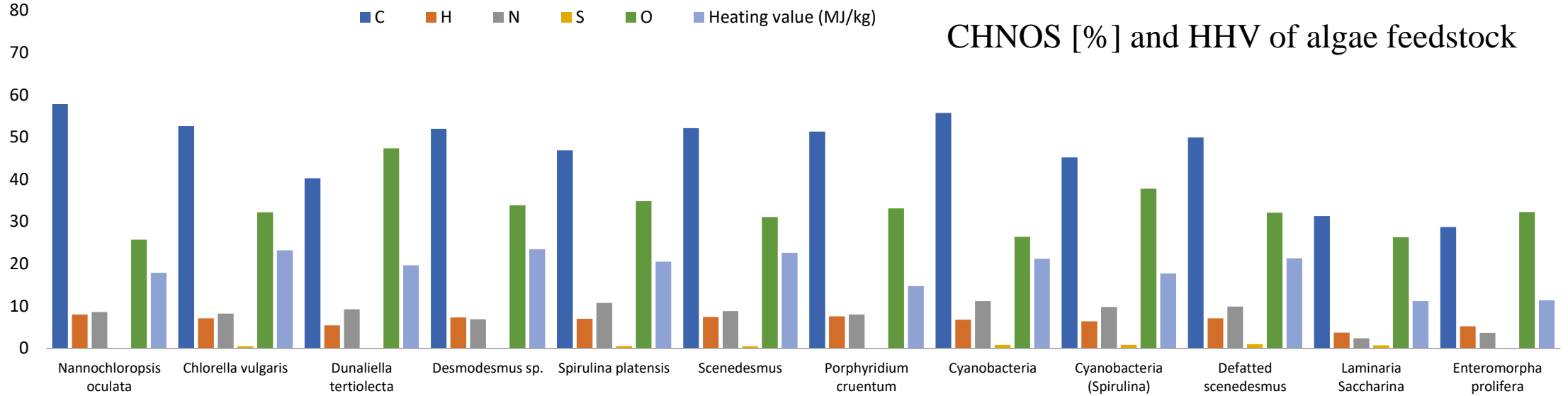


Homogeneous and heterogeneous catalyst effects on biocrude yield from HTL of algae with respect to temperature (Yu et al., 2014).

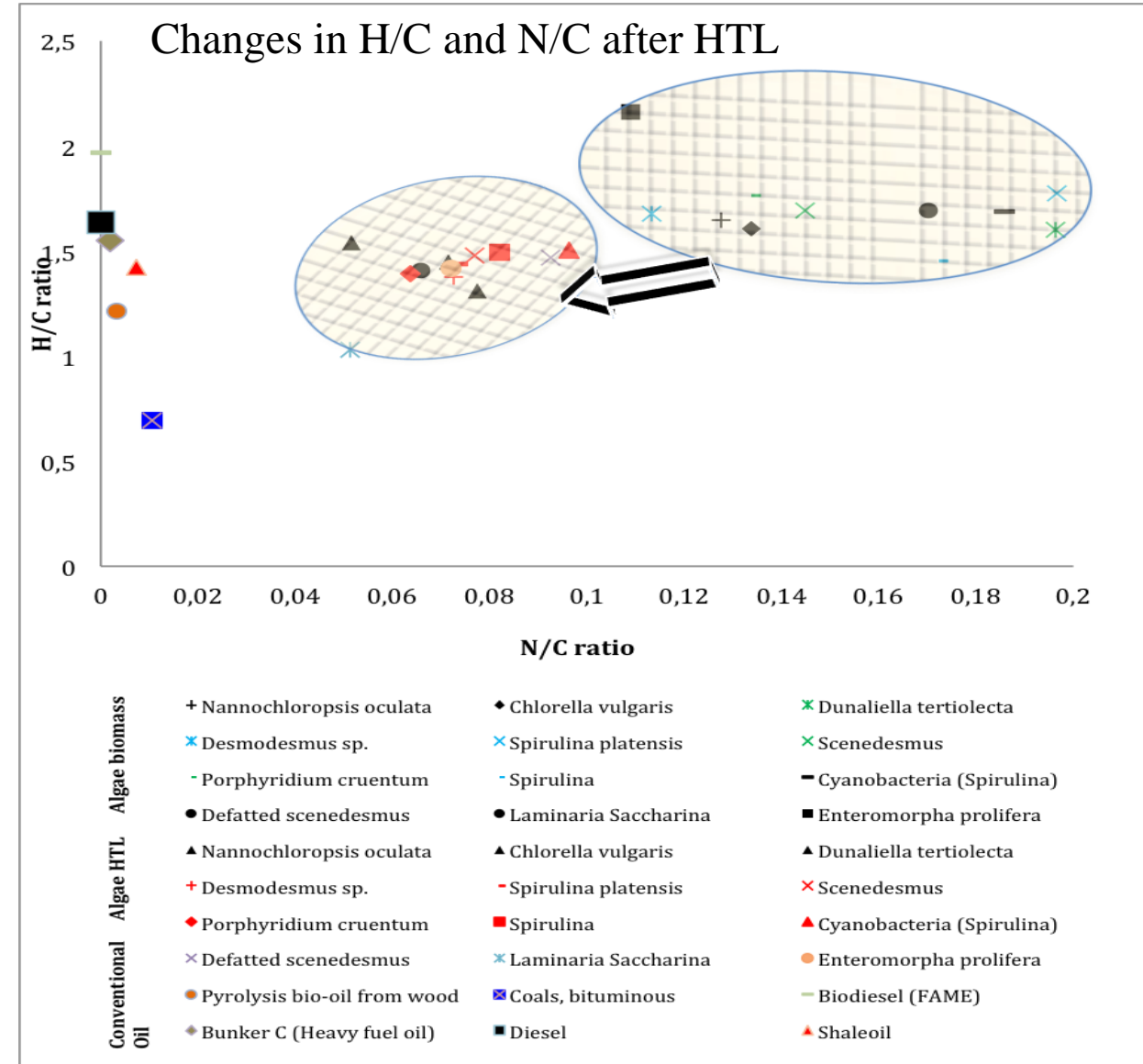
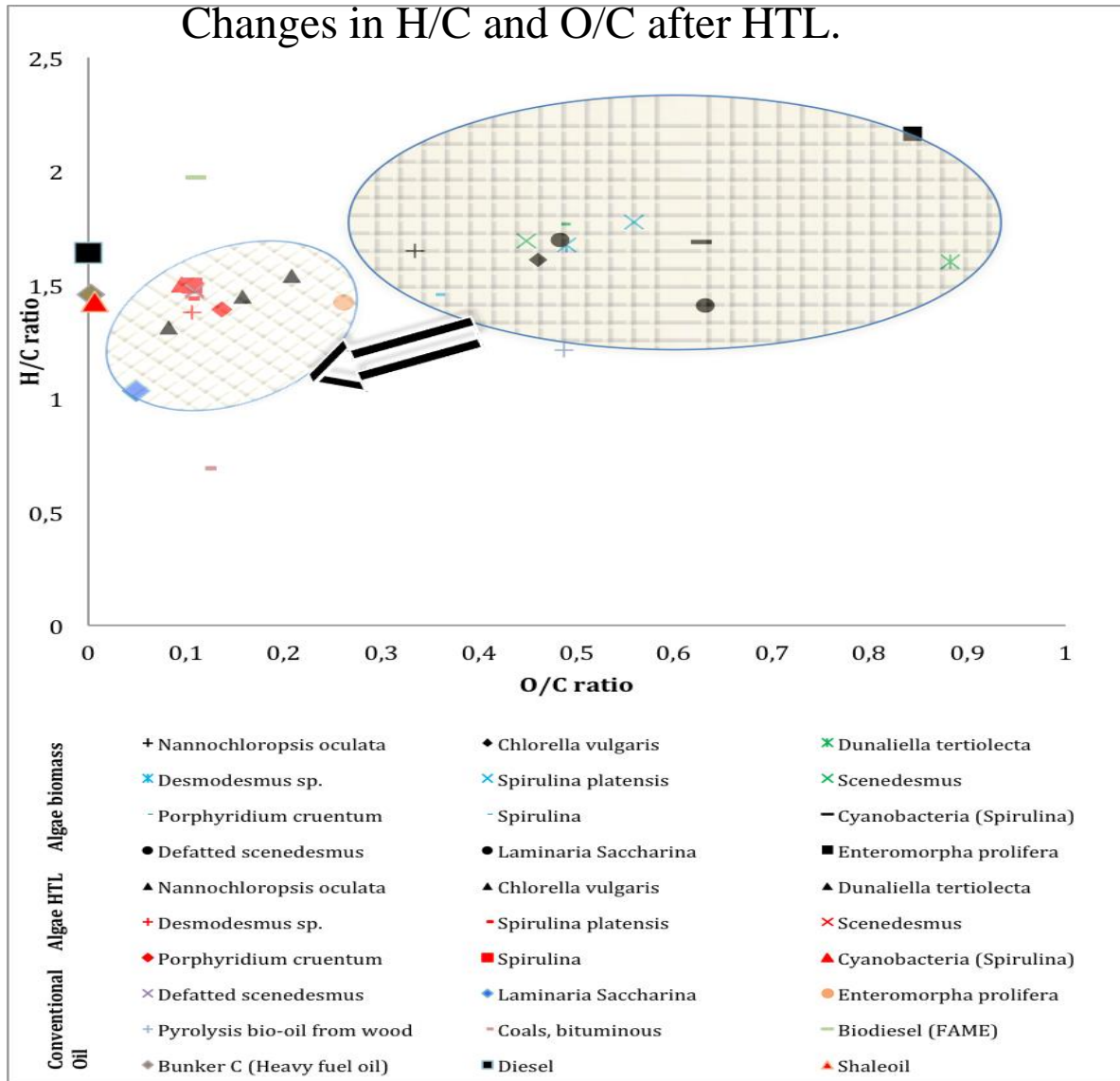


Fast and isothermal HTL in subcritical conditions

# Feedstock and Biocrude yields Analysis



# HTL Biocrude Analysis



## Fast Liquefaction in Continues process

Majority of the HTL research is performed with long residence times ranging from 30-60 mins and temperature from 300-350 °C.

Fast Liquefaction has very short residence times of 30 s to 5 mins and high heating rates up to 585°C/min

Literature shows a fast liquefaction produces bio crude as quality as the conventional liquefaction

Possibility of reduction in size of reactors, reduced energy consumption and feasibility of the process

Could reduce the process cost and reactor sizes significantly if it is taken into an industrial level

Advanced refining methods as well as biomass slurry feeding systems would be a requirement

High heating rates would be a requirement

Continues process is still at laboratory level

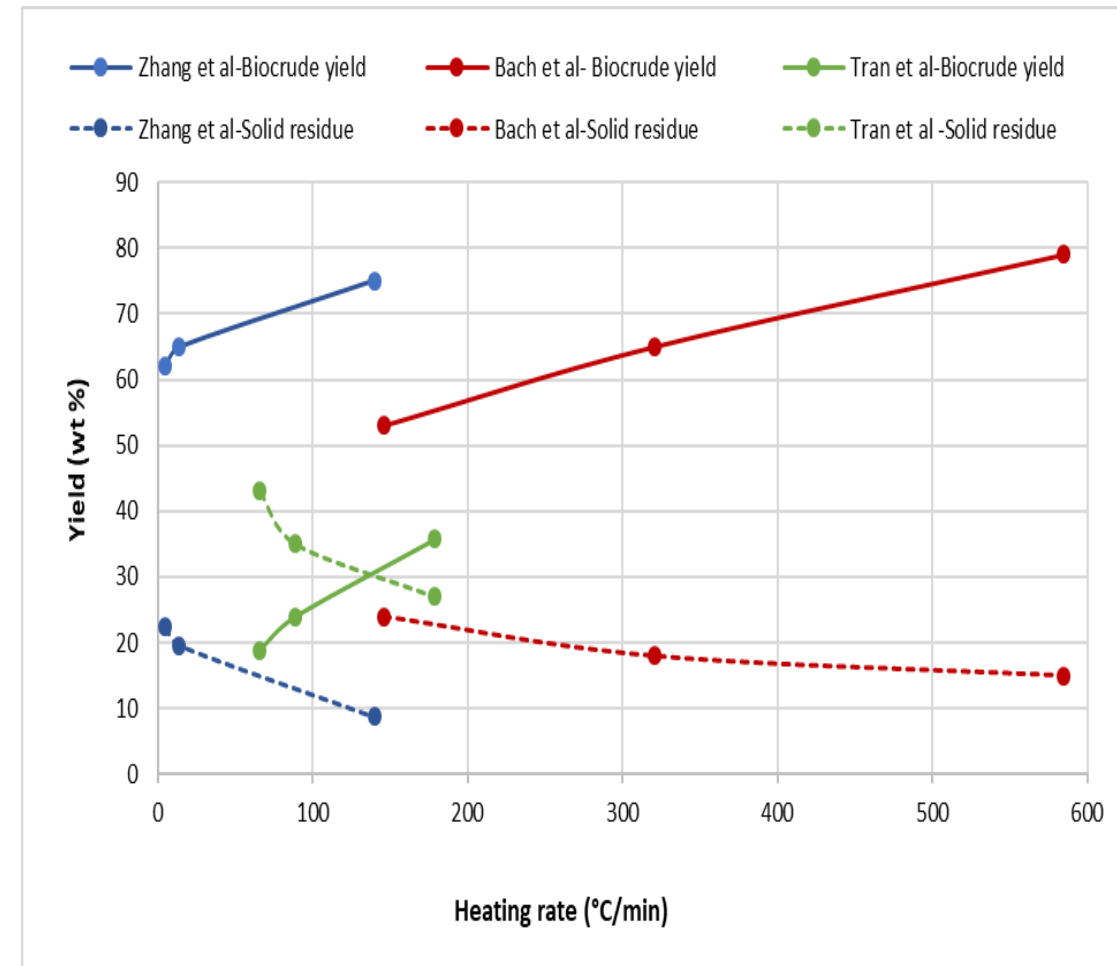
Numerous research groups working on it around the world

Has produced biocrude with HHV from 33-39 MJ/kg while catalyst supported process has produced biocrude with HHV up to 45 MJ/kg

## A comparison of batch and continues process

Reactor type	Temp: (°C)	Residence time(min)	Press: (MPa)	Catalyst	Biomass loading (wt%)	N (%)	HHV (MJ/kg)	Yield %
Batch	300-350	5	NR	No	16	5	32.1–36.7	34–58
Batch	300-350	1-3	±40	No	32	2-6	33.3–36.7	13–66
Continues	250-350	3-5	15-20	No	1-10	6.3-7.8	27.9–33.8	<10–41.7
Continues	350	15	20	No	17-35	4-4.7	39.4–40.1	38–63.6
Continues	300-380	0.5-4	18	No	1.5	2.35-3.9	36.6–39.3	23.13–38.0

## Impact of the Heating rate on the yield



# R&D efforts to improve oil properties

Nitrogen content of the bio crude is one of the main issues encountered .

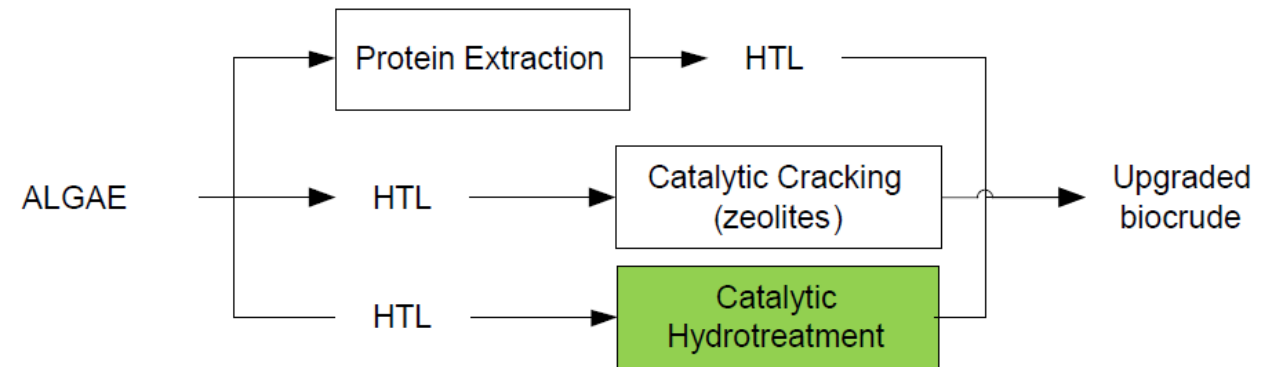
Nitrogen in biocrude can lead to NOx emissions and could harm engines when biodiesel is used as a fuel.

Feedstock with high protein content could lead to generate biocrude with high nitrogen content

Generally, biocrude from microalgae and macroalgae has nitrogen content of 3.7-9 %

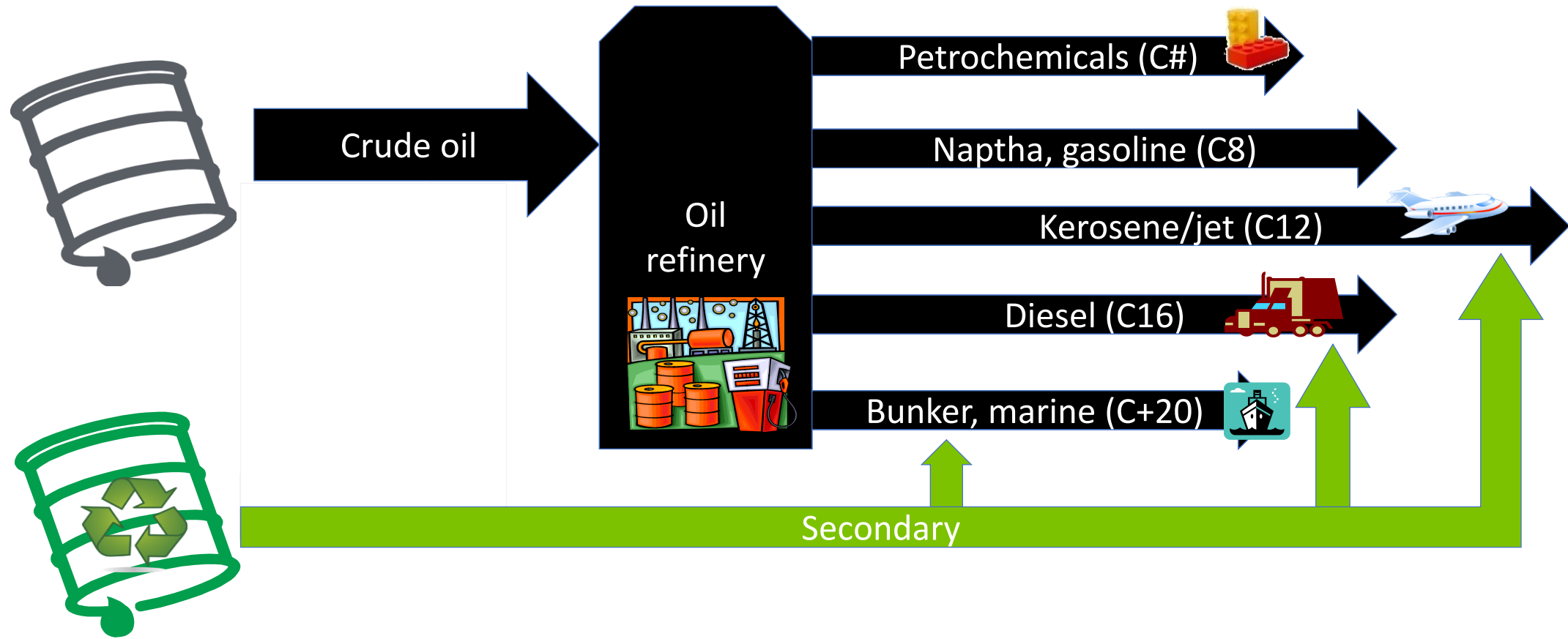
Hydrotreated biofuel has much less nitrogen content, although its not as less as petroleum fuel

Number of techniques are used to reduce nitrogen content in biocrude

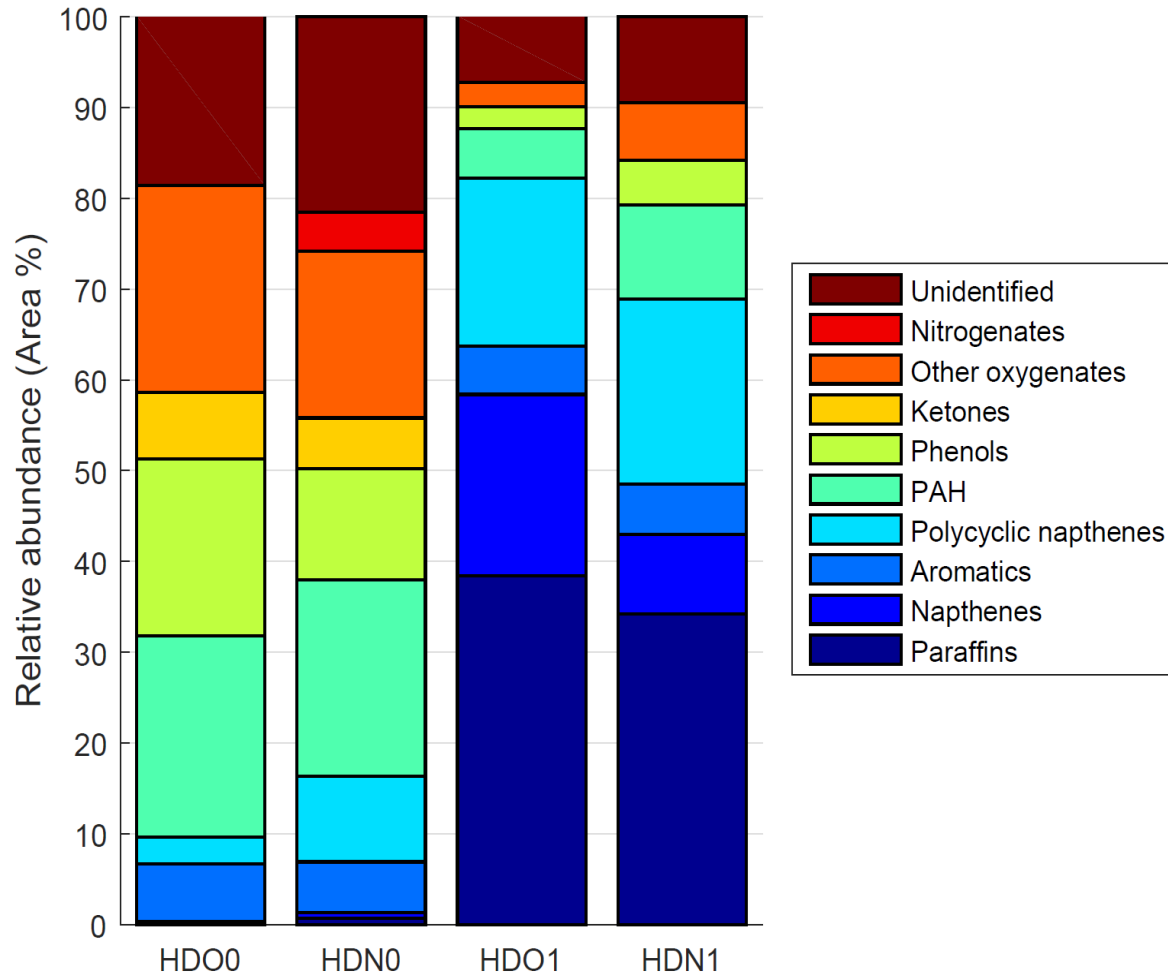


Sample	Elemental composition wt. %				HHV (MJ/kg)
	C	H	N	O	
HTL 350°C, 5 min	74.48	8.99	6.86	9.67	36.0
150 bar H <sub>2</sub> , 400°C, 60 min, no cat.	84.54	11.29	2.68	1.50	42.8
150 bar H <sub>2</sub> , 400°C, 60 min, with cat.	84.92	12.20	2.06	0.82	44.1

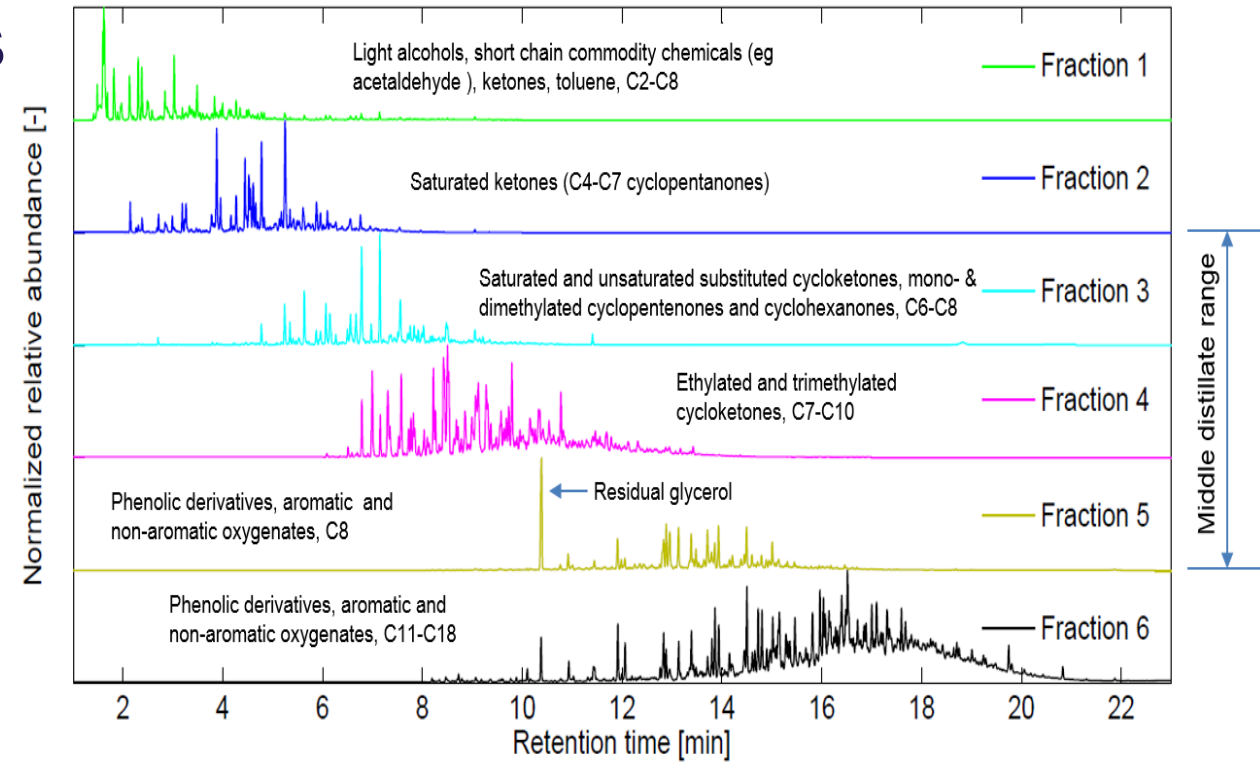
# HTL Bio-Crude to Different fuels



# HTL Bio-Crude to Different fuels



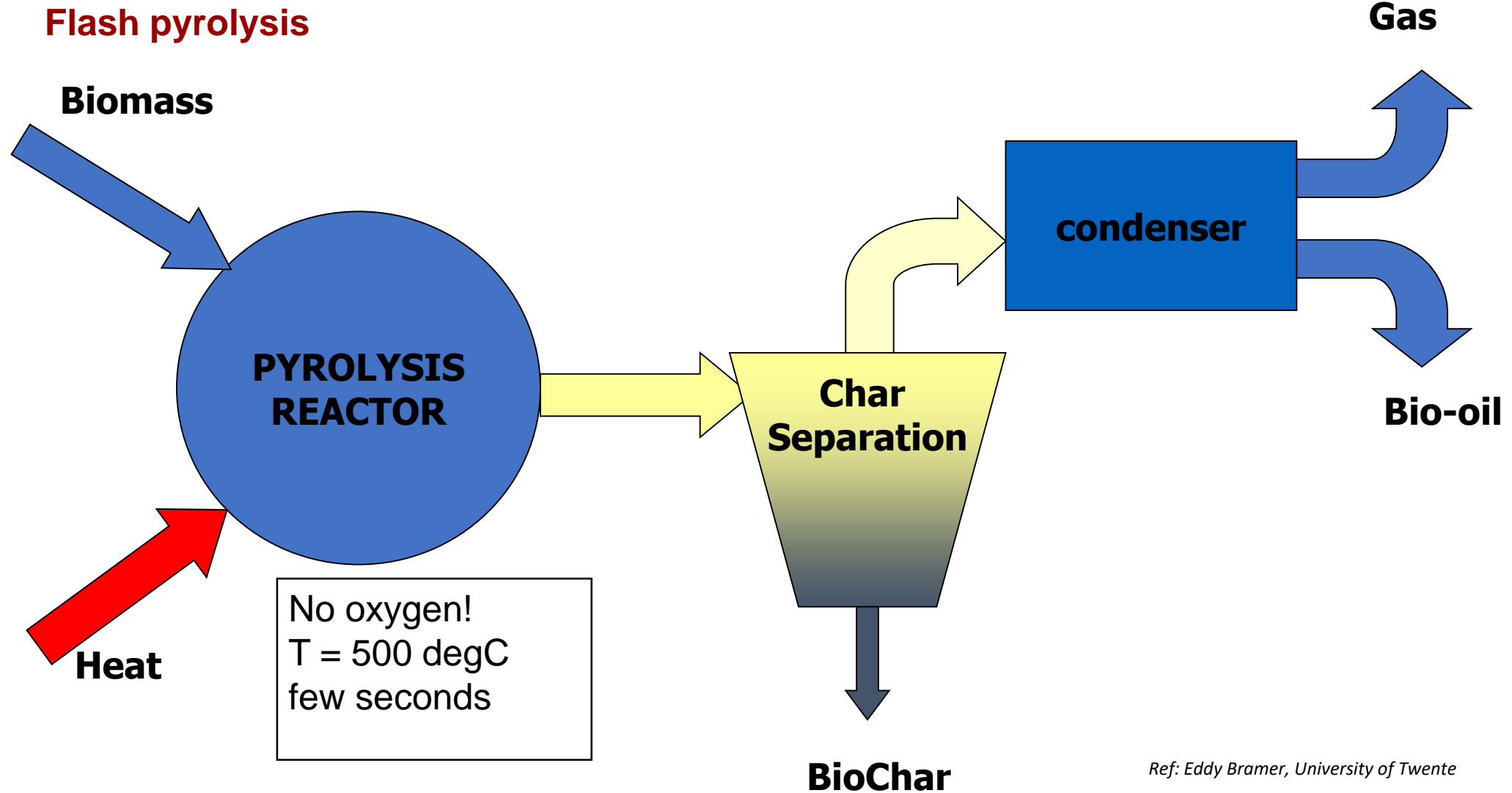
The GCxGC-MS identifications grouped into families



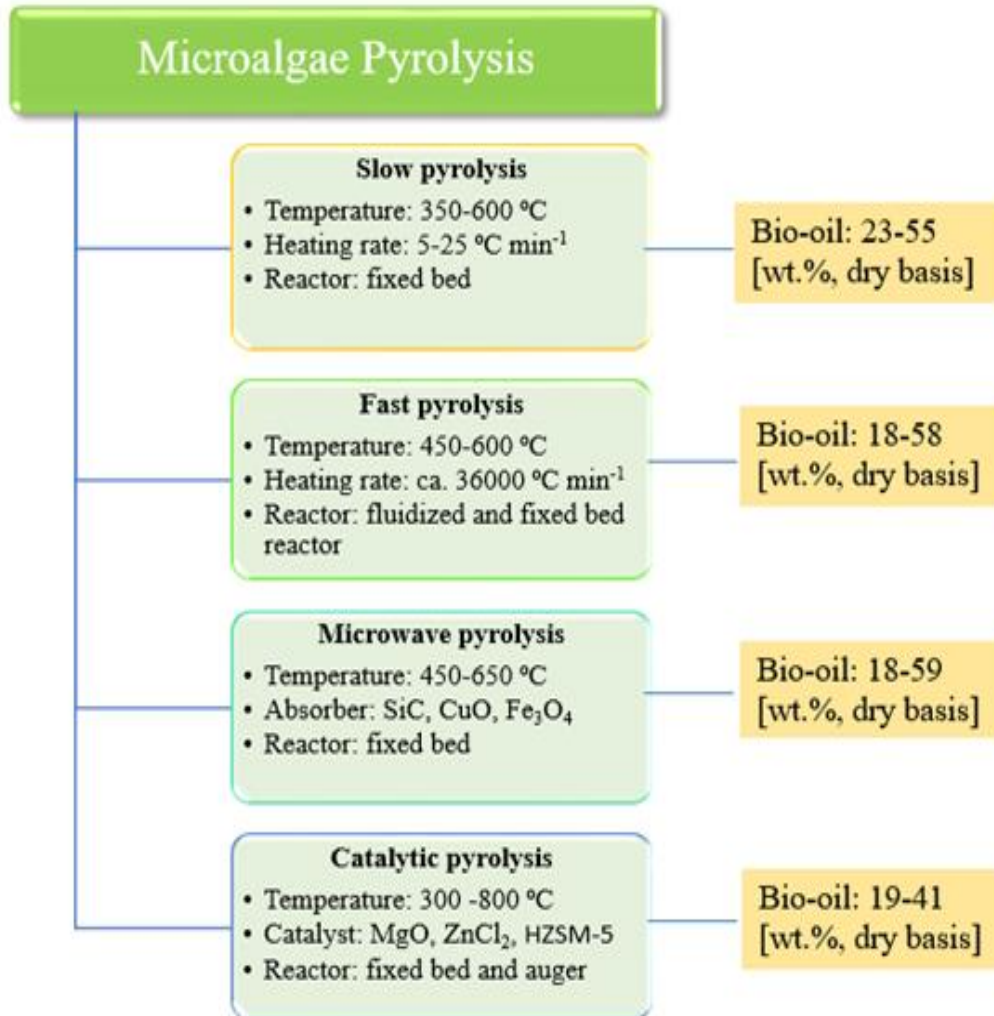
GC-MS chromatograms of the distillate fractions. Chromatograms have been normalized to highest peak.



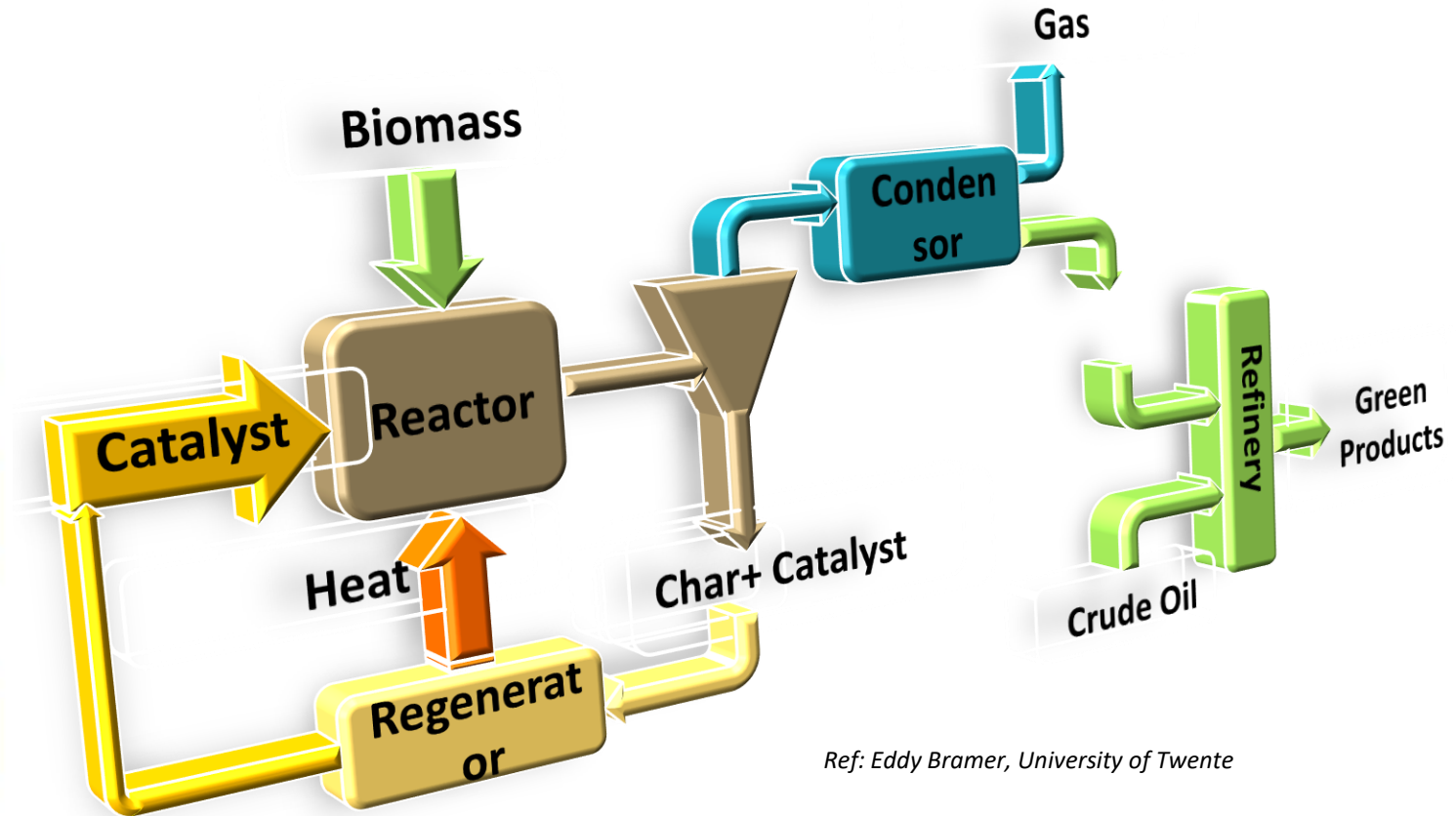
# HTL Vs Pyrolysis



# HTL Vs Pyrolysis



## Pyrolysis Oil Quality Improvement by Catalysis



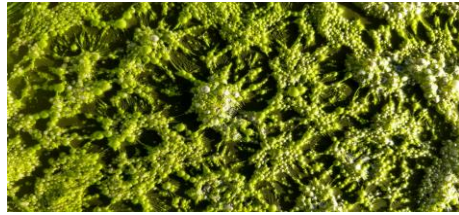
Ref: Eddy Bramer, University of Twente

## HTL Vs Pyrolysis

Pyrolysis Process	Parameter	HTL Process
400-600	Temperature(°C)	250-370
0-3	Pressure (Mpa)	10-25
1-2 s(fast) 10-30 s (intermediate)	Residence time	Up to 1 hr
Gas without Oxygen	Medium	Water

Pyrolysis oil	Parameter	HTL oil
43-55	Biocrude yield(%)	27-64
45-63	Energy recovery (%)	52-78
16-20	HHV(MJ/kg)	34-38
0.4-13	Nitrogen content(%)	0.3-8
7-40	Oxygen content(%)	5-18

## Activities at University of Agder



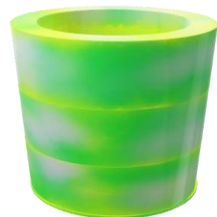
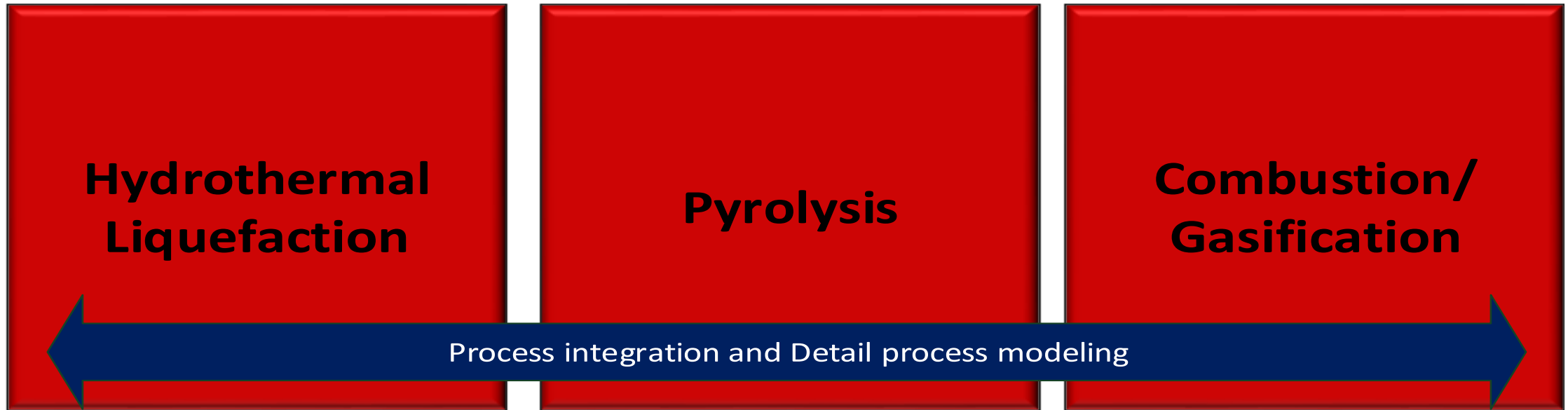
Algae



Wood



Waste / wood



Liquid bio-oil



Bio carbon

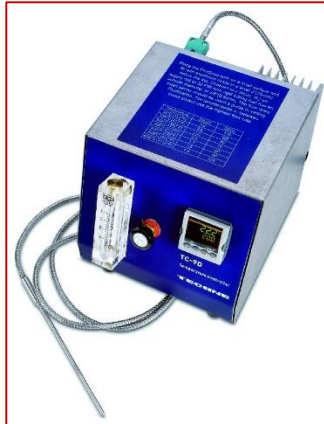


Combine Heat and power

# HTL setup at University of Agder



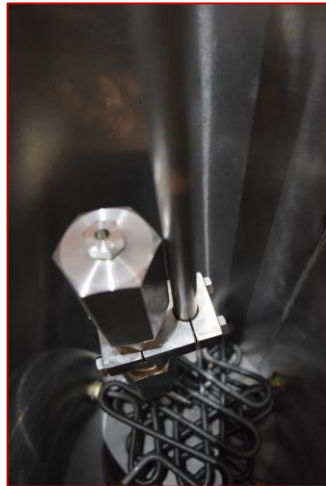
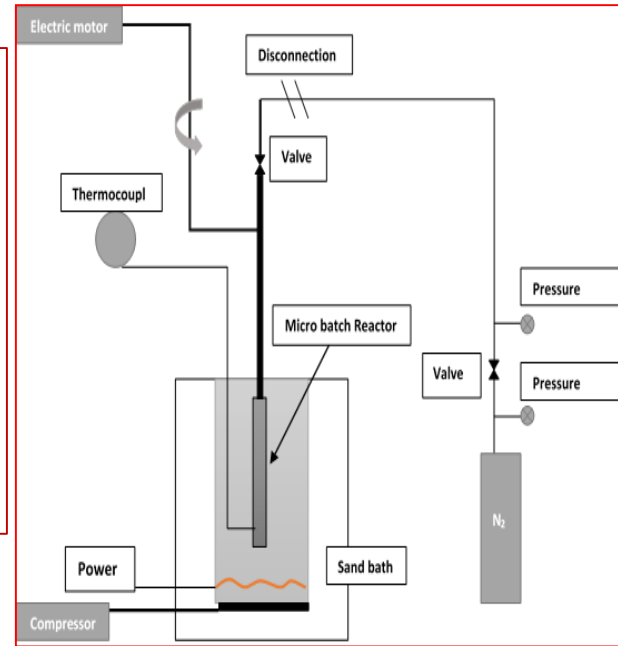
TC-9D temperature controller (°C)



SBL-2D



Keison International Ltd. t/a Keison Products



High Pressure Equipment Company



# Lab instruments at UiA

## Lab scale Reactors for high pressure experiments

- 41-65 mL systems (350 Bar and 500°C.) - Micro batch reactor systems for parametric studies.

## Analysis Equipments

Heating Microscope, 1750 °C , Hesse Instruments HR18

Online producer gas analysis CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, O<sub>2</sub>, ABB Advance Optima AO2000

Portable chilled mirror hygrometer for determination of dew point, Omega RHB-1500-C

Gas chromatograph, Varian

Micro gas chromatograph, Varian

Adiabatic bomb calorimeter for measuring the calorific value, Sanyo Gallenkamp

Elemental analyzer C, H and N, PerkinElmer 2400 Series II System

Thermogravimetric analyzer (TGA). Mettler Toledo TGA/DSC1

Heated muffle furnace for measuring the ash content, 1100 °C, Nabertherm LT 40/11/330

Drying oven for measurement of moisture content, Termaks

Flue gas analysis CO, O<sub>2</sub>, flue gas temperature and draught, Testo 327-1

Measurement of moisture content by means of conductivity, Testo 606-1

Measurement of moisture content capacitive, Testo 635-1

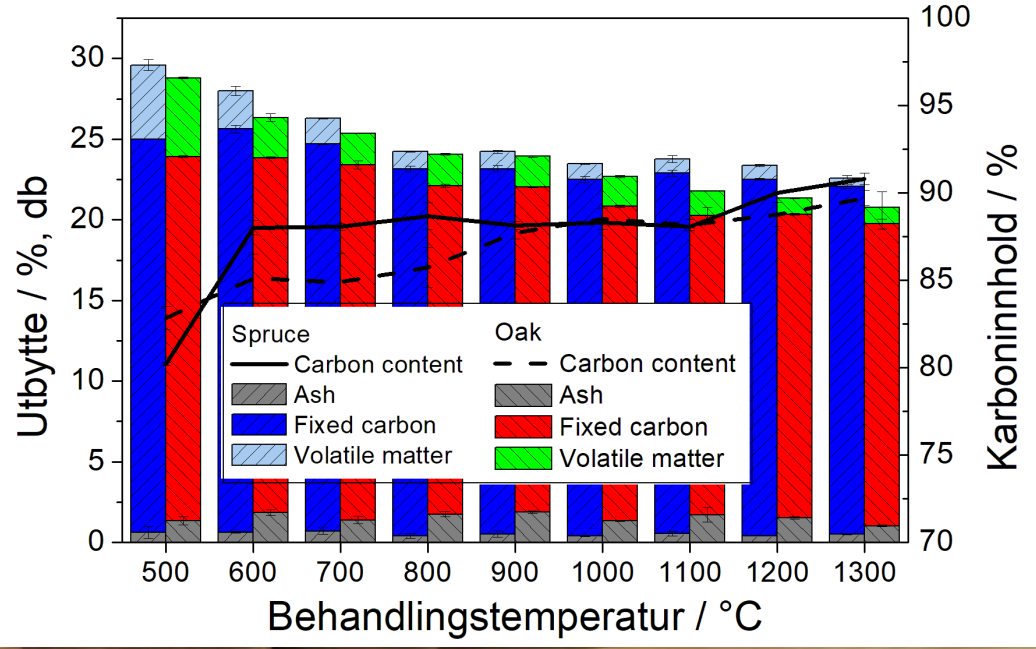
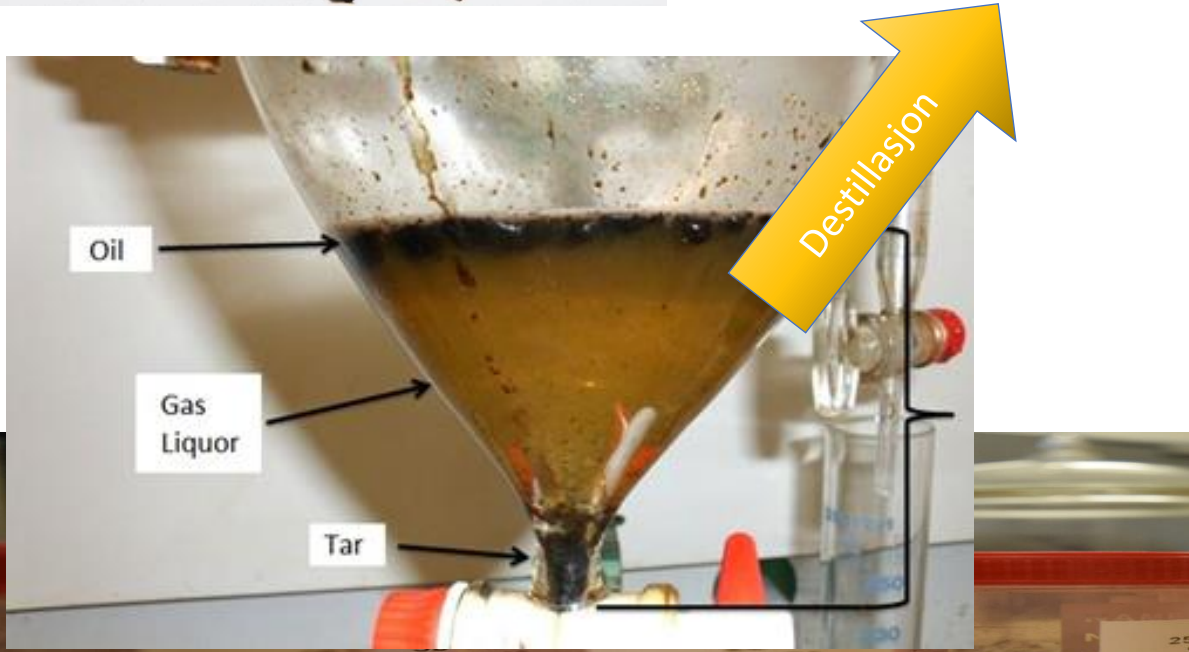
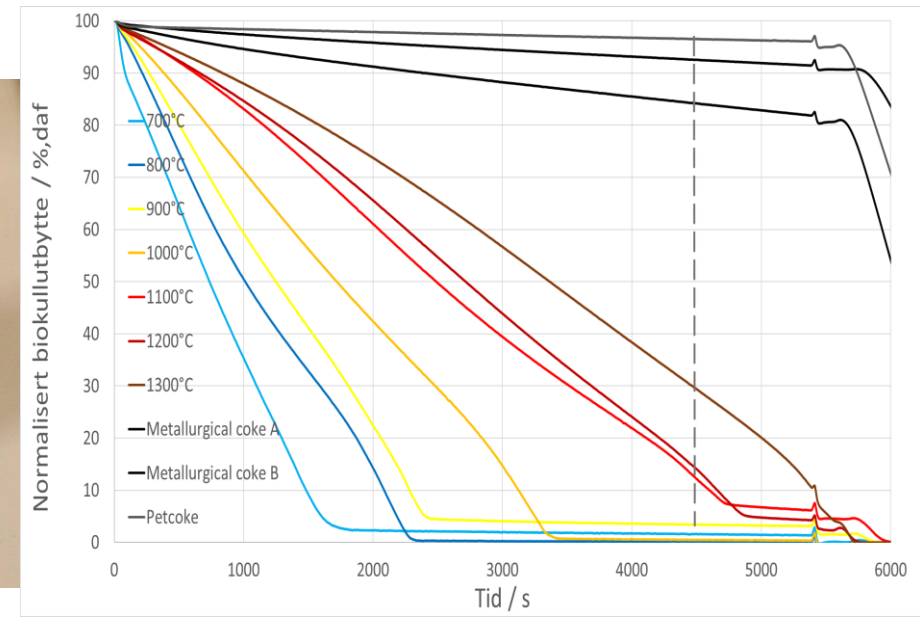
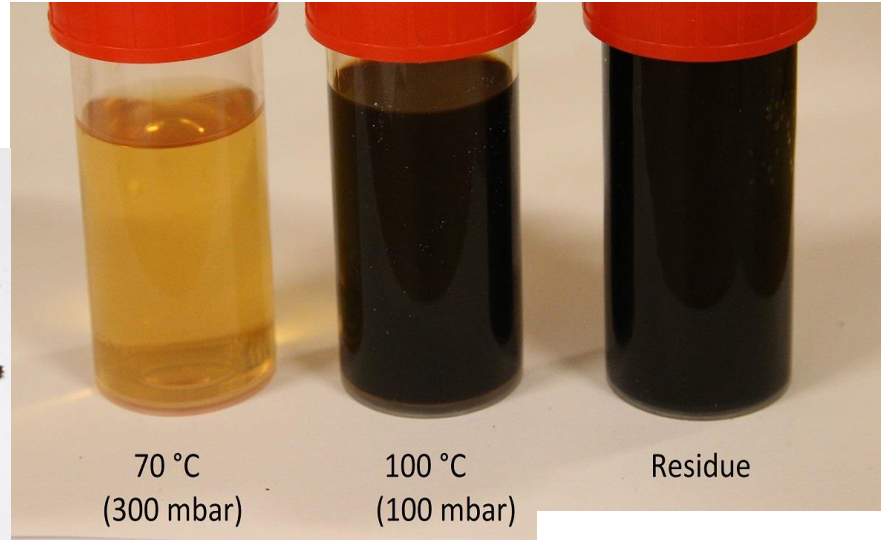
2 food calorimeters for teaching, from skolebutik.dk

Thermocouples for measuring flue gas temperature etc. with Digitron 2029T

3 pallet scales 1500 kg, Scaleit FM pallet scal



# Pyrolysis at UiA



## Modeling of the HTL process

### Kinetic modelling

- Modeling of HTL process by using kinetic data of the reactions and products

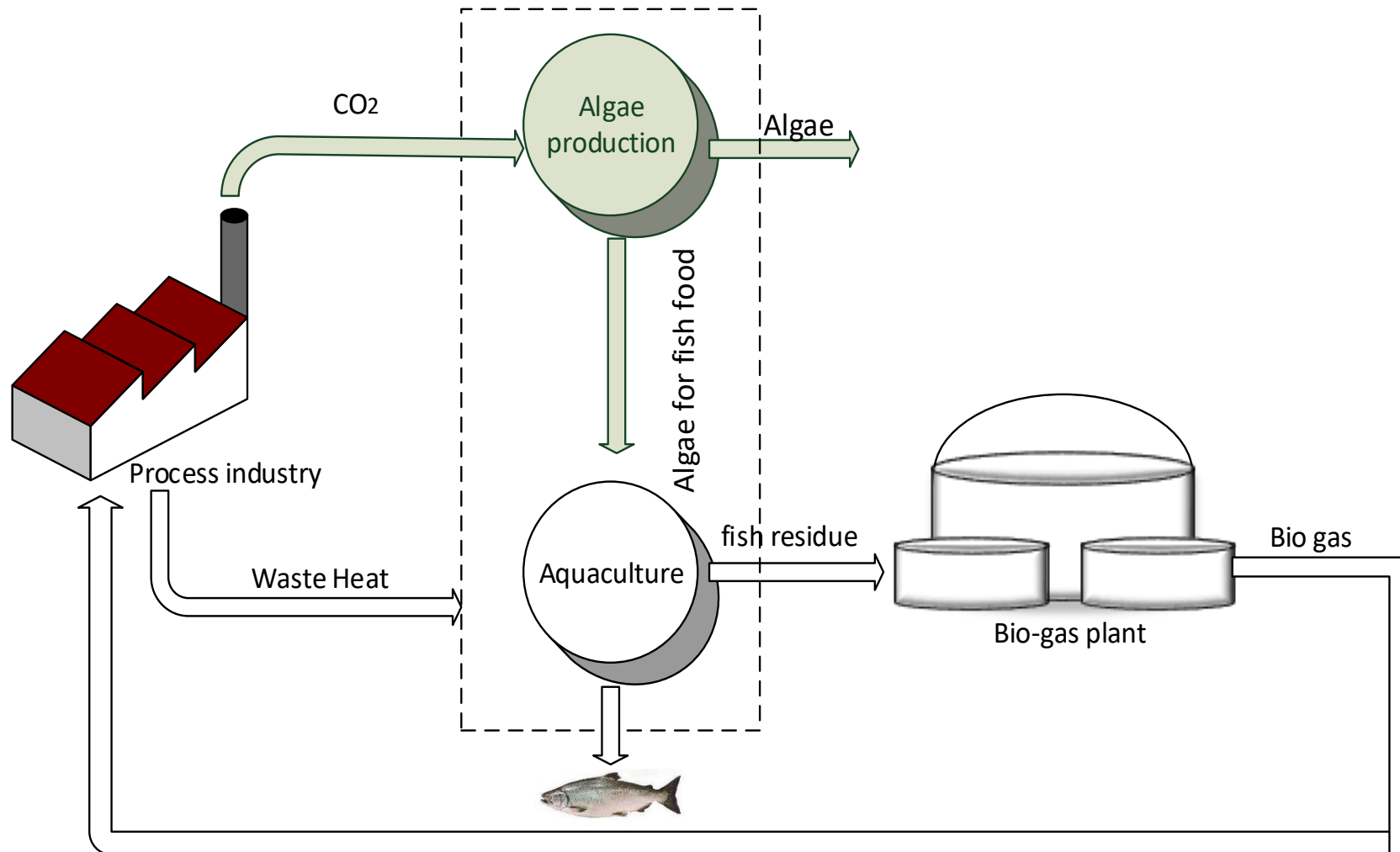
### CFD modelling

- Modeling of HTL process by using computational fluid dynamics concepts, turbulence and particle interaction

### Techno-economic modelling

- Economic analysis of HTL process using energy consumption, efficiencies and feasibility

## CO2 capture and utilization with waste heat integration



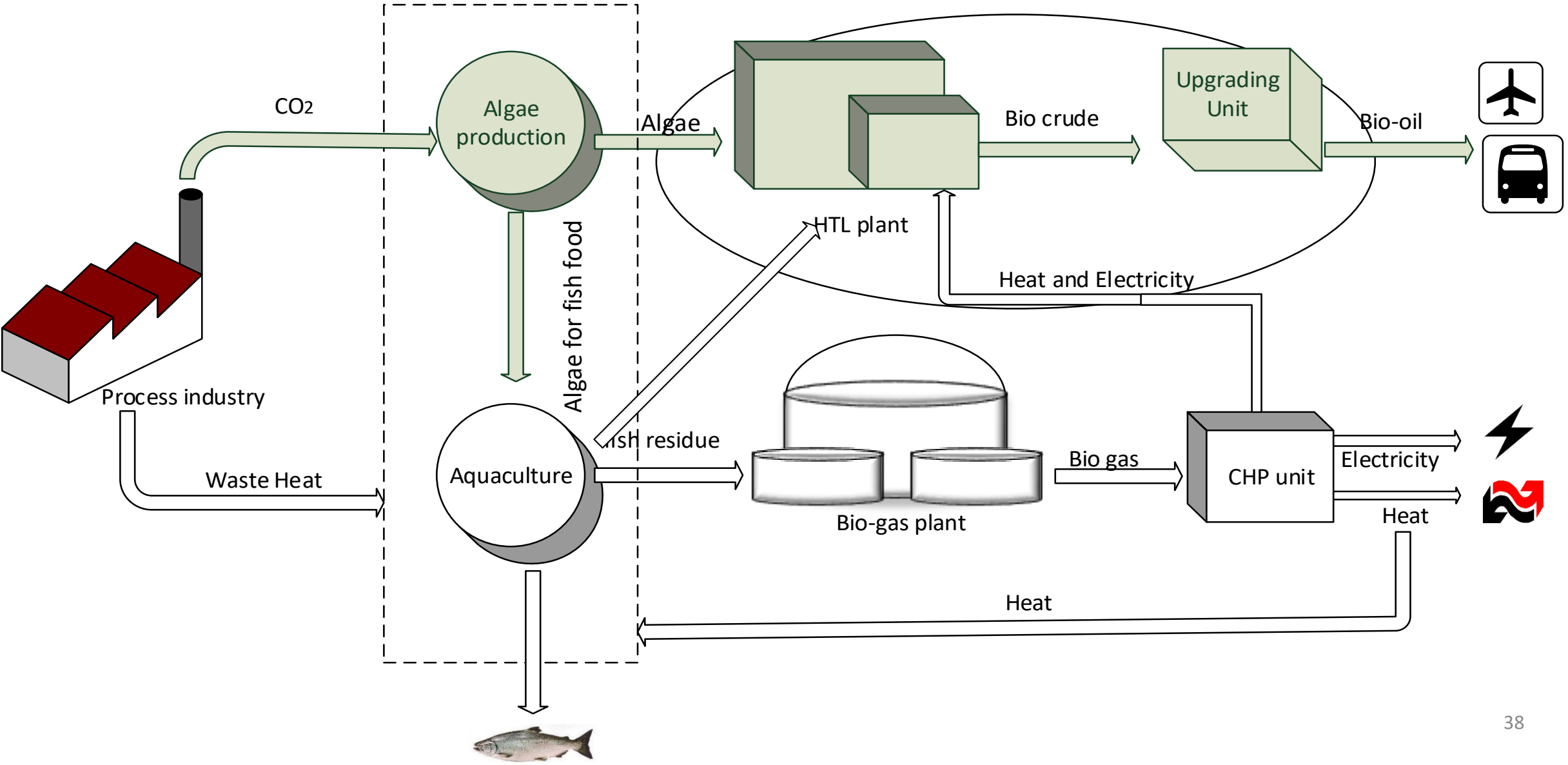
### Process:

- CO2 capture from process industries
- Algae production from captured CO2
- Waste heat utilization from process industries
- Aquaculture from waste heat
- Fish residues for Biogas plant
- Bio gas for process industry

### Products:

- Fish
- Algae (as food both for fish and human)
- Bio gas as feedstock for process industry

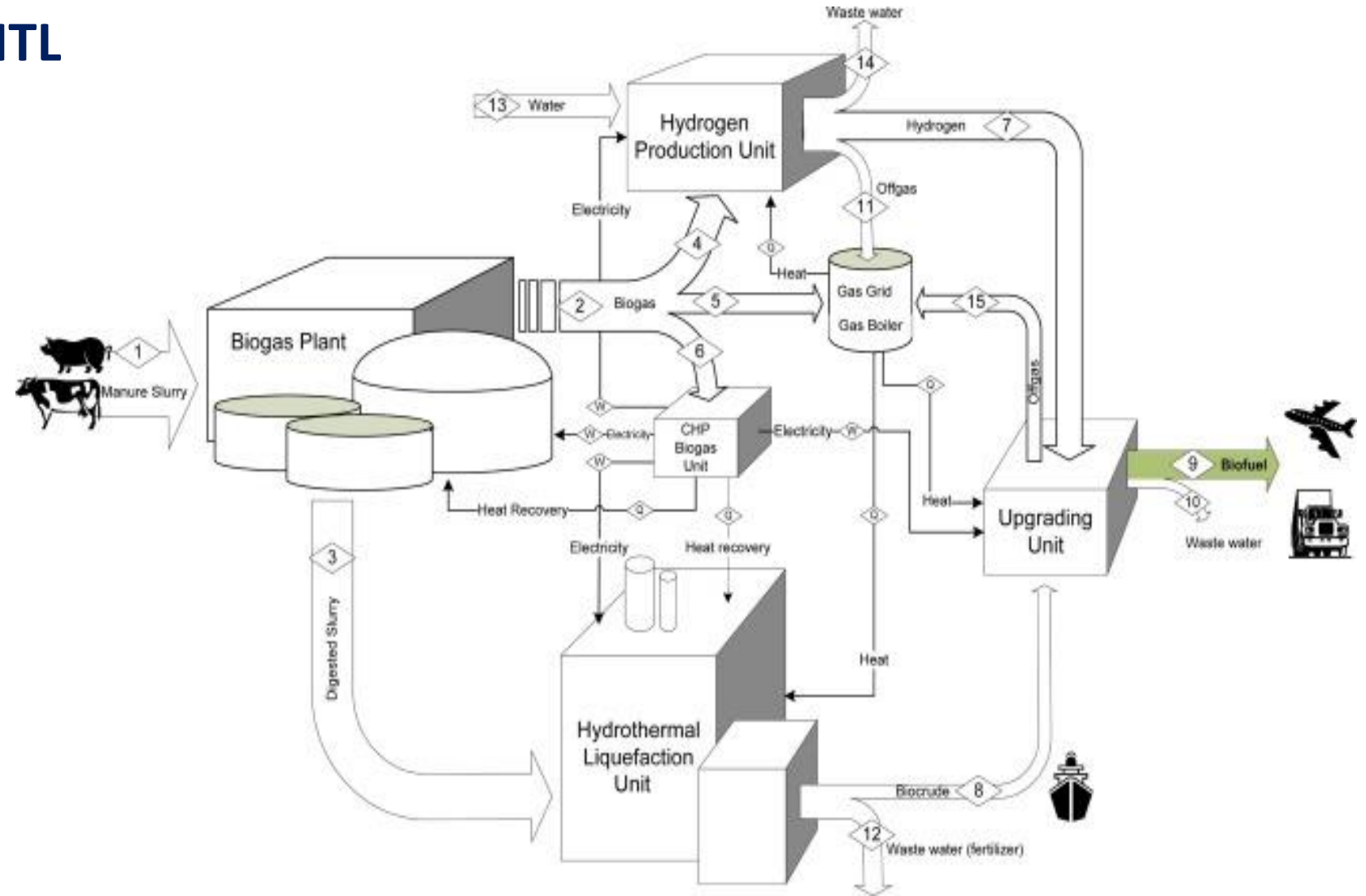
# CO2 capture and utilization with waste heat integration



# Process integration with HTL

The overall process is divided into four independent sections:

- anaerobic biomass digestion (biogas plant),
- hydrogen production,
- hydrothermal liquefaction, and
- upgrading of the biocrude



## Bioenergy And Thermal Energy Group at UiA

### Professors

### Leader



Souman Rudra  
Associate Professor



Henrik Kofoed Nielsen  
Professor



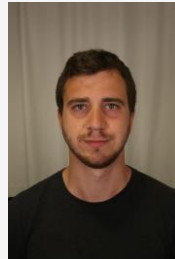
Tore Vehus  
Associate Professor



Nils Randulf Kristiansen  
Assistant Professor



Gerrit Ralf Surup  
PhD Fellow



Lorenzo Riva  
PhD Fellow



Madhawa Jayathilake  
PhD Fellow



Taimur Aktar  
PhD Fellow

### PhDs & Research assistants

### Lab staff



Johan Olav Brakestad  
Senior Engineer



Johnny Finjord



Mariell Skaten



### Students



# Summary

**Produced biocrude from wide range of feedstocks**

**CO<sub>2</sub> emission and Global warming reduction**

**Advance reactor designs and separation improvements**

## **Path To Commercialization-**

- Standardization in terms of Innovation and implementation
- Scale-up
- Low Cost Components
- Business Model Development

**HTL – a future “unit operation” in biorefineries ?**

Thank you!

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