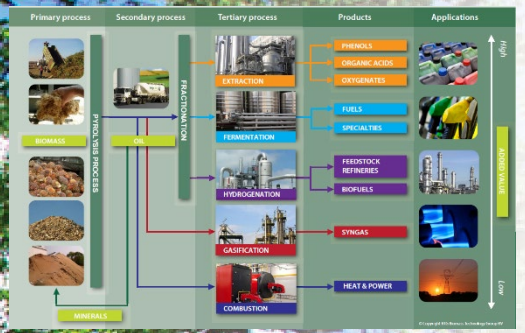


BTG Biomass Technology Group BV

Stabilised pyrolysis oil by mild hydrogenation: status and developments

9/11 2024

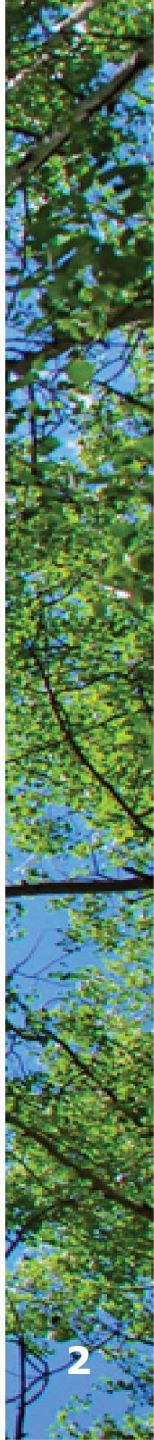
Robbie Venderbosch

biomass technology group

Your partner in bioenergy

Properties		Pyrolysis oils
Water content	wt.%	18 - 25
MW	g/mol	200 – 2,000
MW_{av}	g/mol	600 - 700
EA (daf)		
C	wt.%	53 - 56
H	wt.%	6.4 - 7.0
O (by difference)	wt.%	38 - 45
N	wt.%	<0.01
ash	wt.%	0.01 - 0.1
S	wt.%	< 0.01
Viscosity	cSt	10 - 100
H/C molar, dry	-	1.4 - 1.6
O/C molar, dry	-	0.5 – 0.6
MCRT, a.r.	wt.%	18 - 25
CAN, a.r.	mmol/g	3 - 4
TAN, a.r.	mg_{KOH}/g	60 - 80
pH	-	2.5 – 3.5
Density	kg/m^3	1100 – 1200
Heating value	MJ/kg	16 – 18

Overall Composition $C_2H_5O_2$



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Overall properties of pyrolysis ~~oil~~ liquid

'What we can do in hours is what nature does in millions of years'

Pyrolysis oil

≠

oil

lignitic fragments emulsified in an aqueous syrup solution

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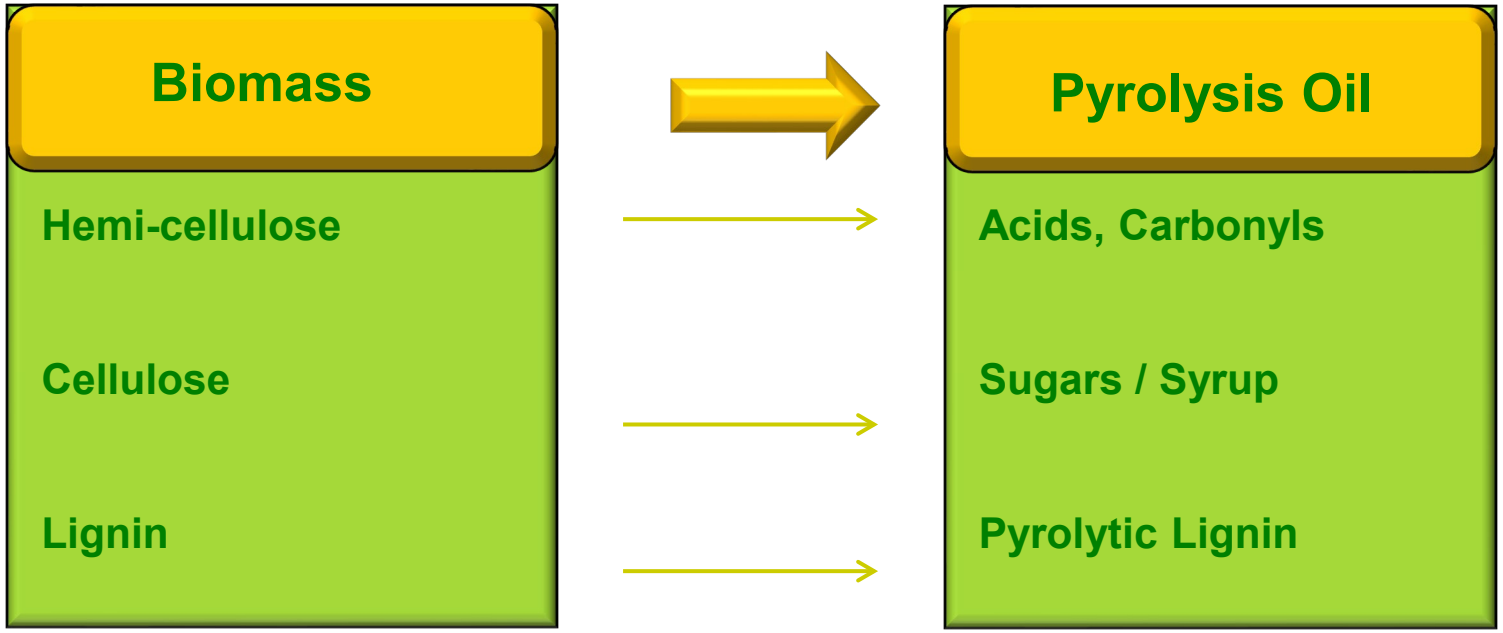
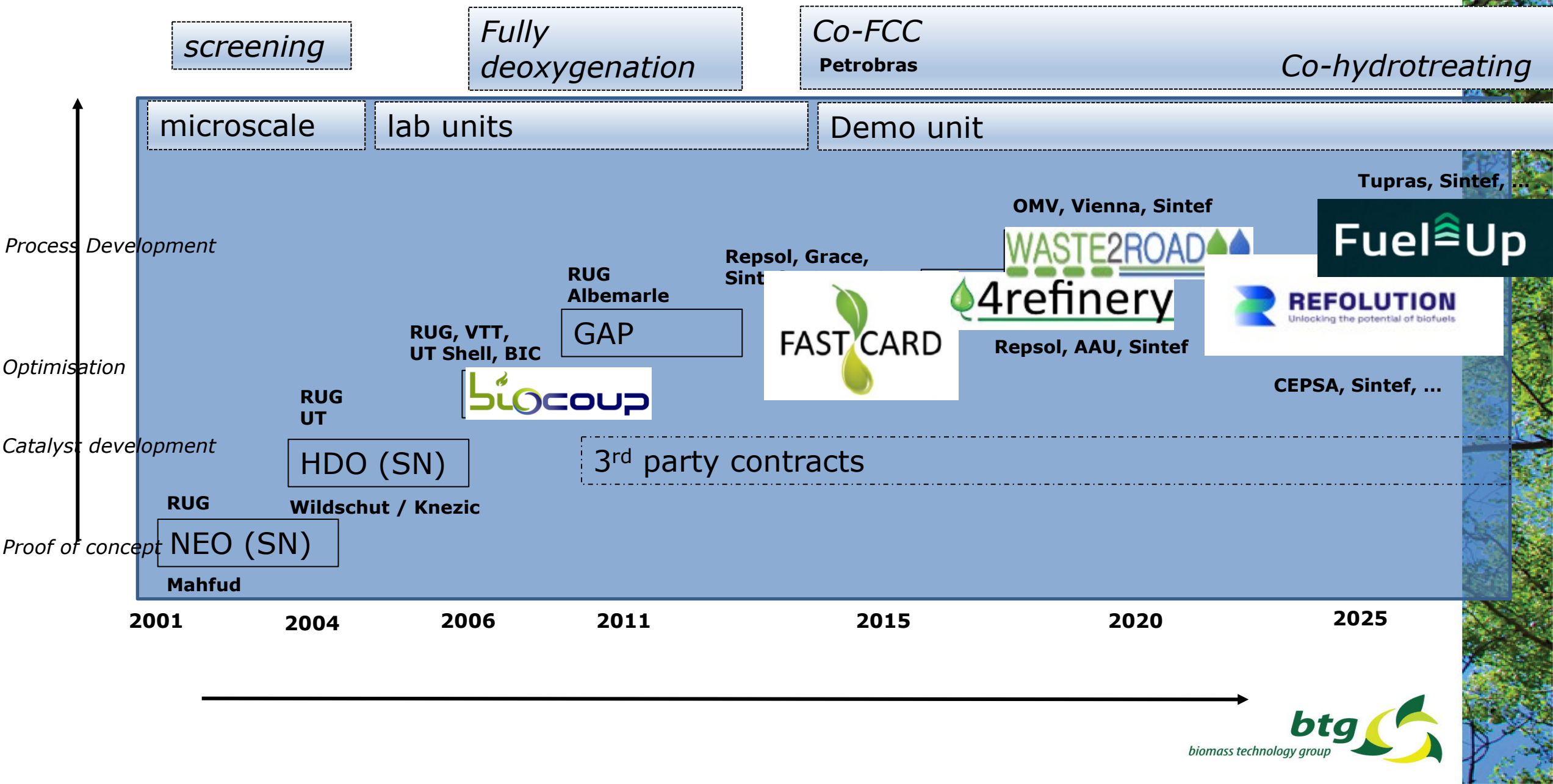
Overall properties of pyrolysis oil

What we do in seconds is what nature does in millions of years?

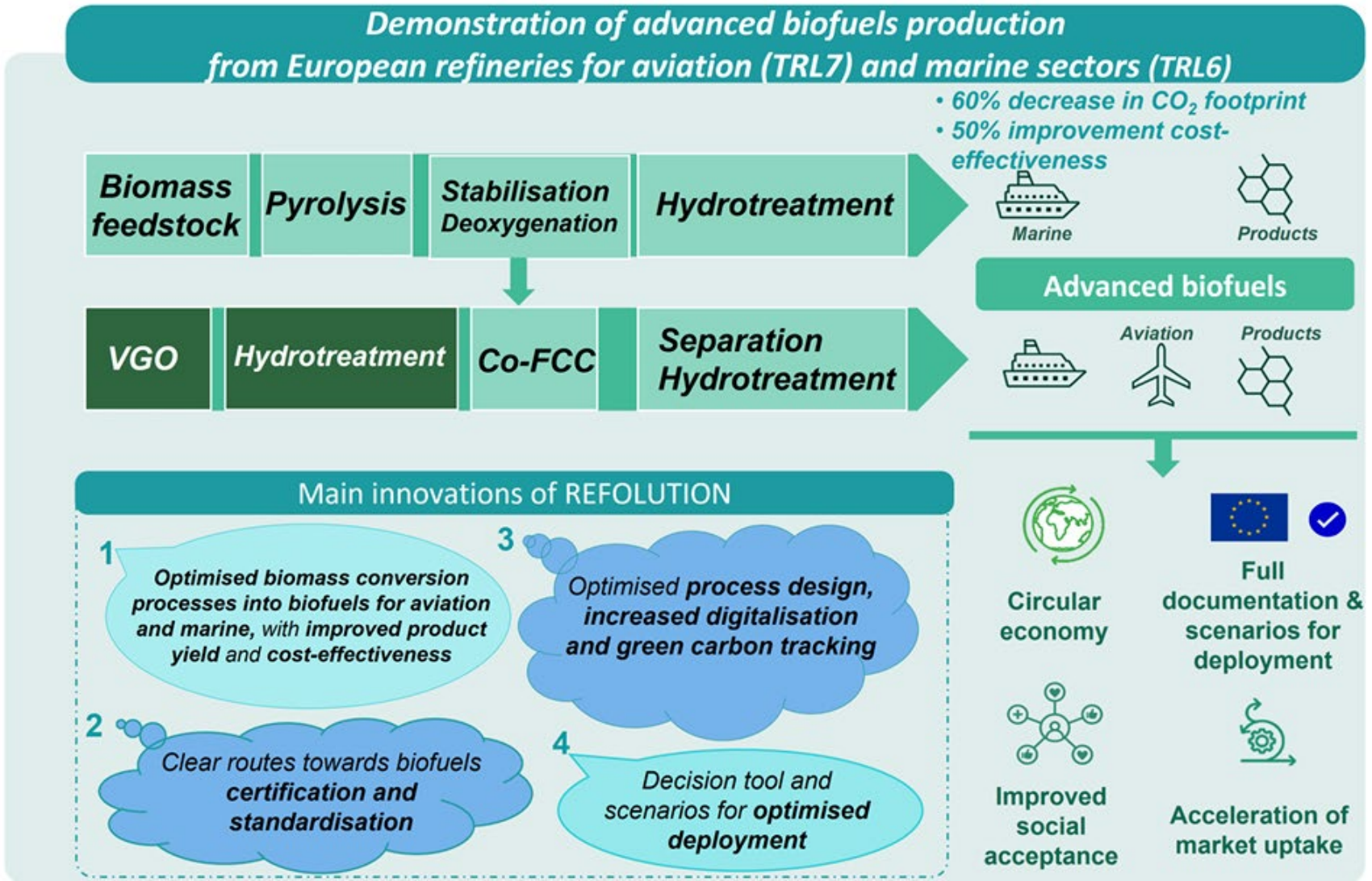


Development stage



REFOLUTION

Unlocking the potential of biofuels



Complete value chain of advance biofuel production from biomass to the engine through pyrolysis route

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Objectives

Demonstrating the simultaneous production of renewable SAF and marine fuels from **100% biogenic waste**.

Achieving up to **80% reduction in GHG emissions** compared to fossil fuels and 47% compared to the state-of-the-art advanced biofuels.

Ensuring that **new value chains** arise by 2030 and replicate by 2035 to then deploy by 2040 in 25 sites among the 12 potential EU countries.

Paving the way to **EU certification** to ensure that production is compatible with practical usage and that it is socially accepted.

FUEL-UP Production Process

FUEL-UP focuses on the production of **stabilized deoxygenated pyrolysis oils** (SDPO) from pyrolysis oils (PO) derived from wood residues that can be subsequently processed towards a fully hydrotreated oil (HPO) in a refinery to ensure transformation of all streams to the key **aviation** and **marine fuels** sectors.

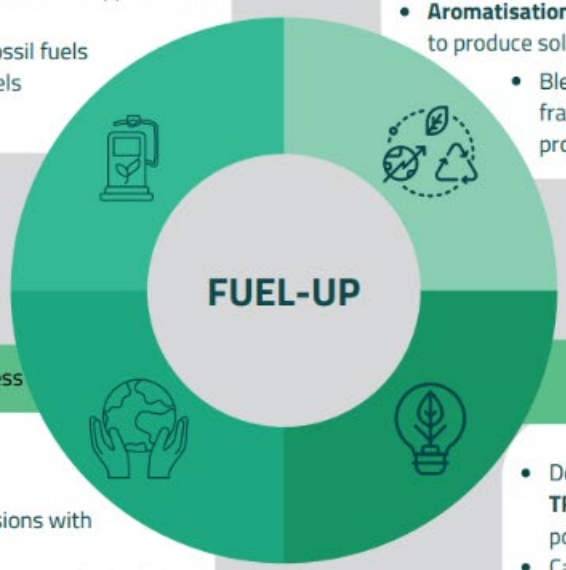
Technology Implementation

Flexible and efficient processing allowing

- **Valorisation** of forest residues and **diversification** of feedstock
- **Different fuel qualities** for two main applications: marine & avaition
- **Blending of biofuels** with fossil fuels and synthetic renewable fuels

Maximising process side streams valorisation

- **Aqueous phase** treatment to produce **biogas** and extract of **alcohols**, **ketones** and **carboxylic acids**
- **Aromatisation** of heavy naphtha fraction to produce solvents
  - Blending of light naphtha fraction to **biomethanol** to produce **marine fuel**



Environmentally friendly process

- Close to **carbon neutral** process with **green H_2**
- **-42% biogenic carbon** emissions with carbon cycle
- **Circular models** to estimate H_2 production from aqueous phase

Ensuring market needs

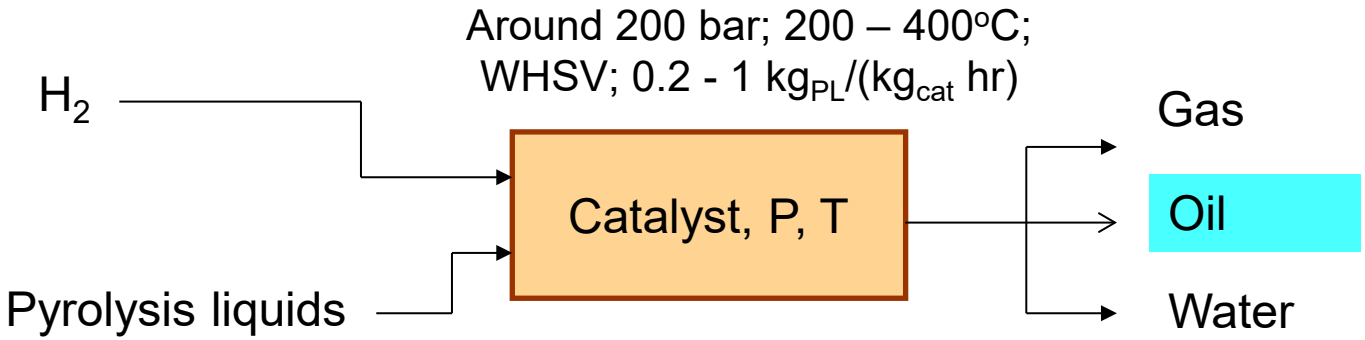
- Derisking of technologies at **TRL7** with **high scalability** potential to commercial scale
- Capacity of 90 kt/HPO by 2030 at commercial scale

Plants (BTG)

200^{+}bar; 400^{+o}C

- ❑ 5 continuous hydrotreaters at lab-scale (~ 1 kg/day)
- ❑ 2 pilot units (~ 50 kg/day) for SPO / SDPO

Hydrotreating pyrolysis oils

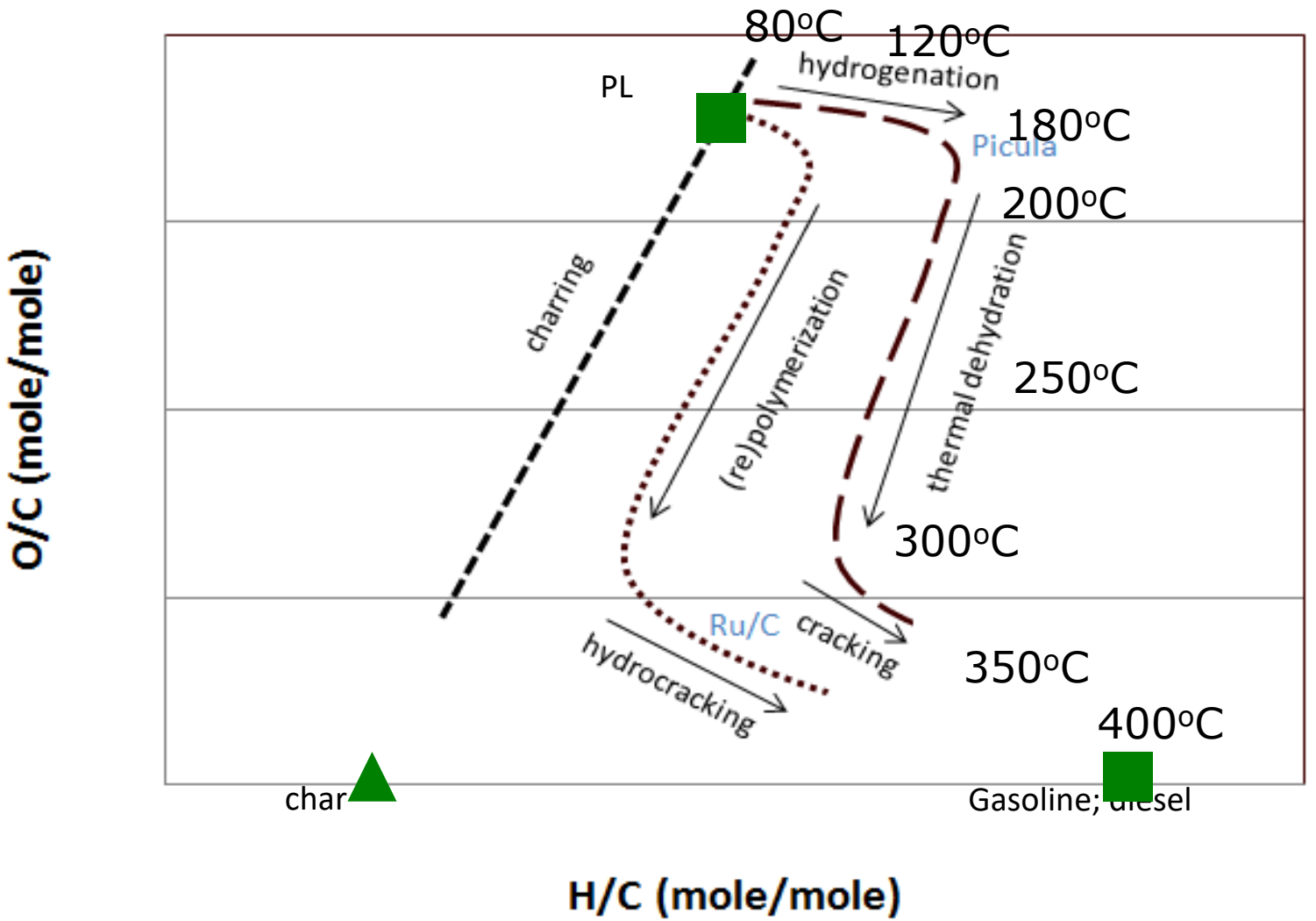


$$(CH_xO_z + H_2O) + H_2 \rightarrow$$
$$- CH_2O - + H_2O + CO_2$$

$$(CH_xO_z + H_2O) + H_2 \rightarrow$$
$$- CH_2 - + H_2O + CO_2 + CH_4$$

Stabilization

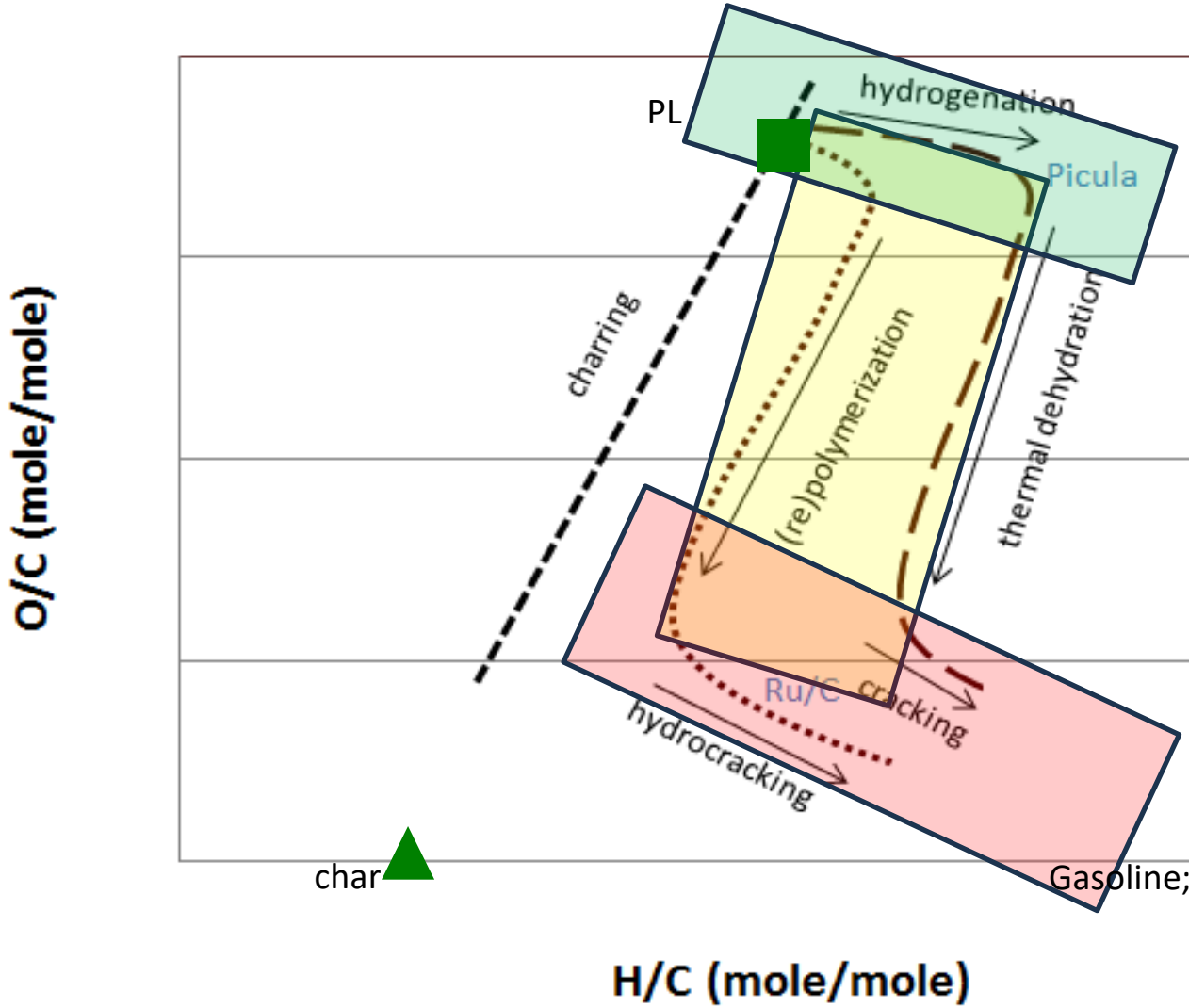
lignitic fragments emulsified in an aqueous syrup solution



SPO:
- Dedicated catalyst
- Sugar chemistry
- Low T, high P

SDPO:
- Mo-s catalyst
- Oil chemistry
- High T, low P

lignitic fragments emulsified in an aqueous syrup solution



SUGAR chemistry

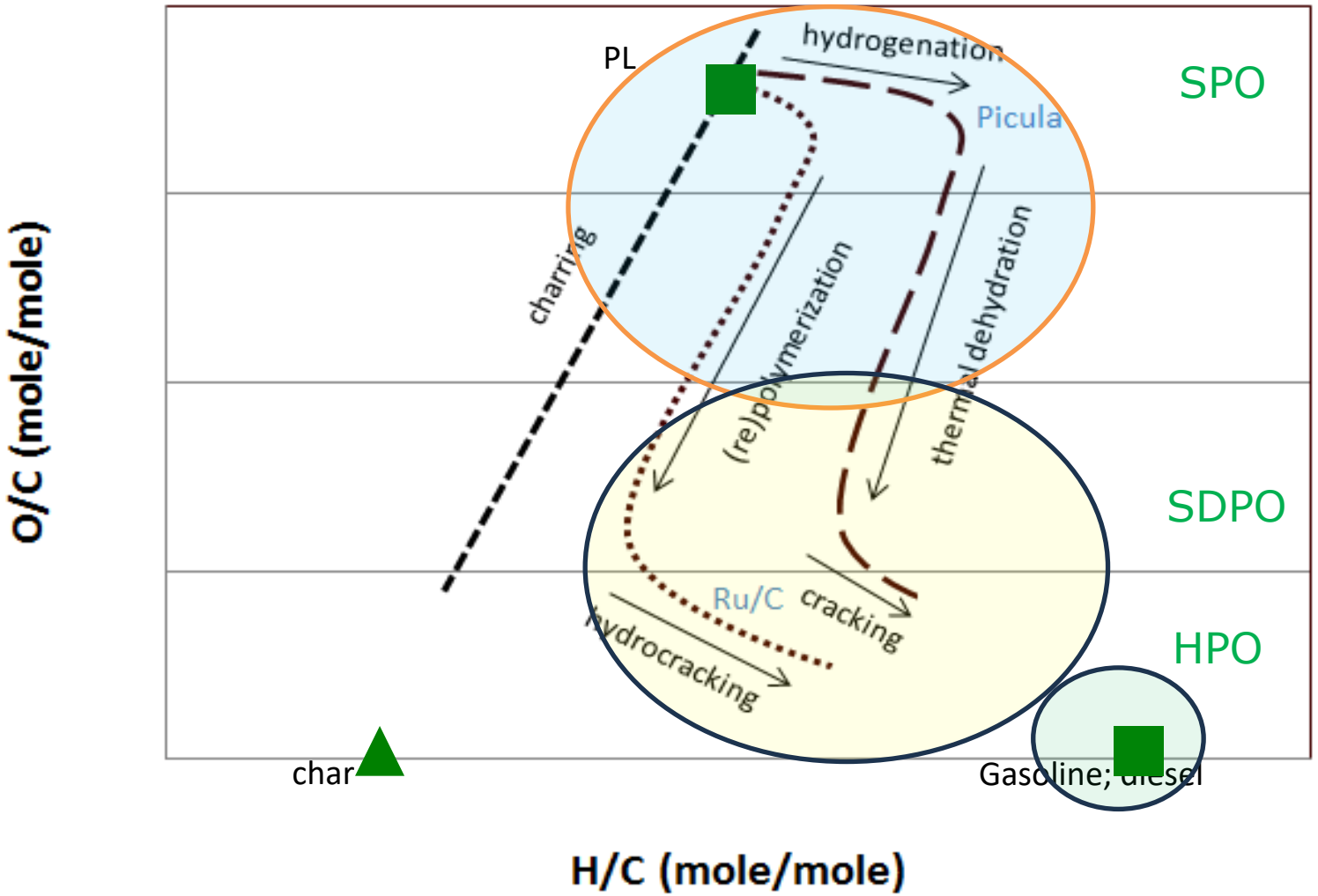
$(CH_xO_z + H_2O) + H_2 \rightarrow (CH_yOH + H_2O)$

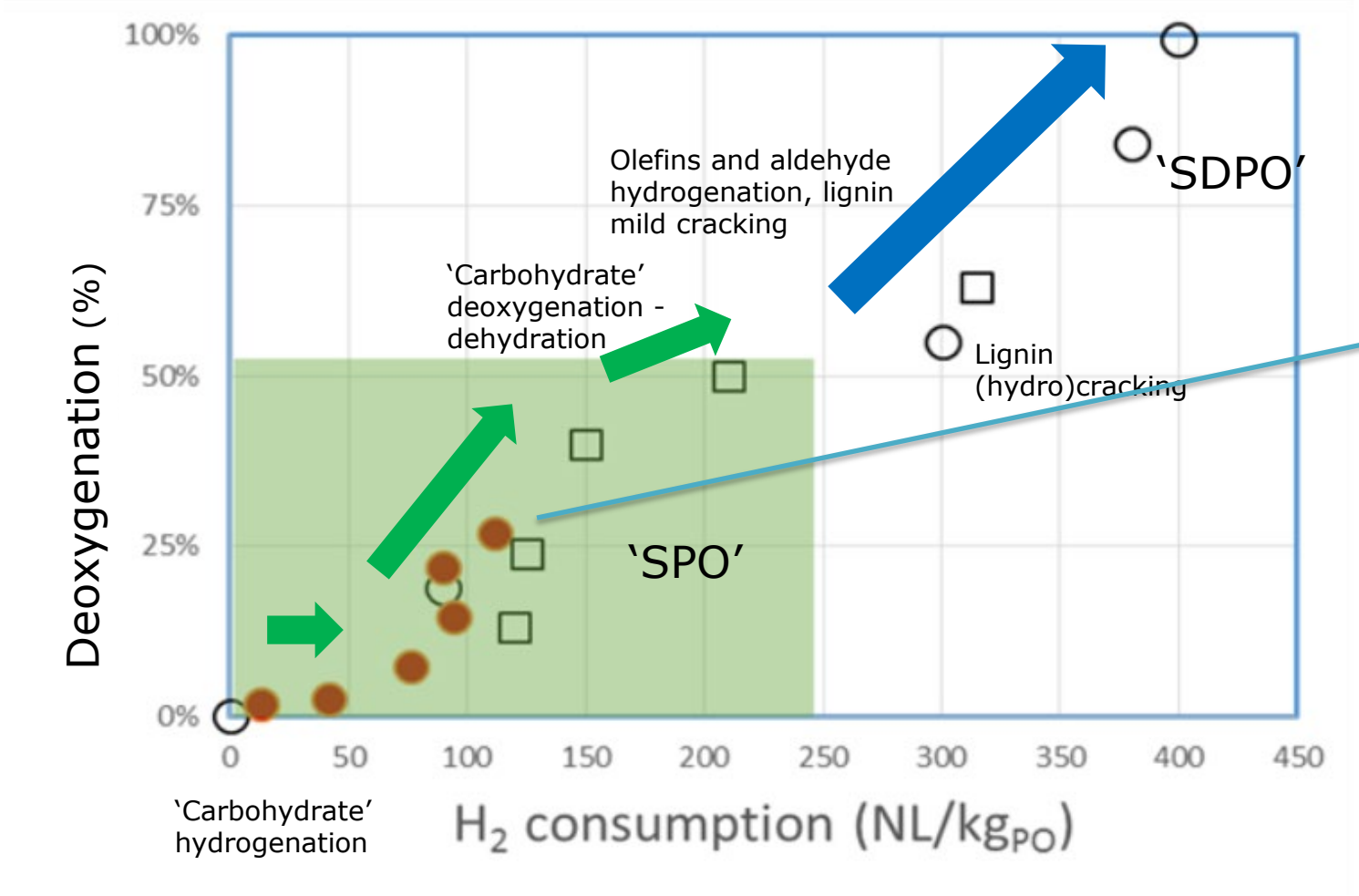
ALCOHOL chemistry
dehydration

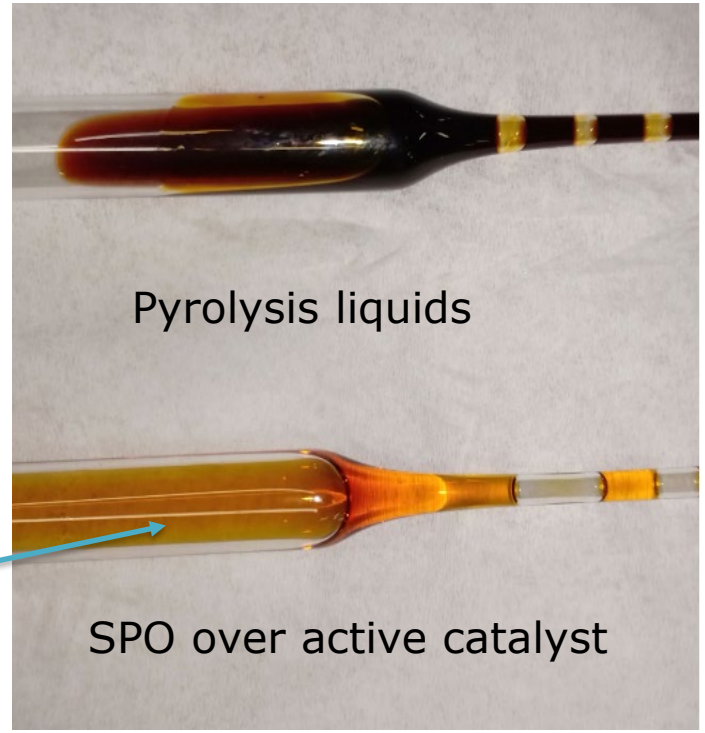
LIGNIN/OIL chemistry

$CH_{x'}OH + H_2 \rightarrow - CH_2 - + H_2O + CO_2 + CH_4$

lignitic fragments emulsified in an aqueous syrup solution







Improved liquid = closer to oil

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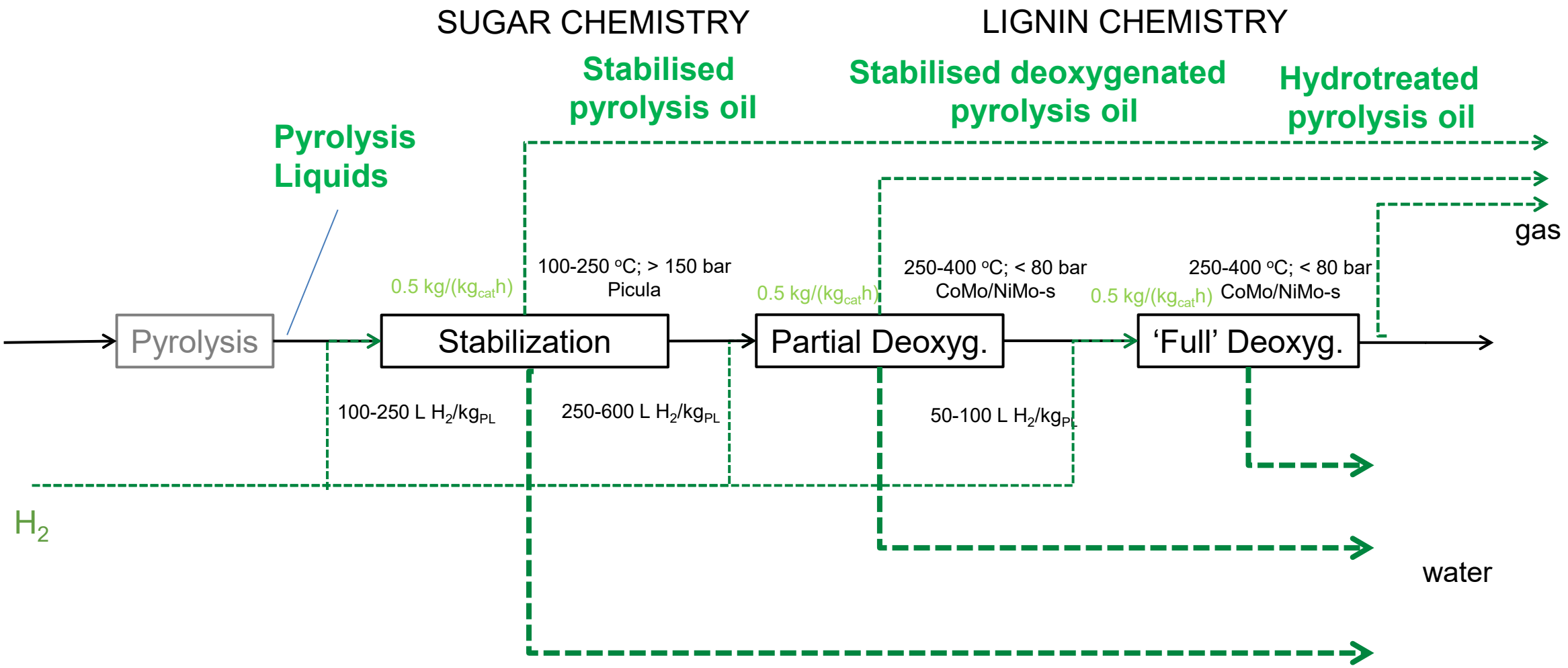
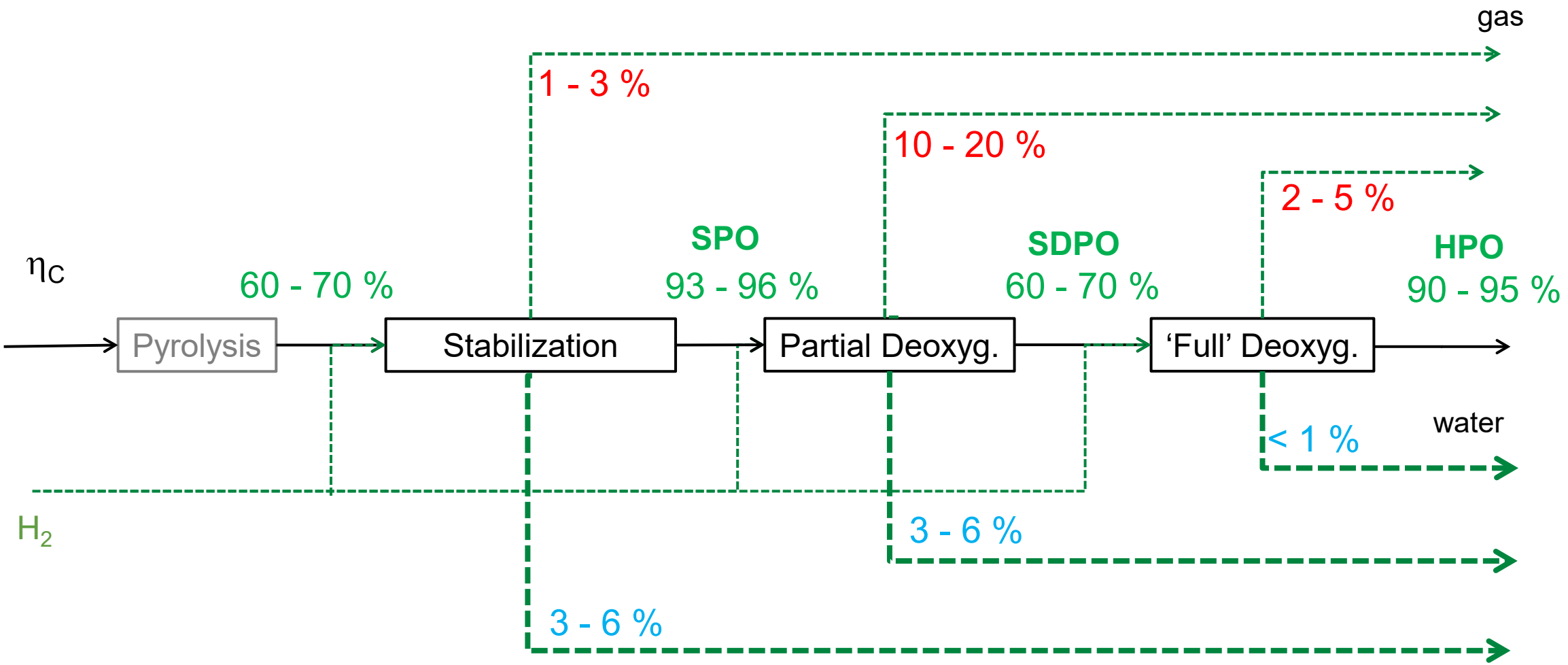
Liquid conversion: sugar chemistry versus lignin chemistry



Liquid conversion: biomass carbon yields



24-30 wt.% yield; η_C= 43 – 48 %

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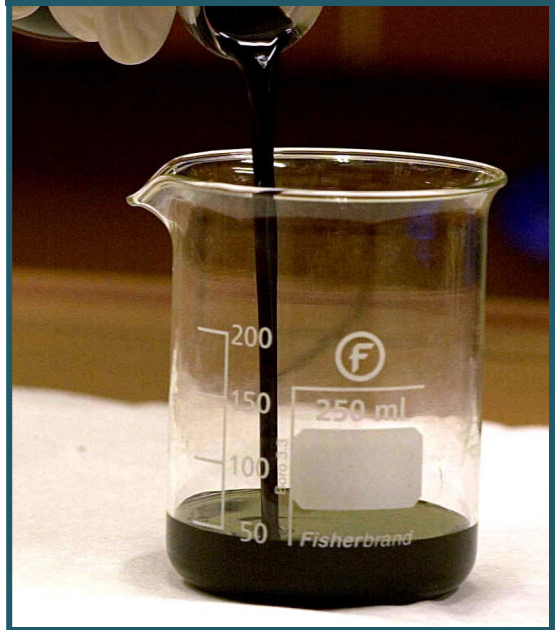
Properties		Pyrolysis oils	Stabilized Pyrolysis Oil (SPO)	Stabilized Deoxygenated Pyrolysis Oil (SDPO)	Hydrotreated Pyrolysis Oil (HPO)
Appearance		dark brown	Dark reddish	Dark brown	Yellowish
Water content	wt.%	18 - 25	5 - 10	1.5 – 2	<< 0.5
MW	g/mol	200 – 2,000			
MW_{av}	g/mol	600 - 700			
EA (a.r.)					
C	wt.%	42 – 48	52 - 65	78 – 82	86 – 88
H	wt.%	7.5 – 8.0	8.5 – 9.5	11 – 11.5	12
O (by difference)	wt.%	45 - 50	20 – 40	7 – 10	< 0.5
N	wt.%	<0.01			
ash	wt.%	0.01 - 0.1			
S	wt.%	< 0.01			
Viscosity	cSt	10 - 100	10 – 100	< 10	< 5
H/C molar, dry	-	1.4 - 1.6	1.6 - 1.7	1.7 - 1.8	> 1.8
O/C molar, dry	-	0.5 – 0.6	0.4 – 0.6	< 0.1	< 0.05
MCRT, a.r.	wt.%	18 - 25	< 10	< 1	<< 1
CAN, a.r.	mmol/g	3 - 6	2	< 0.5	<< 0.1
TAN, a.r.	mg_{KOH}/g	60 - 80	60 - 80	< 10	< 0.1
pH	-	2.5 – 3.5	2.5 – 3.5	N/A	N/A
Density	kg/m^3	1100 – 1200	1000 - 1100	900 - 950	800- 900
Heating value	MJ/kg	16 – 18	20 - 25	30 - 40	> 40

Fuel Properties

Water content	25	wt%
Density	1,170	kg/m^3
LHV	16	MJ/kg
Acid Number	70	mg$_{KOH}$/g
Sulfur	< 0.05	wt%
FlashPoint	?	°C
Cetane Number	< 20	-
MCRT	> 15	wt%



Fast Pyrolysis Oil - **FPBO**

Water content	< 0.1	wt%
Density	870	kg/m^3
LHV	> 40	MJ/kg
Acid Number	< 0.15	mg$_{KOH}$/g
Sulfur	< 0.05	wt%
FlashPoint	25	°C
Cetane Number	?	-
MCRT	<< 1	wt%

Biofuel from FPBO **- HPO**

Water content	-	wt%
Density	< 890	kg/m^3
LHV	42	MJ/kg
Acid Number	< 0.5	mg$_{KOH}$/g
Sulfur	< 0.1	wt%
FlashPoint	> 60	°C
Cetane Number	> 40	-
MCRT	<< 1	wt%

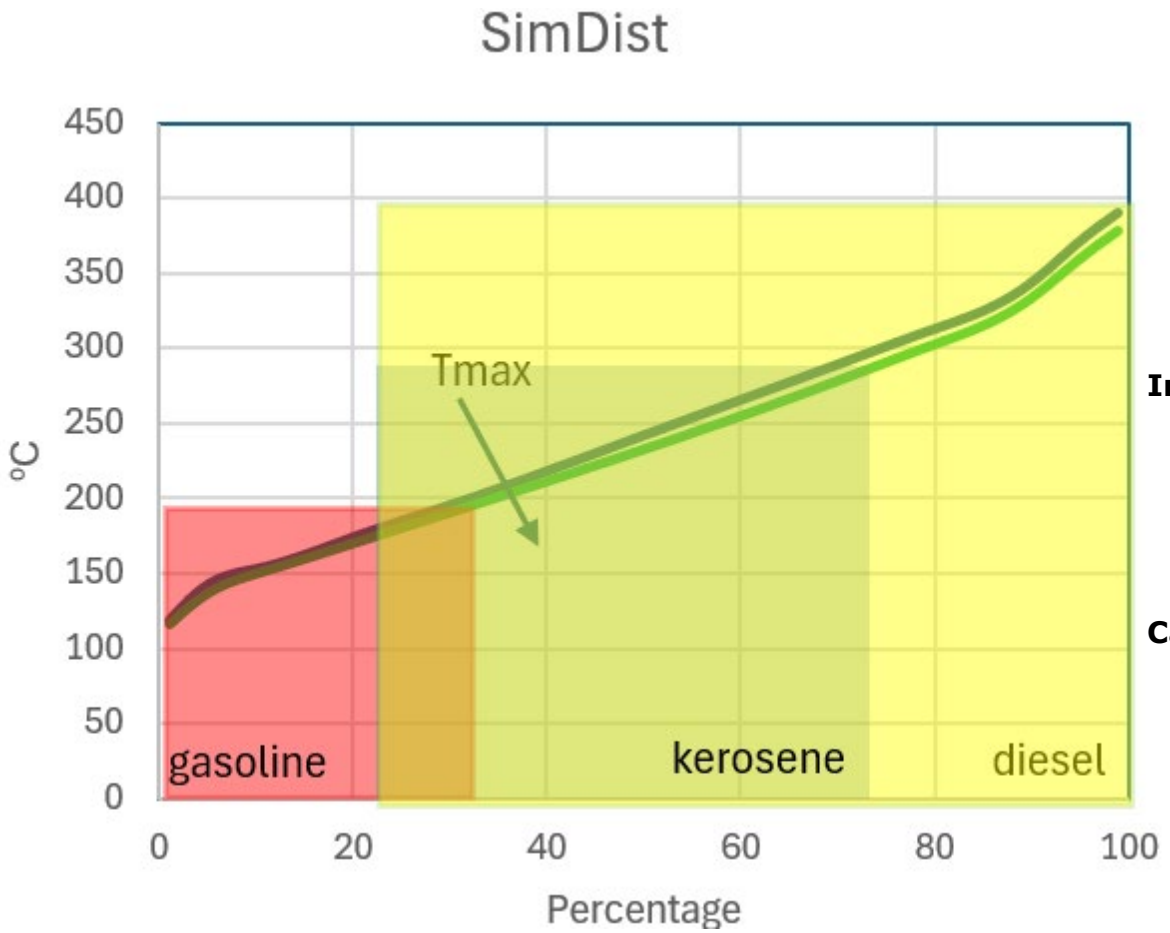
Fossil Marine Fuel - **DMA**

SimDist / GC

24-30% yield; 2/3 in MD range

Composition analyses HPO

Boiling point range wider than marine distillate oils
Composed of hydrocarbons, mostly cyclic, aliphatic and aromatic
No oxygenated compounds detected



20 : 40 : 40 (kerosene)
20 : 0 : 80 (marine)

Integrated hydro-pyrolysis/catalytic hydro-treatment (IH2®)
- Developed by Gas Technology Institute
- 15-35 bar H_2, 340-470 °C, 370-400 °C
- 25-28% liquid yields, 2/3 gasoline and 1/3 in the MD range

Catalytic pyrolysis followed by catalytic hydro-treatment
- Scaled-up by KiOR: Khosla Ventures and BIOeCON
- 10 wt.% yield, most in the gasoline range

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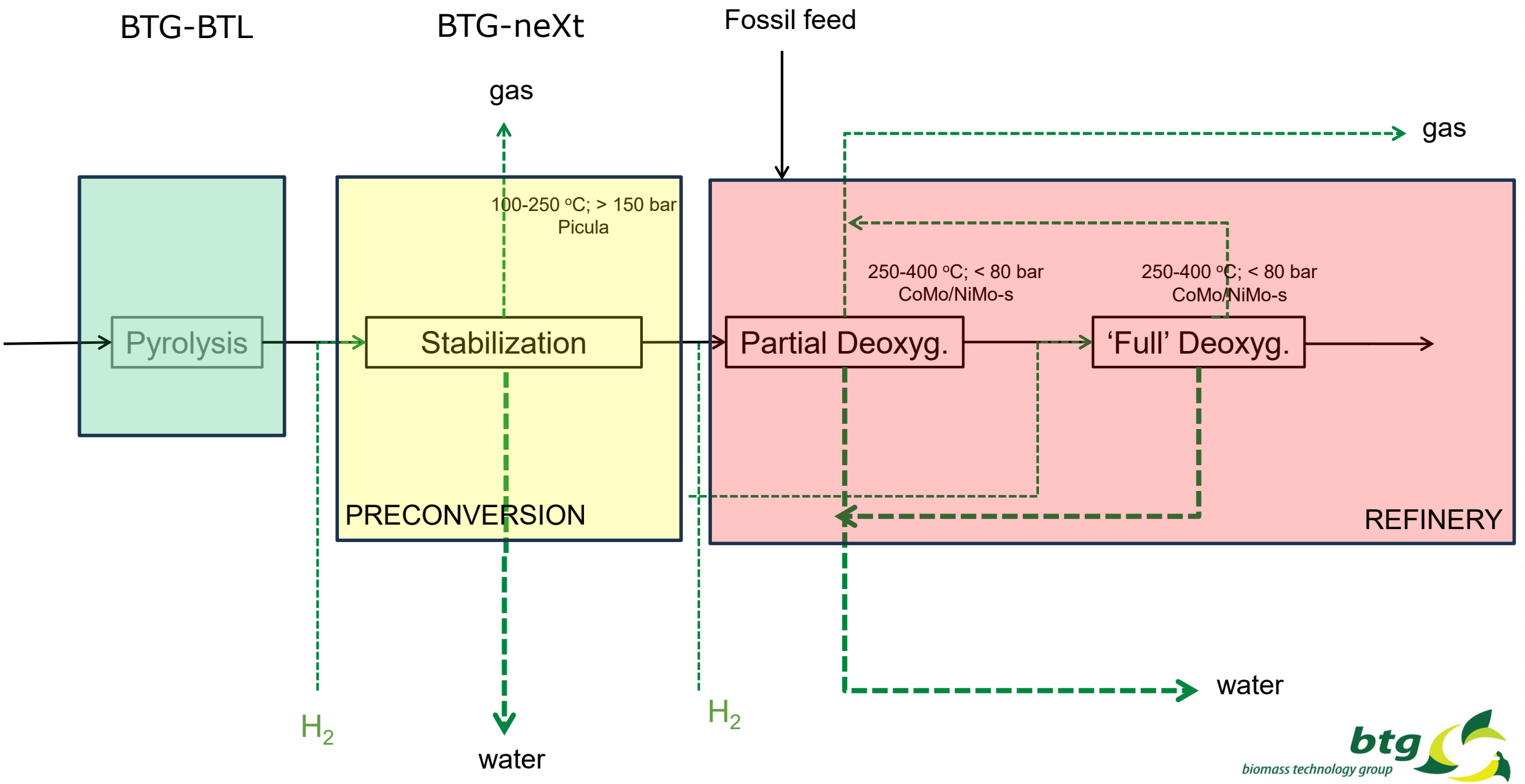
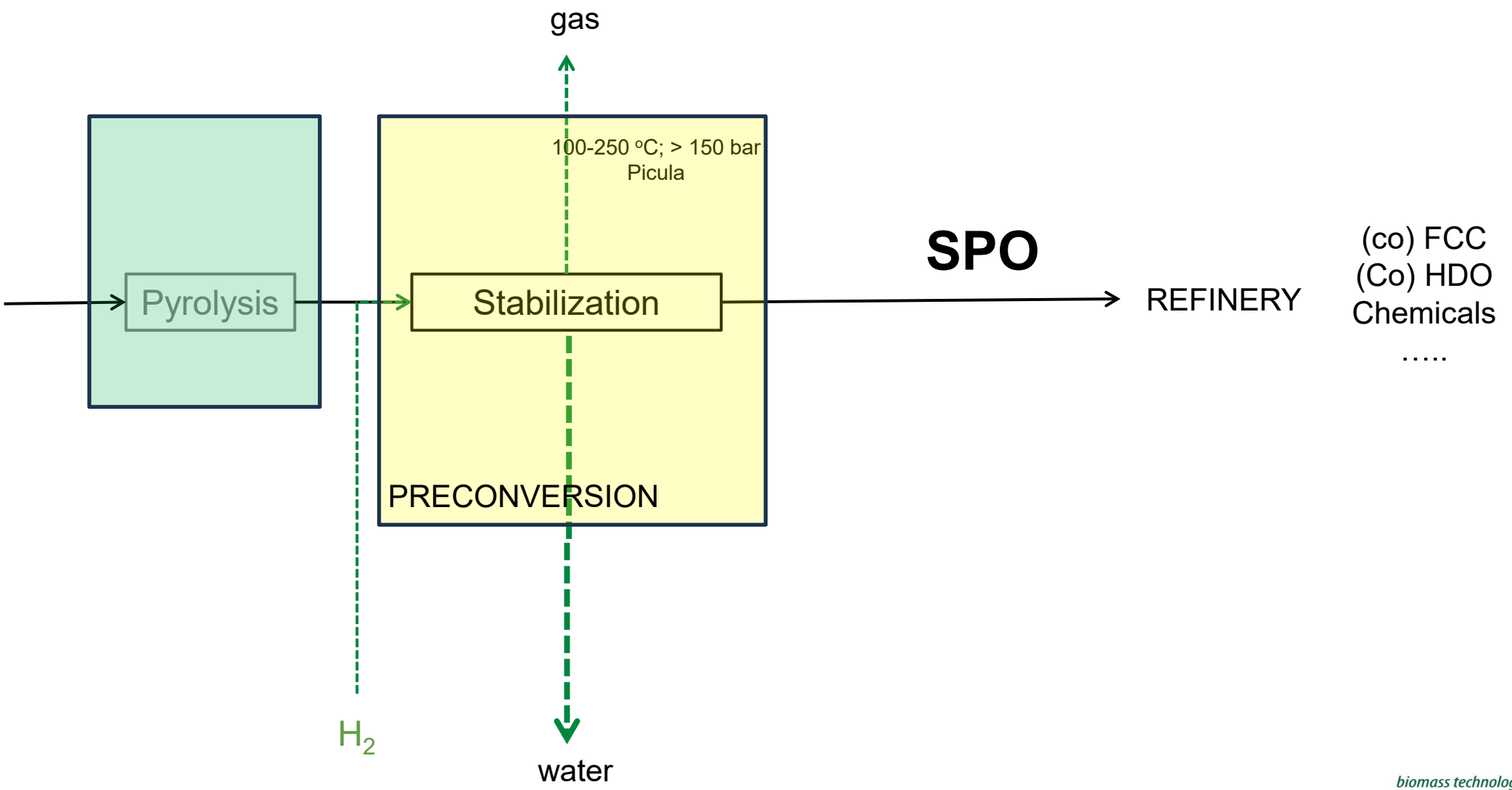
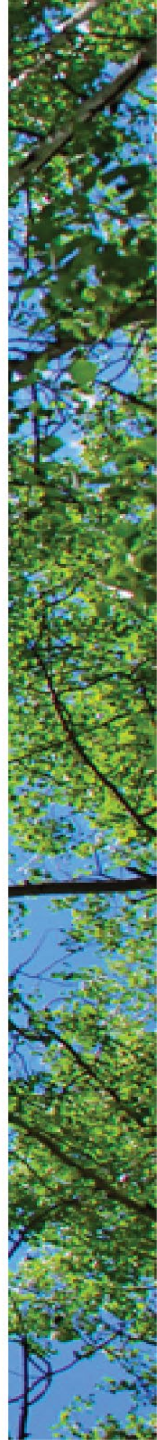
Pathways for integration into an existing structure



BTG-BTL

BTG-neXt





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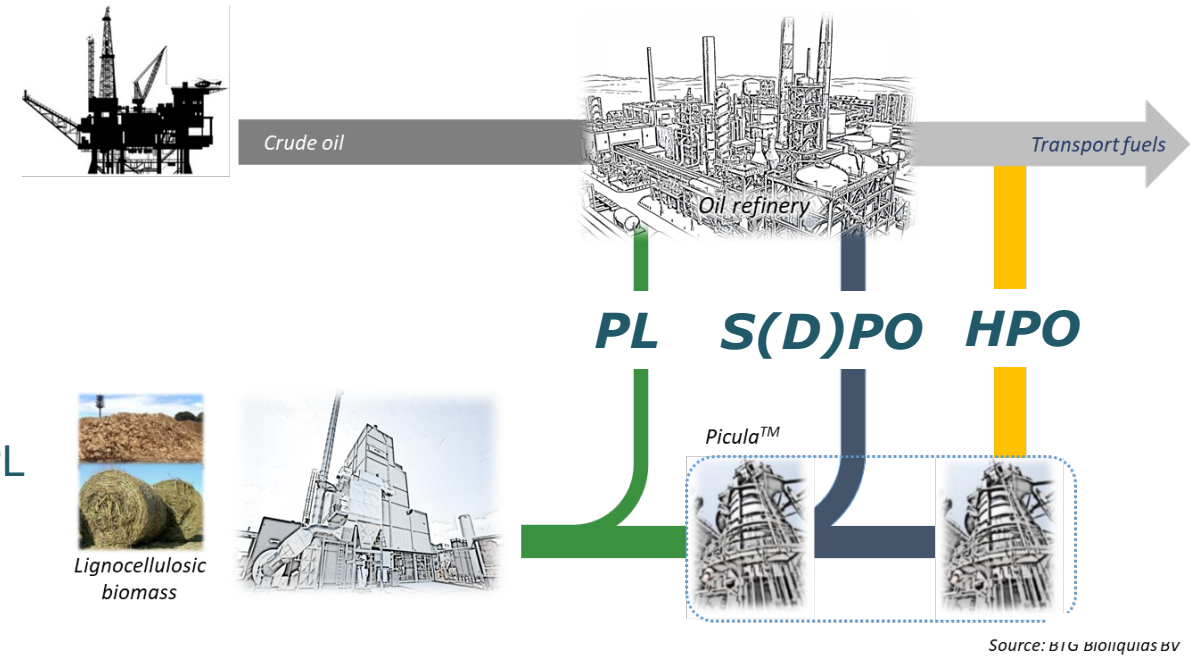
Advanced biofuels from pyrolysis liquids

Options to produce a fuels

1. Co-feed of PL with VGO in FCC unit
- Extensive testing by Petrobras
- Demonstrated full-scale by Preem (2021)
- Max co-feed around 5 wt%

2. Co-feed of treated SPO with VGO in FCC unit
- Lab- and pilot testing
- Higher co-feed ratio's possible (20 - 30 wt%) ?
- Less impact on product slate compared to crude PL

3. Stand-alone upgrading of PL to drop-in
- Lab- and pilot testing
- Multi-step hydrotreating process
- Product (HPO) is fully miscible with fossil fuels
- (co-)distill CDU



Source: BTG Biofuels BV

***PL** = Fast Pyrolysis Bio-Oil*
***S(D)PO** = Stabilized (Deoxygenated) Pyrolysis Oil*
***HPO** = Mixed Transportation Fuel*

https://doi.org/10.1016/j.fuel.2016.10.032;
10.1021/acs.iecr.5b03008

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Take home messages

Catalytic stabilisation is key to upgrading pyrolysis oils

If SPO could be directly derived by pyrolysis of biomass, we would never had a fossil fuel oil industry

- Extensive testing by BTG (20 years exp.)
- Sugar-like hydrogenation: low temperature; high pressure
- Main specifications - required / obtainable - known: MCRT < 10 wt%
- High carbon yield from pyrolysis oil (> 95%)
- Dedicated catalyst available – now being optimized irt stand times
- Couple of patent families (catalysts – methods) in progress
- Oils transferred - supplied all over the world (L, 100's L)
- Looking for cooperations

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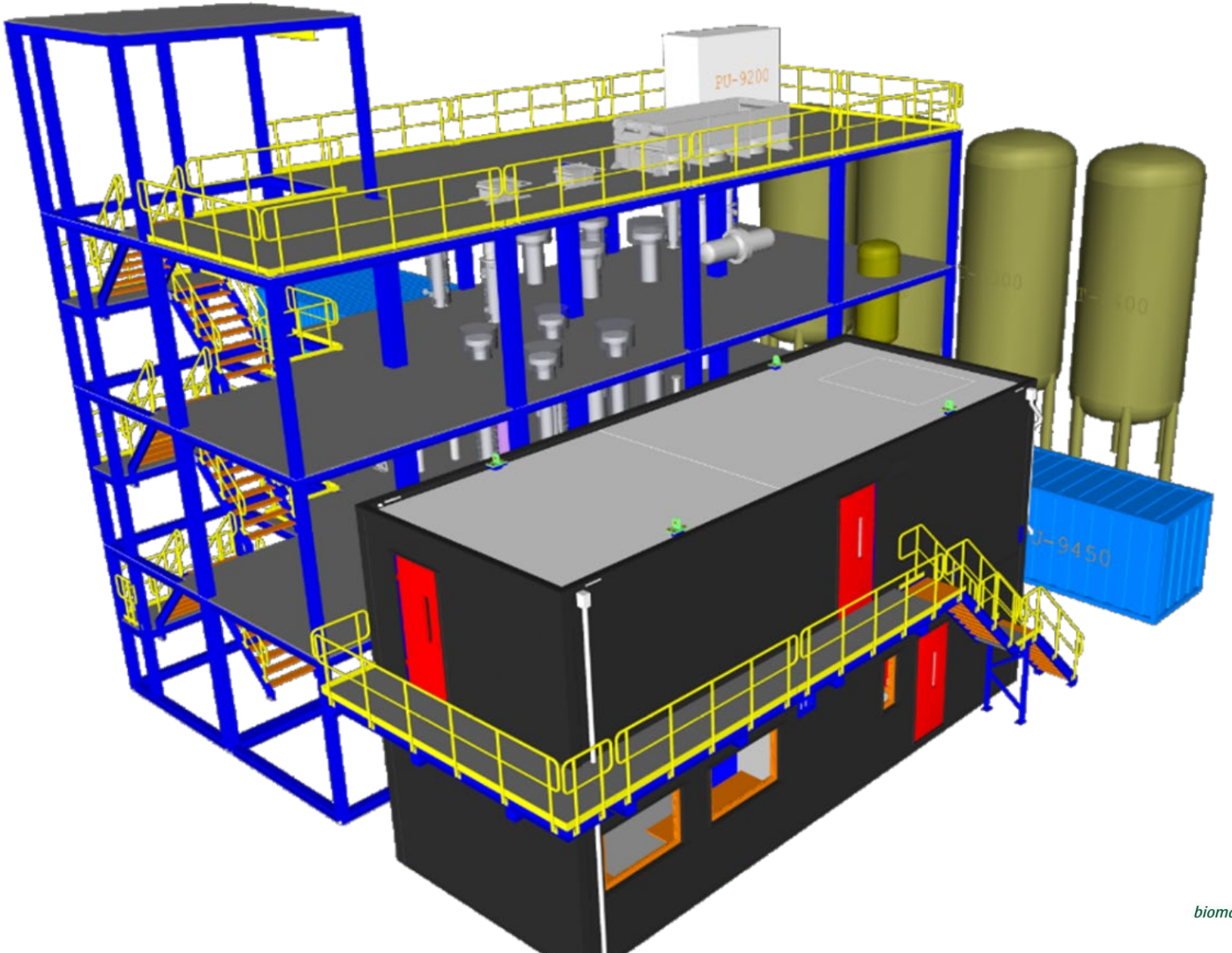
PU-9200
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Thanks for your attention

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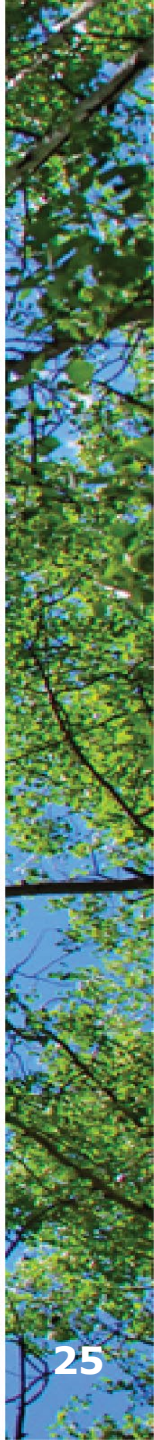
4REFINERY project, grant agreement **727531**

WASTE2ROAD project, grant agreement **818120**

REFOLUTION, grant agreement 101096780

FUEL-UP, grant agreement 101136123



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