Modelling of fast pyrolysis processes using COCO software

Robbie Venderbosch

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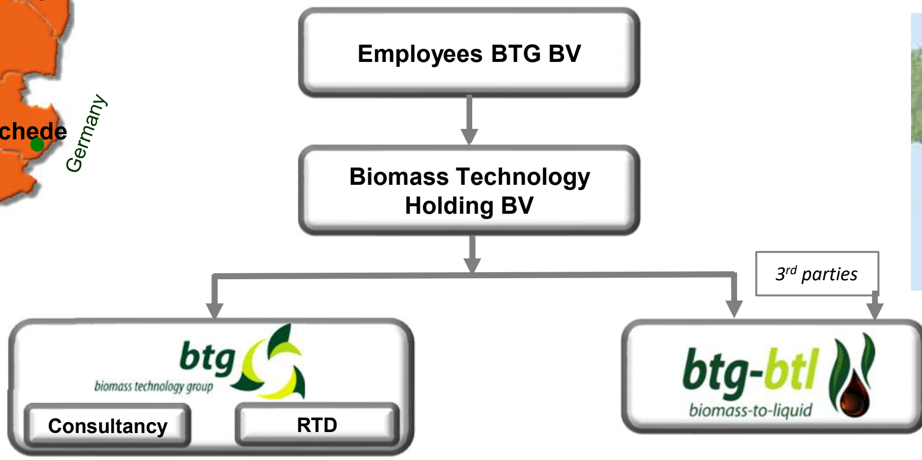
biomass technology group

Date 20-04-2021

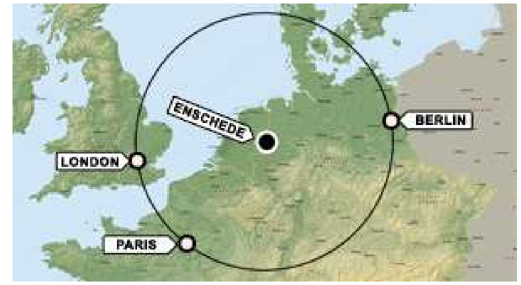
Your partner in bioenergy

BTG Biomass Technology Group B.V.

Amsterdam 160 km



Approx.30 people



Berlin 445 km
Paris 485 km
London 490 km

It is timing and stamina

Fast Pyrolysis – development timeline BTG

Roll-out

BTL

- 2019 Empyro sold to Twence; roll out thrugh GreenFuelNordic and Pyrocello
- 2015 Start-up Empyro plant & Boiler at FrieslandCampina
- 2014 Start construction 120 t/d Empyro plant
- 2013 Long-term FPBO supply contract signed

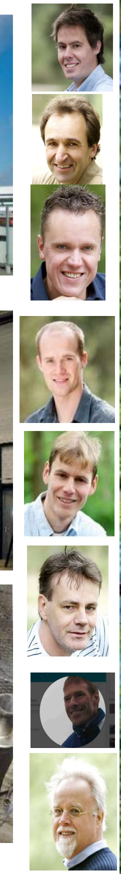
development

- 2009 Establishment of Empyro BV to demonstrate 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
- 1987 Rotating cone reactor 'invented' at University of Twente (UT)

UT



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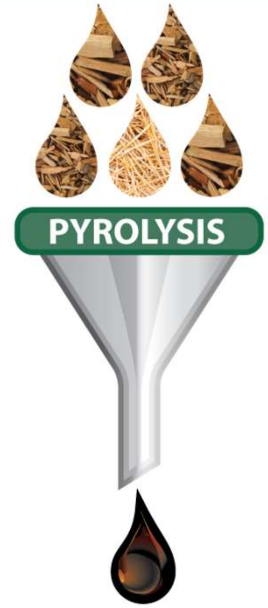
Pyrolysis of biomass

Thermal cracking of organic material w/o oxygen

Main product: liquid ‘bio-oil’

400 - 600 °C; atmospheric pressure



Why?

- liquid products as main product from biomass (≤70%)
- Minerals remain in char / ash
- Feed flexibility
- Increase in energy density with a factor of 4 - 5 (wood) to 10 - 20 (fibrous, wet EFB)
- 60-70 % carbon yield (biomass-to-oil)

For competiveness: SOLVE LOGISTICS FIRST !!
There must be much of it, it must be dense, available at low costs and readily available

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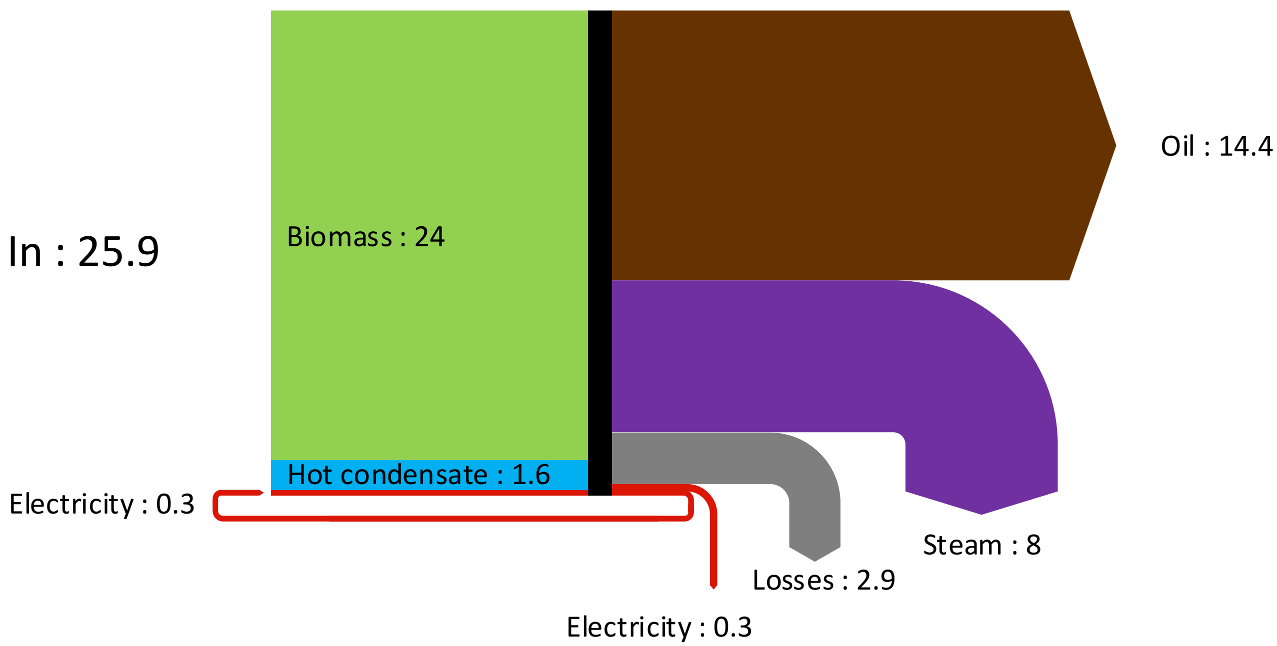
Empyro efficiency (MW_{th})



Overall Efficiency : 85 %

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Overall properties of pyrolysis oil

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

Biomass	→	Pyrolysis Oil
Hemi-cellulose	→	Acids, Carbonyls
Cellulose	→	Sugars / Syrup
Lignin	→	Pyrolytic Lignin

Overall Composition	$C_2H_5O_2$
Oxygen content	≈ 45 - 50 %
pH	≈ 2,5 - 3,5
Density	1.15 kg/l
Heating Value	16 -18 MJ/kg
Viscosity	25 cP
Ash	< 0.1 wt.%

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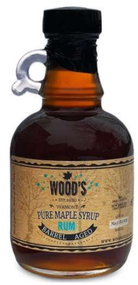
Overall properties of pyrolysis ~~oil~~ liquid

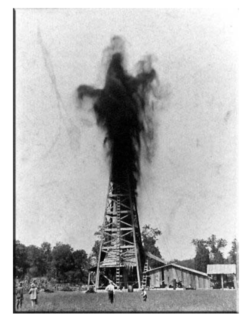
What we can do in hours is what nature does in millions of years



Pyrolysis oil

≠

oil



lignitic fragments emulsified in an aqueous syrup solution

Change in oxygen functionality!

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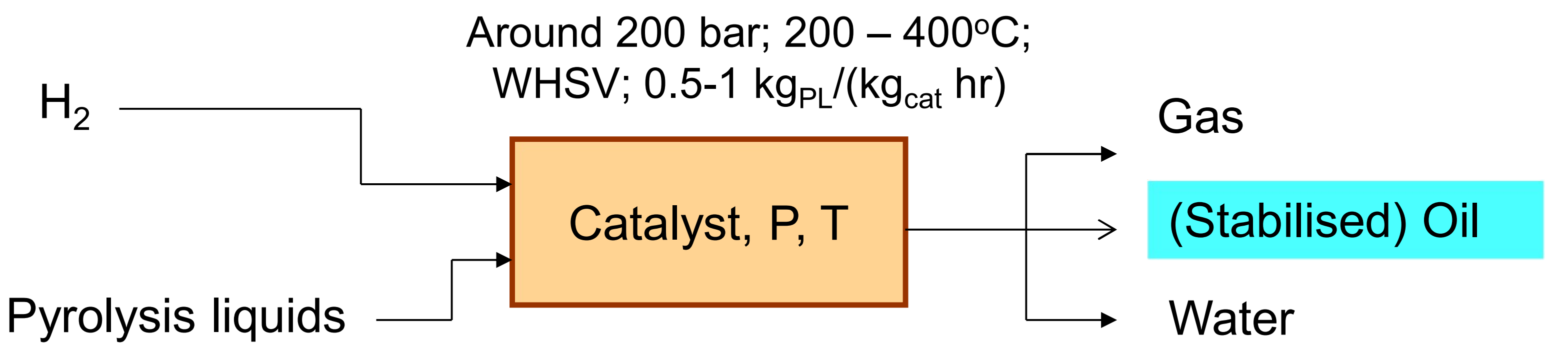
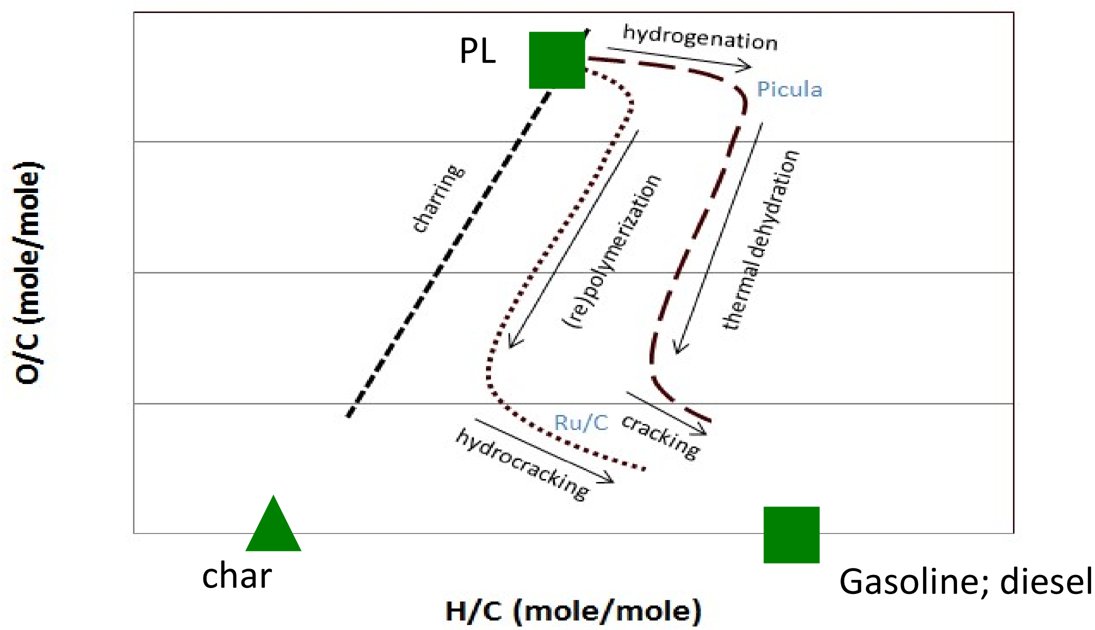
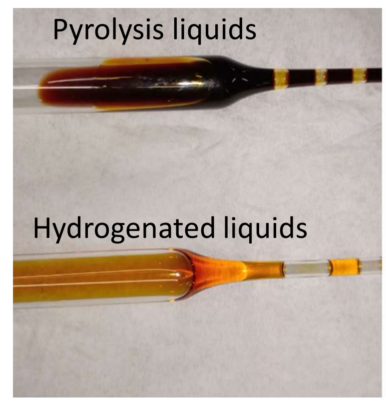
Catalytic Hydrotreatment (activities from BTG since 2001)



$$(CH_xO_z + b\ H_2O) + c\ H_2 \rightarrow (CH_{x'}OH + b'\ H_2O)$$

$$CH_{x'}OH + \alpha\ H_2 \rightarrow \beta\ CH_{x''} + \chi\ H_2O + \delta\ CO_2 + \varepsilon\ CH_4$$





char

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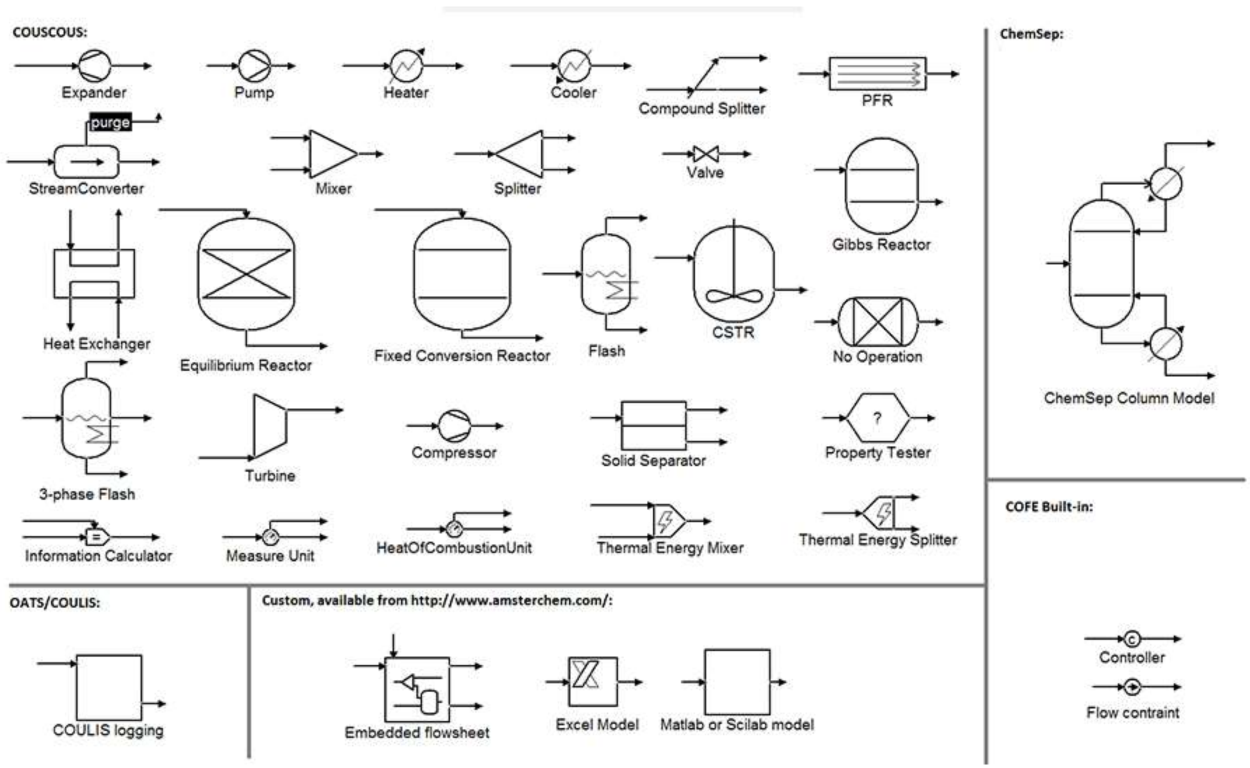
Freeware flowsheeting

https://www.cocosimulator.org/

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



Example model components

Component selection

- Main assumptions
  - Model compounds
  - Conversion reactors
  - No pressure drop
  - 1.4 bar

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	C20H26O
High MW Lignin B	C21H26O
Nitrogen compounds	2,4,6-trimethylpyridine
Sulfur compounds	Dibenzothiophene

Figure 1: Pyrolysis model compounds

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

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Pacific Northwest National Laboratory

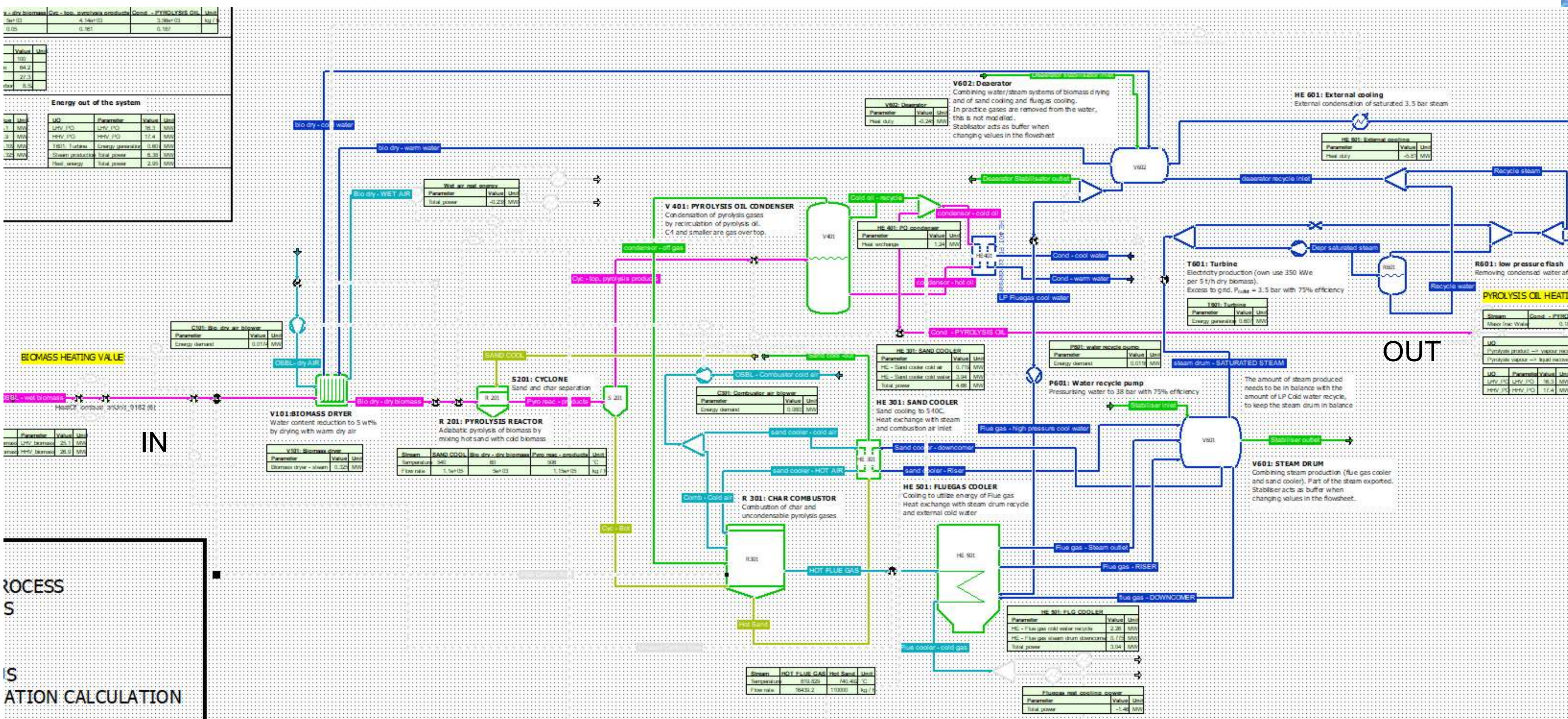
Eric Tan, Abhijit Dutta
National Renewable Energy Laboratory

Jacob Jacobson, Kara Cafferty
Idaho National Laboratory

PNNL-23053
NREL/TP-5100-61178

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

Model pyrolysis



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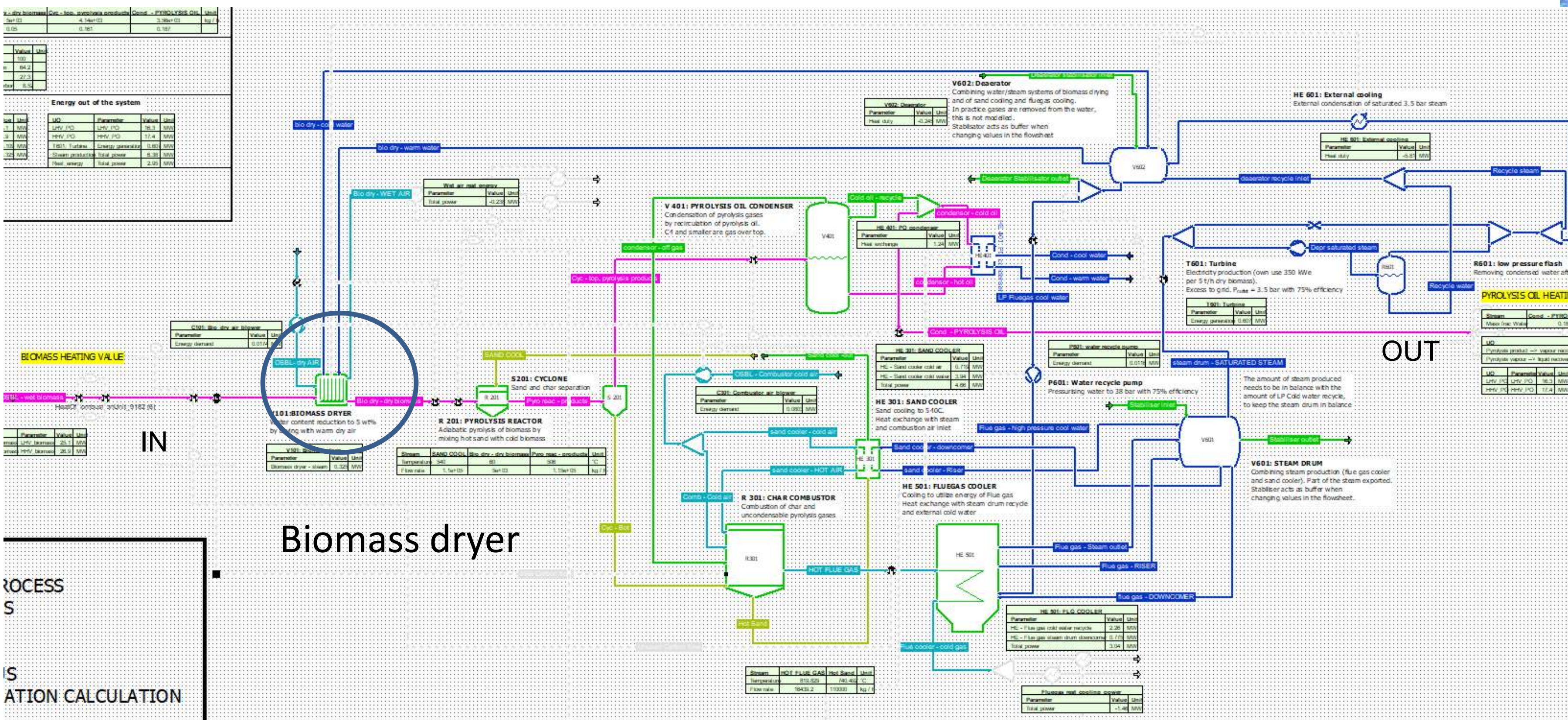
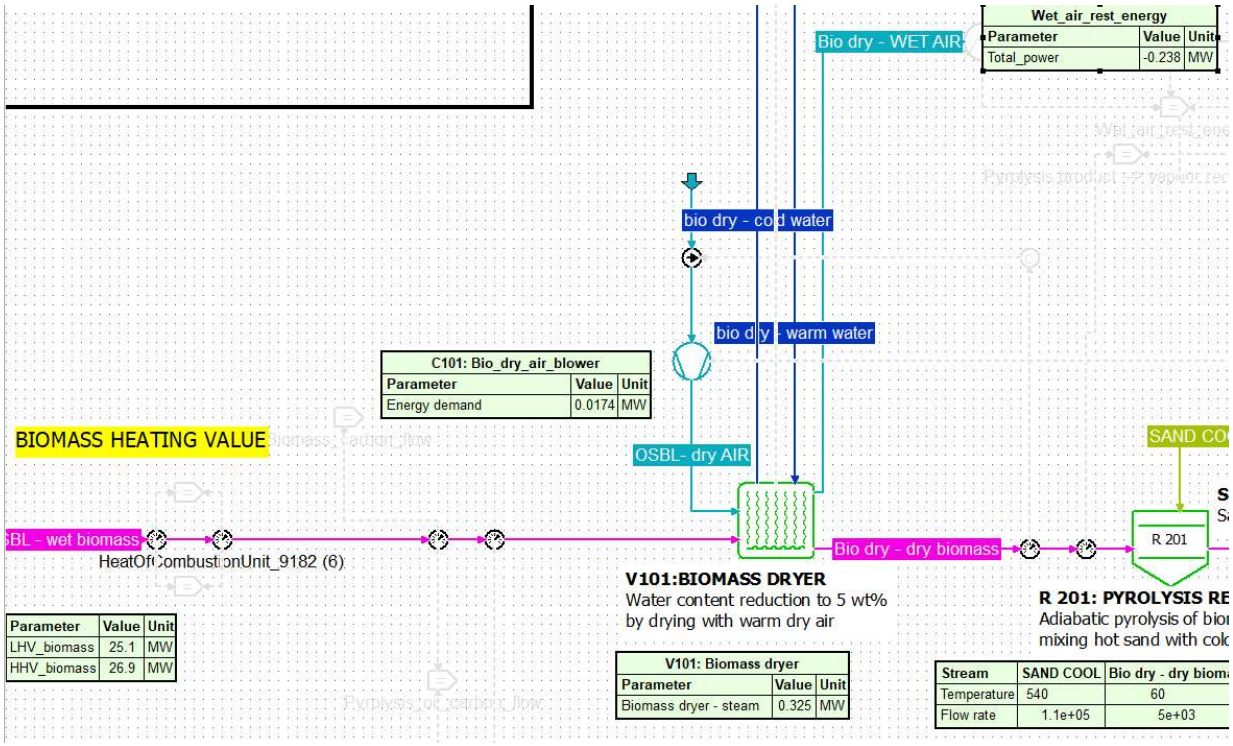
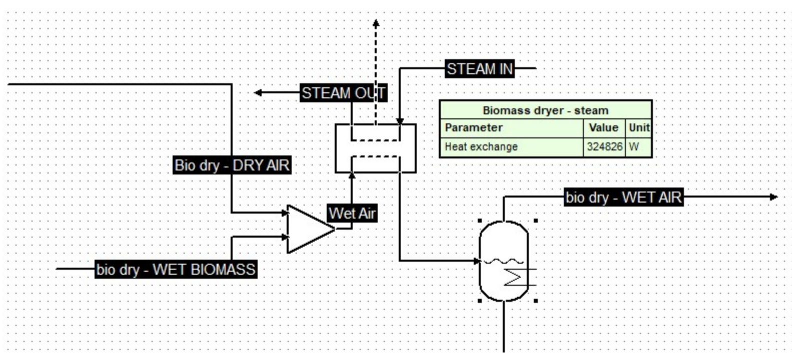
Model pyrolysis



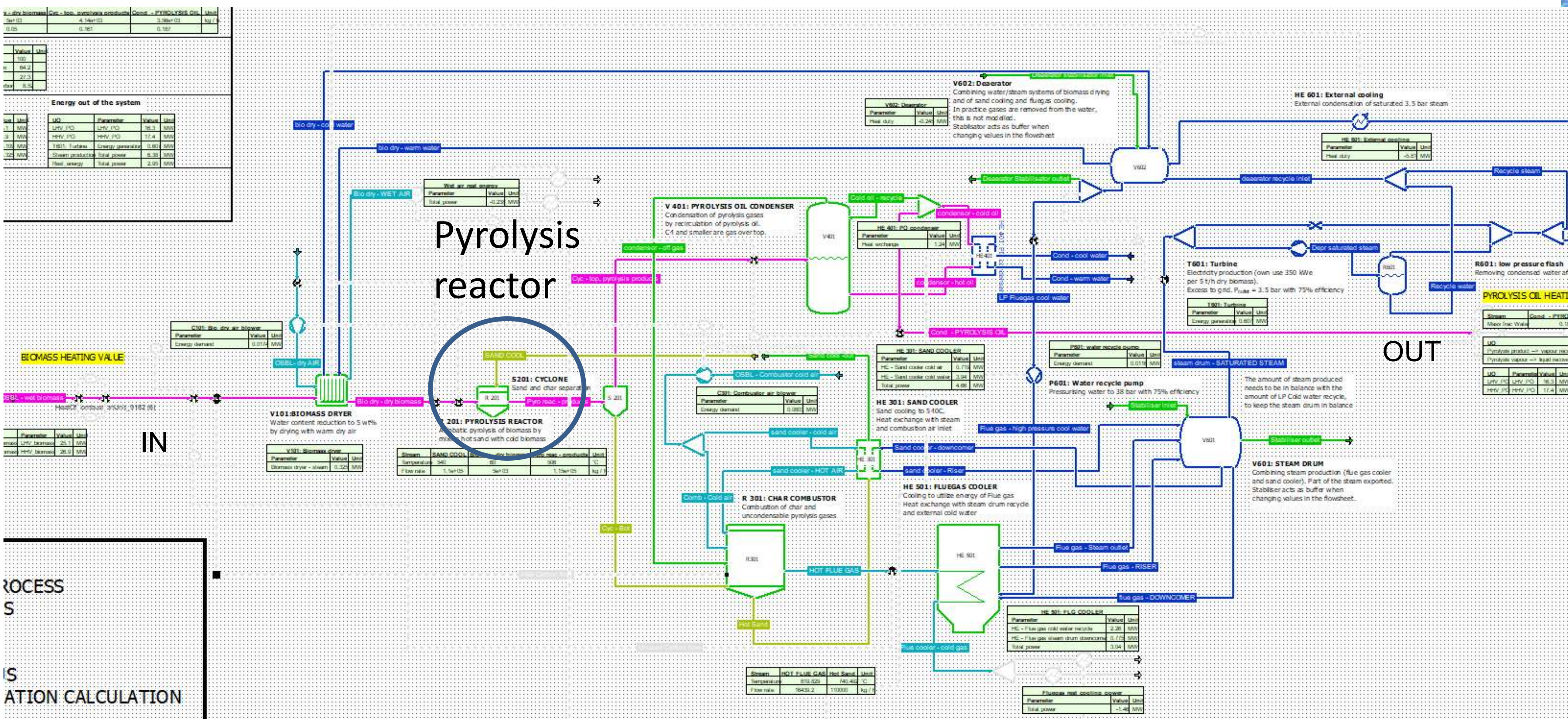
Detailed sections – biomass dryer

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





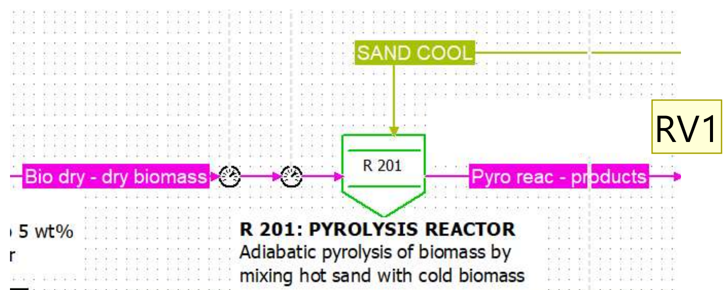
Model pyrolysis



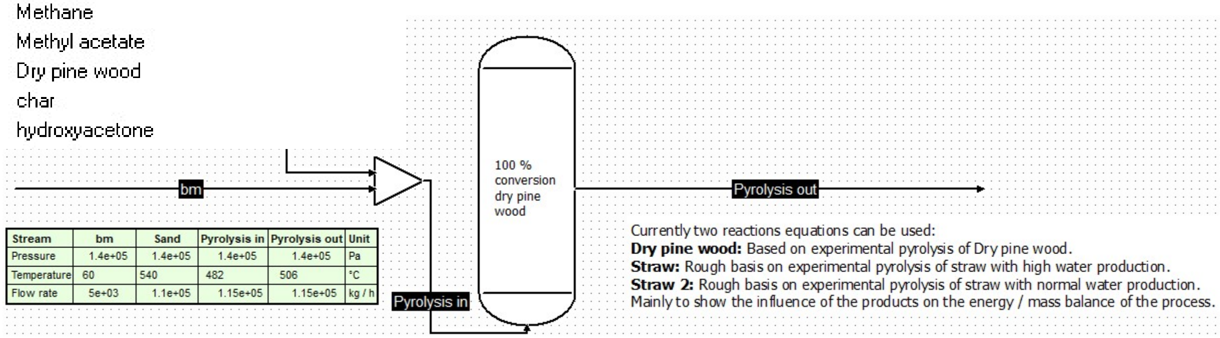
Detailed sections – pyrolysis reactor

- 3 reaction packages, obtained with excel solver.
- Compounds defined in PCD manager.
- 22:1 ratio sand:biomass
- ~Slightly exothermic

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.

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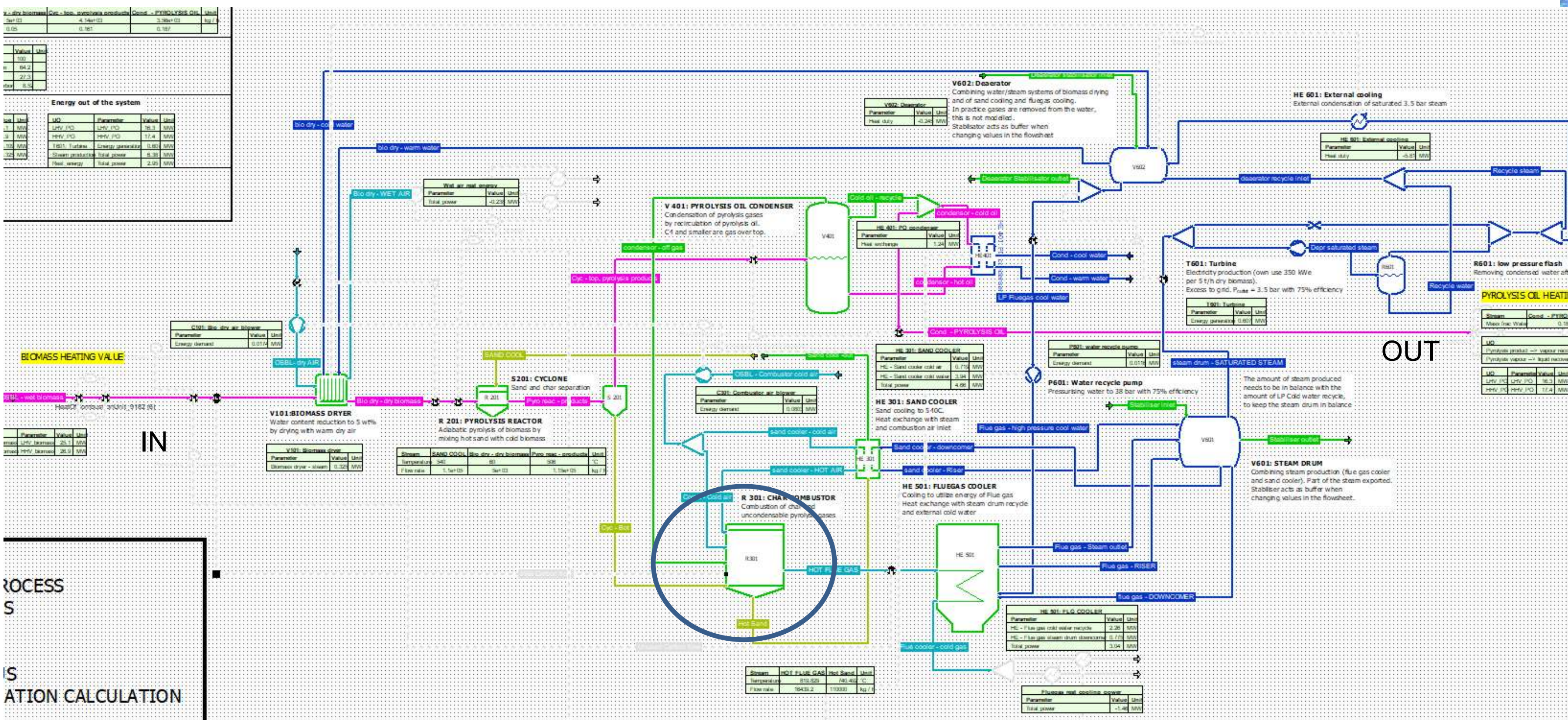
Slide 15

RV1 Robbie Venderbosch, 4/19/2021

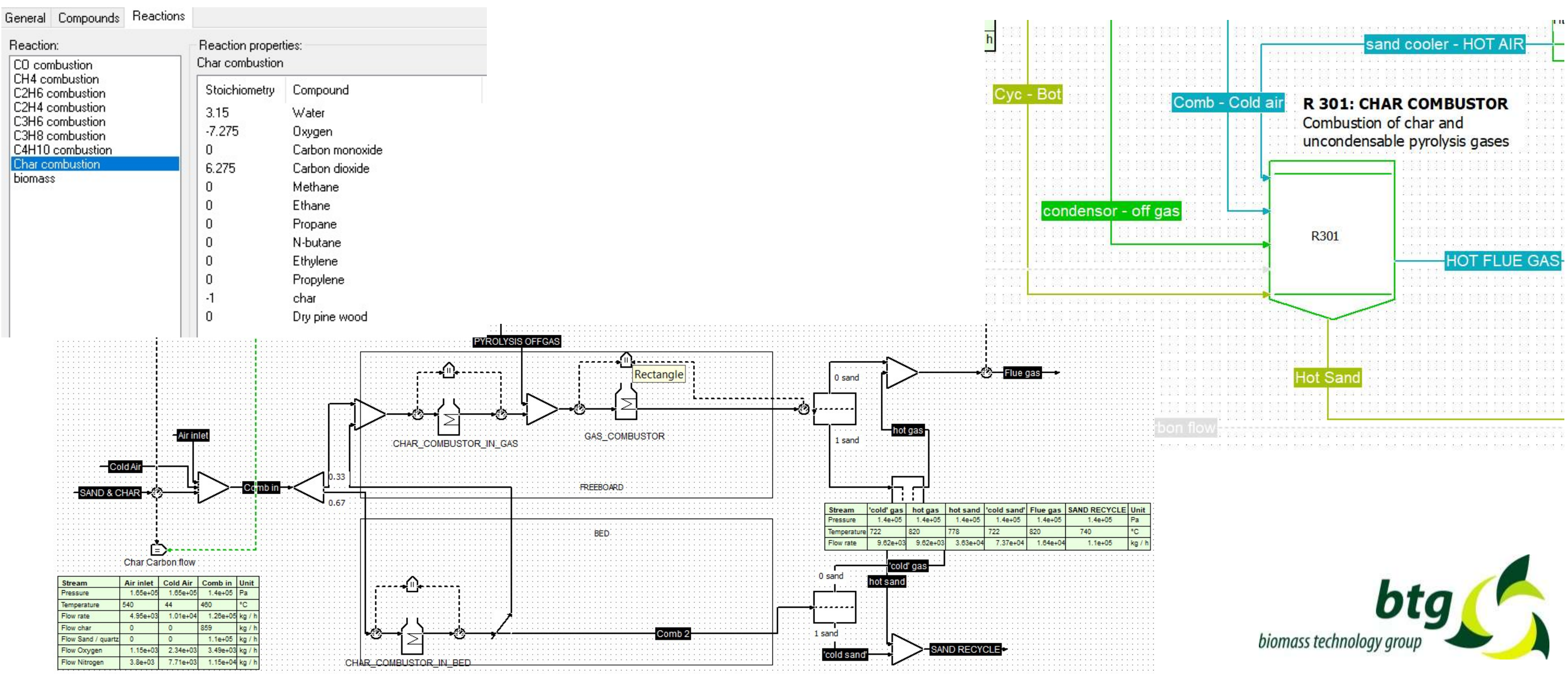
Model pyrolysis



Char combustor

Detailed sections – combustor reactor

- Char and light gases combusted
- Bed and freeboard reactions: oxygen transported to free board
- Some heat exchange between bed and board
- $T_{fluegas} = 820^oC$, $T_{sand} = 740^oC$



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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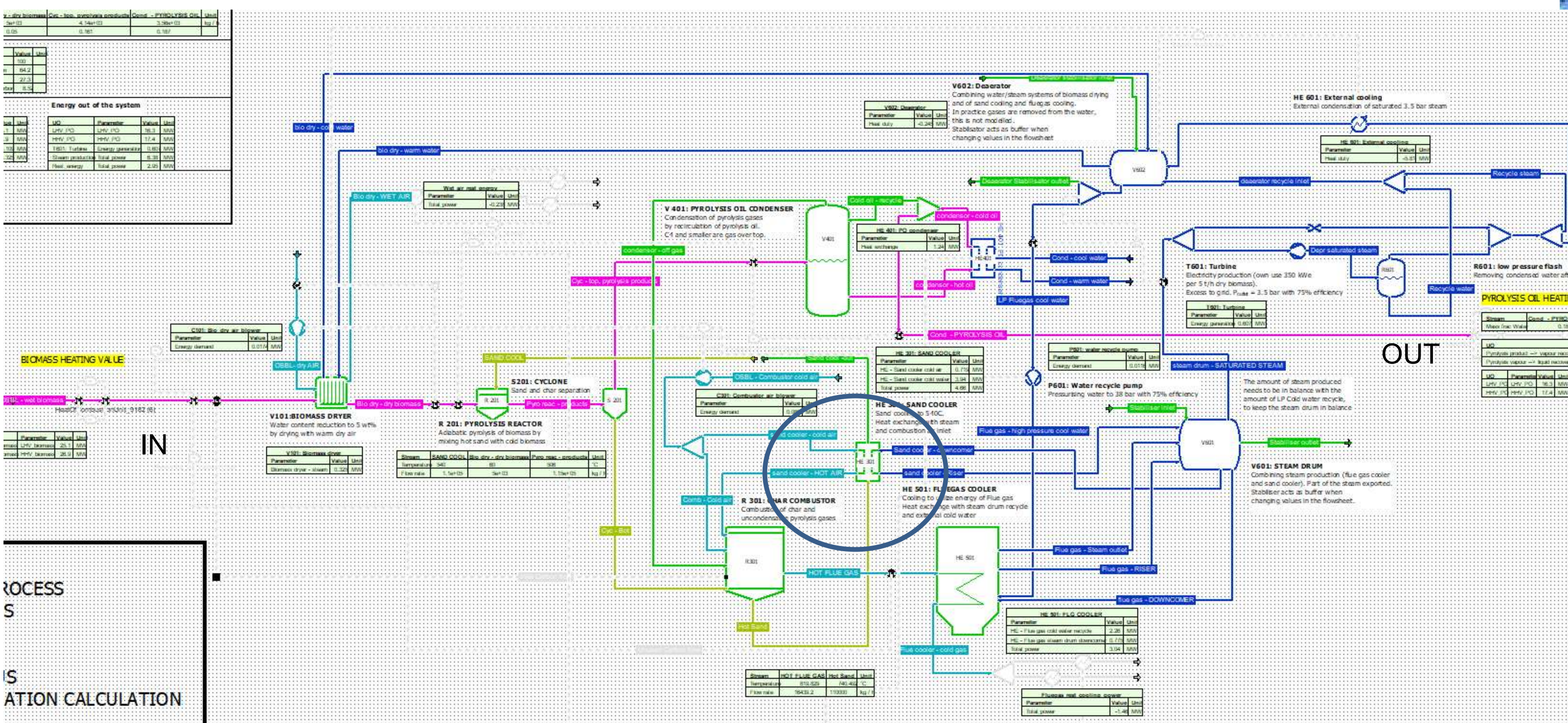
Model pyrolysis



Sand cooler

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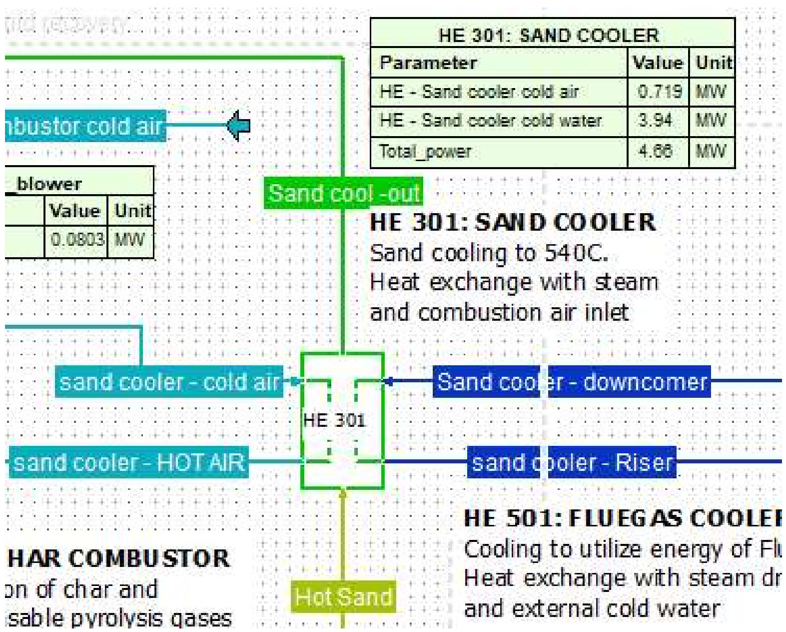
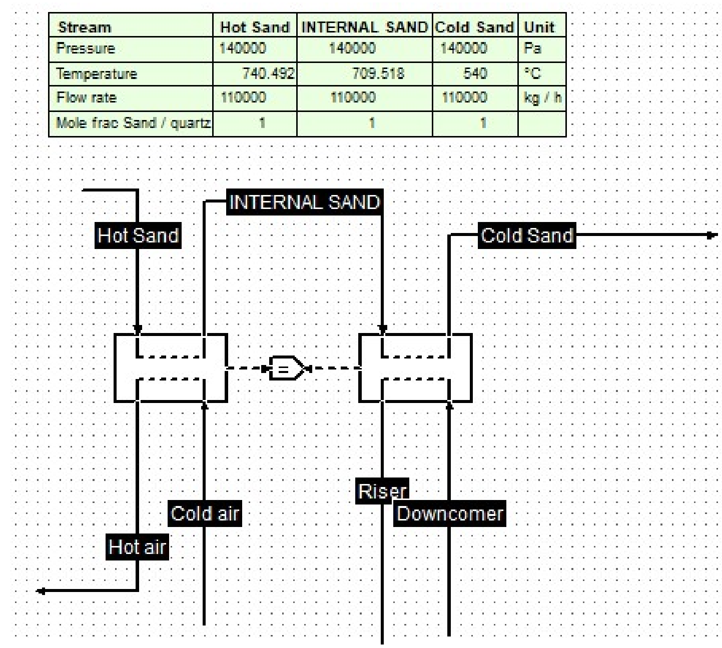
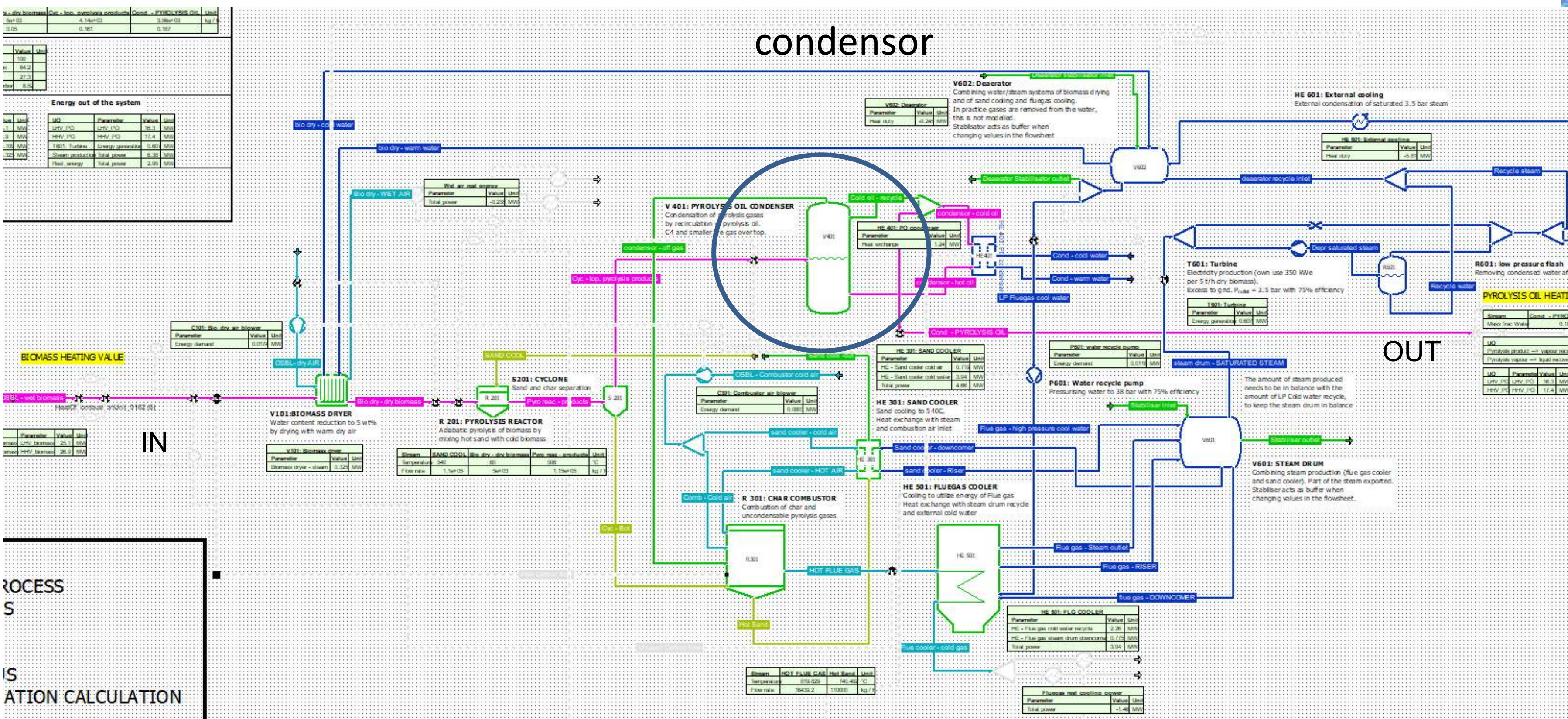
Detailed sections – Sand cooler

- Sand recycle temperature set.
- First air cooling, then steam recycle.





Model pyrolysis



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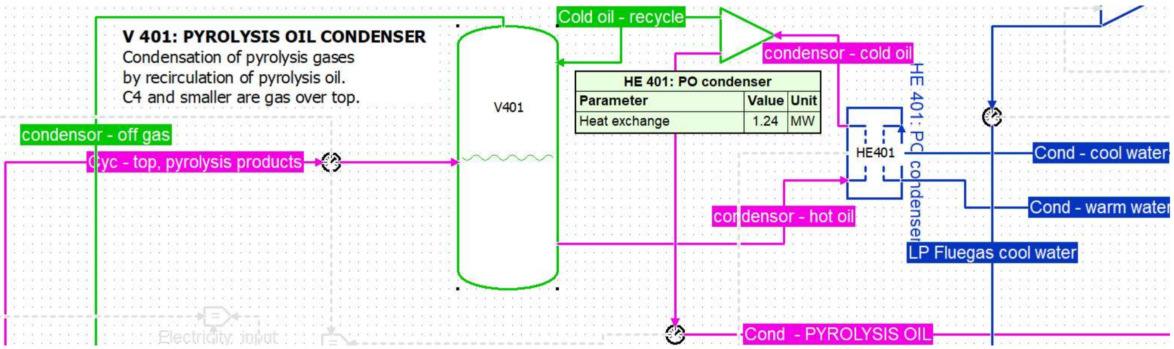
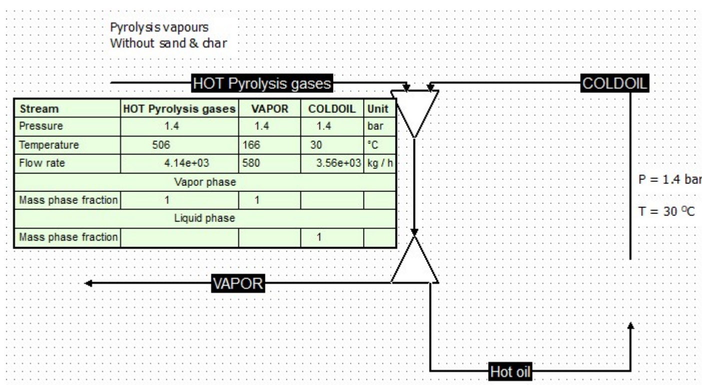
Detailed sections - condenser

- C_4 and smaller as gas over top.
- Quenching with 50% of cold oil.





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	

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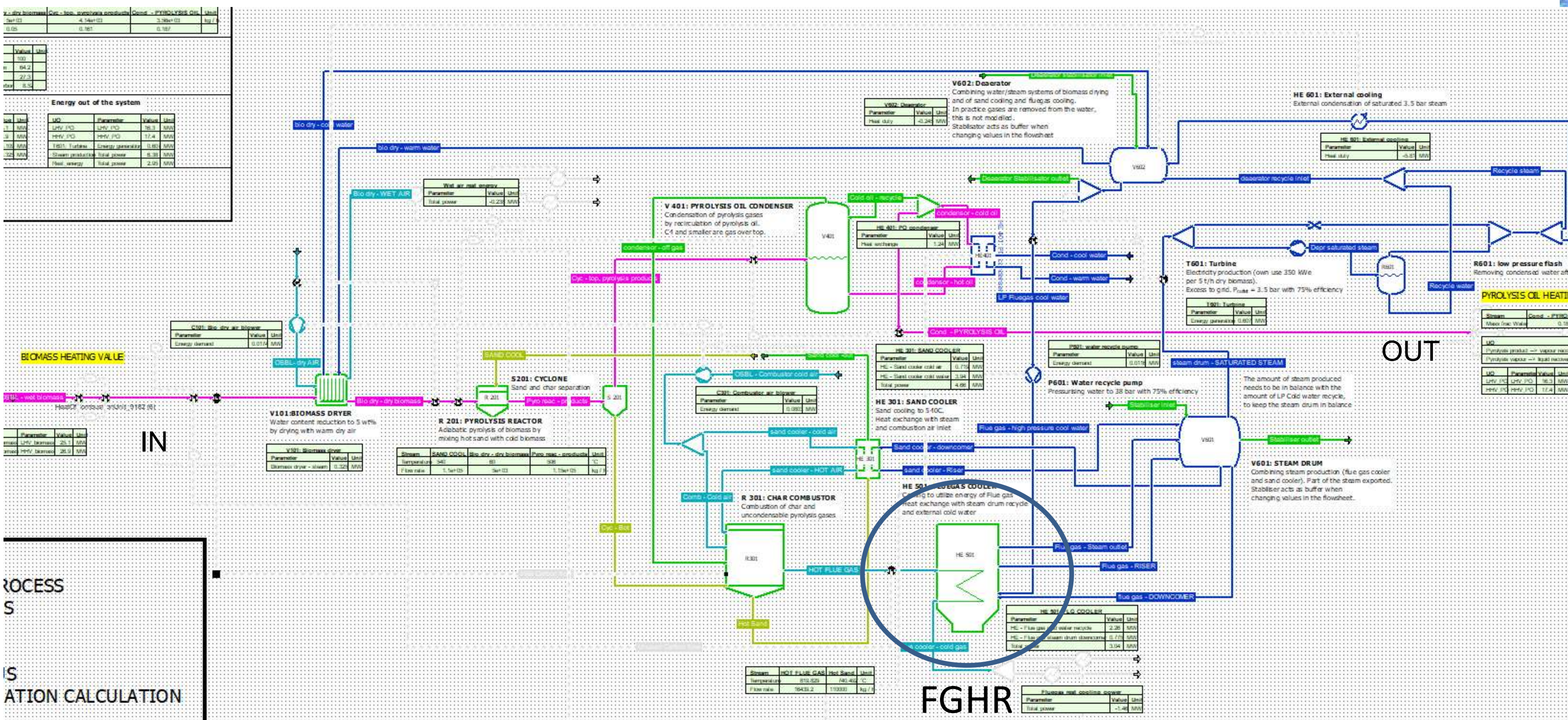
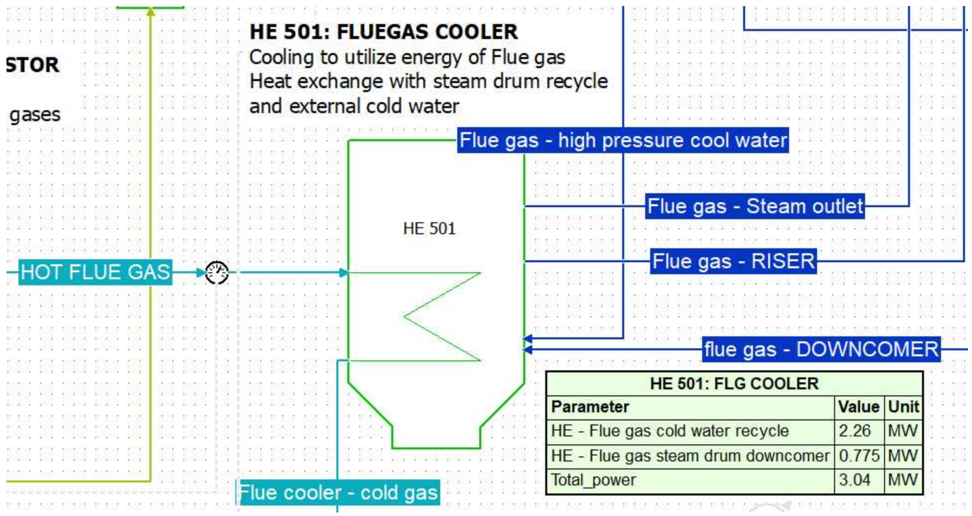
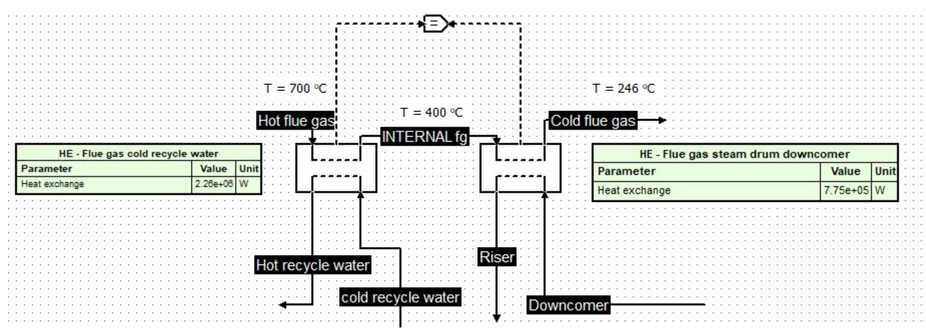
Model pyrolysis



Detailed sections – Flue gas cooler

- Recycle cool water
- Steam drum recycle





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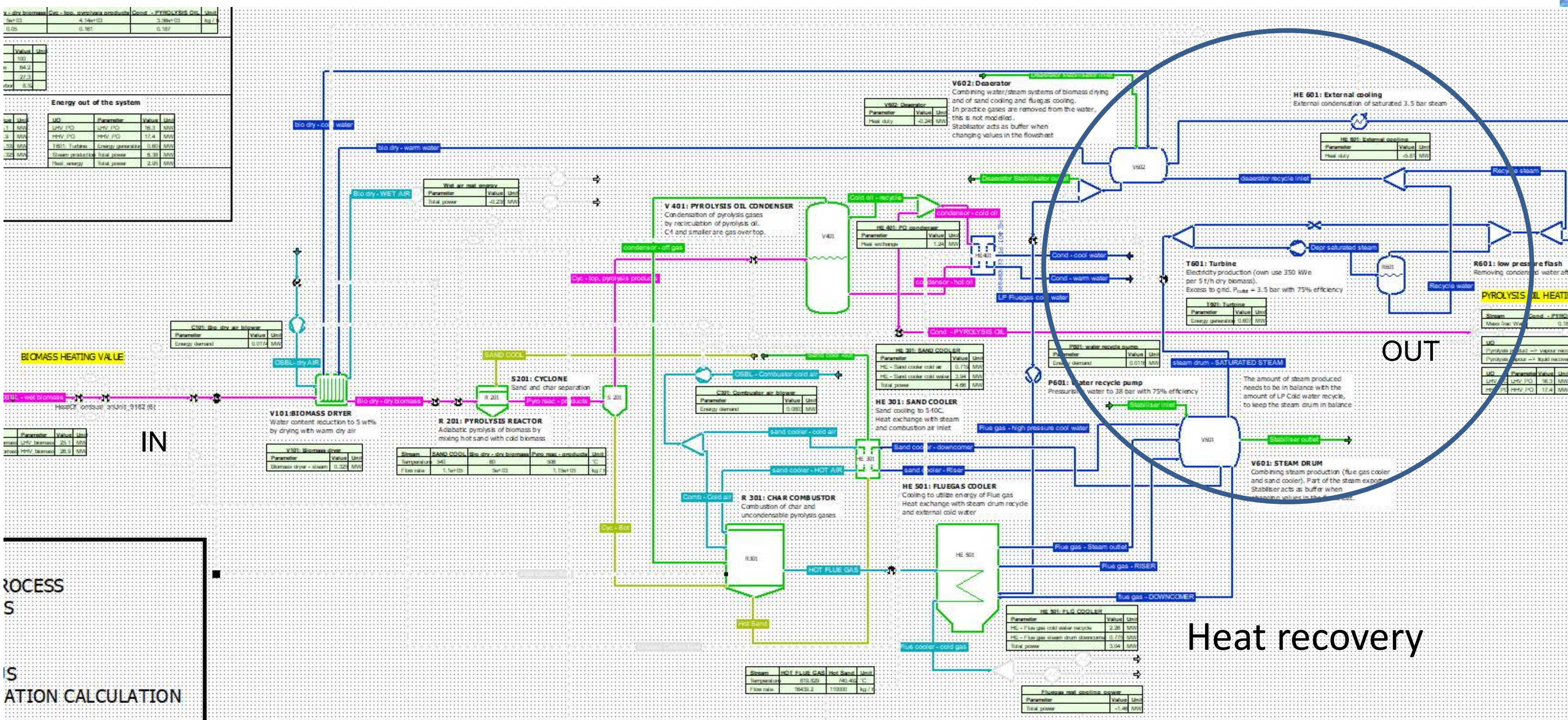
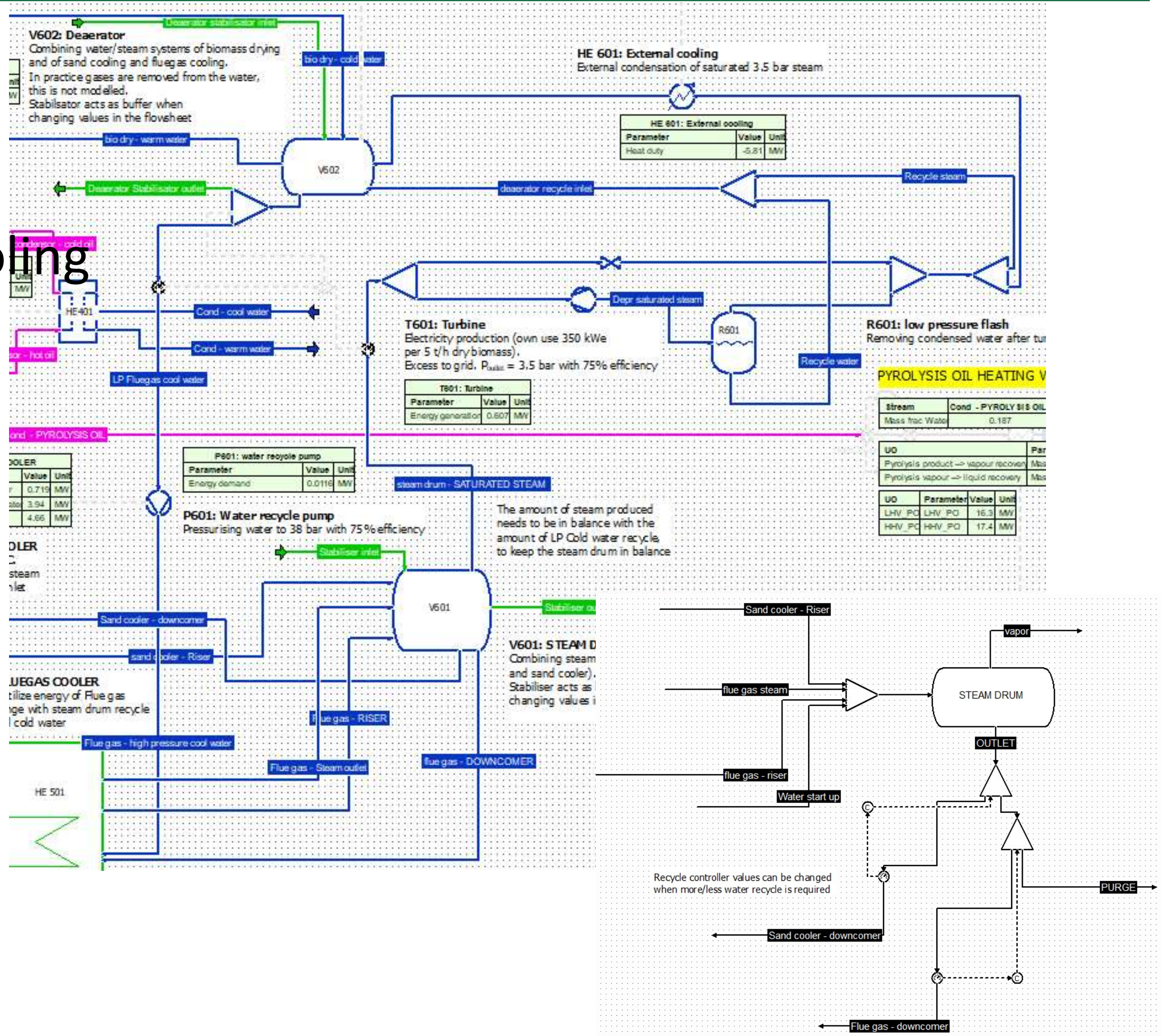
Model pyrolysis



Detailed sections – Steam system

- Steam drum
- Turbine
- External cooling
- Deaerator



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Mass balance (Intrinsically correct due to mass and atom check in program)

- Over flowsheet and unit operations
- Quick values for 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	

Process flow diagram – iterative / recycling

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Energy Balance (intrinsically correct with EnthalpyF.)

- Energy flows for whole model and unit operations.
  - Checked (LHV/HHV calculator).
  - 0.1 - 0.3% errors
- Electricity only used in pressure adjusters.

HHV - corresponds to 25C
LHV - corresponds to 150C
HHV should be used for the energy balance

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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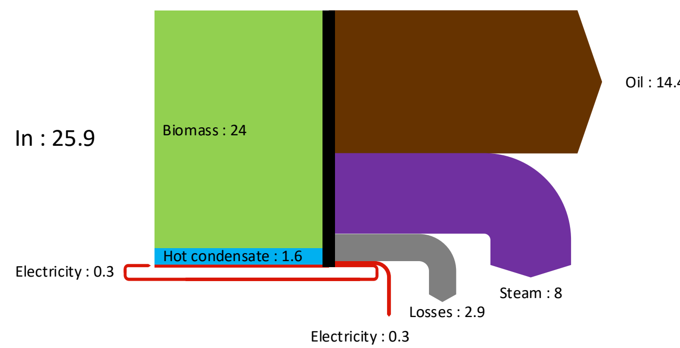
Energy balance comparison

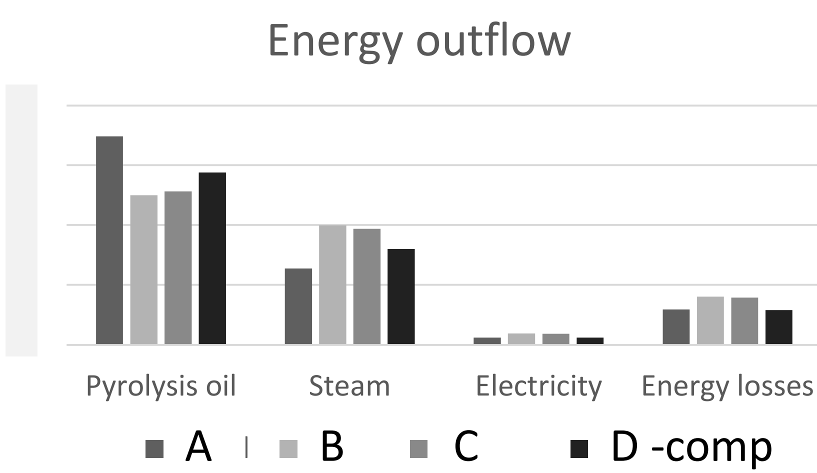
- Variation stoechiometries
  - Wood; straw; …
- Comparable with experimental data.

	A in	A out	B in	B out	C in	Cout	D in	D out
HHV	26.9	17.4	26.9	12.4	26.9	12.8	24	14.4
Steam	0.325	6.38	0.325	9.97	0.325	9.69	1.6	8.0
Electricity	0.109	0.607	0.169	0.949	0.169	0.922	0.3	0.6
Losses		2.95		4.03		3.94		2.9
Total	27.33	27.34	27.39	27.35	27.39	27.35	25.9	25.9

90%

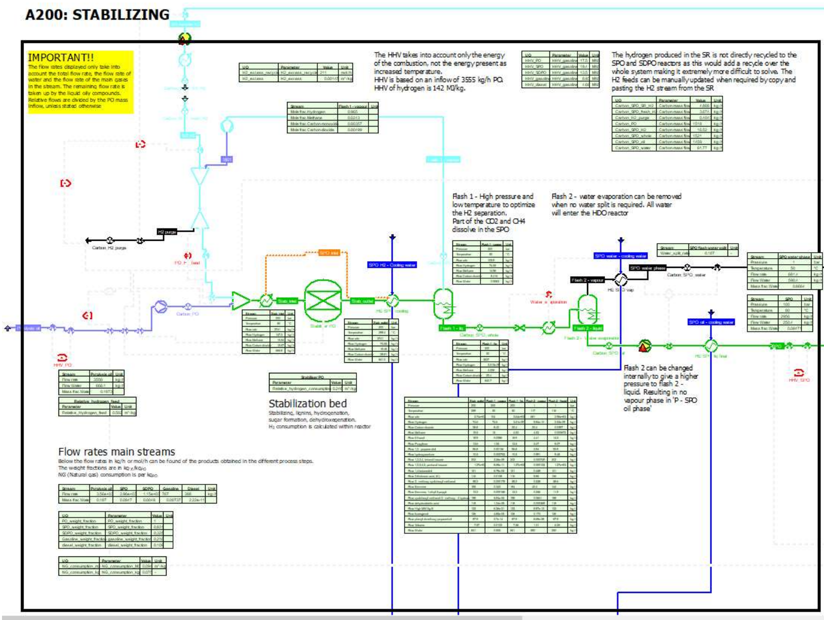
Pyrolysis energy flow, in MW with 5 ton/hr inflow.

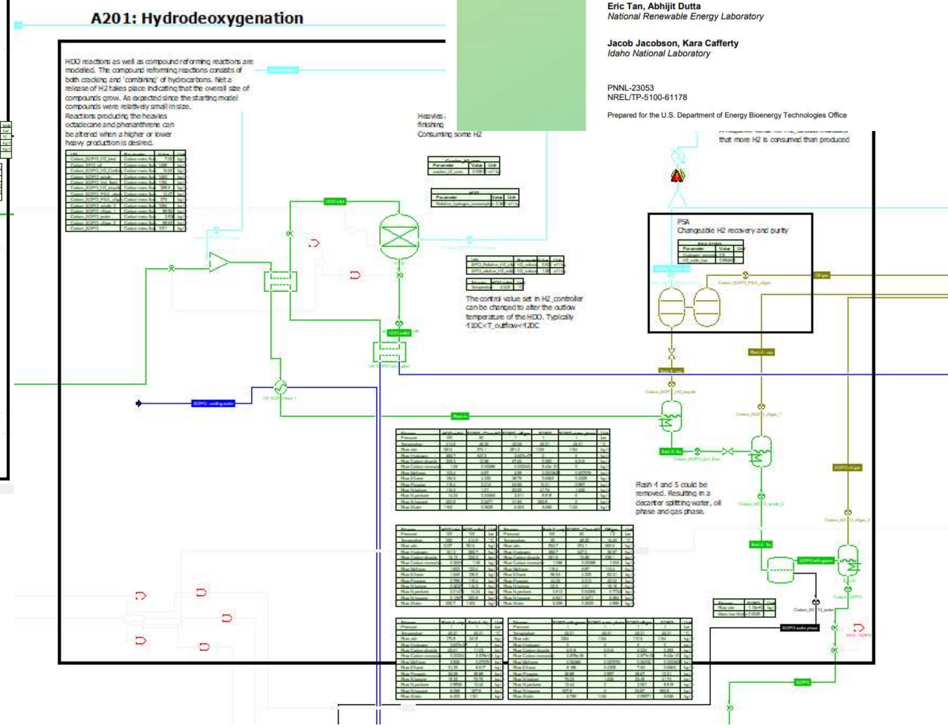


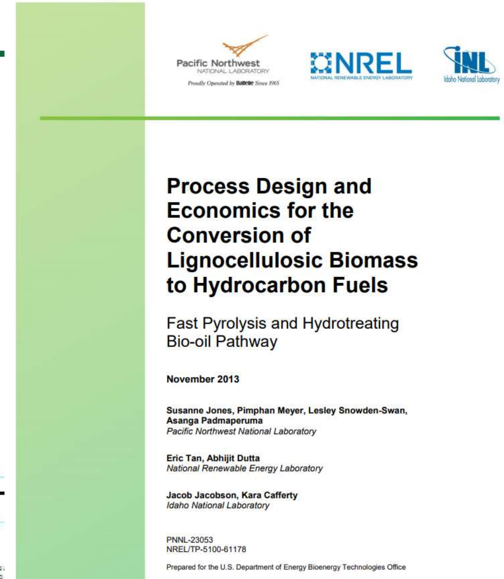


Graph 1: Pyrolysis energy flow, in MW with 5 ton/hr inflow.

Modelling further deoxygenation







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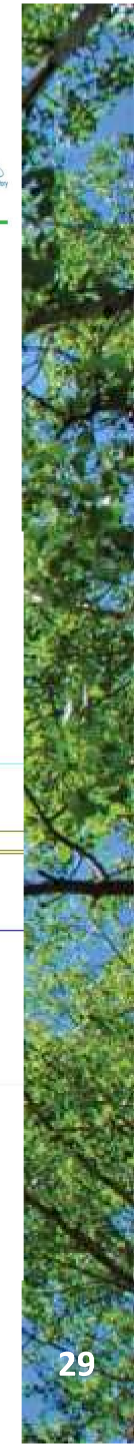

WASTE2ROAD

4refinery

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Take-home messages flow sheeting

Open resource /open access

For us COCO is a valuable **Freeware** tool for process modelling

- Understanding mass / energy balance
  - Component selection
  - Process flow diagram – iterative / recycling
- Data
  - Compiling
  - Analysis
  - Missing
  - 'Anchoring'
  - Documenting / **sharing**
- Improving overall process (also auxiliary equipment)

Engineering purposes

Provide the arguments so the potential clients will convince themselves

Garbage in = Garbage out !

Occam's razor

'entities should not be multiplied without necessity'
= 'the simplest explanation is usually the right one'

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Questions

Thanks for your attention

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