BTG Biomass Technology Group BV

Insights in the hydrotreating of pyrolysis liquids

October 8 2019, TCBiomass 2019

Robbie Venderbosch

btg biomass technology group

Your partner in bioenergy

BTG Biomass Technology Group BV

Employees BTG BV

↓

Biomass Technology Holding BV

↓

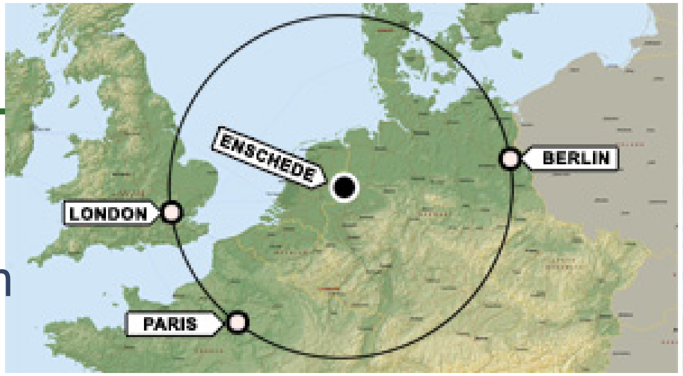
3rd parties

btg biomass technology group — **Consultancy** | **RTD**

Around 30 employees

btg-btl biomass-to-liquid

Around 10 employees



Berlin 445 km
Paris 485 km
London 490 km

Amsterdam 160 km

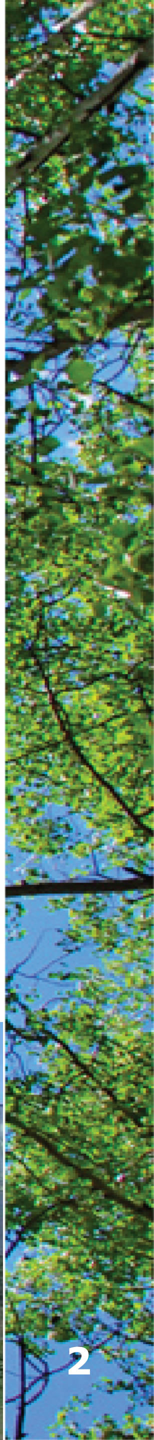
Twence®

↓

EMPYRO energy & materials from pyrolysis

As of 2019

*waste processing company established by 14 municipalities in Twente



Content

Background
- BTG-BTL's pyrolysis process

Short and long term perspective
- co-FCC pure liquids
- co-FCC hydrotreated liquids

Hydrotreatment of pyrolysis liquids

Insights in hydrotreatment - catalyst deactivation

Concluding remarks

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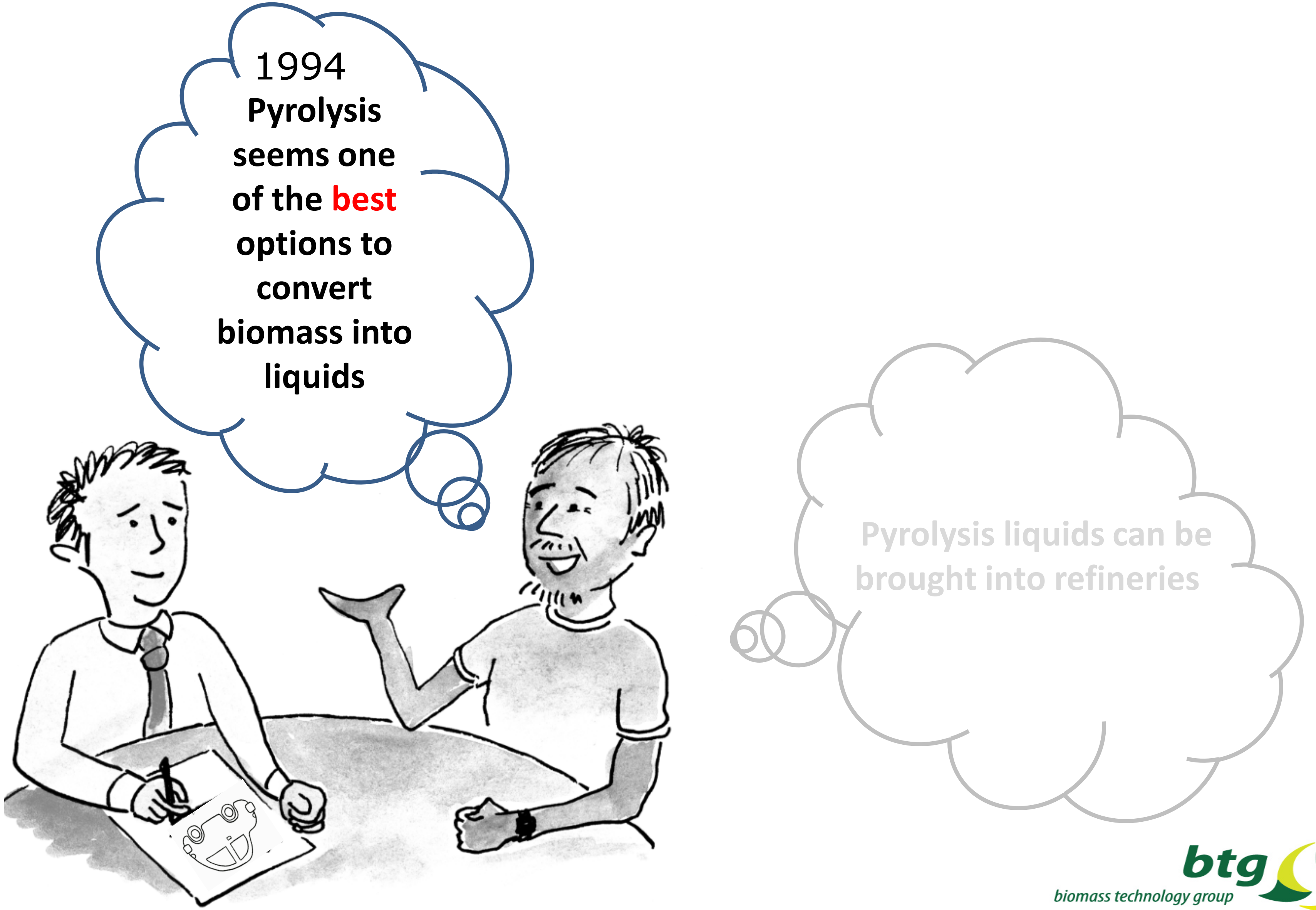
Biomass problem: solve logistics first

Pyrolysis is a cheap pretreatment ‘to solve logistics first’



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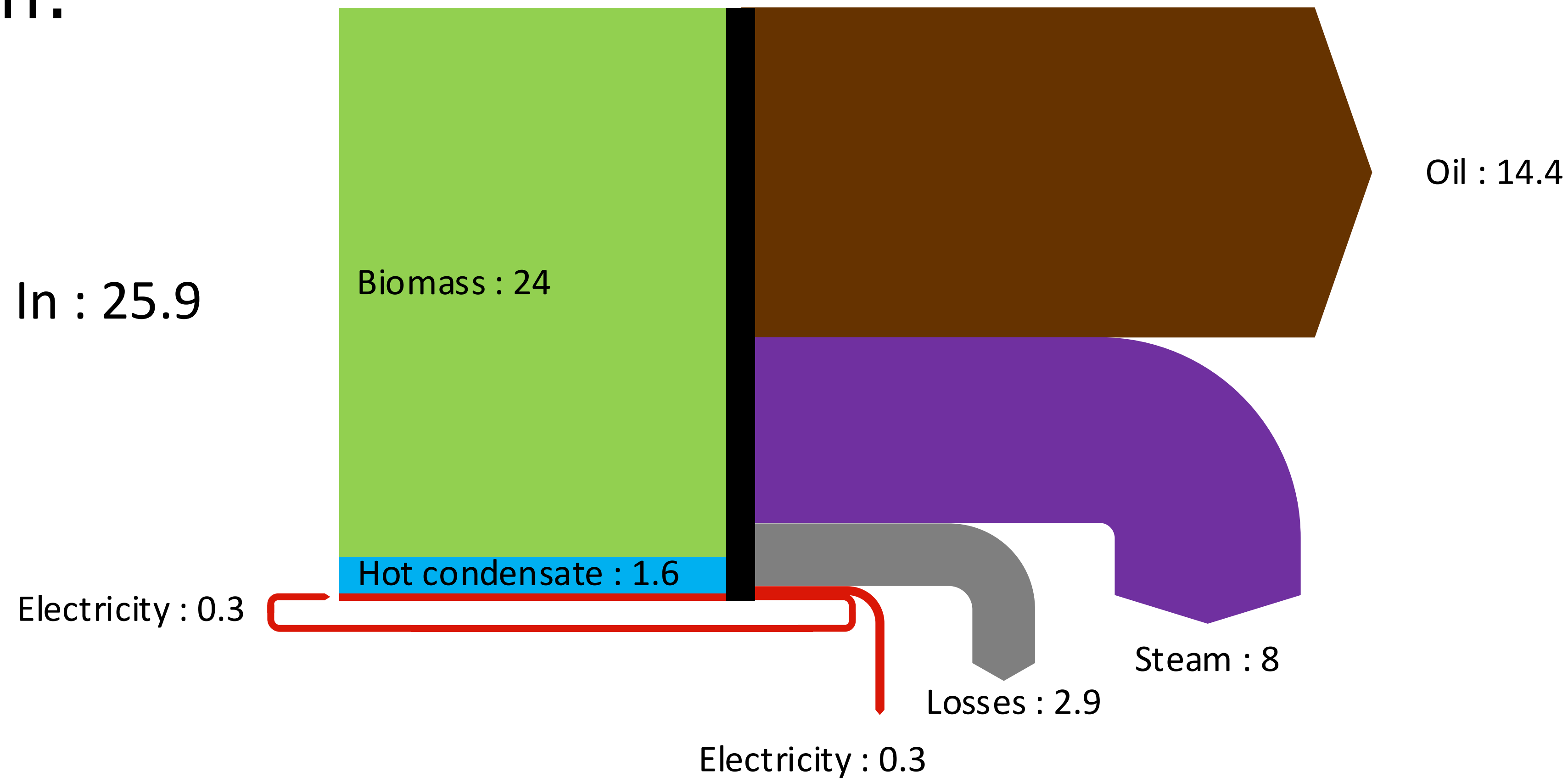

Overall Efficiency : 85 - 89 %

https://www.cocosimulator.org/index_sample.html

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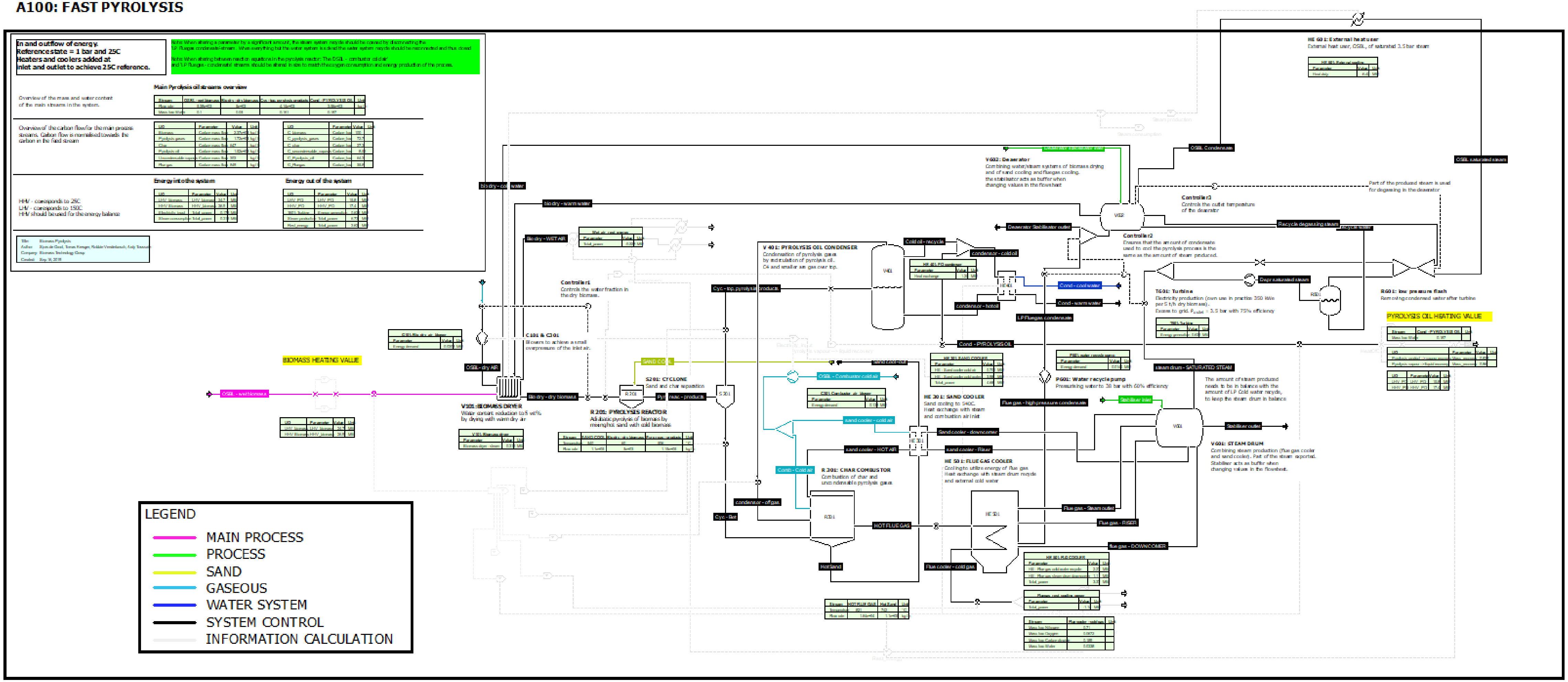
https://www.cocosimulator.org/index_sample.html

A100: FAST PYROLYSIS



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Biomass problem: solve logistics first

Pyrolysis is a cheap pretreatment ‘to solve logistics first’

Pyrolysis seems one of the best options to convert biomass into liquids

1998:

Pyrolysis liquids can be brought into refineries

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Bio-óleo a partir da pirólise rápida, térmica ou catalítica, da palha da cana-de-açúcar e seu co-processamento com gasóleo em craqueamento catalítico

Marlon Brando Bezerra de Almeida

Escola de Química/UFRJ
M.Sc.

Orientadores:
Prof. Donato Alexandre Gomes Aranda, D.Sc.
Yiu Lau Lam, Ph.D

Rio de Janeiro-RJ-Brasil
Março, 2008

DE GRUYTER DOI 10.1515/pac-2013-0914 — Pure Appl. Chem. 2014; 86(5): 859–865

Pyrolysis liquids from BTG-BTL (2014)

Conference paper

Andrea de Rezende Pinho*, Marlon Brando Bezerra de Almeida, Fabio Leal Mendes and Vitor Loureiro Ximenes

Production of lignocellulosic gasoline using fast pyrolysis of biomass and a conventional refining scheme

Pyrolysis liquids from Ensyn (2015/2017)

'uel 188 (2017) 462–473

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Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locat

Full Length Article

Fast pyrolysis oil from pinewood chips co-processing wi oil in an FCC unit for second generation fuel production

Andrea de Rezende Pinho [a,*], Marlon B.B. de Almeida [a], Fabio Leal Mend Michael S. Talmadge [c], Christopher M. Kinchin [c], Helena L. Chum [c]

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Fuel Processing Technology 131 (2015) 159–166

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Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Co-processing raw bio-oil and gasoil in an FCC Unit

CrossMark

Andrea de Rezende Pinho [a,*], Marlon B.B. de Almeida [a], Fabio Leal Mendes [a], Vitor Loureiro Ximenes [a], Luiz Carlos Casavechia [b]

[a] PETROBRAS, Centro de Pesquisas e Desenvolvimento Leopoldo A. Miguez de Mello (CENPES), Ilha do Fundão, Av. Horácio Macedo, 950, Rio de Janeiro, RJ, Brazil
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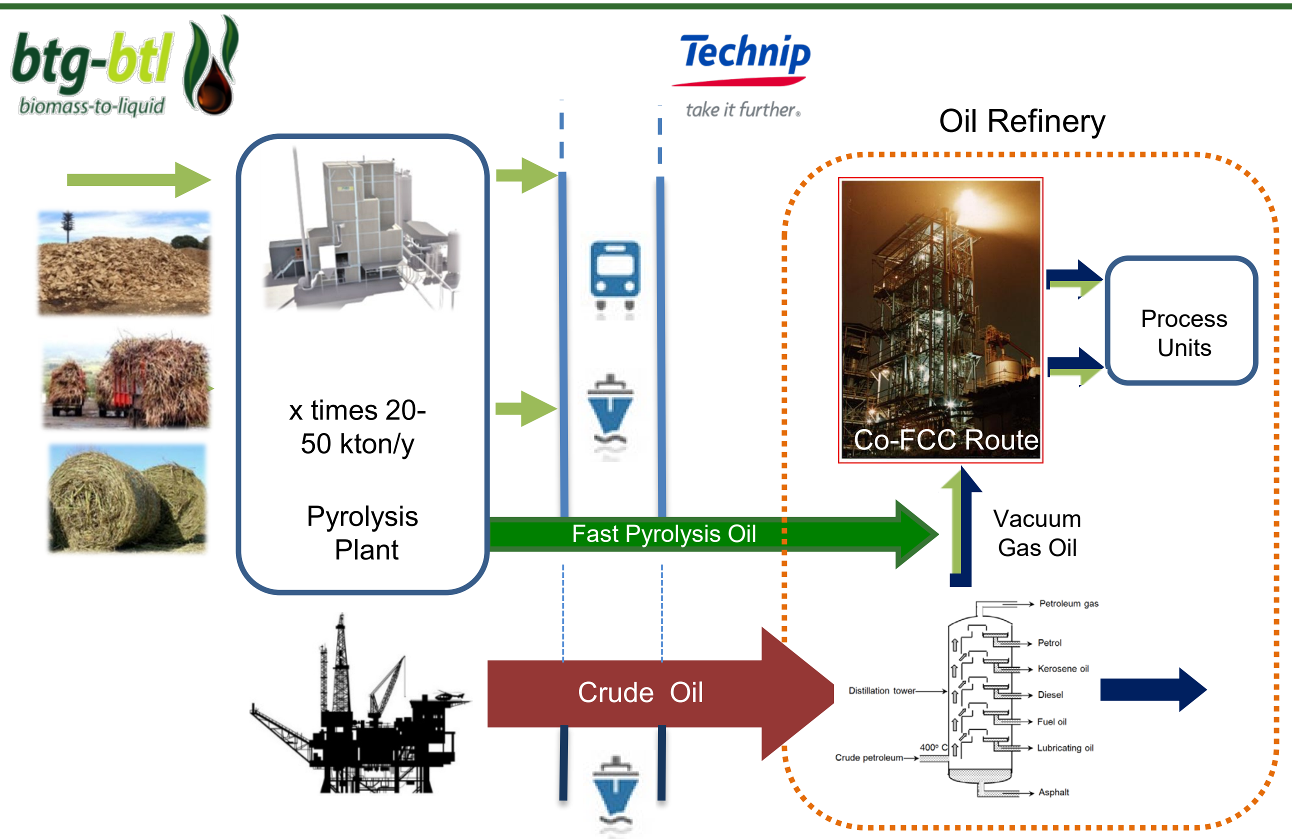
Shortcut to refineries: co-FCC FPBO based on the short term



Co-refining PL in FCC enables production of **2^{nd}G bio-fuels** utilizing existing refining infrastructure.

Feedstock	VGO	90% VGO + 10% Bio-oil	80% VGO + 20% Bio-oil
CO	0.1	1.9	3.1
CO_2	0.1	0.5	0.8
Water	0.0	2.3	7.3
Dry Gas	3.9	2.8	2.5
LPG (C_3-C_4)	15.2	12.9	9.9
Gasoline (C_5-220°C)	40.4	40.7	37.7
Diesel (220-344°C)	18.1	17.4	16.5
Bottoms (+ 344°C)	14.8	14.0	13.7
Coke	7.4	7.5	8.5

1 wt.% substitution = 1 Empyro
Europe = 80 refineries with FCC (US > 100; worldwide > 400)
1 Empyro = 25 M€

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Forest and saw mill bi-products and residue liquefaction and valorization

- Preem has further interests in pyrolysis technologies
- Setra and Preem has started a JV, Pyrocell AB to build a fast pyrolysis plant Gävle. The plant would use saw dust from the Setra saw mill "Kastet"
- The pyrolysis oil would be used as a refinery feedstock

Setra

Pyrocell selects BTG-BTL's fast pyrolysis technology

Alan Sherrard · Technology & Suppliers · September 16, 2019

In Sweden, Pyrocell AB has announced that it has selected the Dutch companies TechnipFMC and BTG BioLiquids (BTG-BTL) to design and build a production facility in which sawmill residues from Setra Group's Kastet sawmill will be converted into bio-oil. It will be the first plant in the world where 'green fuel' will be produced and further processed into road transportation fuels at an oil refinery – Preem's Lysekil refinery.

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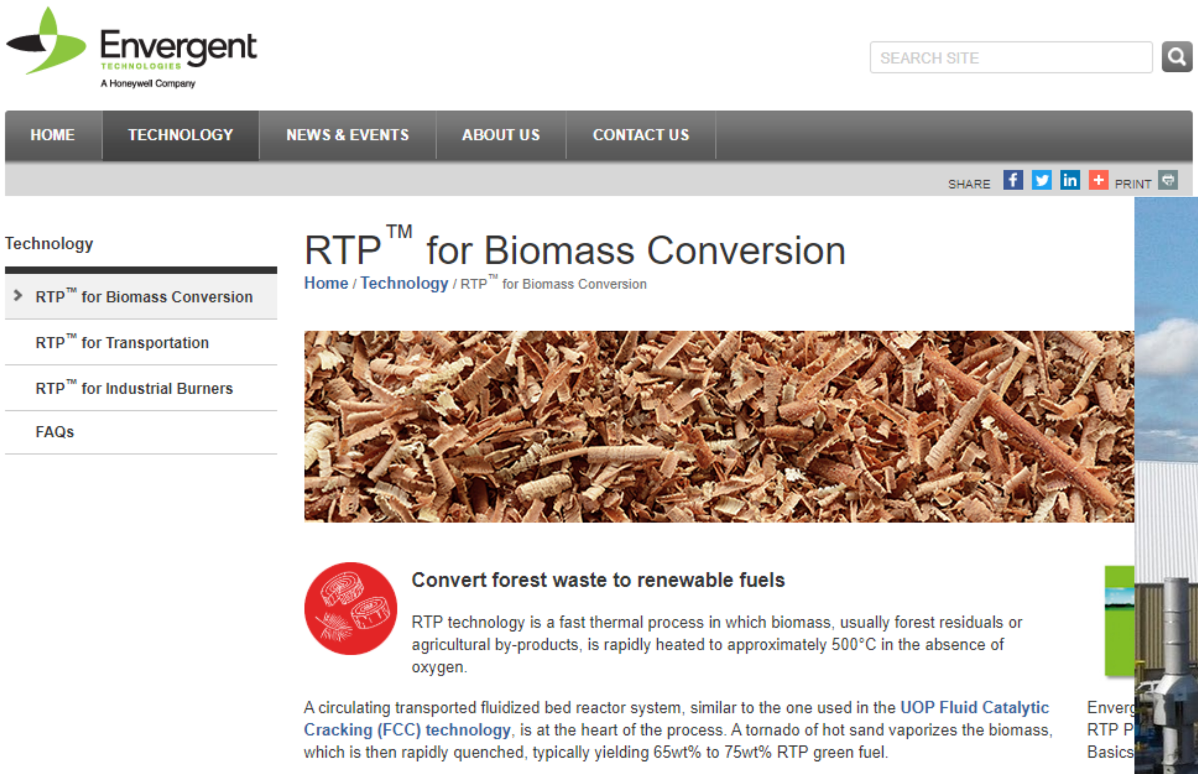
Envergent TECHNOLOGIES A Honeywell Company

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Convert forest waste to renewable fuels

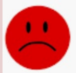
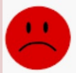
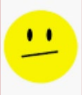
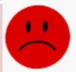
RTP technology is a fast thermal process in which biomass, usually forest residuals or agricultural by-products, is rapidly heated to approximately 500°C in the absence of oxygen.

A circulating transported fluidized bed reactor system, similar to the one used in the UOP Fluid Catalytic Cracking (FCC) technology, is at the heart of the process. A tornado of hot sand vaporizes the biomass, which is then rapidly quenched, typically yielding 65wt% to 75wt% RTP green fuel.

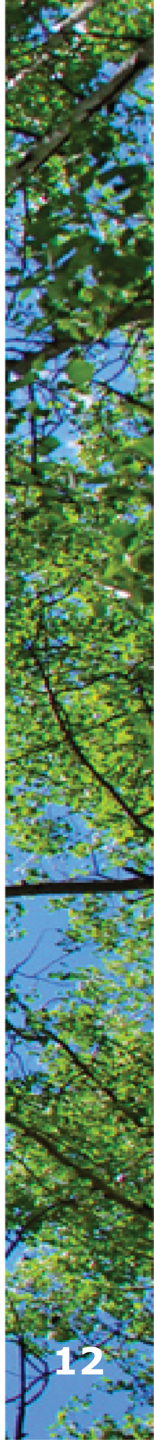
Energ
RTP P
Basics

CÔTE NORD (Port-Cartier, Quebec)
Envergent / Arbec Forest Products / Groupe Rémabec
65,000 kt/y woody biomass to sell liquids to customers (US/Can) for **heating purposes** and **refinery co-processing**.

Shortcut to refineries: co-FCC FPBO based on the short term

Feedstock	VGO	90% VGO + 20% Bio-oil	
CO	0.1	3.1	
CO_2	0.1	0.8	
Water	0.0	7.3	
Dry Gas	3.9	2.5	
LPG (C_3-C_4)	15.2	9.9	
Gasoline (C_5-220°C)	40.4	37.7	
Diesel (220-344°C)	18.1	16.5	
Bottoms (+344°C)	14.8	13.7	
Coke	7.4	8.5	

Petrochemicals?



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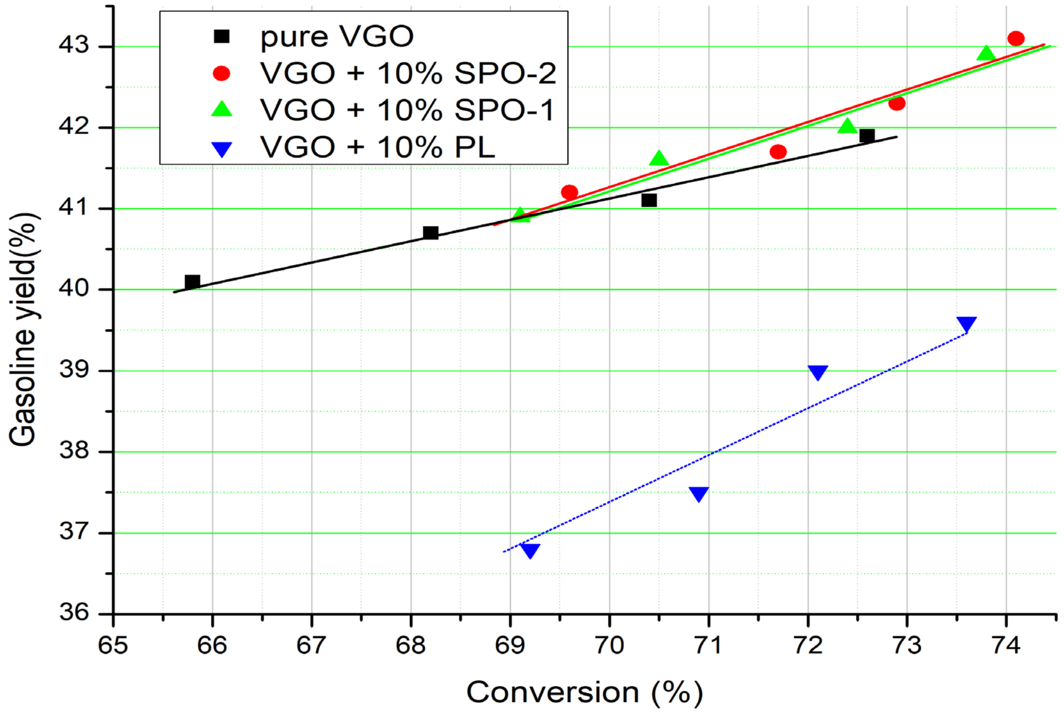

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Fuel
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Full Length Article

Optimizing the bio-gasoline quantity and quality in fluid catalytic cracking co-refining

CrossMark

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Co-processing of crude and hydrotreated pyrolysis liquids and VGO in a pilot scale FCC riser setup

ARTICLE INFO

Keywords:
Pyrolysis liquids
Mild hydro-upgrading
Bimetallic Ni-based catalyst
FCC co-processing

ABSTRACT

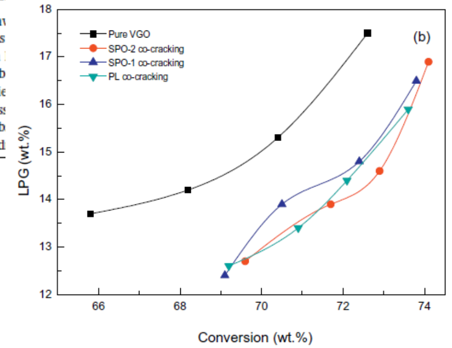
Untreated and mildly hydrotreated pyrolysis derived liquids are evaluated in FCC processing by co-feeding with vacuum gas oil ('VGO'). Pyrolysis liquids (PLs) applied are from the Empyro plant in the Netherlands. The treated PLs are produced by BTG employing novel bimetallic Ni-based catalyst (Picula), at 200 bar hydrogen pressure and two temperatures, 120 °C and 225 °C.

A pilot scale riser setup (riser: I.D. = 7 mm, length = 9 m; combustor: I.D. = 78 mm) is employed to process the liquids with VGO. The riser is operated at a riser outlet temperature of 525 °C, atmospheric pressures and Cat-to-Oil ('C/O') ratio ranging from 5 to 8. Co-processing ratios are kept constant at 10:90 (PLs:VGO).

The most relevant observa

– At all C/O ratios, the conv
– The yield of coke, dry gas
– At such high substitution ... htly higher yield of LCO and b
– The treated bio-liquids yie

During crude PL co-process ... ure VGO. Renewable carbon is ob ... ysis oil (SPO), while the mild hyd



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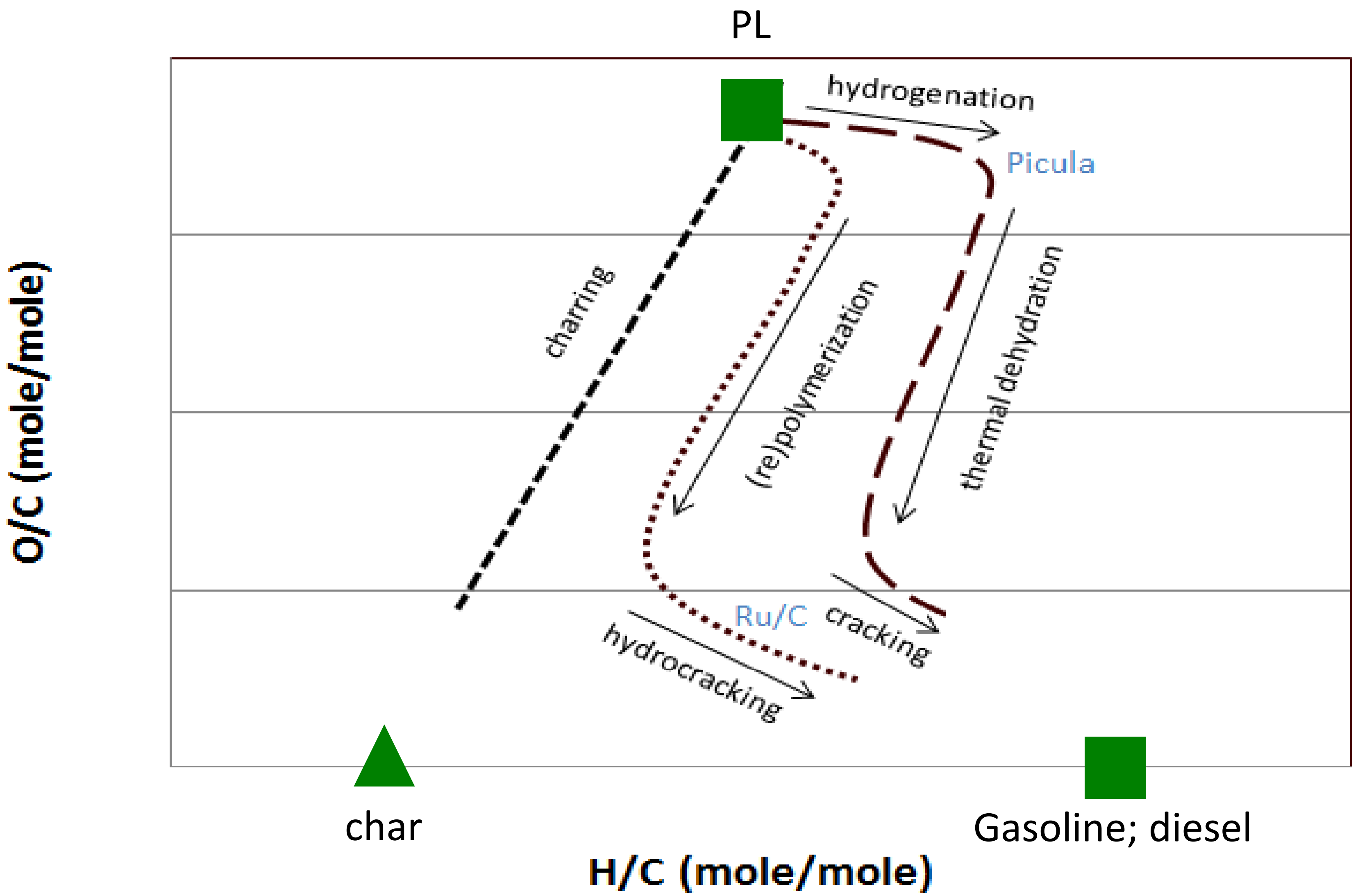
What is PL hydrotreating?

It is not and all, it is all sugar chemistry..



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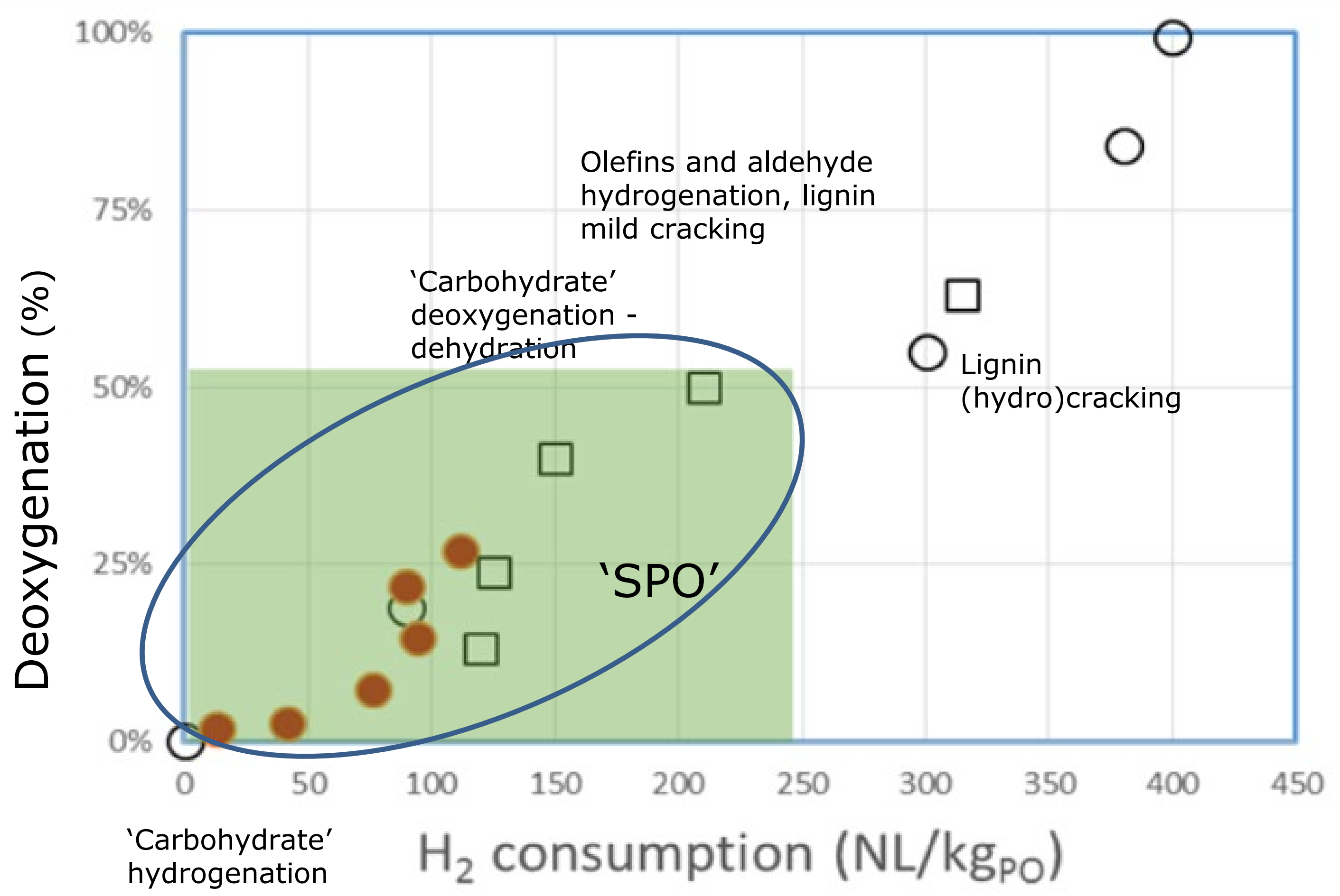
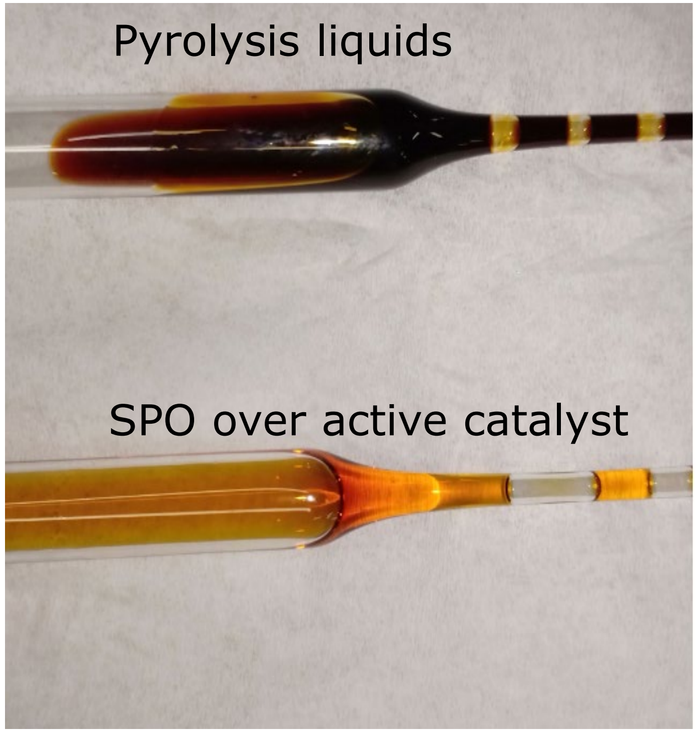
What is PL hydrotreating?





Improved liquid = closer to oil

MCRT<10 wt.%; $H_{2,cons}$ > 150 L/kg_{PL}

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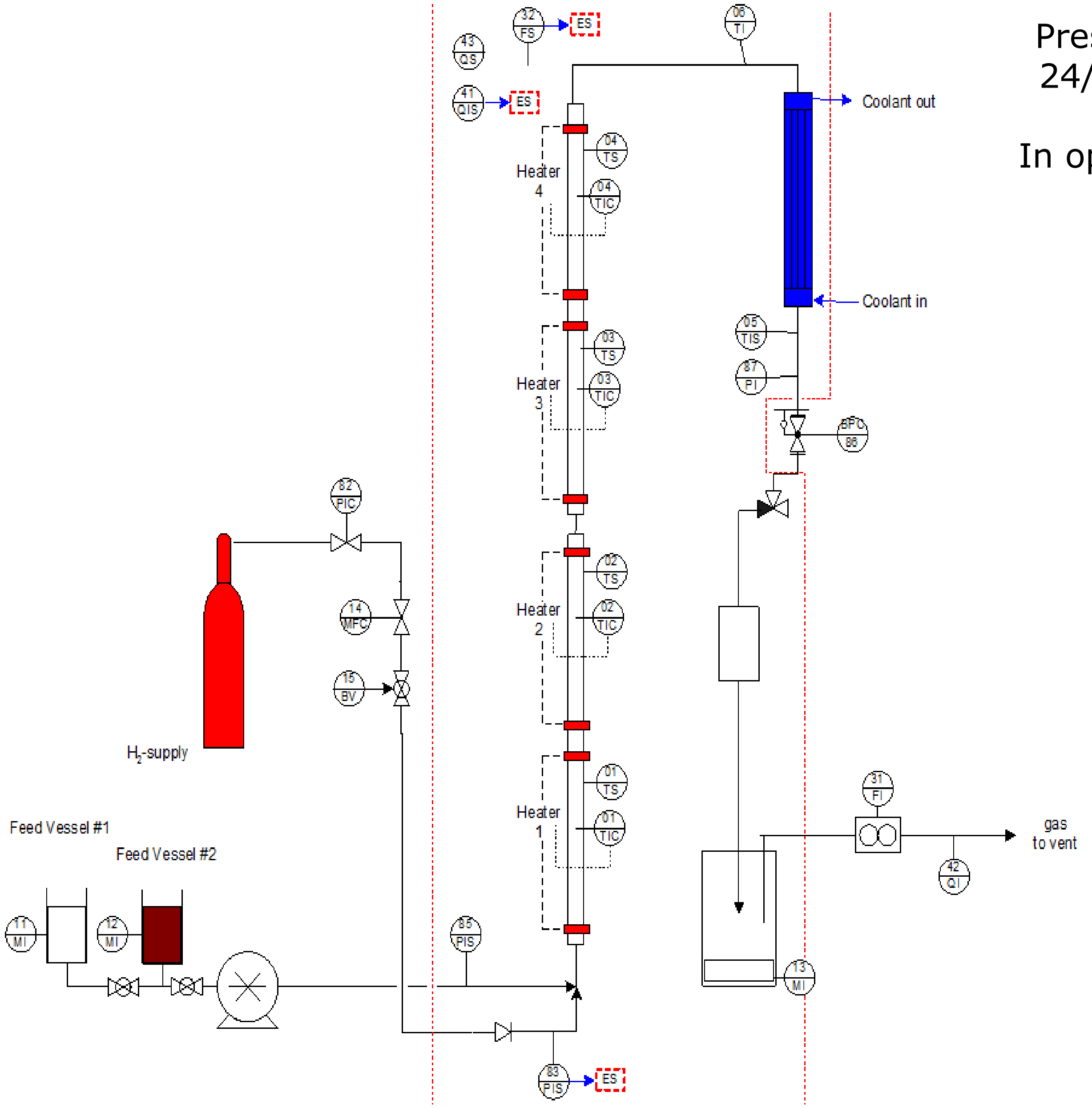
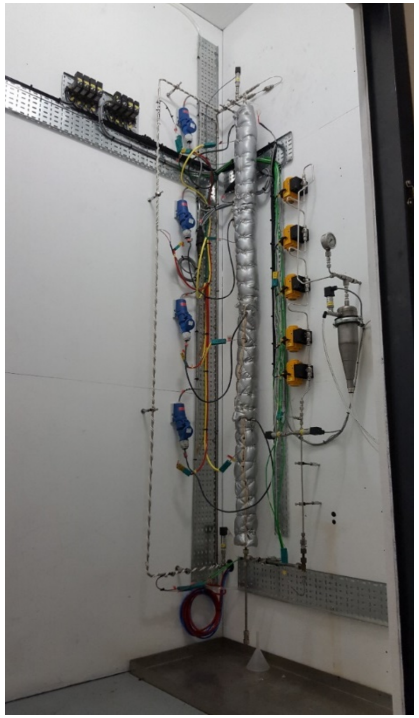
1 - 20 L of product



Pressure 100-200 bar
24/7; 100 ml volume
Up to 450^{o}C
In operation since 2006



50 - 200 litres of product

Pressure 100-200 bar
24/7; 6 L volume (below 300°C)
In operation since 2018

Feed section   4 reactor in series   G/L separator   Product collection

each reactor
1.5 L

6 kg Picula™

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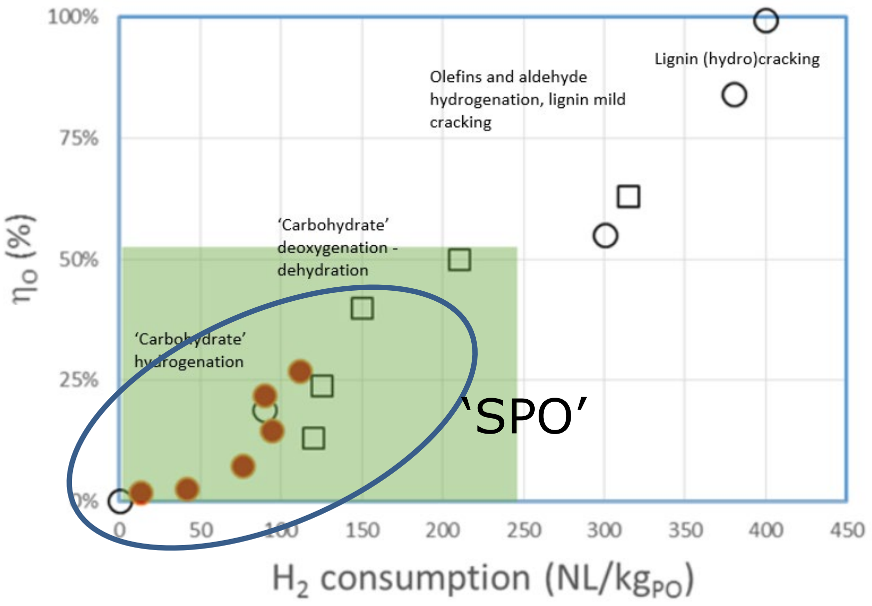
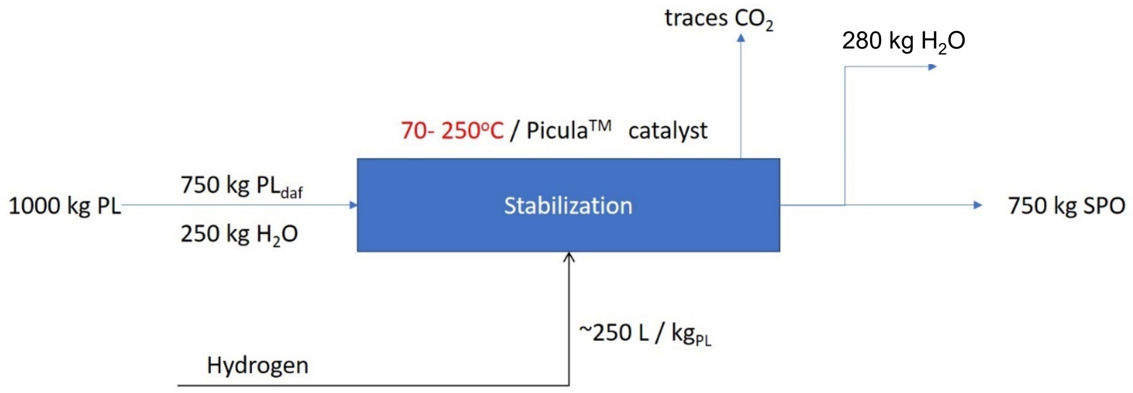
Status / M&E balance SPO and Quality





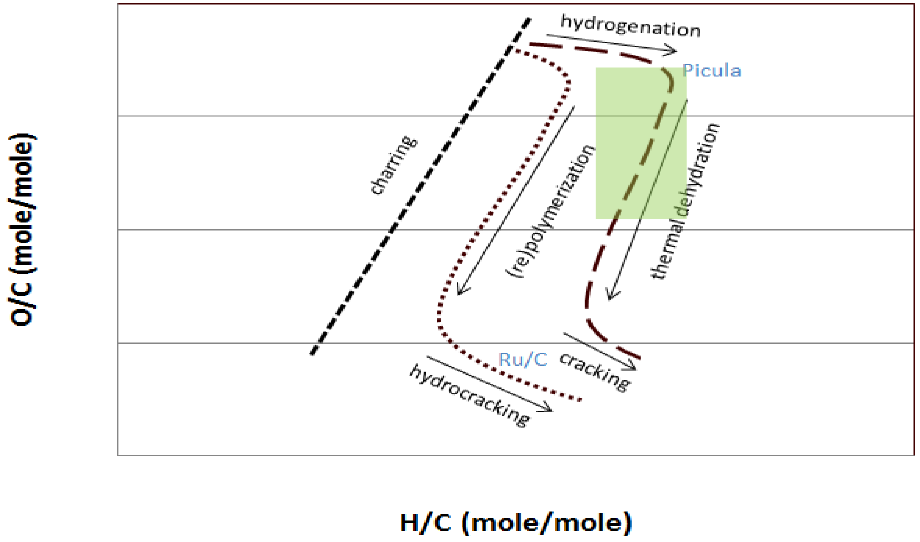
PL

wt. %	
C_{ar}	43.0
H_{ar}	7.5
O_{ar}	49.5
H_2O	25.0

SPO

wt. %	
C_{ar}	54.0
H_{ar}	8.6
O_{ar}	37.4
H_2O	8.4

SPO		
Physical property		
Elemental analysis (as received)	[wt.%]	
C		52 – 56
H		8.2 – 9.2
N		-
S		-
O (by difference)		
Ash		N/A
MCRT		8 – 12
Water content		5 – 10
Viscosity	[cP]	N/A
Acid number	[mg KOH/g]	20 – 40
Carbonyl content	[mg BuO/g]	< 10
pH	[-]	3.2 – 4.2

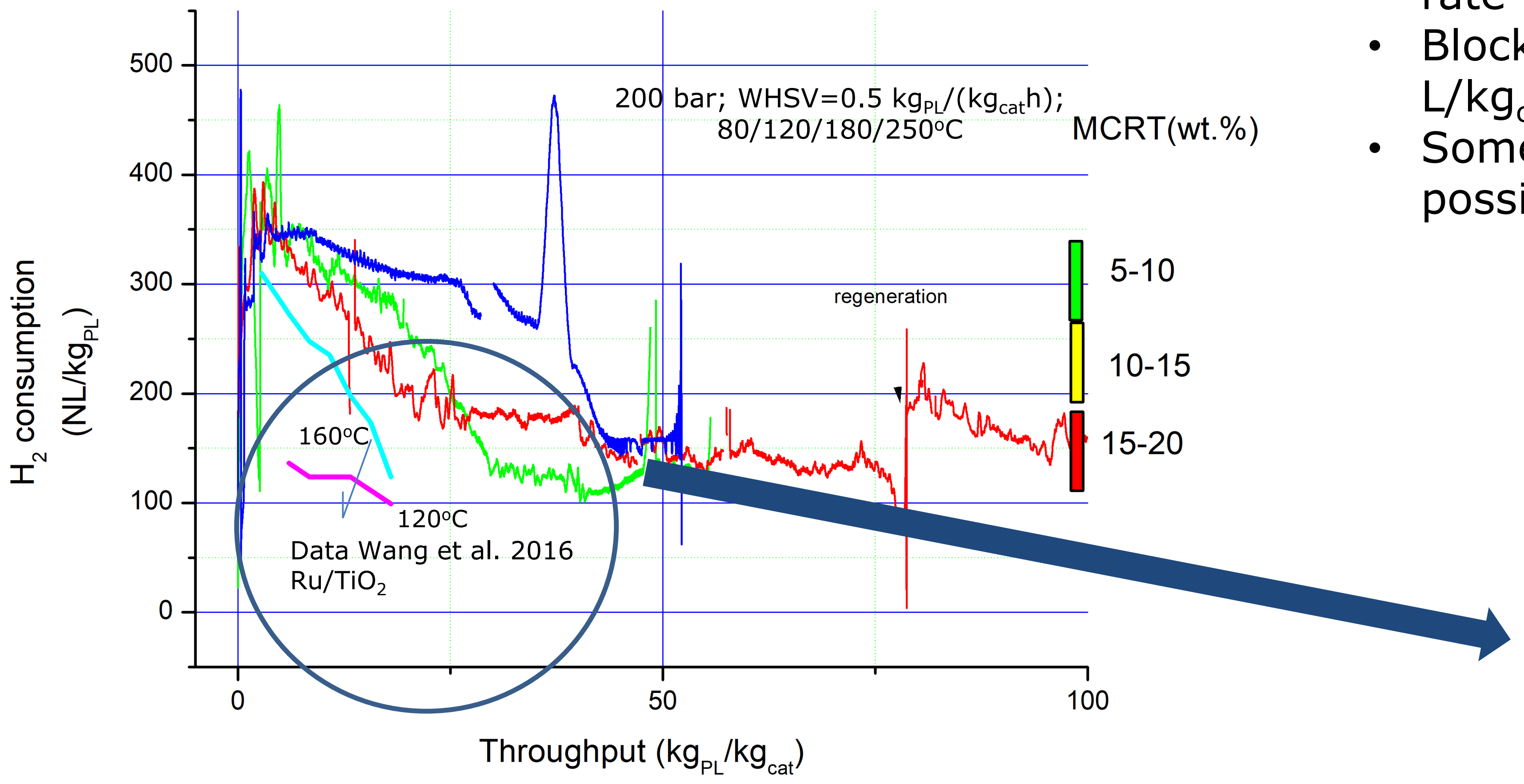


Deactivation vs liquid throughput

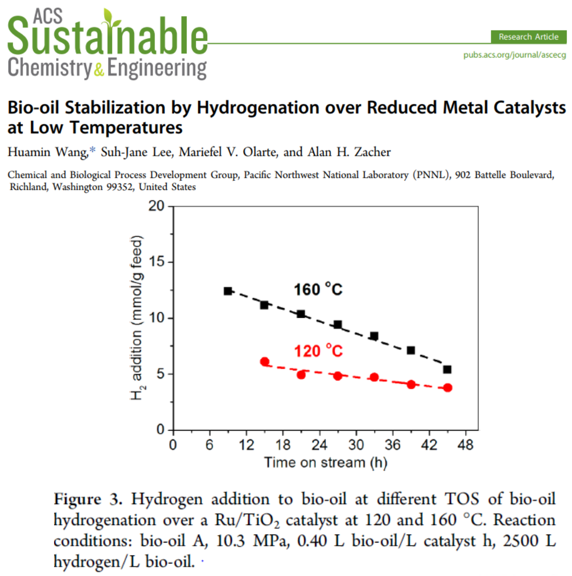
red = benchmark Picula

green = copy Picula from 3rd party

blue = commercially pelletised



- Similar pattern for different types of Picula catalysts (A1-A2-A3)
- 4-stage deactivation?
- Initial high deactivation rate
- Blockage at $H_2/kg_{PL} \approx 150$ L/kg_{cat}
- Some regeneration possible


ACS Sustainable Chemistry & Engineering

Research Article

pubs.acs.org/journal/ascecg

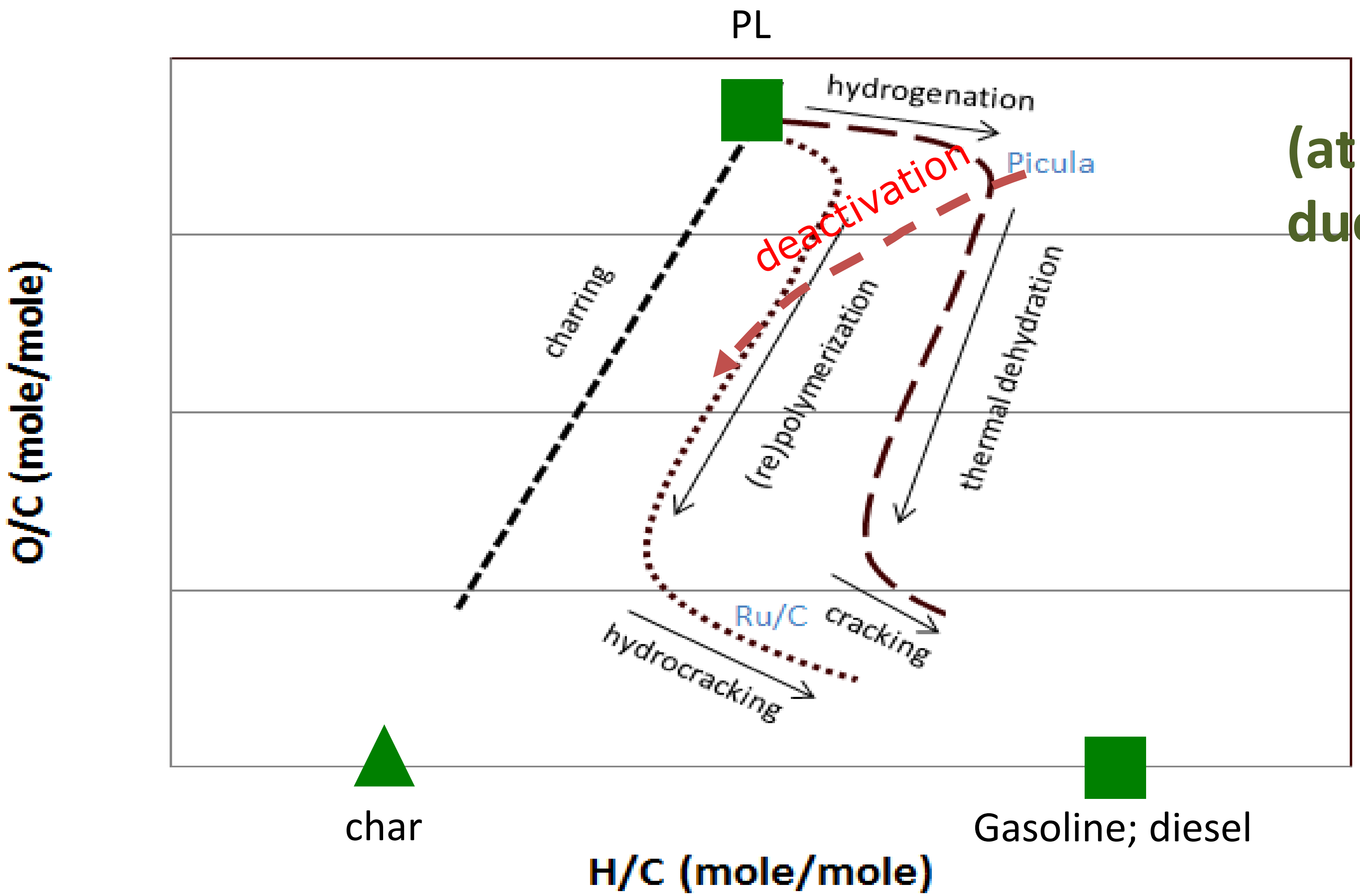
Bio-oil Stabilization by Hydrogenation over Reduced Metal Catalysts at Low Temperatures

Huamin Wang,* Suh-Jane Lee, Mariefel V. Olarte, and Alan H. Zacher

Chemical and Biological Process Development Group, Pacific Northwest National Laboratory (PNNL), 902 Battelle Boulevard, Richland, Washington 99352, United States

Figure 3. Hydrogen addition to bio-oil at different TOS of bio-oil hydrogenation over a Ru/TiO_2 catalyst at 120 and 160 °C. Reaction conditions: bio-oil A, 10.3 MPa, 0.40 L bio-oil/L catalyst h, 2500 L hydrogen/L bio-oil.

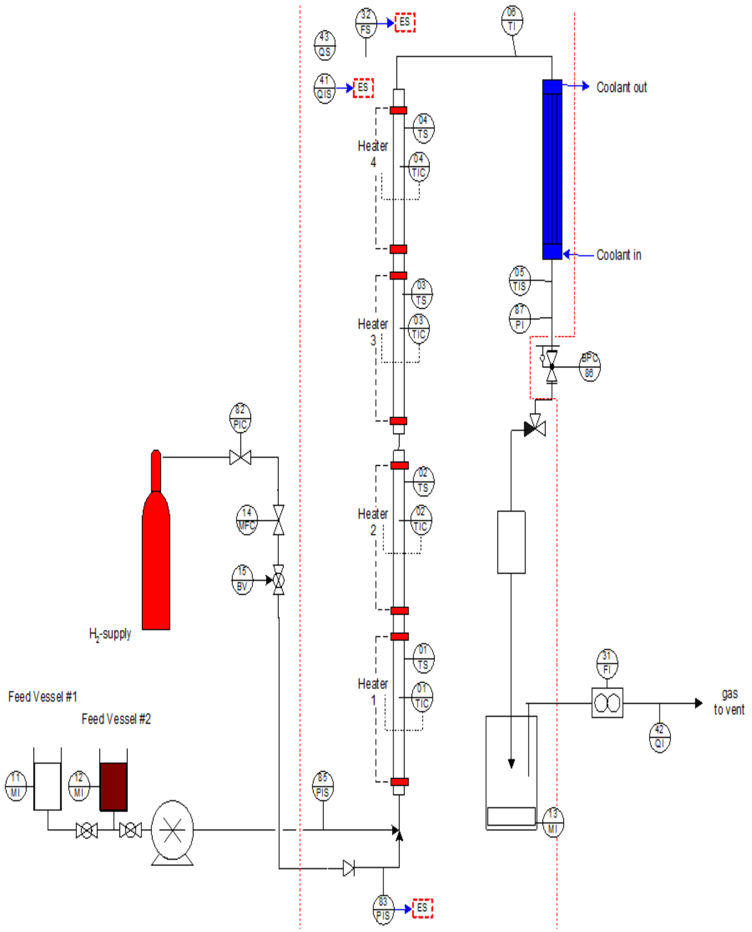
What is deactivation?

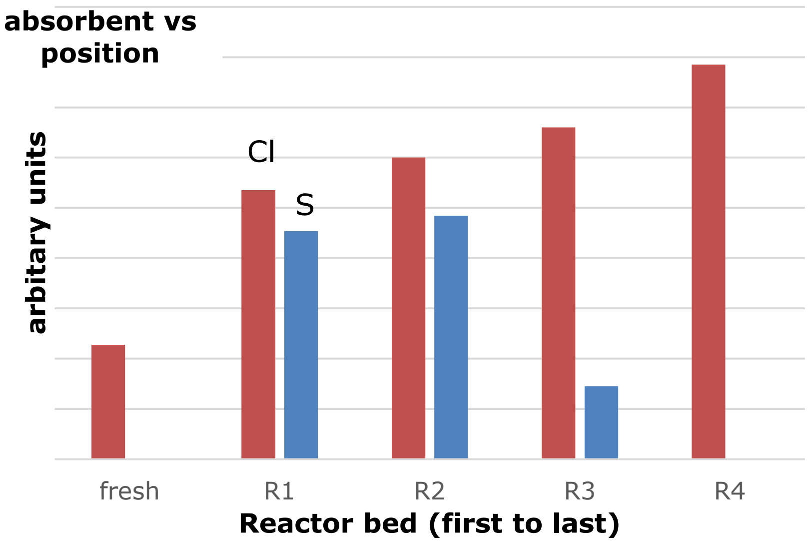


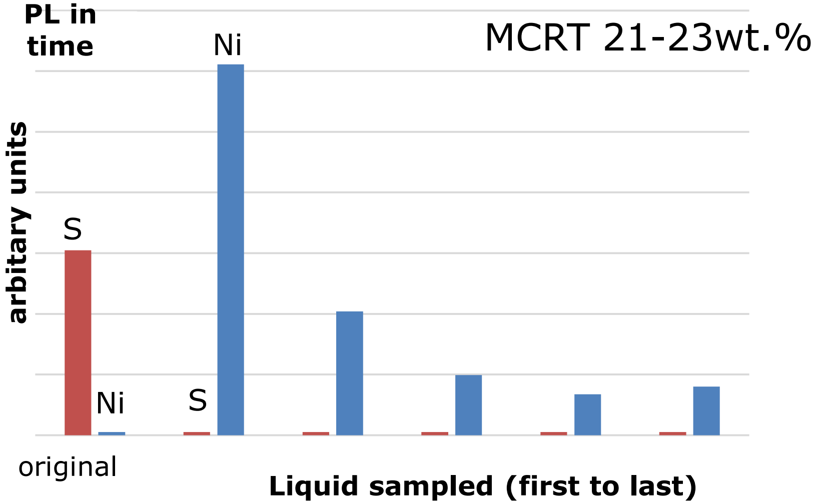
(at least partially) due to S

Prior pretreatment PL over absorbent - S/Cl through XRF (Malvern/RUG)

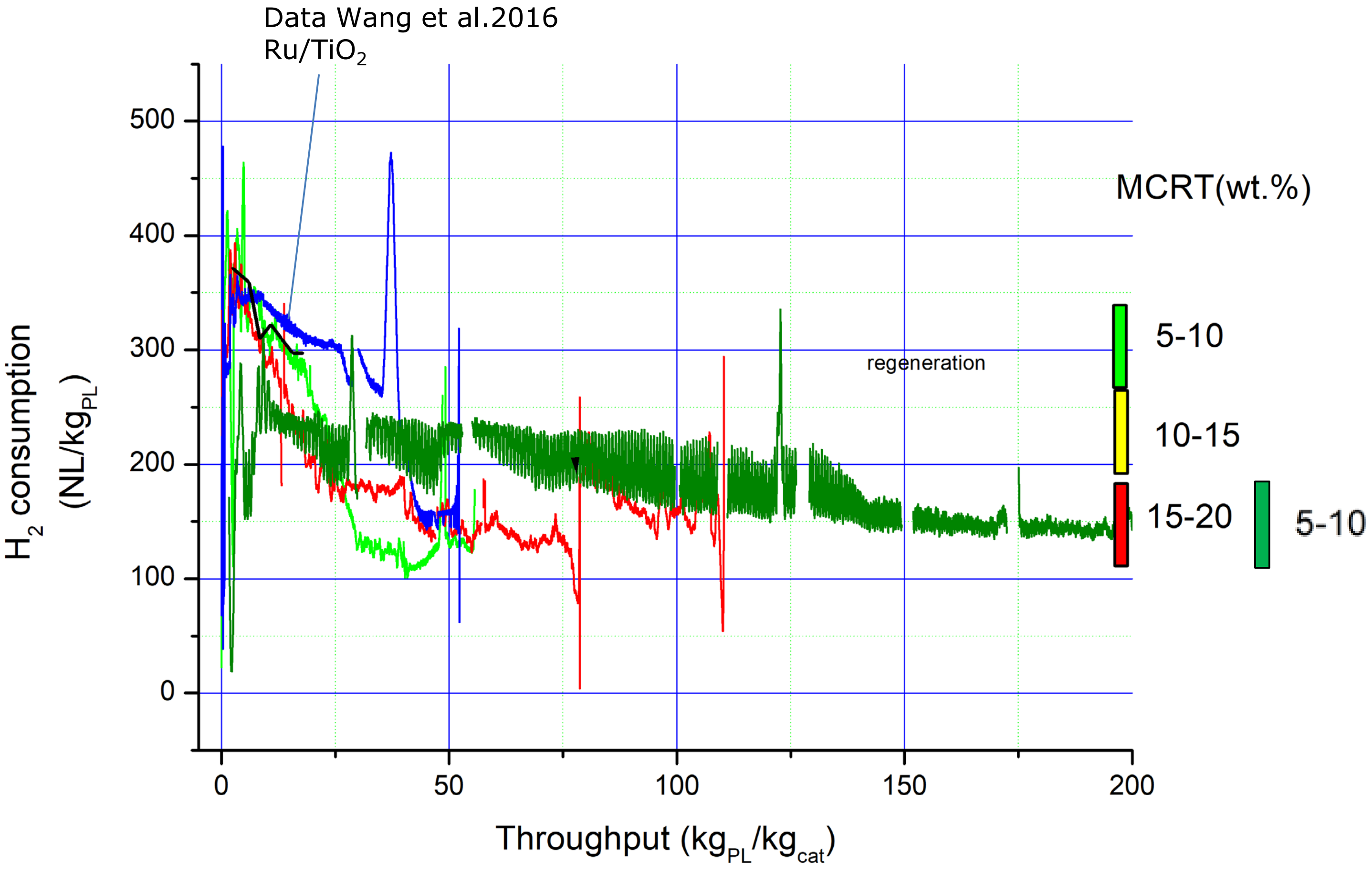
Elevated pressure; 24/7
A few hundreds hours







Deactivation vs liquid throughput
Prior treatment (B1)



- More stable (factor 2)
- Different pattern of deactivation → Different deactivation mechanism
- Blockage due to other reasons (structure)
- Initial slightly lower activity than earlier catalysts
- No regeneration done

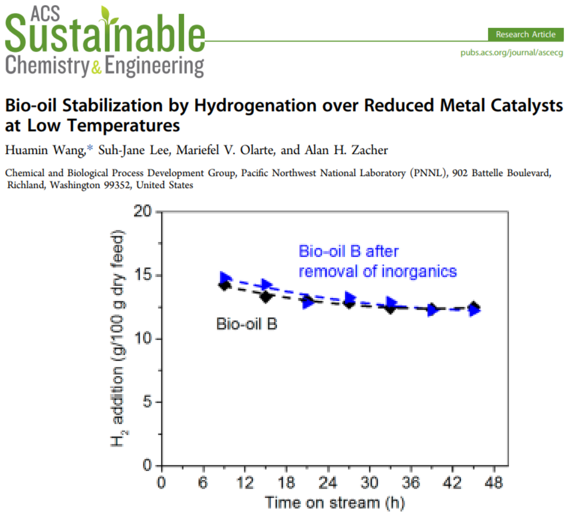


Figure 11. Effect of inorganics in bio-oil B in their hydrogenation performance. The hydrogen consumption, hydrogen-to-carbon ratio, and carbonyl contents of two hydrogenation tests using bio-oil B feed with different inorganic content. Reaction conditions: 160 °C, 1500 psig, 0.40 L bio-oil/L catalyst h, 2500 L hydrogen/L bio-oil.

Spent catalyst info

- Different pattern of deactivation → loss of support material / loss of active metal
- Initial slightly lower activity than earlier catalysts → it is suggested that the (most) reactive parts are converted at the low temperatures already
- At low temperatures encapsulation of catalyst structures by a film layer
- Sulfur may contribute to the deactivation of the catalyst, but one should be aware that it may not be the only reason for the deactivation.

Analysis based on XRF: data on S/Cl not yet fully decisive due to calibration issues

Concluding remarks

Roll-out pyrolysis

- Short term:
  - To demonstrate biomass to fuels by co-FCC pure PL at low substitution ratios
  - Increase substitution ratios by making the liquid available
- Longer term: To increase η_C by co-FCC of mildly treated liquids ('SPO')

This work:

- Sulphur is important in the deactivation mechanism of our Ni based hydrotreating catalysts (not as severe as for Ru-based catalysts)
- Sulphur can be removed by prior treatment (from 100 to 200 kg PL/kg_{cat}): we need to go to 5,000 kg PL/kg_{cat}
- Next step is to improve structural stability (in relation to acidity) – BTG / 4REFINERY

- Data co-FCC in bench scale unit, not (only) MAT or ACE

Sofar, Picula^{TM} catalysts are the best catalysts we have used for stabilization during the last 15 years

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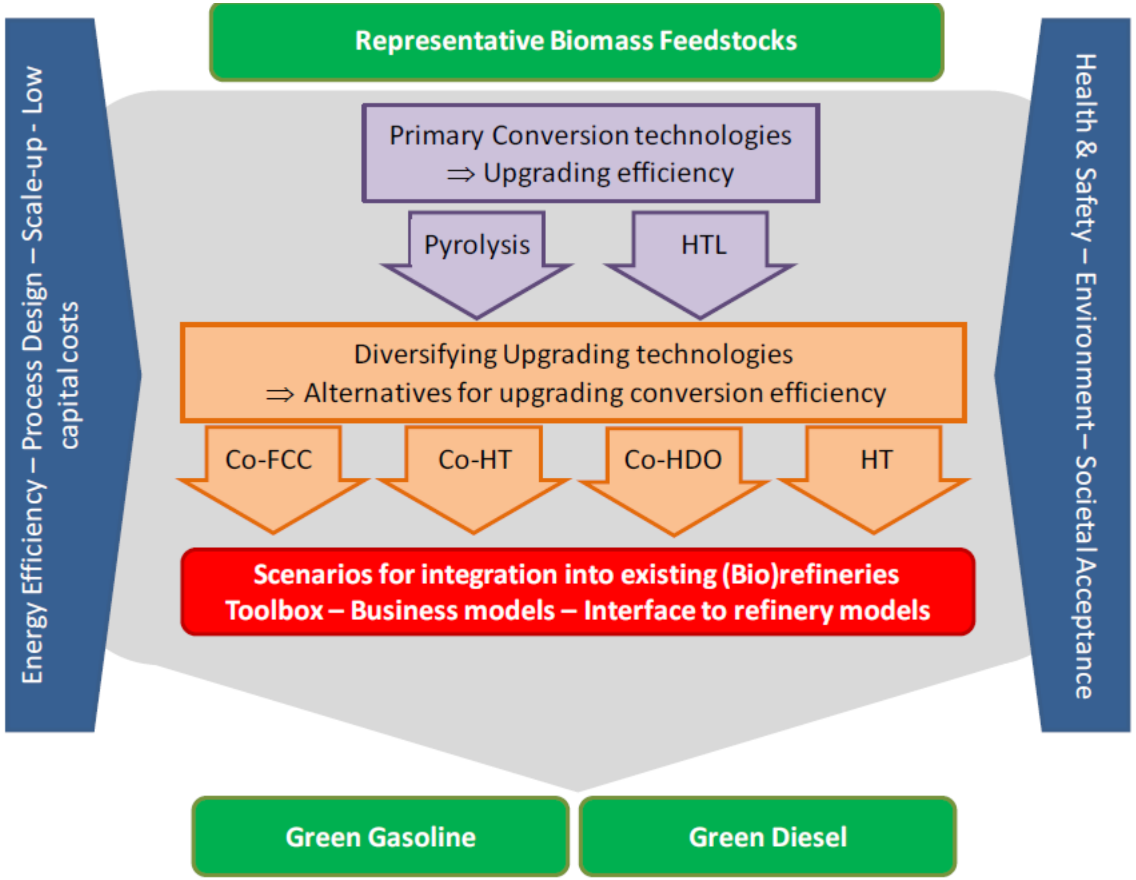
Acknowledgments

4refinery



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FASTCARD project, grant agreement **604277**

FAST CARD

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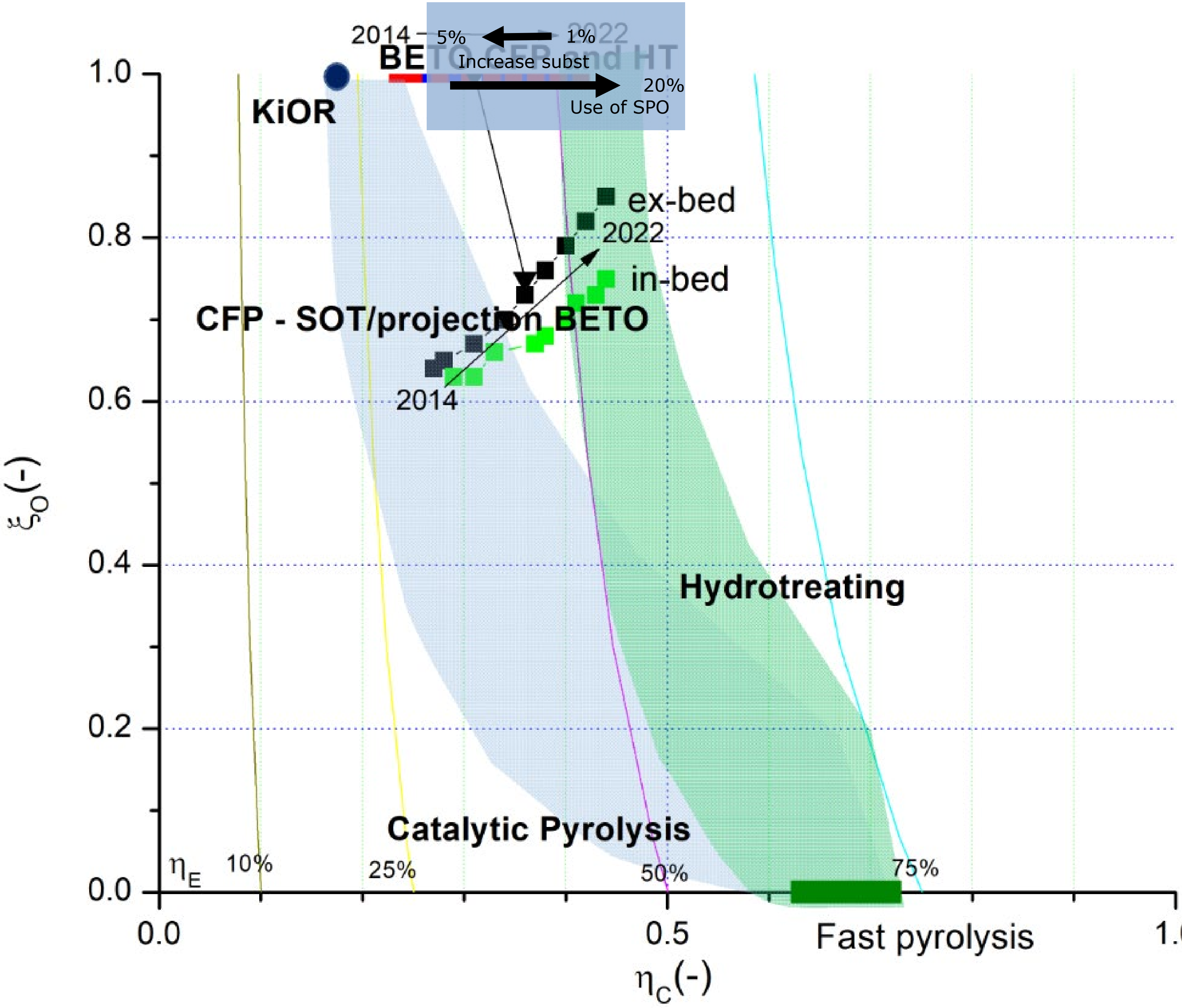
2014
5%
1%
2022
BETO CFP and HT
Increase subst
20%
Use of SPO
KiOR
ex-bed
2022
in-bed
CFP - SOT/projection BETO
2014
Hydrotreating
Catalytic Pyrolysis
η_E
10%
25%
50%
75%
Fast pyrolysis
ξ_O(-)
η_C(-)
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.5
1.0