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Advanced Biofuels from co-processing Fast Pyrolysis Bio-Oil

BioFIT webinar

24 March 2021, Tijs Lammens



Agenda

1. About BTG Bioliquids and our commercial fast pyrolysis bio-oil production facilities

2. FPBO co-processing: green content tracking

3. Summary and Conclusions



Company introduction

- As a **technology provider** and **product leader** we are committed to the commercial deployment of our fast pyrolysis technology.
- Fast Pyrolysis Bio-Oil is explicitly made from biomass residues and is known as **second generation** (2G) or **advanced biofuel**. It does not compete with the food chain.





Our company milestones



1987

BTG starts as a spin-off from the University of Twente



2008

BTG Bioliquids is established by BTG



2015

Start up of Empyro in the Netherlands



2016

Cooperation agreement with TechnipFMC

Starting BTG Bioliquids webshop



2019

Empyro sold to Twence, the Netherlands

Green Fuel Nordic, Finland

Pyrocell, Sweden

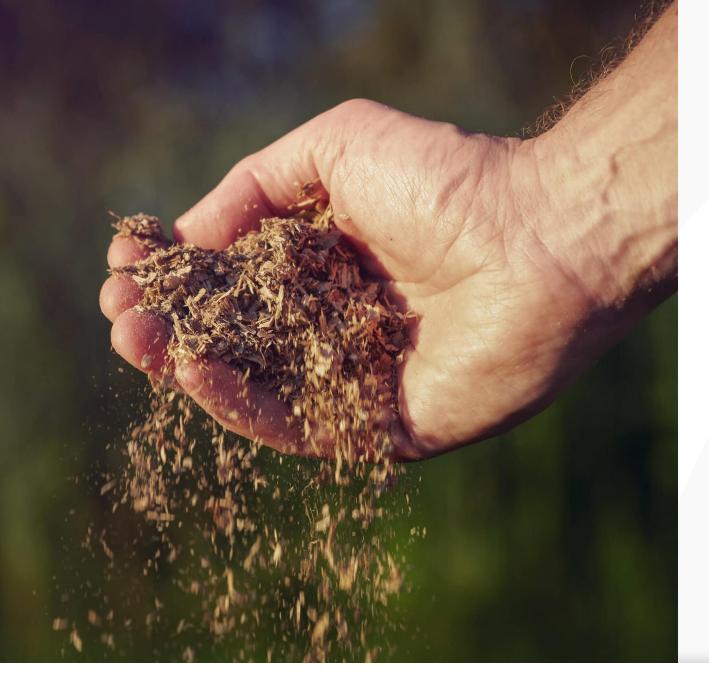


2020

Start up of Green Fuel Nordic plant in Finland

Pyrocell plant under construction

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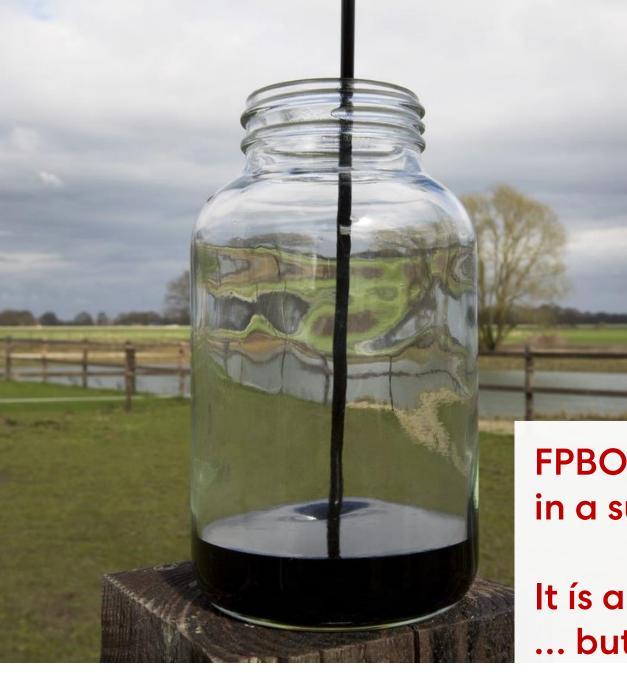
Fast pyrolysis technology

- Thermochemical decomposition of biomass residues through rapid heating (450-600 °C) in absence of oxygen.
- Different types of biomass residues can be converted into one homogeneous energy carrier: **Fast Pyrolysis Bio Oil** (FPBO).
- By products are **heat** (steam) and **power** (electricity)





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Properties of Fast Pyrolysis Bio-Oil

- Lignocellulosic: made from sawdust, forestry residues, straw, etc.
- Water content: 20 25 wt-%
- Oxygen content: 45 50 wt-%
- **Density:** 1.1 1.2 kg/L

FPBO is "an emulsion of lignin fragments in a sugar syrup".

Ash and solids contents: < 0.1 wt-%</p>

It ís a dark liquid... ... but not a typical refinery feedstock!

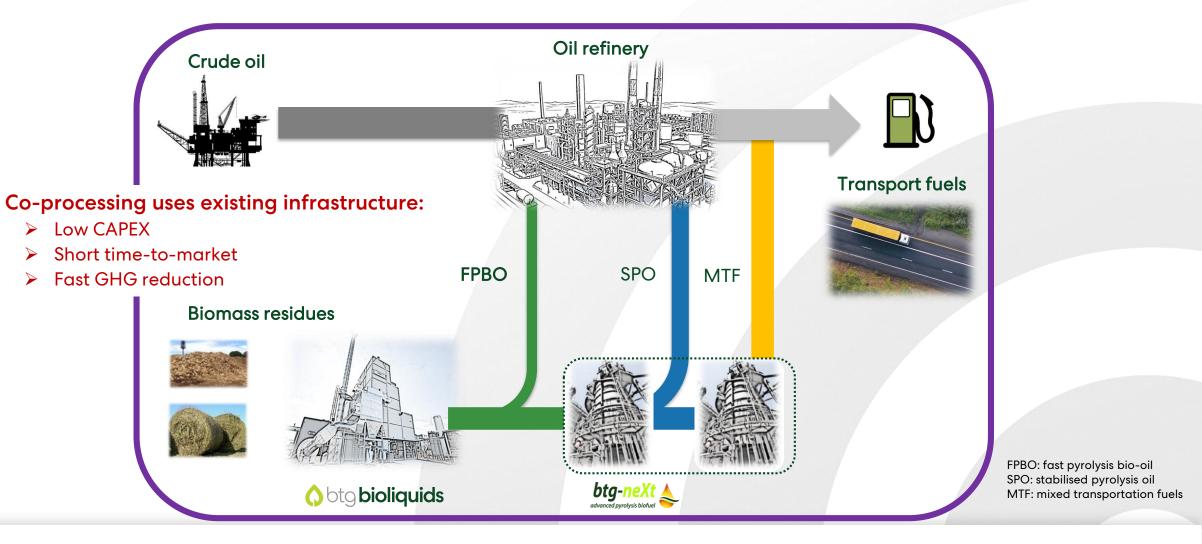




Co-processing FPBO

and green content tracking

Routes from FPBO to transport fuels

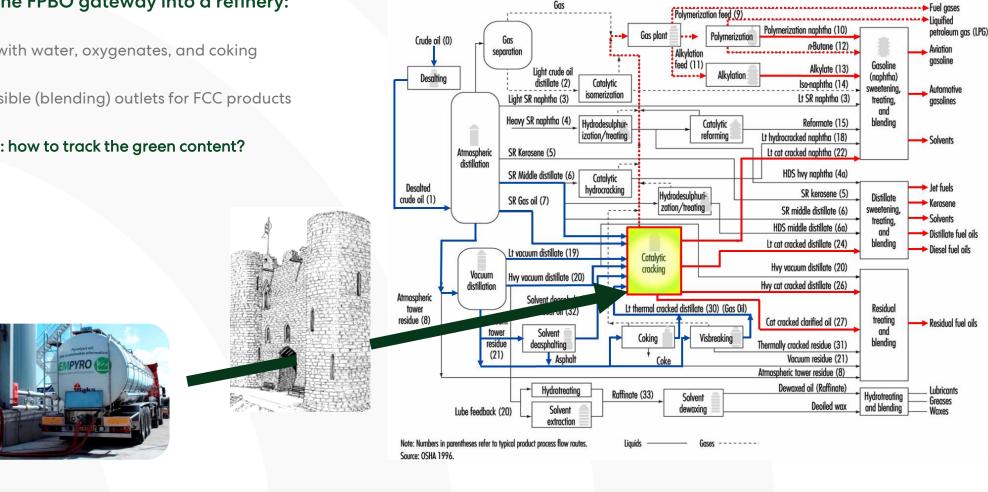




Fluid Catalytic Cracker (FCC)

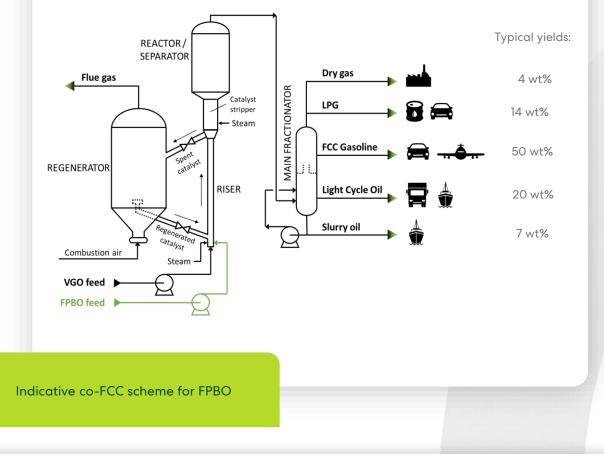
FCC unit is the FPBO gateway into a refinery:

- Can deal with water, oxygenates, and coking 0
- 0 Many possible (blending) outlets for FCC products
- Challenge: how to track the green content? 0





Co-FCC of FPBO how does it work?

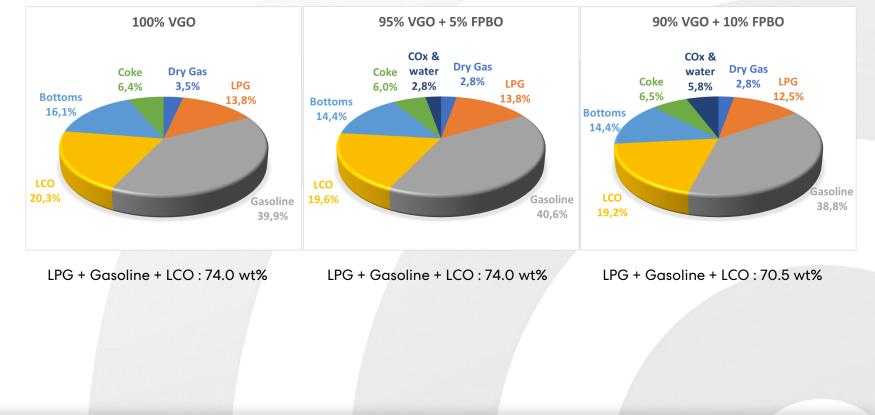


- FPBO is injected via separate nozzles into the FCC riser
- Biomolecules cracked together with the regular FCC feed
- Acidity disappears upon contact with the hot catalyst
- Green content is distributed across the different products
- Operability proven for 5 wt-% FPBO at commercial scale
- Operability proven for 10 wt-% FPBO at pilot scale

FPBO impact on FCC product yields

FPBO co-processing has little impact on overall FCC product yields (Pinho *et al.*):

- 5 wt-%: slight increase of gasoline production and decrease of heavies.
- At 10 wt-%: overall decrease in product yields, due to oxygen/water in FPBO.
- Oxygenates in FPBO result in CO, CO₂ and water production.
- > Where does the green content go?



Tracing green content

- Tracing biogenic content through a supply chain is easy and well-established for products with a high biogenic content.
- Co-processing vegetable oils in hydrotreaters to produce HVO is also well-established
- Certification systems exist for such pathways, such as ISCC. These rely on:
 - 1. Either radiocarbon determination (^{+14}C ")
 - 2. Or bookkeeping methods (e.g. mass / energy balance)
- However, the combination of challenges for FCC co-processing of FPBO is unique:
 - > Scale difference between a fast pyrolysis plant and FCCU is typically 1 : 100
 - > FPBO co-processing volume is limited to ~ 5 wt-%
 - > Green content is distributed across many refinery products
- This makes radiocarbon analysis unfeasible (as will be shown...)



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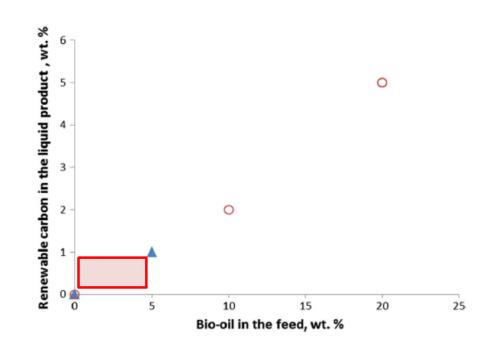


Fig. 7. Renewable carbon content in the liquid product at different bio-oil feed percentages: present study (▲), Literature [16] (□).

¹⁴C data published by Pinho *et al.* (2017)

A deep-dive into ¹⁴C analysis

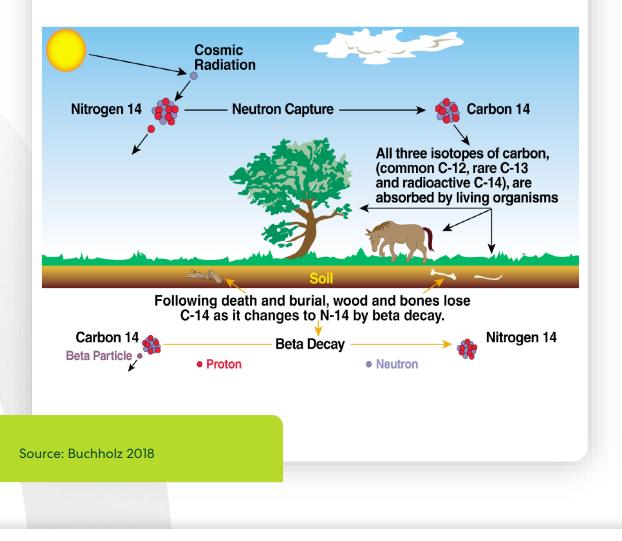
- Radiocarbon ("¹⁴C") analysis appears to be the ideal method to determine the green content of fuels from co-processing.
- Pinho *et al.* published ¹⁴C data of the liquid product from coprocessing FPBO.
- 75 wt-% of the total product volume (the liquids) contained about 40 wt-% of the bio-carbon.
- 60 wt-% of the bio-carbon was unaccounted for. It could not be traced by ¹⁴C.
- Thus, the bio-carbon percentage in the gases and coke would be over 4 times higher than in the liquids, which is very unlikely.
 - How reliable is ¹⁴C analysis? Especially below 5 wt-%?



About ¹⁴C analysis

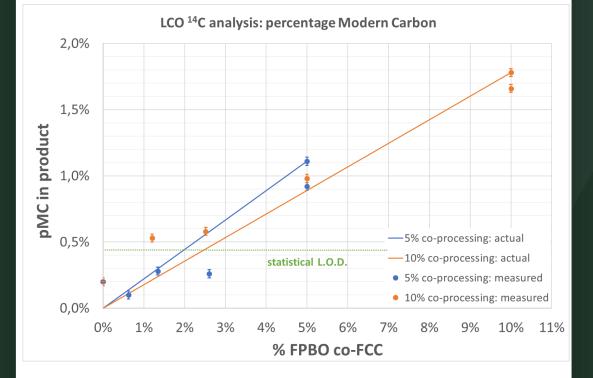
- Radiocarbon $({}^{14}C)$ is formed in the atmosphere by radiation.
- Living plants absorb ${}^{14}CO_2$ and turn it into biomass.
- ¹⁴C in dead matter gradually decays. Hence fossil fuels do not contain ¹⁴C and biofuels do.
- ¹⁴C can be detected by a.o. Accelerator Mass Spectrometry.
- The ratio ¹²C : ¹⁴C in the sample is compared to a reference standard. This gives the Percentage Modern Carbon (pMC). The statistical limit of detection is 0.44% pMC.
- Bio-carbon percentage is pMC multiplied by Atmospheric Adjustment Factor (AAF), to compensate for ¹⁴C fluctuations in the atmosphere over time (e.g. by "A-bomb").

The way in which radiocarbon forms and decays



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Percentage Modern Carbon in FCC diesel (LCO) samples



Error margins are those that were provided by the analytical lab.

Our own ¹⁴C data

- Gasoline and diesel (LCO) samples from the co-processing of 5 and 10 wt-% FPBO were diluted with defined amounts of fossil fuel, to mimic co-processing lower percentages FPBO.
- If ¹⁴C analysis is accurate, linear dilution of samples containing biocarbon with fossil fuel should result in linear ¹⁴C concentration trends.
- Results are shown here for the diesel samples.
- Data scatter was found to be significant, especially below the "statistical limit of detection (LOD)".
- For individual samples, the observed deviations were much larger than the indicated error margins.

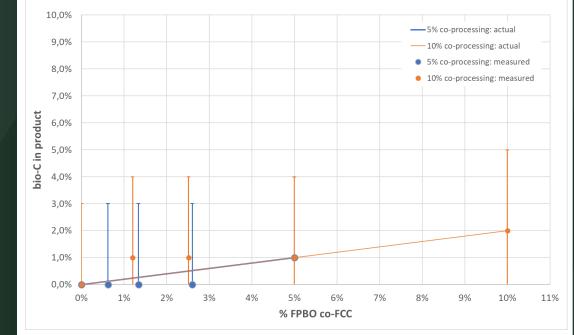
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¹⁴C to bio-carbon

- Biogenic carbon percentages derived from the PMC values are indicated.
- ASTM prescribes an absolute error of 3 wt-% biogenic carbon when using ¹⁴C analysis, because of the know inaccuracies with this method, e.g. the "bomb effect" that effects the Atmospheric Adjustment Factor.
- When incorporating those error margins, the data become meaningless.
- Conclusion: ¹⁴C analysis is unsuitable for these low coprocessing percentages (<10 wt-% FPBO).
- Paper with more detailed info: www.btg-bioliquids.com

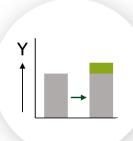
Resulting biogenic carbon in FCC diesel (LCO) samples

LCO ¹⁴C analysis: percentage Biogenic Carbon (ASTM D6866-18-B)



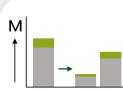
Error margins are those prescribed by the ASTM method.

Bookkeeping methods



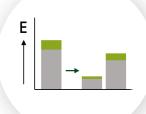
Observed yields

- Difference in product yields between a fossil baseline and that baseline plus co-processing
- 95 t/h fossil feed *vs.* 95 t/h fossil + 5 t/h bio
- Yield increase is then the biofuel yield
- Also referred to as "incremental yields"



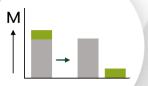
Mass balance

- Mass of bio-feed is a fraction of total feed
- Bio-fraction is equally distributed across all products
- Can also be done as "carbon-mass balance"
- CO, CO₂ and water need to be excluded



Energy balance

- Energy content of bio-feed is a fraction of energy content of fossil- plus bio-feed
- Bio-fraction is equally distributed across all products

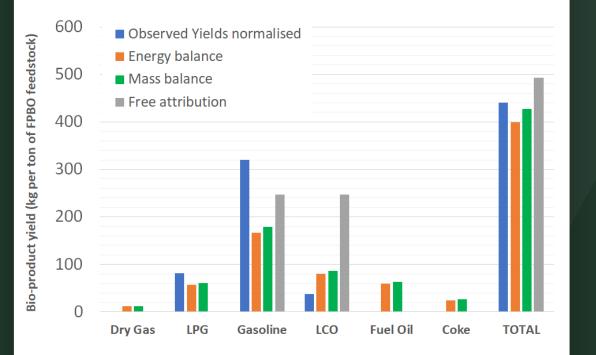


Free attribution

- Operator can choose to which product the bio-fraction is allocated
- Used for bio-based chemicals in ISCC PLUS, e.g. for co-processing in steamcracker



Co-processing yields from bookkeeping methods

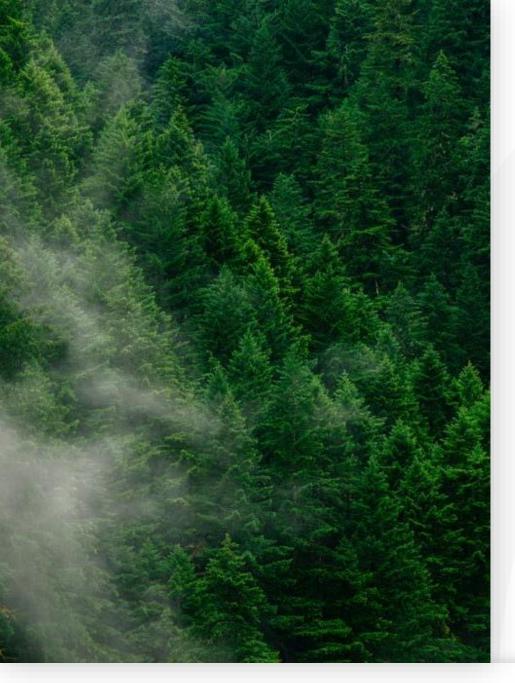


Note: FCC product yields from 5 wt-% FPBO co-processing and fossil baseline scenario were taken from data published by Pinho et al.

Bookkeeping case study

- Observed yields method gave both positive and negative yields (due to "synergistic effects"). The existing method was adapted to avoid overestimation of biofuel yields.
- Carbon mass and total mass balance methods gave different results, probably due to inaccuracies in oxygen balance.
- Energy balance method gave lower yields than mass balance, perhaps due to inaccuracies in energy contents.
- Free attribution is straightforward and easy to implement, but its "fairness" is being challenged.
- Observed yields and energy balance methods strike a good balance between implementability and accuracy.

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Summary and Conclusions

• FCC co-processing of FPBO has a high potential as pathway to advanced biofuels

- Low CAPEX
- Short time-to-market
- Fast GHG emissions reduction

• Biogenic content tracing is particularly challenging for this pathway

- Scale difference between a pyrolysis plant and FCCU is typically 1:100
- FPBO co-processing percentages are limited to ~ 5 wt-%
- Green carbon is distributed across many refinery products

• Radiocarbon analysis is unfeasible for commercial purposes

> Experimental results showed large data scatter and "bomb effect"

• Bookkeeping methods are not perfect, but they are appropriate for this pathway

- Observed yields (modified) and energy balance are the most suitable methods
- > Verification of renewable input could be done with ¹⁴C analysis of the FPBO





Thank you

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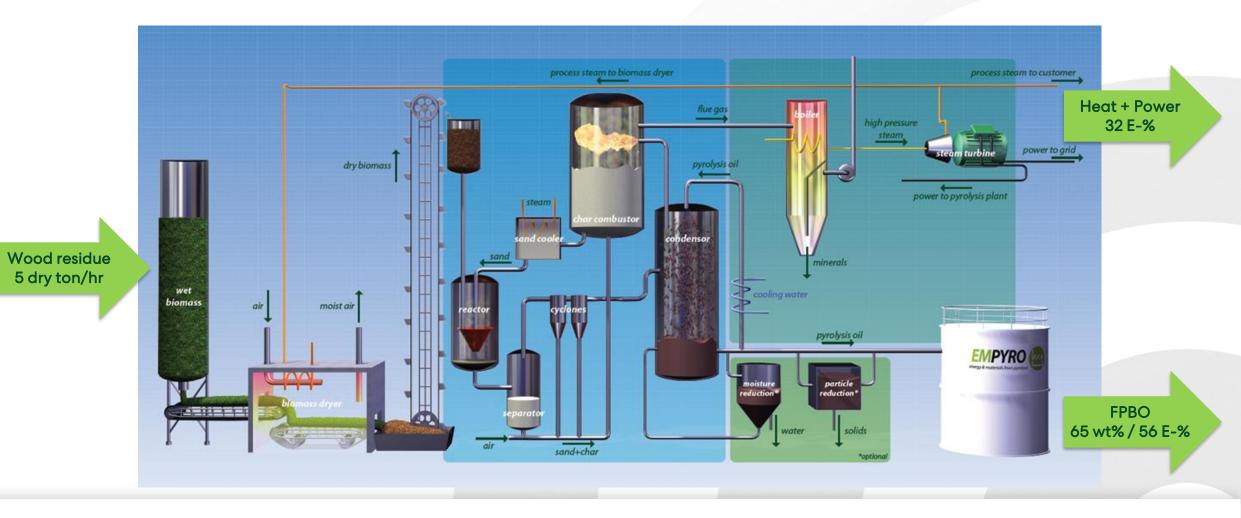




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Back-up slides

Our process from biomass to FPBO





The FPBO supply chain

Biomass conversion

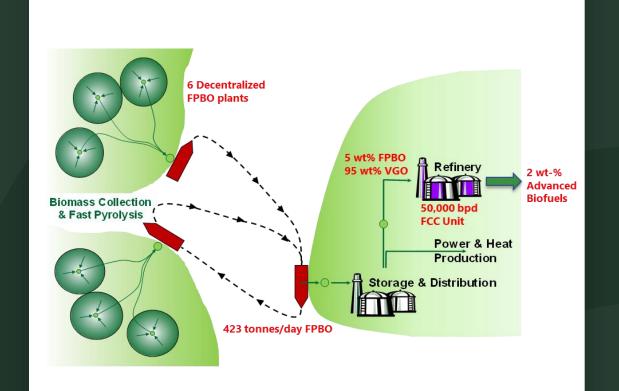
- Local processing of biomass residue feedstock
- Returning minerals to the soil

FPBO transportation

- Biomass liquified
- 10x densified versus raw biomass feedstock

FPBO processing and disctribution

- Centralized location
- Make use of existing infrastructure





Empyro The Netherlands

In 24/7 operation since 2015

First commercial FPBO plant in the world that runs 24/7. Empyro was sold to Twence early 2019.

- Biomass feedstock wood residue
- Biomass input 36.000 ton/year
- FPBO output 24.000 ton/year
- Steam output 80.000 ton/year
- Electricity output 2.200 MWh/year



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FPBO application at FrieslandCampina

- FPBO replaces 10 million m³ natural gas
- Sustainable heat is used for producing dairy products
- Switch from gas to FPBO provides 90% GHG reduction
- Boiler runs without problems; processed all FPBO from Empyro
- Borculo site reduced overall CO₂ footprint by 15%

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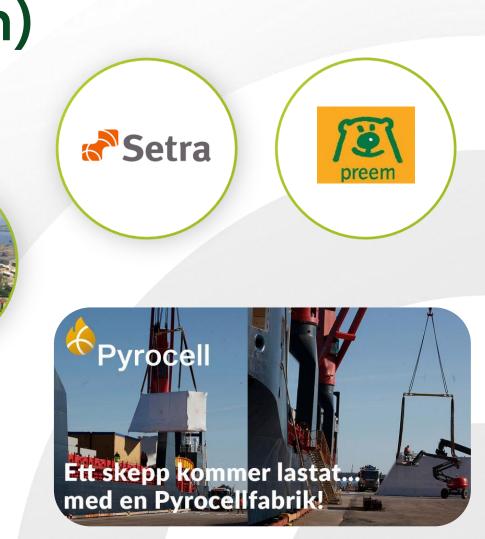
Green Fuel Nordic (Finland) a true trailblazer

- Location: Lieksa, Finland
- Biomass residue is clean sawdust
- Start on-site reassembly of modules August 2020
- First FPBO production on December 2, 2020
- FPBO as part of carbon neutral energy strategy of customer Savon Voima Joensuu heating plant
- Further investments and expansion are planned

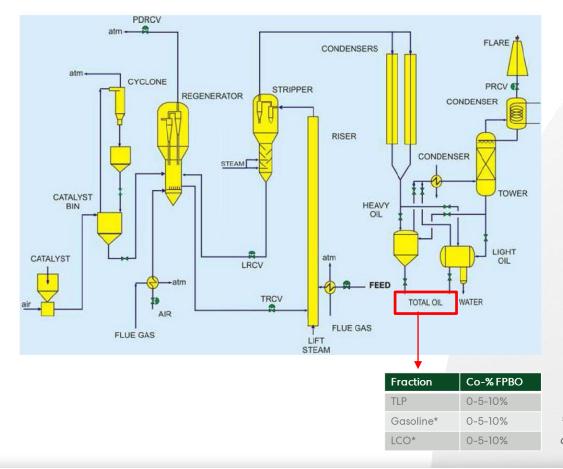


Pyrocell project (Sweden) from sawdust to tank

- Pyrocell is Joint Venture of Setra and Preem
- Production of FPBO from sawdust start-up in 2021
- Fast pyrolysis technology annual FPBO production 25,000 tonnes GHG reduction of 80-90%
- FPBO will be co-processed in Preem refinery
- Equivalent of 15,000 family cars powered per year
- Advanced biofuels under EU RED II directive



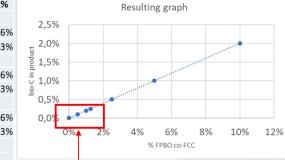
¹⁴C experiment: approach



- We have samples of 5 & 10 wt% co-FCC, which contain 1 & 2 wt-% bio-C
- By preparing a dilution set (diluting with the same product from 0 % co-FCC, we can go down in the range between 0.1 and 5 wt% bio-C
- Also analysed: 4 samples of FPBO (100% bio-C) with fossil butanol to test conversion pMC > bio-C

samples	wt% co-FCC	dil. fact	eq wt%	dil. fact	eq wt%	dil. fact	eq wt%
gasoline	0						
gasoline	5%	2	2.5%	4	1.3%	8	0.6%
gasoline	10%	2	5.0%	4	2.5%	8	1.3%
diesel	0						
diesel	5%	2	2.5%	4	1.3%	8	0.6%
diesel	10%	2	5.0%	4	2.5%	8	1.3%
TLP	0						
TLP	5%	2	2.5%	4	1.3%	8	0.6%
TLP	10%	2	5.0%	4	2.5%	8	1.3%

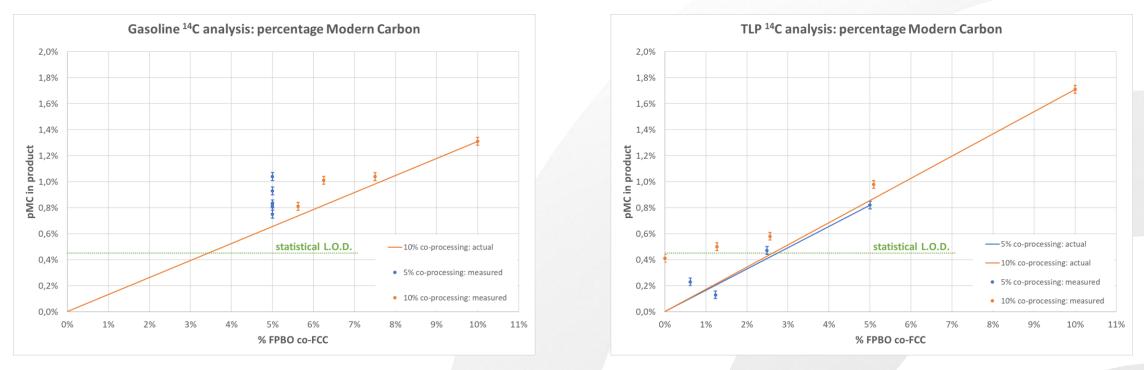
number of samples to be analysed: 27



"data below LOD"

*) Gasoline and LCO were prepared by Petrobras by distillation of Total Liquid Product (TLP); cutpoints: 220 °C and 344 °C

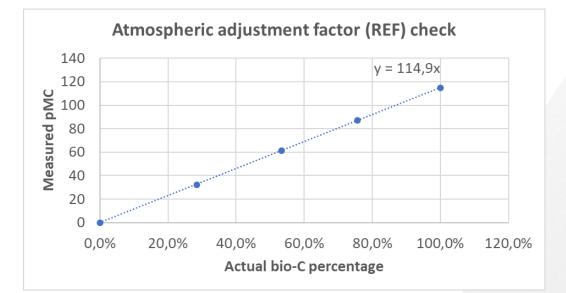
¹⁴C results: Gasoline & TLP



- Gasoline sample was diluted with product from 5 wt-% co-FCC instead of 0 wt-% co-FCC, due to inaccurate labelling of the gasoline product container.
- Uncertainties are again significant, also data scatter above limit of detection. Gasoline samples of 5 wt-% show a relative error margin of 33 %. (values between 0.75 and 1.05)
- TLP samples paint the same picture as gasoline and LCO.

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¹⁴C results: Atmospheric Adjustment Factor



Observations:

- The atmospheric adjustment factor prescribed by ASTM for converting pMC into bio-C-% was checked by measuring the pMC of FPBO samples with known bio-C content.
- For all samples the measured pMC was 15% higher than the actual bio-C content (see graph).
- This observation was discussed with the ¹⁴C lab and together the conclusion was drawn that this is probably due to the "bomb curve": the sawdust-FPBO contains more radiocarbon than the current average radiocarbon concentration in the atmosphere.



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we replace fossil fuels