Pyrolysis in CoCo flowsheeting

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Date 27-10-2021

biomass technology group

Your partner in bioenergy

Contents

BTG Biomass Technology Group BV

Research & Technology Development

Enschede, The Netherlands

RTD - Thermochemical Biomass conversion

- Fast Pyrolysis process
- Pyrolysis oil conditioning & analysis
- Pyrolysis oil applications
  - Energy
  - Biofuels
  - Chemicals & Materials
- Staged Catalytic Gasification
- Torrefaction & Carbonisation
- High Pressure Processing
  - Reforming in Supercritical water
  - Liquid Phase Reforming

Supply of products (kg's – tonnes)

- Pyrolysis oil
- Stabilized & upgraded Oil
- Oil fractions (e.g. Sugar syrup, Lignin)
- Torrefied biomass / biochar

Contract Research

- Feedstock testing
- Processes under elevated pressure;
- Feedstock & Product Analysis

Design & supply of (test) units

- Conceptual & basic designs
- RTD test units for biomass conversion

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Fast Pyrolysis

- Thermal cracking of organic material in absence of oxygen
- Main product: **liquid** bio-oil (70% yield)
- Other products: gas and char
- Typical Process conditions
  - T = 400 - 600 °C
  - P = atmospheric
  - τ_{gas} ~ seconds

Pyrolysis liquids as an intermediate between biomass and end-users (i.e. refineries)

Fast Pyrolysis – development timeline

Roll-out

2018 Co-production of FPBO, process steam and electricity
3 years operational experience: production and use

2015 Start-up Empyro plant & Process steam boiler at FrieslandCampina

development

2014 Start construction 120 t/d Empyro plant in Hengelo (NL)

2013 Long-term FPBO supply contract signed

2009 Establishment of Empyro BV to demonstrate FP technology

2007 Establishment of BTG Bioliquids BV to commercialize BTG Fast Pyrolysis technology

2005 Delivery of 50 t/d FP-plant to Malaysia

2004 Large-scale co-firing test at Harculo Power Plant

research

1998 Start-up of 200 kg/hr FP pilot plant in BTG Laboratory

1994 Delivery semi-continous test unit (50 kg/hr) to Shenyang (China)

1993 Knowledge transferred from UT to BTG

1989 Rotating cone reactor ‘invented’ at University of Twente (UT)

1987

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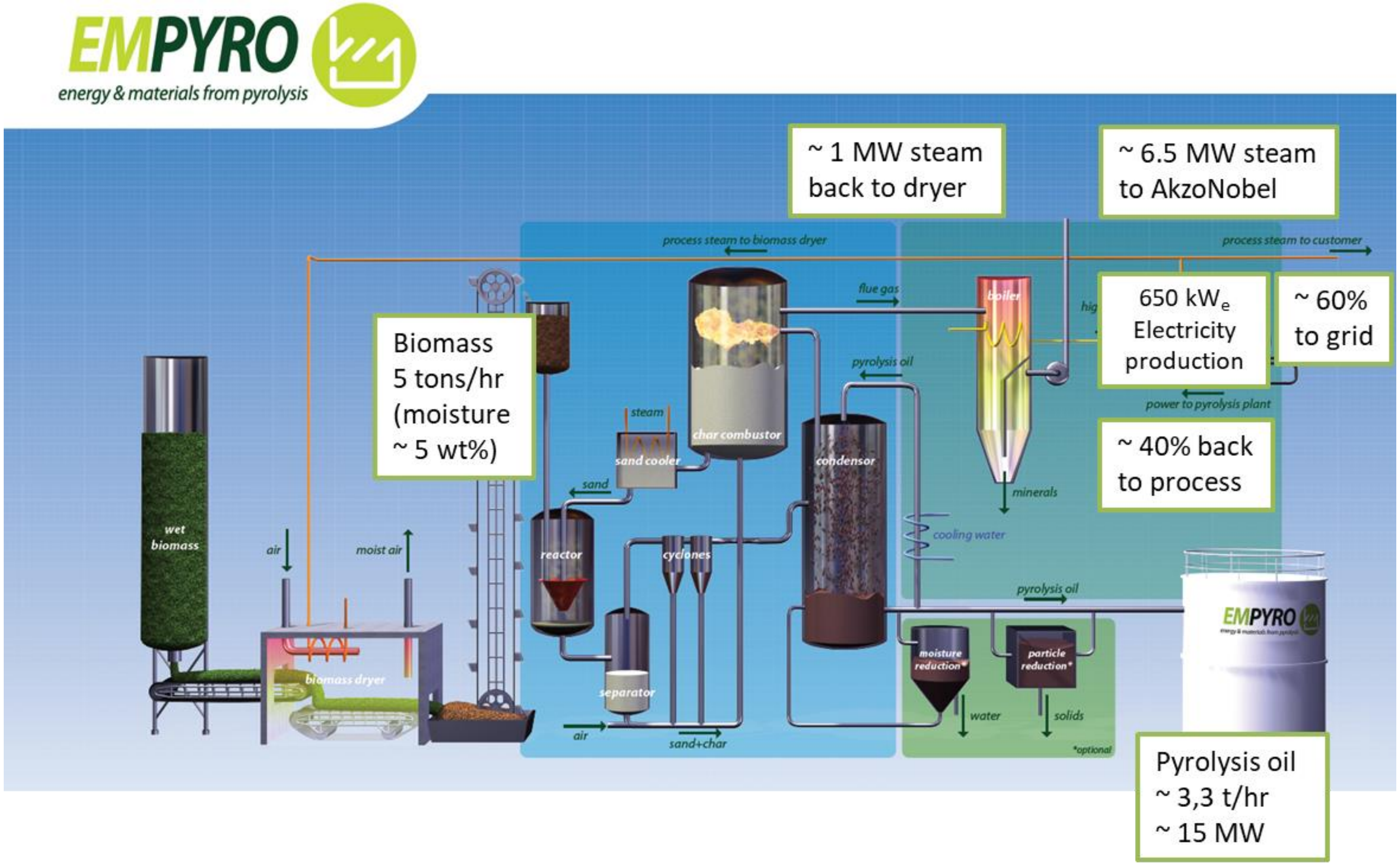
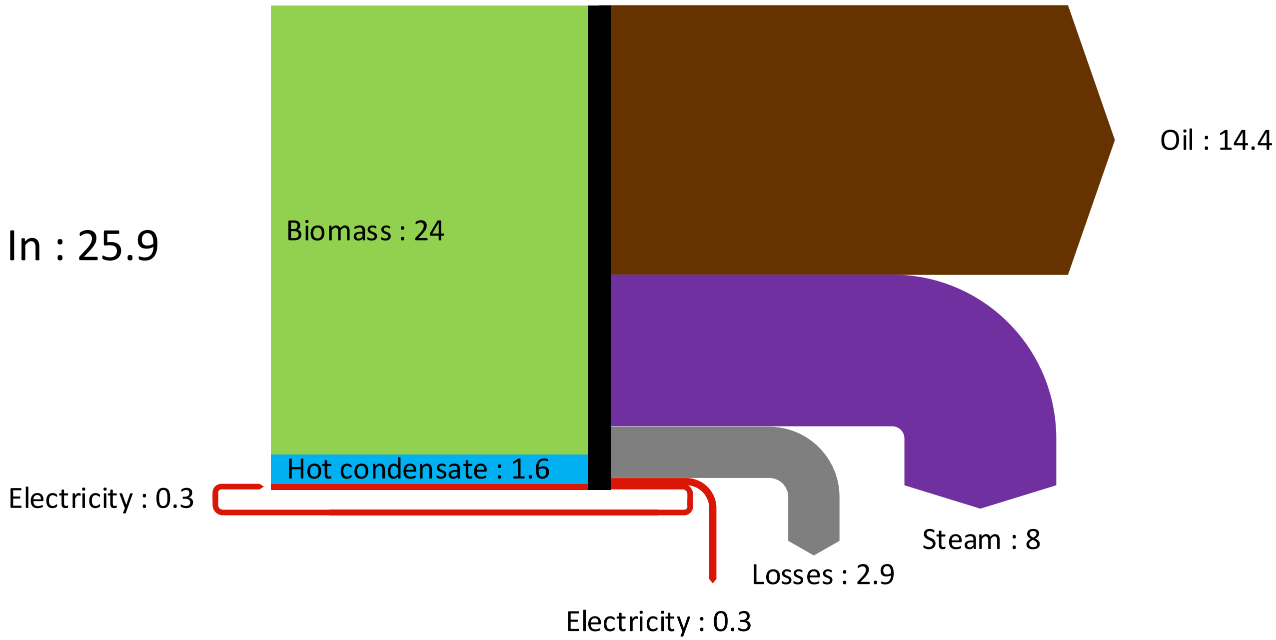

EMPYRO
energy & materials from pyrolysis
~ 1 MW steam back to dryer
~ 6.5 MW steam to AkzoNobel
process steam to biomass dryer
process steam to customer
flue gas
boiler
650 kW$_e$ Electricity production
~ 60% to grid
Biomass 5 tons/hr (moisture ~ 5 wt%)
pyrolysis oil
power to pyrolysis plant
steam
char combustor
sand cooler
condensor
~ 40% back to process
sand
minerals
cooling water
wet biomass
air
moist air
reactor
cyclones
pyrolysis oil
moisture reduction*
particle reduction*
biomass dryer
separator
water
solids
air
sand+char
*optional
Pyrolysis oil ~ 3,3 t/hr ~ 15 MW

Empyro efficiency (MW_{th})



Overall Efficiency > 85 %

Relative low investment costs

Small scale (5 t/h biomass)


EMPYRO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bioliquids


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bioliquids
GREEN FUEL
Nordic Oy


ZETON
PILOT PLANT TECHNOLOGY
btg bioliquids

Pyrocell commences production

MON, SEP 20, 2021 13:35 CET

Production is now underway at Pyrocell's groundbreaking plant in Gävle. The new and pioneering plant converts sawdust into bio-oil.

Pyrocell, which is jointly owned by Setra and Preem, was formed in 2018 based on the business concept of producing bio-oil from sawdust. Production at the groundbreaking plant is now underway – and is the country's first pyrolysis oil plant for biofuel.

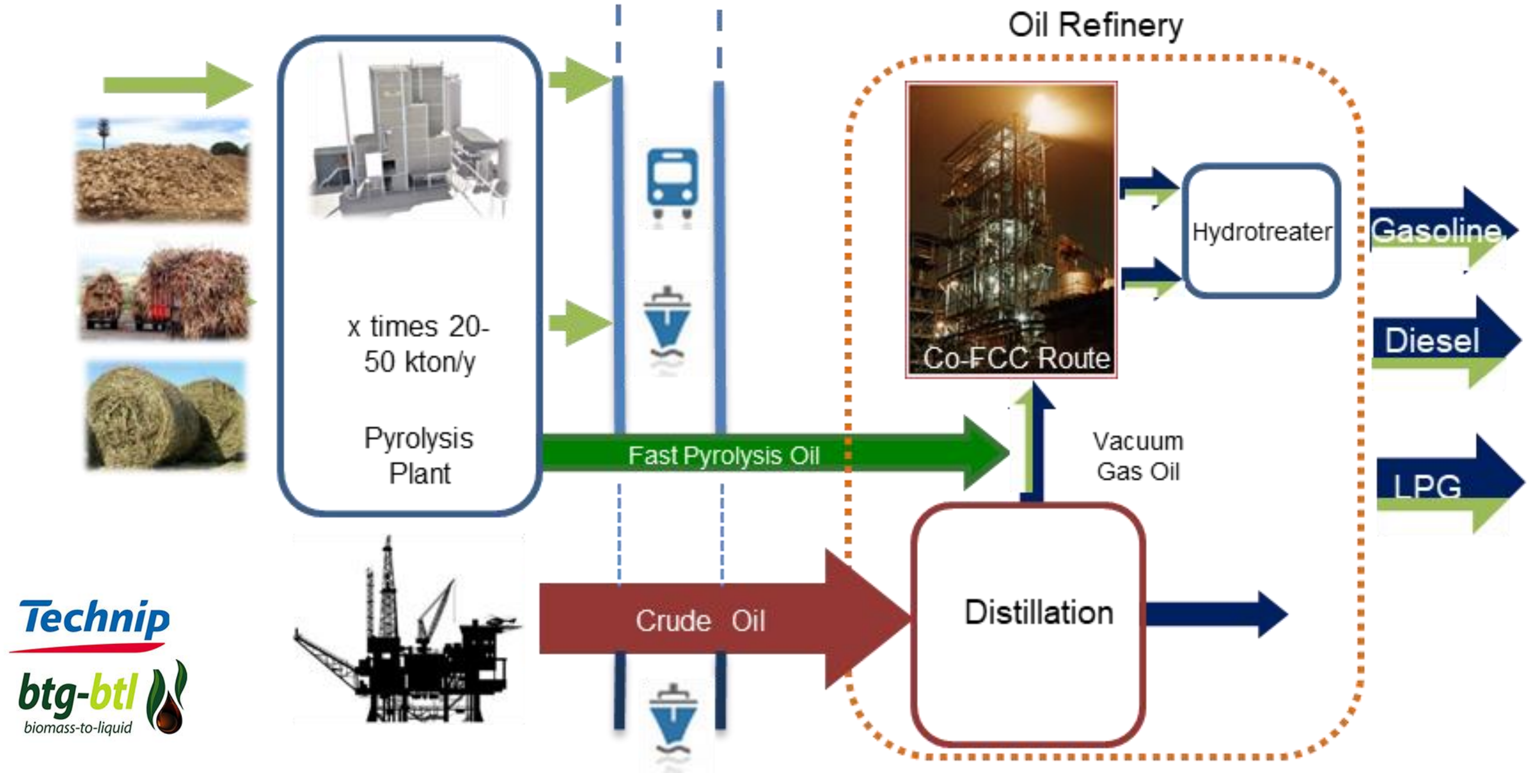
"The commence of production at Pyrocell signals another concrete step in our transition and in our work to achieve large-scale renewable production," says Magnus Heimburg, CEO of Preem.

Pyrocell's plant is located next to Setra Kastet sawmill in Gävle. There, sawdust, which is a residual product in Setra's industrial process, is converted into non-fossil pyrolysis oil. The pyrolysis oil is then refined into renewable diesel and petrol at Preem's refinery in Lysekil.

"Pyrocell is a unique industrial investment that enables a sustainable value chain from forest to tank," says Pontus Friberg, acting Chairperson of Pyrocell. "We are replacing fossil fuels and contributing to an increased proportion of renewables in fuels that result in lower carbon dioxide emissions."

The plant will produce around 25,000 tons of non-fossil pyrolysis oil per year, corresponding to the annual fuel consumption of 15,000 passenger cars.

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



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Why flowsheeting

Flowsheeting:

Provide facts / arguments
Transparency / retrace data
Collect data
Data management
Data transfer
Understanding
Optimisation

CoCo:

Open resource (EU projects)
Impact!

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965
NREL NATIONAL RENEWABLE ENERGY LABORATORY
INL Idaho National Laboratory

Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels

Fast Pyrolysis and Hydrotreating Bio-oil Pathway

November 2013

Susanne Jones, Pimphan Meyer, Lesley Snowden-Swan, Asanga Padmaperuma
Pacific Northwest National Laboratory

Eric Tan, Abhijit Dutta
National Renewable Energy Laboratory

Jacob Jacobson, Kara Cafferty
Idaho National Laboratory

PNNL-23053
NREL/TP-5100-61178

Prepared for the U.S. Department of Energy Bioenergy Technologies Office

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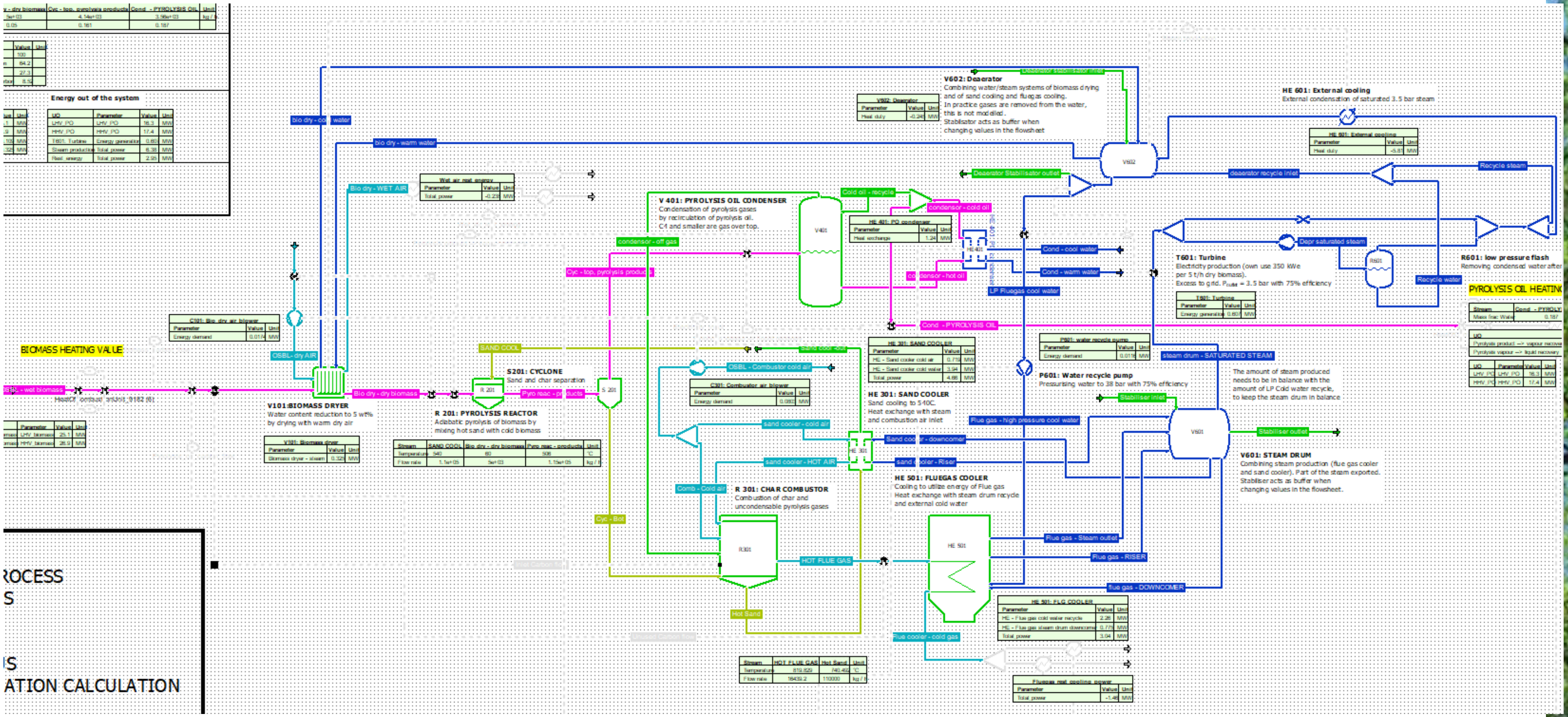
Model overview



https://www.cocosimulator.org/down.php?dl=BTG_pyrolysis.fsd

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Overview model

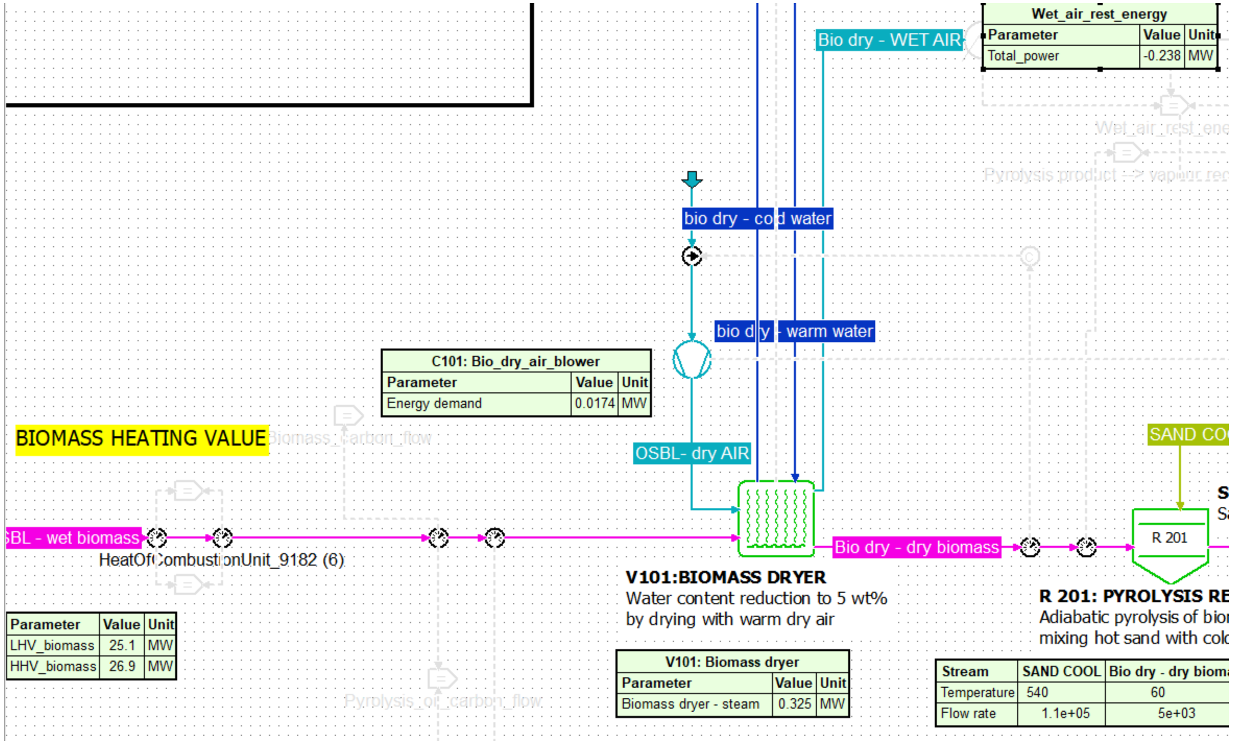
- Main assumptions
  - Model compounds
  - Conversion reactors
  - No pressure drop
  - Slightly over pressure

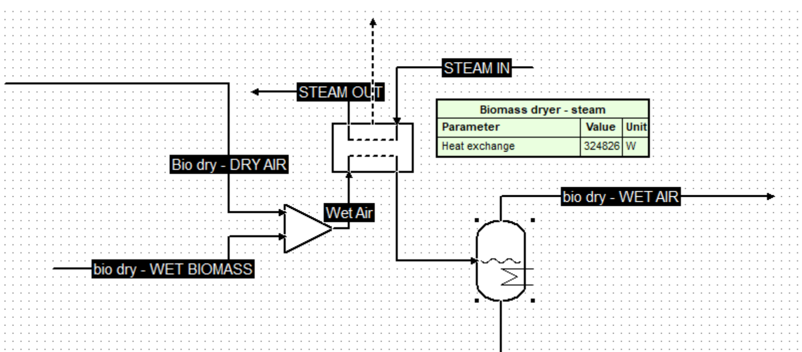
Compound group	**Model compound**
Water soluble	
Acids	Crotonic acid
Alcohols	1,4-benzenediol
Ketones	Hydroxyacetone
Aldehydes	3-metoxy-4-hydroxybenzaldehyde
Guaiacols	Isoeugenol
Low MW sugar	Levoglucosan
High MW sugar	Cellbiose
Water Insouluble	
Low MW Lignin A	Dimethoxy stillbene
Low MW Lignin B	Dibenzofurane
Extractives	Dehydroabietic acid
High MW Lignin A	$C_{20}H_{26}O$
High MW Lignin B	$C_{21}H_{26}O$
Nitrogen compounds	2,4,6-trimethylpyridine
Sulfur compounds	Dibenzothiophene

Figure 1: Pyrolysis model compounds (+ 'wood')

Detailed sections – biomass dryer

- 5 wt% water in biomass fed, controlled by air flow.

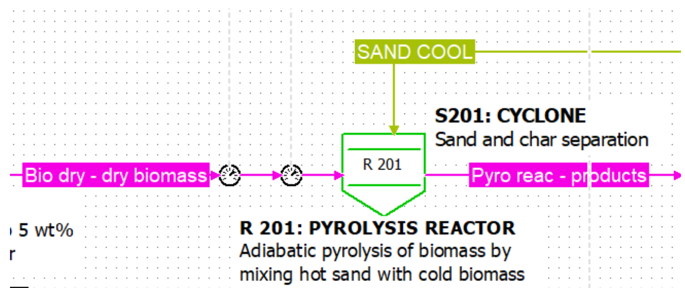




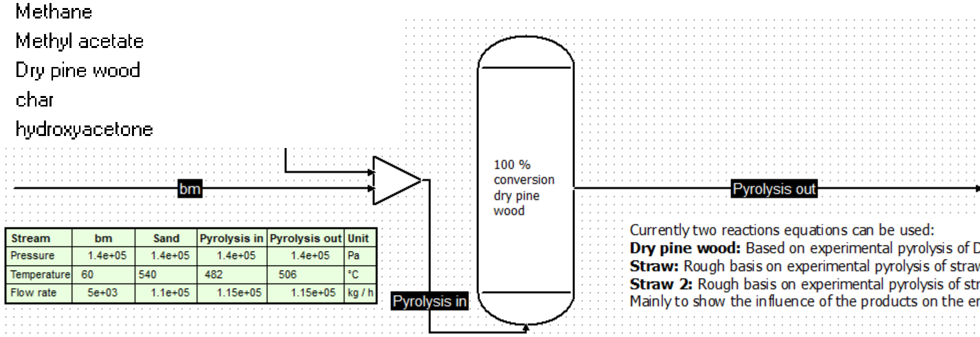
Detailed sections – pyrolysis reactor

- reaction packages obtained with (external) excel solver.
- 20 : 1 ratio sand : biomass
- ~Slightly exothermic behaviour predicted

Stoichiometry	Compound
0.5638	Water
0.02172	Oxygen
0.01	High MW lig A
0.01	High MW lig B
0.0302	Benzaldehyde, 3-hydroxy-4-metho...
0.0728	2-Butenoic acid, (E)-
0.0096	dehydroabietic acid
0.0187	Isoeugenol
0.07382	levoglucosan
0.07235	maltose
0.0575	p-hydroquinone
0.20558	Carbon monoxide
0.1572	Carbon dioxide
0.0463	Methane
0	Methyl acetate
-4.802	Dry pine wood
0.209	char
0.0345	hydroxyacetone



Stream	SAND COOL	Bio dry - dry biomass	Pyro reac - products	Unit
Temperature	540	60	506	°C
Flow rate	1.1e+05	5e+03	1.15e+05	kg / h

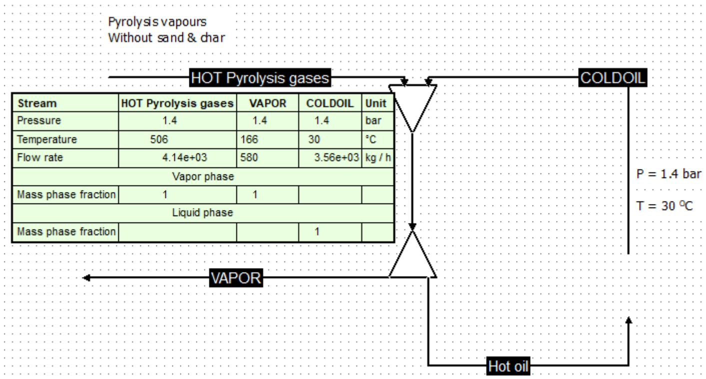


Stream	bm	Sand	Pyrolysis in	Pyrolysis out	Unit
Pressure	1.4e+05	1.4e+05	1.4e+05	1.4e+05	Pa
Temperature	60	540	482	506	°C
Flow rate	5e+03	1.1e+05	1.15e+05	1.15e+05	kg / h

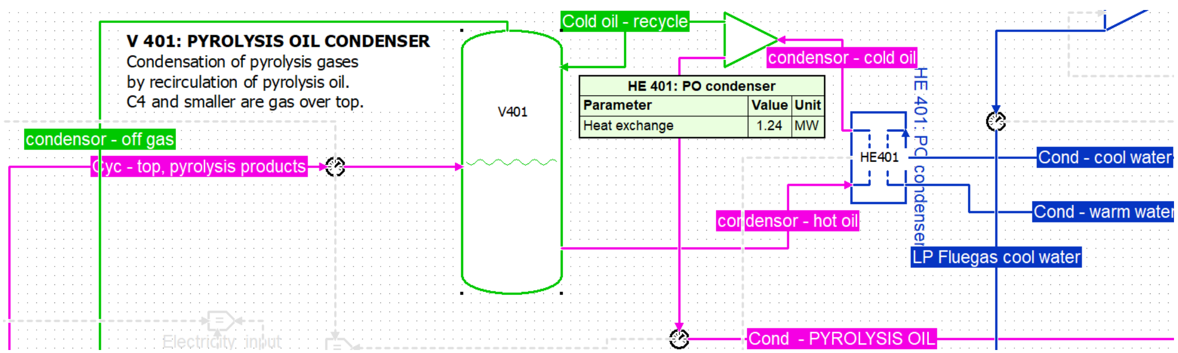
Currently two reactions equations can be used:
Dry pine wood: Based on experimental pyrolysis of Dry pine wood.
Straw: Rough basis on experimental pyrolysis of straw with high water production.
Straw 2: Rough basis on experimental pyrolysis of straw with normal water production.
Mainly to show the influence of the products on the energy / mass balance of the process.

Detailed sections - condenser

- <C_4 as gas over top; Quenching with cold oil.
- Temperatures nicely predicted



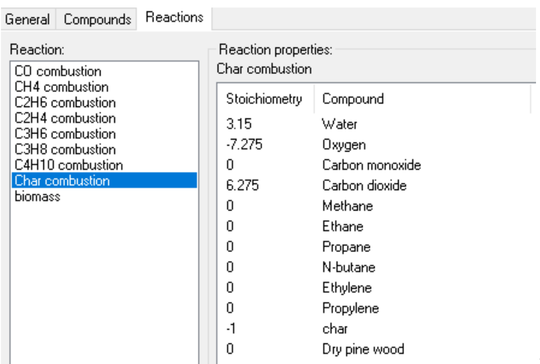
Stream	HOT Pyrolysis gases	VAPOR	COLDOIL	Unit
Pressure	1.4	1.4	1.4	bar
Temperature	506	166	30	°C
Flow rate	4.14e+03	580	3.56e+03	kg / h
Vapor phase				
Mass phase fraction	1	1		
Liquid phase				
Mass phase fraction			1	



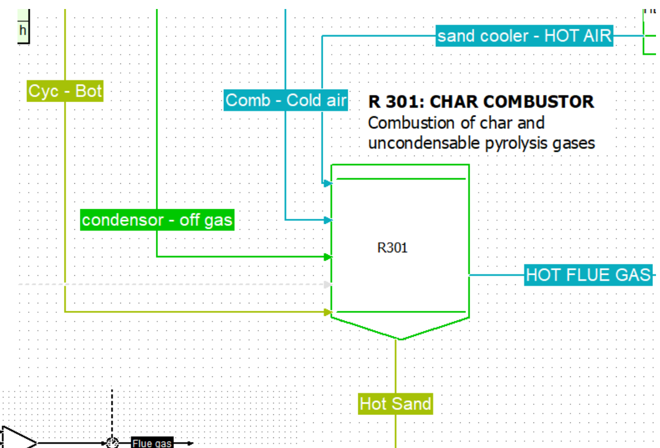
HE 401: PO condenser		
Parameter	Value	Unit
Heat exchange	1.24	MW

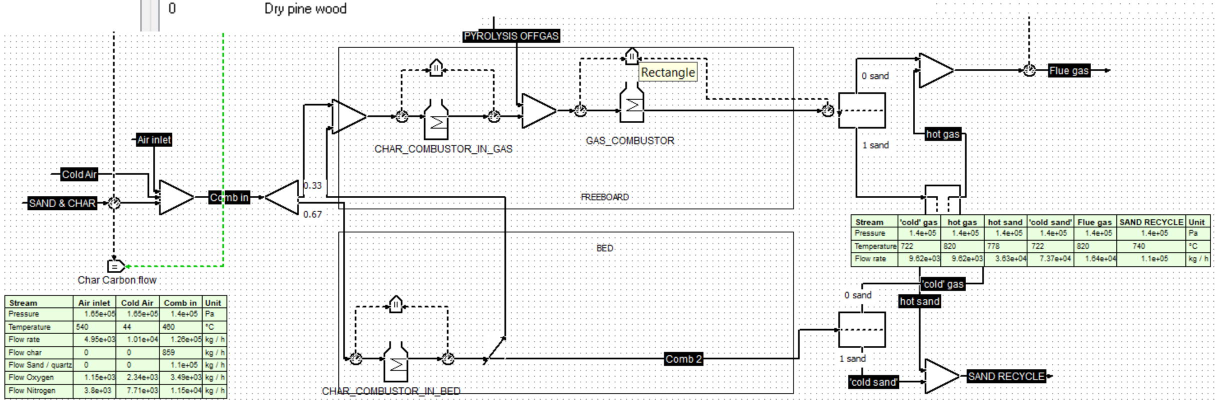
Detailed sections – combustor reactor

- Char and light gases combustion
- Oxygen transported to board
- Slight heat exchange between bed and board
- $T_{fluegas}$ and T_{sand} accurately predicted



Stoichiometry	Compound
3.15	Water
-7.275	Oxygen
0	Carbon monoxide
6.275	Carbon dioxide
0	Methane
0	Ethane
0	Propane
0	N-butane
0	Ethylene
0	Propylene
-1	char
0	Dry pine wood





Stream	Air inlet	Cold Air	Comb in	Unit
Pressure	1.65e+05	1.65e+05	1.4e+05	Pa
Temperature	540	44	460	°C
Flow rate	4.95e+03	1.01e+04	1.26e+05	kg / h
Flow char	0	0	859	kg / h
Flow Sand / quartz	0	0	1.1e+05	kg / h
Flow Oxygen	1.15e+03	2.34e+03	3.49e+03	kg / h
Flow Nitrogen	3.8e+03	7.71e+03	1.15e+04	kg / h

Stream	'cold' gas	hot gas	hot sand	'cold sand'	Flue gas	SAND RECYCLE	Unit
Pressure	1.4e+05	1.4e+05	1.4e+05	1.4e+05	1.4e+05	1.4e+05	Pa
Temperature	722	820	778	722	820	740	°C
Flow rate	9.62e+03	9.62e+03	3.63e+04	7.37e+04	1.64e+04	1.1e+05	kg / h

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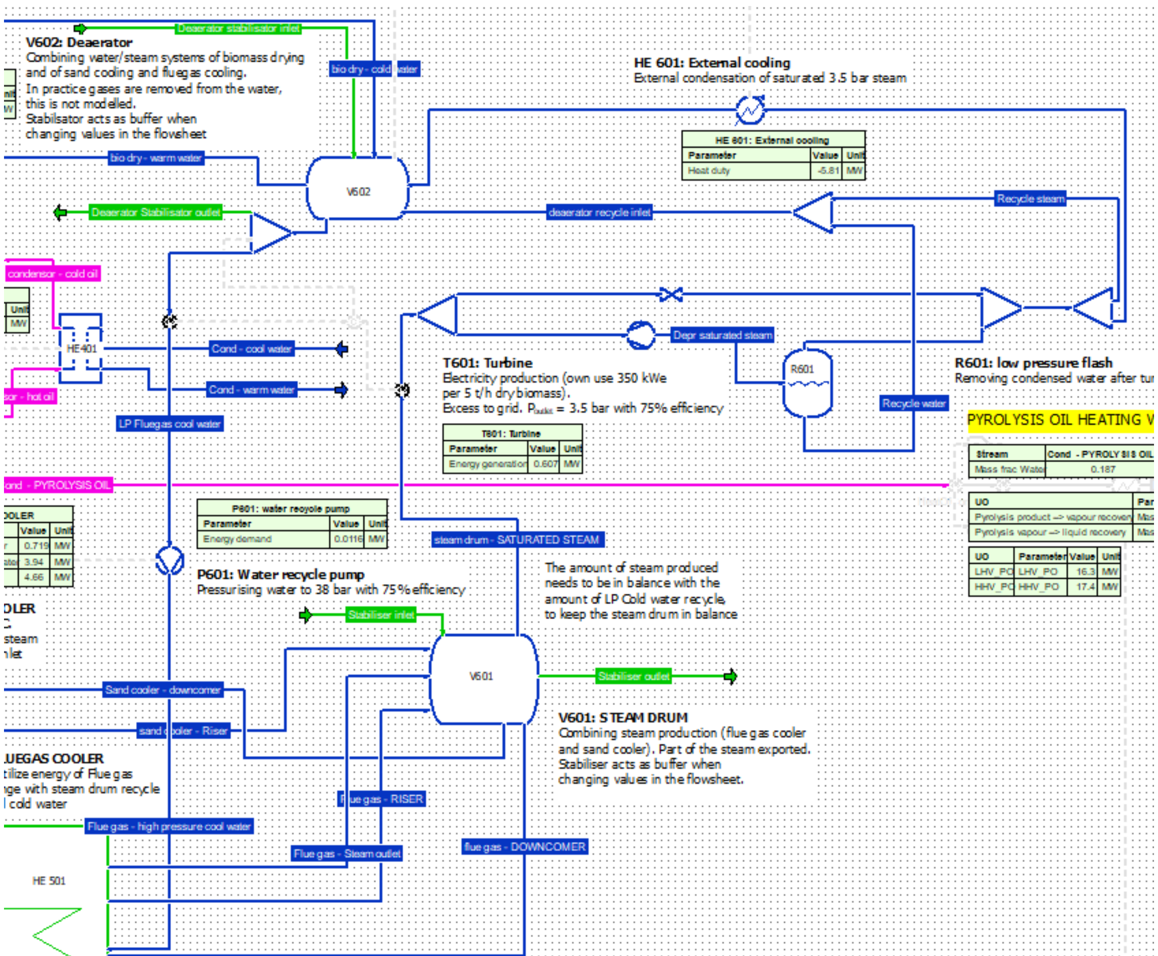
Detailed sections – Steam system

- Steam drum; Turbine; External cooling; Deaerator
- All pressure / temperatures nicely predicted



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Mass balance

- Checked over complete flowsheet and unit operations.
- Intrinsicly correct due to mass and atom check in program.
- Carbon Efficiency.
- Mass and water flow.

Main Pyrolysis oil streams overview

Overview of the mass and water content of the main streams in the system.

Stream	OSBL - wet biomass	Bio dry - dry biomass	Cyc - top, pyrolysis products	Cond - PYROLYSIS OIL	Unit
Flow rate	5.28e+03	5e+03	4.14e+03	3.56e+03	kg / h
Mass frac Water	0.1	0.05	0.161	0.187	

Overview of the carbon flow for the main process streams. Carbon flow is normalised towards the carbon in the feed stream

UO	Parameter	Value	Unit
Biomass_carbon_flow	Inlet_Carbon	100	
Pyrolysis_oil_carbon_flow	Pyrolysis_oil_carbon	64.2	
R301: CHAR COMBUSTOR	Char_Carbon	27.3	
R301: CHAR COMBUSTOR	Uncondensable_Carbon	8.52	

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Energy Balance

- Energy internally intrinsically correct.
- Visualised energy flows for whole model and unit operations.
  - Checked with build in LHV/HHV calculator build in.
  - 0.1 - 0.3% errors

Energy into the system

UO	Parameter	Value	Unit
LHV_biomass	LHV_biomass	25.1	MW
HHV Biomass	HHV_biomass	26.9	MW
Electricity_input	Total_power	0.109	MW
V101: Biomass dryer	Biomass dryer - steam	0.325	MW

Energy out of the system

UO	Parameter	Value	Unit
LHV_PO	LHV_PO	16.3	MW
HHV_PO	HHV_PO	17.4	MW
T601: Turbine	Energy generation	0.607	MW
Steam production	Total_power	6.38	MW
Rest_energy	Total_power	2.95	MW

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Future perspectives wrt CoCo flowsheeting

Three individual constituents

Cellulose ; hemicellulose; lignin

Process

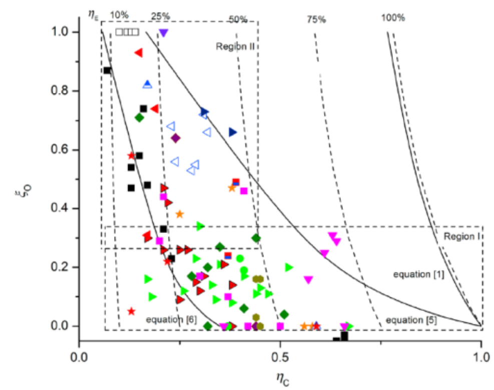
Pyrolysis does not yield an oil ≠ crude oil

Syrup in which lignitic fragments are emulsified

Reactive sugars versus stable lignins
Relatively high contaminant level – alien to fossil fuel

Product

Sugar chemistry versus lignin chemistry



Catalysis within the pyrolysis process a 'tricky' choice

Hydrotreating pyrolysis liquids

10.1002/cssc.201500115

btg-neXt advanced pyrolysis biofuel

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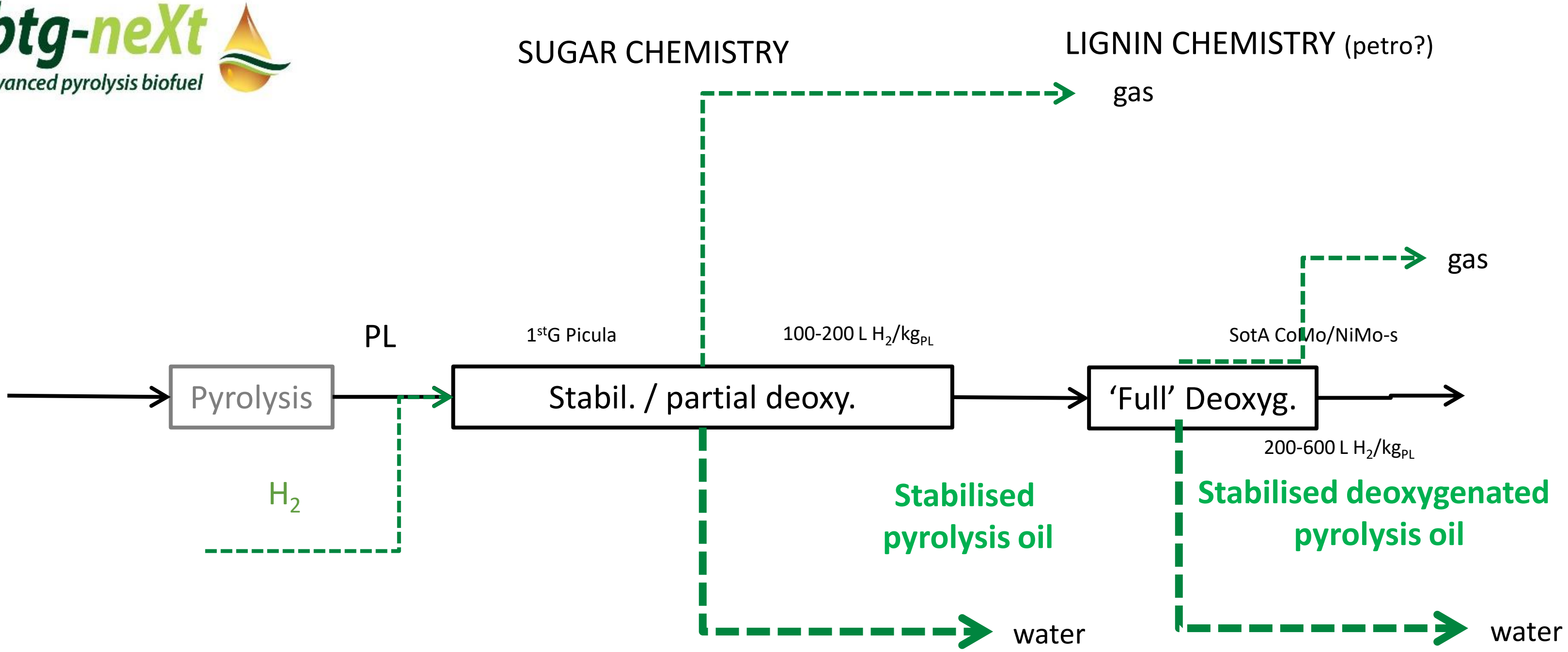
Preliminary models of Stabilization and Deoxygenation in CoCo Simulator (standard feedstock)

Liquid conversion: sugar chemistry versus lignin chemistry



Advanced biofuels from pyrolysis liquids by refinery integration

Options to produce a drop-in fuel

1. Co-feed of PL with VGO in FCC unit

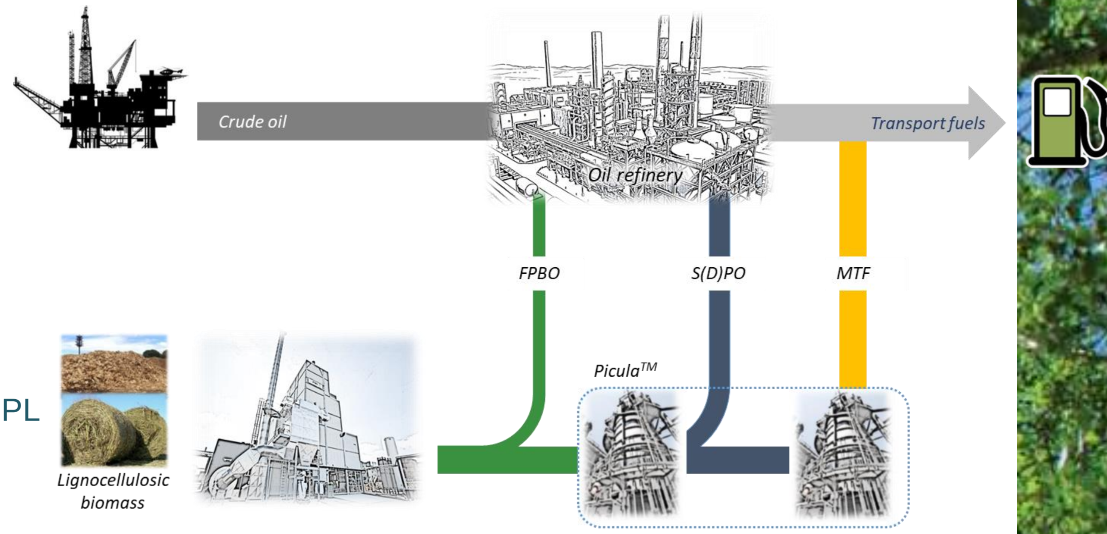
- Extensive testing by Petrobras (and others)
- To be demonstrated full-scale by Preem (2021)
- Max co-feed around 5-10 wt%

2. Co-feed of treated PL 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 (MTF) is fully miscible with fossil fuels



Source: BTG Bioliquids BV

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

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

Challenges

- Fluid catalytic cracking models – custom made operation
  - Aspen / Hysis: (excel) add-on
    - rigorous HYSYS models for modelling the FCC step do not take into account oxygen containing feedstocks
  - Alternatively experimental modelling software. Fitting models to obtain data sets requires extensive testing (with variables as feedstock, process conditions and product yields)

Development reactor tool through integration with other open resource applications (PythonUnitOperations)

- FCC – refinery approach
- Electrochemical transformations (EBIO / Sintef)

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Take-home messages

- COFE sheeting in this open resource application straightforward and very useful (European commission / Saxion / Twente University / VTT ..)
- Development of models in other applications in biofuel arena ongoing (ethanol / lignin conversion /...)
- Efficient use in quick and dirty screening of specific pathways / routes
- **unique plus; open resource; easy access; relatively intuitive approach**

- Dynamic simulations?
- Integration with other open resource applications: PythonUnitOperation

Acknowledgments

4REFINERY (GA 727531); Waste2Road (GA 818120)
Jasper van Baten (also to solve any flaws / bugs during the last 5 years)

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Questions?

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