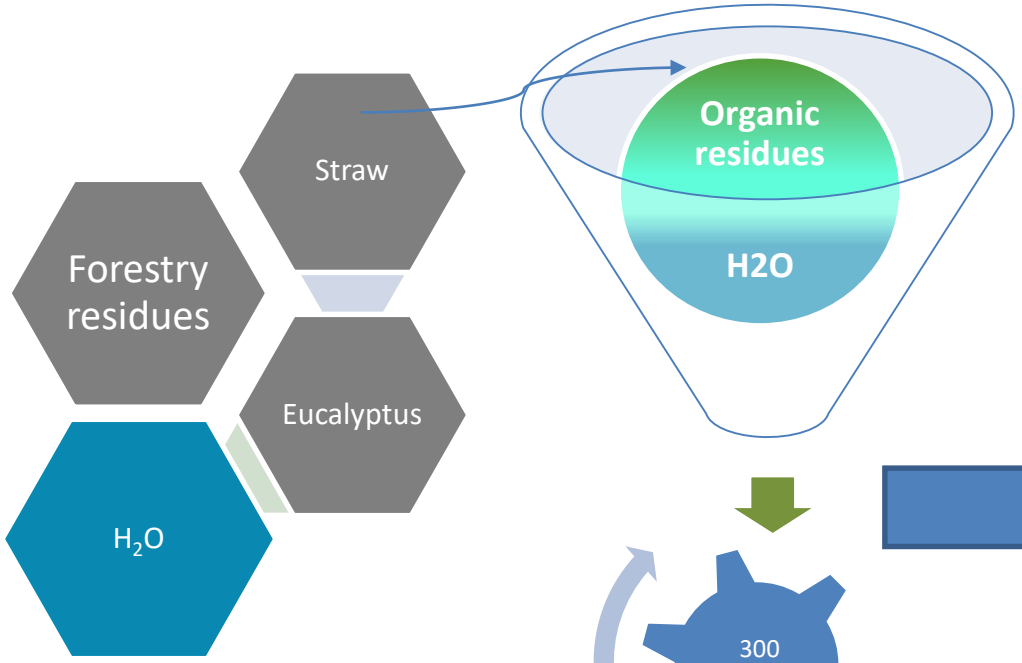
Modelling the hydrothermal liquefaction process

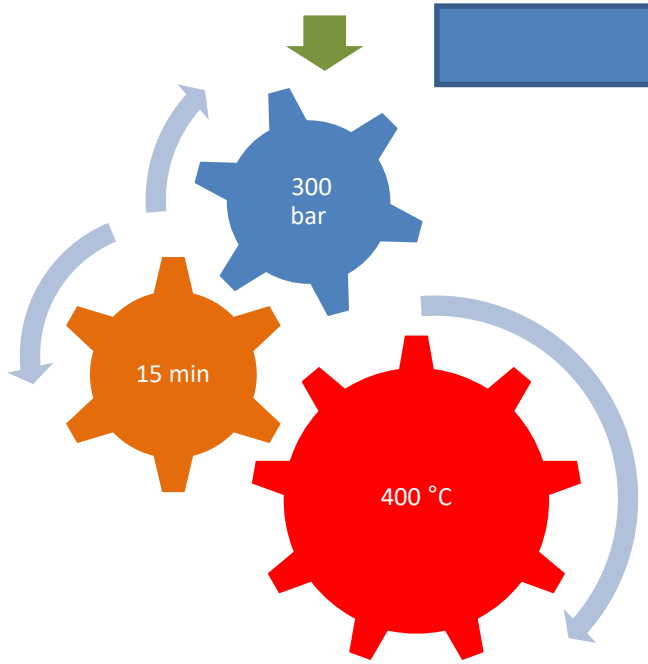
Associate professor Thomas Helmer, AAU, Denmark

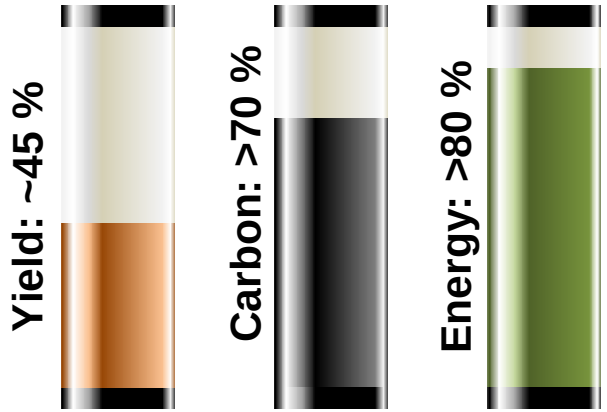
April 20nd 2021

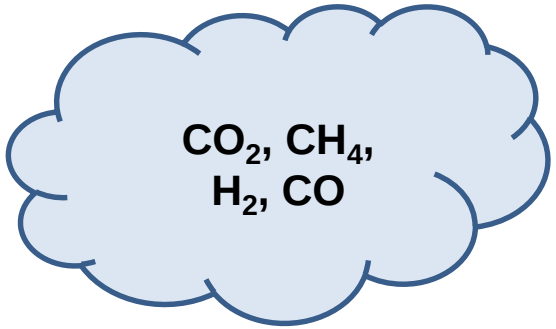
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 727531.

What is HTL – the simple version









Gas production

Char & nutrients

Mimics the natural process for crude oil production.

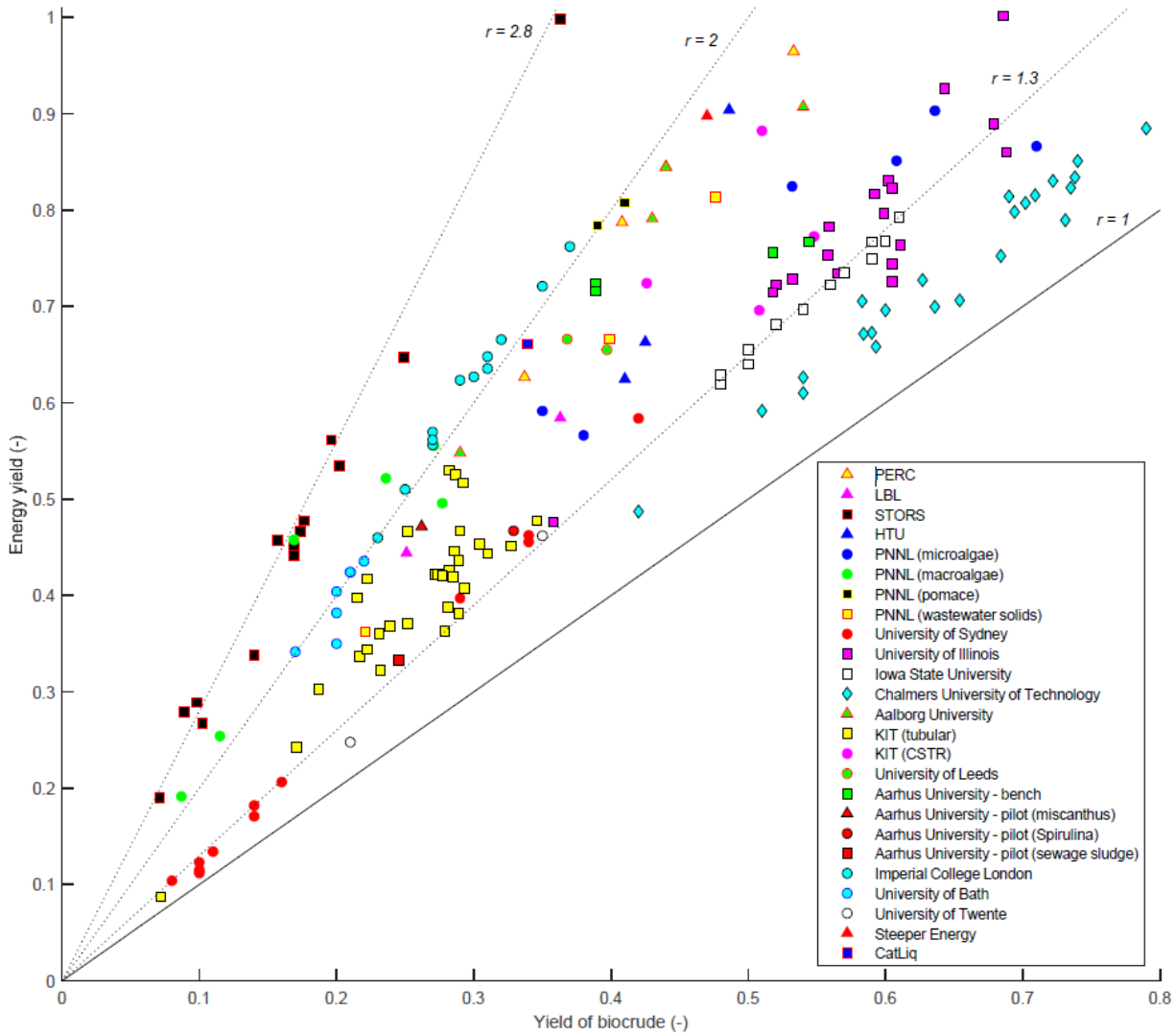
Time reduction: 100 mio. yrs vs. 15 min!

Biocrude ≠ crude oil

European Union's Horizon 2020 research and innovation programme, GA No. 727531

Biocrude yield and quality

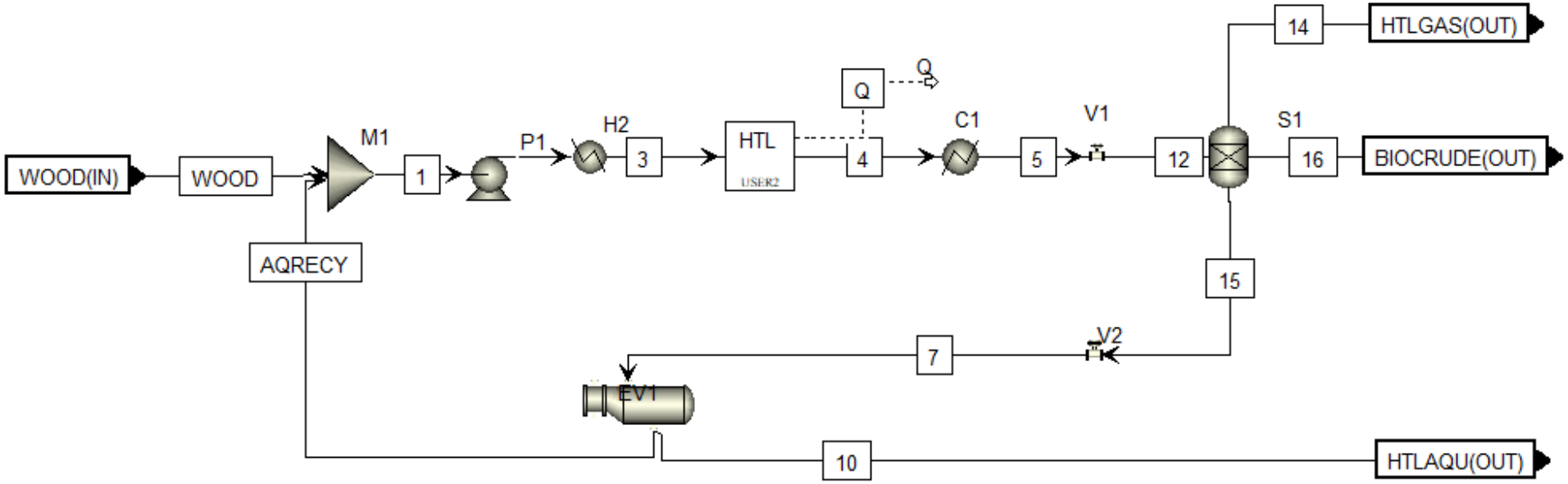
- Biocrude composition dedicated by the feedstock.
- Energy ratio, $\mathrm{r} = \frac{HHV_{bc}}{HHV_{feed}}$, follows iso-lines, determined by the feedstock
  - High HHV_{feed}; low energy ratio
  - Low HHV_{feed}; high energy ratio
- Yields can be greatly influenced by the process implementation



European Union's Horizon 2020 research and innovation programme, GA No. 727531

Energies 2018; doi:10.3390/en11113165

HTL process implementation

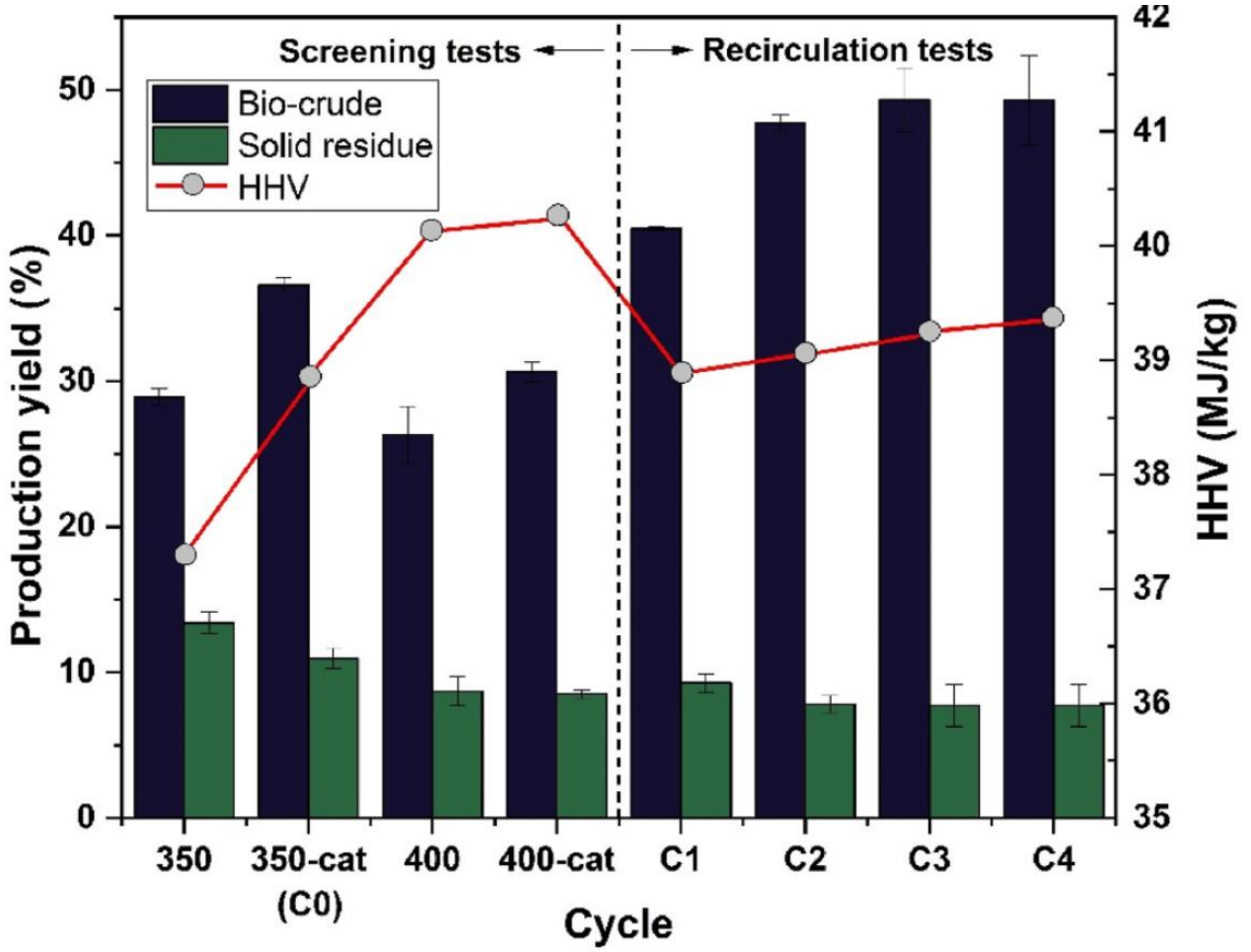


- Gas phase is combusted for internal heat recovery
- Bio-crude is demineralized and hydro-processed to fuels
- Aqueous organics can be recycled, waste water is processed by e.g. AD or HTG
- Important: Based on design data – HTL is not commercial!

European Union's Horizon 2020 research and innovation programme, GA No. 727531

Biocrude yield and quality

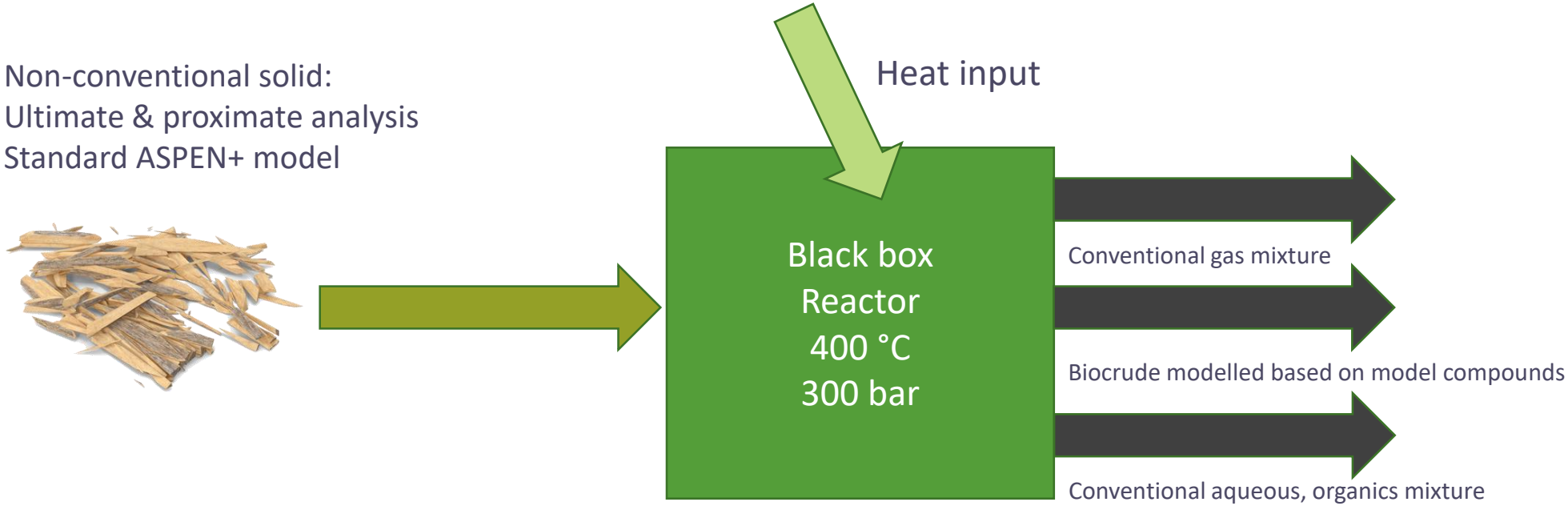
- Higher temperature, higher HHV
- Alkali agents (cat) increases carbon and mass yields
- Recirculating the aqueous phase organics increases biocrude yield.
- Energy recovery, $\mathrm{ER} = Y \cdot \frac{HHV_{bc}}{HHV_{feed}}$, governed by the biocrude yield



https://doi.org/10.1016/j.biombioe.2021.10603

HTL modelling in ASPEN+: General consideration in energy calculations

- The HTL chemistry of biomass is simply too complex to model!
- The pragmatic approach:



- *Yield approach*, eventually coupled with predictive yield models calibrated by experimental data.

European Union's Horizon 2020 research and innovation programme, GA No. 727531

Modelling of biomass (in ASPEN+)

- Non-conventional solid (coal based, approx. 140 samples)
- Enthalpy and density models need to be specified:

$$h_{wood}^{T,P} = h_f^0 + \Delta h = h_f^0 + C_p(T) \cdot \Delta T$$

  - Heat of formation
  - Heat capacity
  - *Heat of formation* via the *heat of combustion*

Option Code Number	Option Code Value†	Calculation Method	Parameter Names	Component Attributes
1 Heat of Combustion				
	1	Boie correlation	BOIEC	ULTANAL SULFANAL PROXANAL
	2	Dulong correlation	DLNGC	ULTANAL SULFANAL PROXANAL
	3	Grummel and Davis correlation	GMLDC	ULTANAL SULFANAL PROXANAL
	4	Mott and Spooner correlation	MTSPC	ULTANAL SULFANAL PROXANAL
	5	IGT correlation	CIGTC	ULTANAL PROXANAL
	6	User input value	HCOMB	ULTANAL PROXANAL
	7	Revised IGT correlation	CIGT2	ULTANAL PROXANAL

Option Code Number	Option Code Value†	Calculation Method	Parameter Names	Component Attributes
2 Standard Heat of Formation				
	1	Heat-of-combustion-based correlation	—	ULTANAL SULFANAL
	2	Direct correlation	HFC	ULTANAL SULFANAL PROXANAL COALMISC

Option Code Number	Option Code Value†	Calculation Method	Parameter Names	Component Attributes
3 Heat Capacity				
	1	Kirov correlation	CP1C	PROXANAL
	2	Cubic temperature equation	CP2C	—

Modelling of biomass

- Calculating the enthalpy of formation, $\Delta h_{f,biomass}^{0,daf}$

Stoichiometric balancing the complete combustion reaction:

$$C_\varphi H_\alpha O_\beta N_\gamma S_\delta + \left(\varphi + \frac{\alpha}{4} - \frac{\beta}{2} + \gamma + \delta\right) O_2 \rightarrow \varphi CO_2 + \frac{\alpha}{2} H_2O + \gamma NO_2 + \delta SO_2$$

Consider the energy energy:

$$HHV = \Delta h_{f,biomass}^{0} + \left(\varphi + \frac{\alpha}{4} - \frac{\beta}{2} + \gamma + \delta\right) \Delta_f h_{O_2}^{0} - \varphi \Delta_f h_{CO_2}^{0} - \frac{\alpha}{2} \Delta_f h_{H_2O}^{0} - \delta \Delta_f h_{SO_2}^{0} - \gamma \Delta_f h_{NO_2}^{0} \left[\frac{J}{kg}\right]$$

Isolating and converting from molar to mass basis:

$$\Delta h_{f,biomass}^{0,daf} = HHV^{daf} - \left(3{,}278 * 10^5 \, w_C^{daf} + 1{,}418 * 10^6 w_H^{daf} + 9{,}264 * 10^4 \, w_S^{daf} - 2{,}418 * 10^4 \, w_N^{daf}\right) * 10^2 \left[\frac{J}{kg}\right]$$

European Union's Horizon 2020 research and innovation programme, GA No. 727531

Modelling of biomass

- Indirect methods in ASPEN+:

$$\Delta h_{f,biomass}^{0,daf} = HHV^{daf} - \left(3{,}278 * 10^5\, w_C^{daf} + 1{,}418 * 10^6 w_H^{daf} + 9{,}264 * 10^4\, w_S^{daf} - 2{,}418 * 10^4\, w_N^{daf}\right) * 10^2 \left[\frac{J}{kg}\right]$$

  - HHV is estimated from multiple empirical correlations, e.g. BOIE or DULONG formula

- Direct methods in ASPEN+:

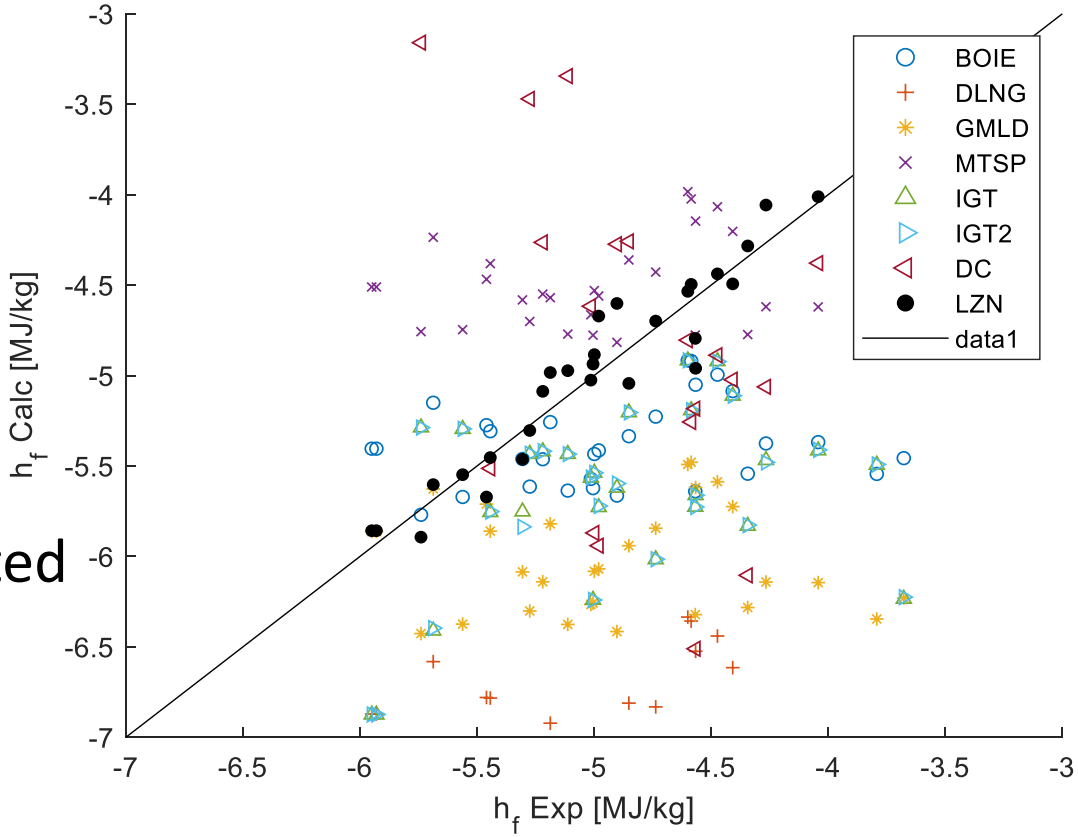
$$\Delta h_f^{0,daf} = \left[\left(a_1 w_C^{dm} + a_2 w_H^{dm} + a_3 w_H^{d}\right)10^2 + \left(a_4\left(w_C^{d} - w_{FC}^{d}\right) + a_5 w_{VM}^{d}\right) 10^2\right.$$

- $\Delta h_{f,biomass}^{0}$ is estimated from proximate and ultimate analysis, solely, from an empirical correlation.

European Union's Horizon 2020 research and innovation programme, GA No. 727531

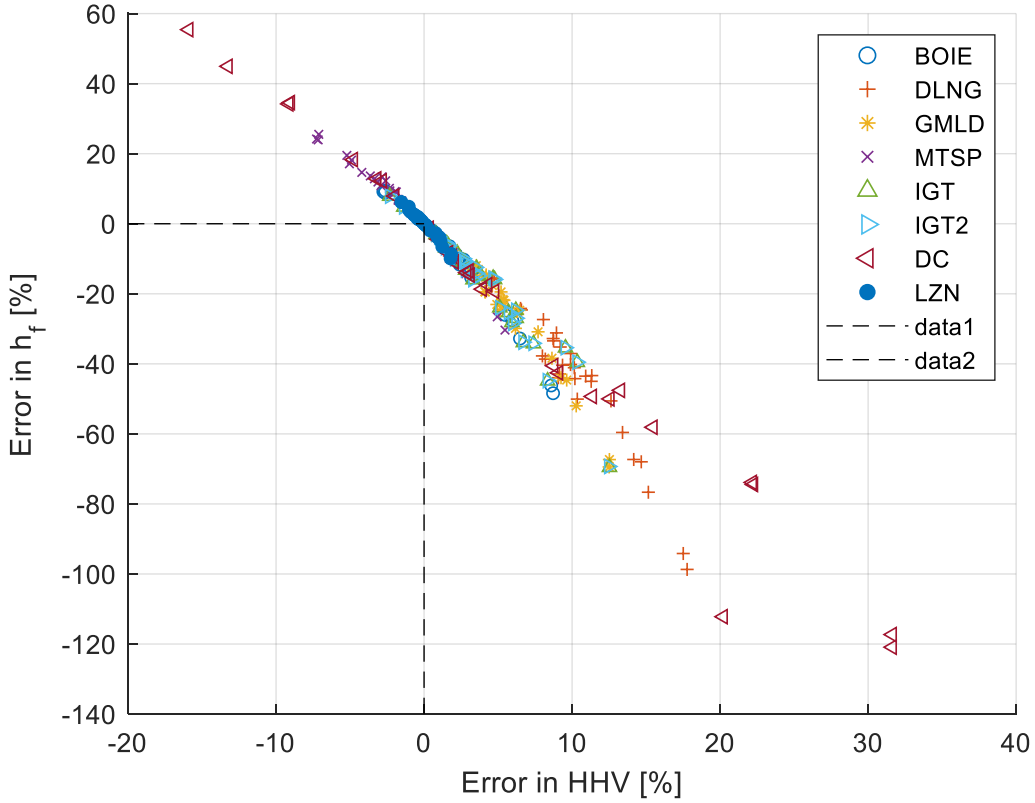
Modelling of biomass

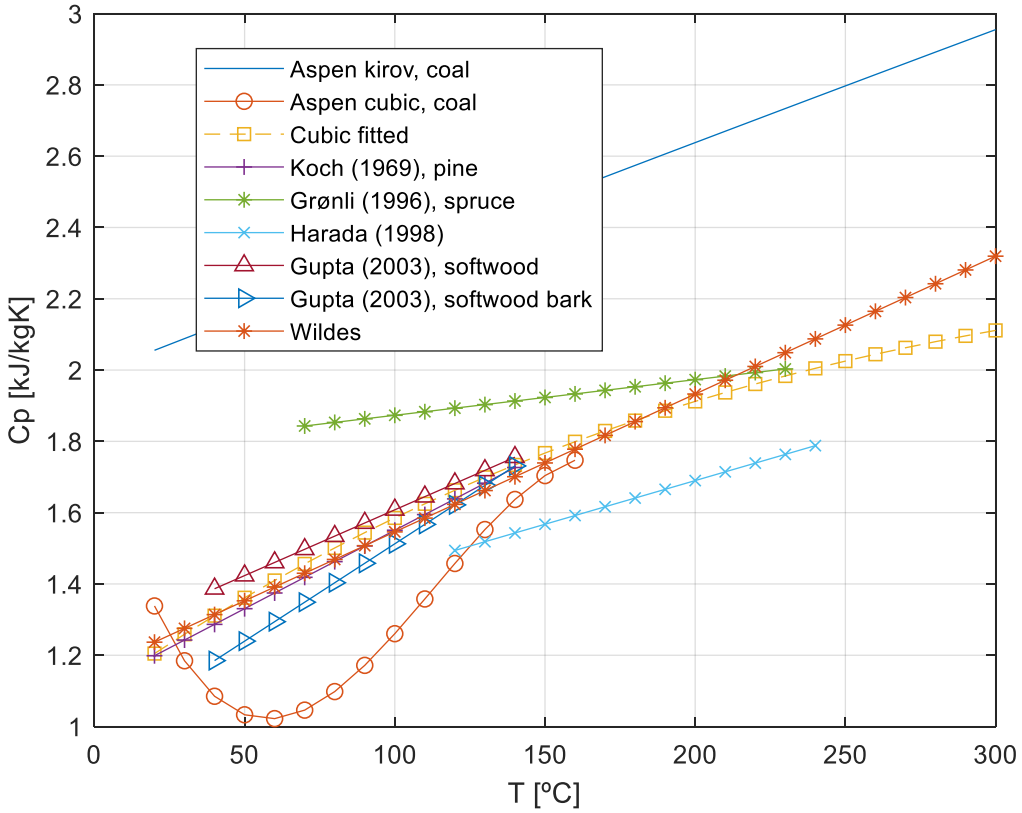
- Verification using 20 different wood samples (Phyllis data base)
- All direct and indirect methods perform unsatisfactory.
- The solution: Fit your own *direct method!*
- Note: Correlation parameters can easily be imported to ASPEN+.



10.1016/J.APENERGY.2019.113654

Modelling of biomass





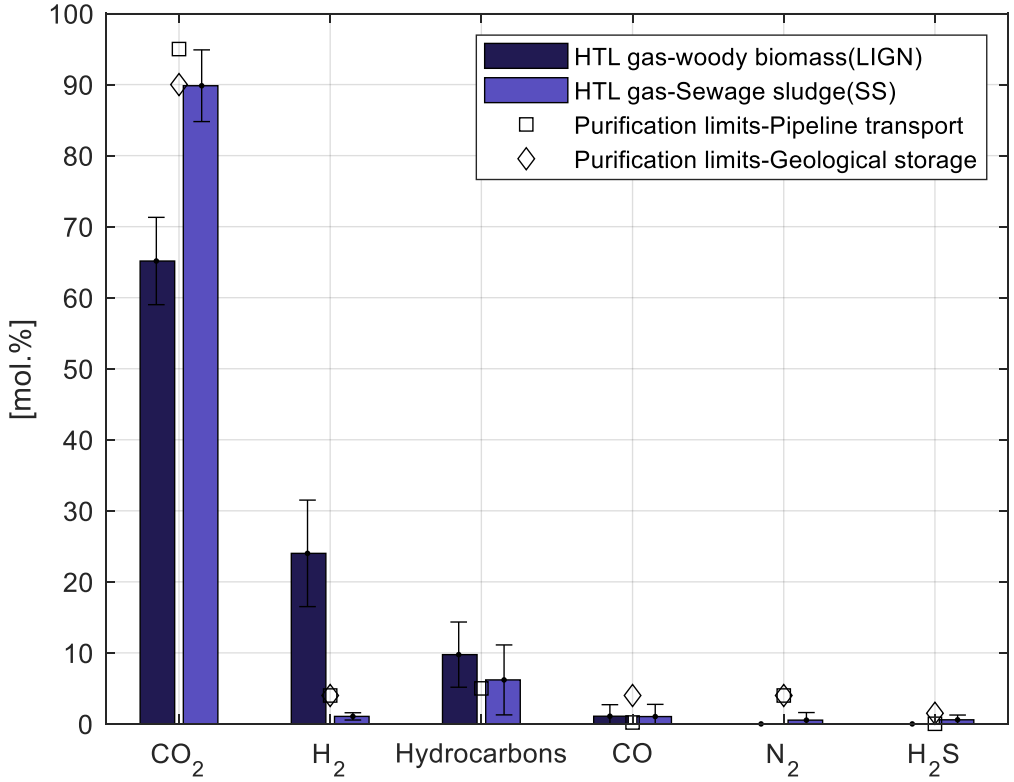
- Specific heat capacity of wood is NOT accurately calculated by the standard ASPEN+ correlation

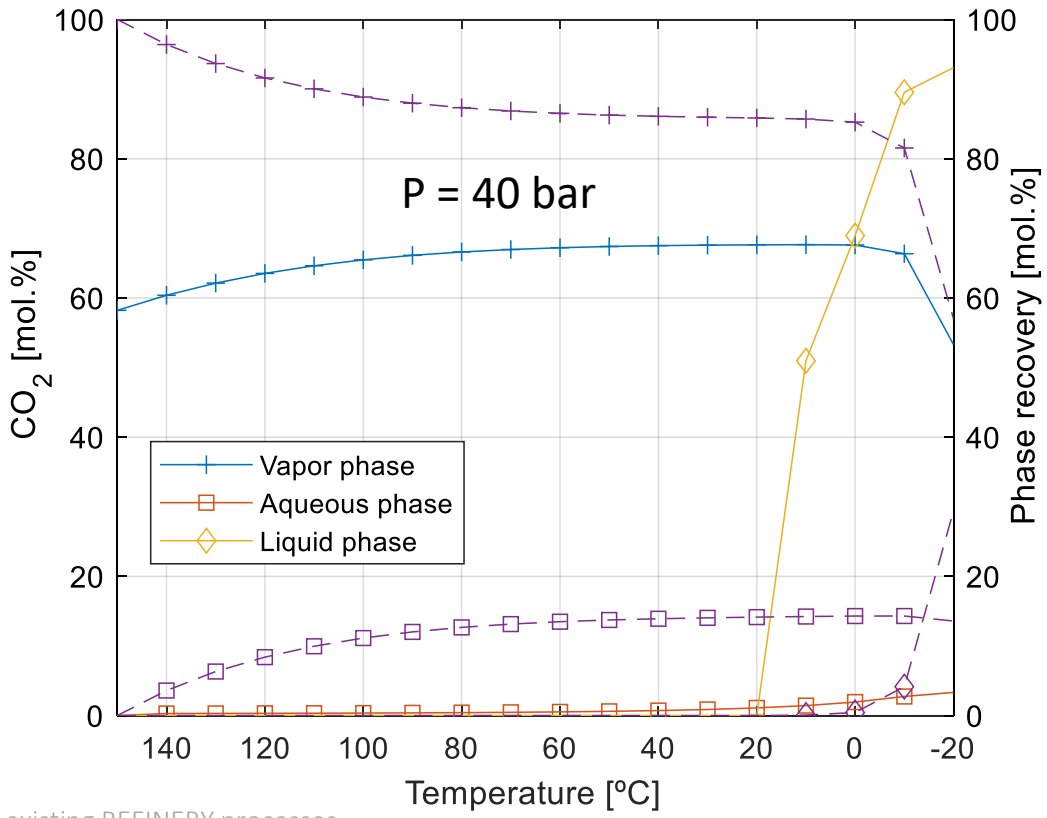
$$\mathrm{h}_{\mathrm{wood}}^{\mathrm{T,P}} = \mathrm{h}_f^0 + \Delta h = \mathrm{h}_f^0 + C_p(T) \cdot \Delta T$$

European Union's Horizon 2020 research and innovation programme, GA No. 727531

Gas phase considerations

- The gas phase is mainly CO_2. Modelled by a cubic equation or similar.
- Note; gas cooling at high pressure can initiate a VLE-situation.





European Union's Horizon 2020 research and innovation programme, GA No. 727531

Modelling of HTL biocrude

- Biocrude modelling is typically by a model cpound approach
- ”Finger printing” the biocrude by e.g. GC-MS analysis has limitations.

	mg/g of biocrude	Norm. Mass fraction
2-Cyclopenten-1-one, 2,3-dimethyl-	1.13	2.2%
Phenol	0.92	1.8%
2-Cyclopenten-1-one, 3,4,4-trimethyl-	1.27	2.5%
Caproic acid	0.50	1.0%
2-Cyclopenten-1-one, 3,4,4-trimethyl-	1.13	2.2%
2-Cyclopenten-1-one, 2,3,4,5-tetramethyl-	0.52	1.0%
2-Methylphenol	1.02	2.0%
Phenol, 4-methyl	2.29	4.5%
Heptanoic acid	0.91	1.8%
2,5-Dimethylphenol	1.07	2.1%
2,3-Dimethylphenol	2.76	5.4%
Phenol, 2,6-dimethyl	1.28	2.5%
Octanoic acid	1.09	2.1%
4-methyl catechol	7.20	14.1%
Benzeneacetic acid, 3-hydroxy	2.94	5.8%
Palmitic acid	4.92	9.6%
Myristic acid	2.38	4.7%
Octadecanoic acid	8.53	16.7%
SUM =	51.00	100%
% identified of the whole biocrude	**5%**	-

Modelling objectives

Bulk biocrude — Sum of model compounds

$$\mathrm{HHV_{exp}} - \sum_{i=1}^{n} x_i \, \mathrm{HHV_i} = 0$$

$$\mathrm{C(wt\%)} - \sum_{i=1}^{n} x_i \, \mathrm{C_i(wt\%)} = 0$$

$$\mathrm{H(wt\%)} - \sum_{i=1}^{n} x_i \, \mathrm{H_i(wt\%)} = 0$$

$$\mathrm{O\ (wt\%)} - \sum_{i=1}^{n} x_i \, \mathrm{O_i(wt\%)} = 0$$

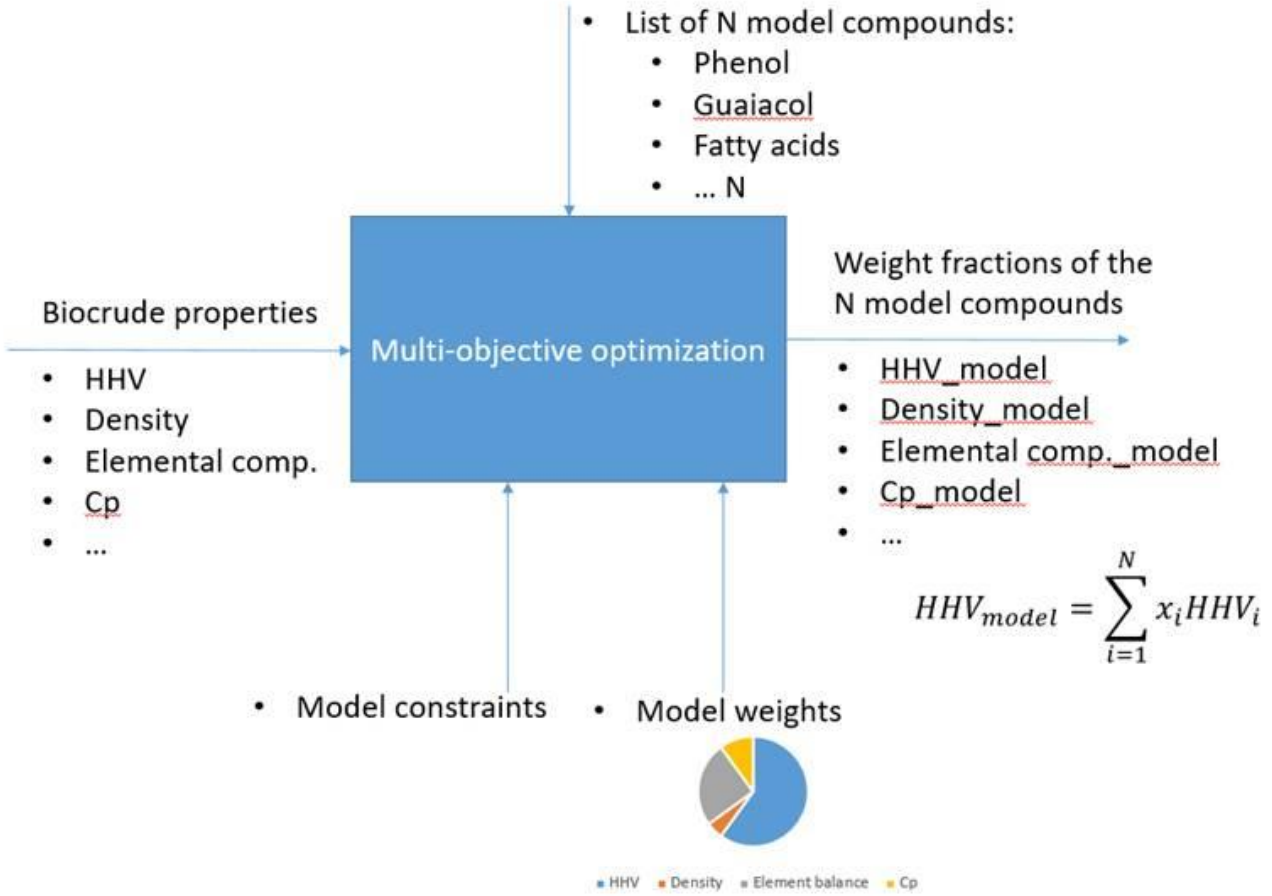
$$\rho_{exp} - \sum_{i=1}^{n} x_i \, \rho_{,i} = 0$$

$$\mathrm{Cp_{exp}} - \sum_{i=1}^{n} x_i \mathrm{C_p} = 0$$

European Union's Horizon 2020 research and innovation programme, GA No. 727531

Modelling of HTL biocrude

- Model compounds approach – selection of compounds



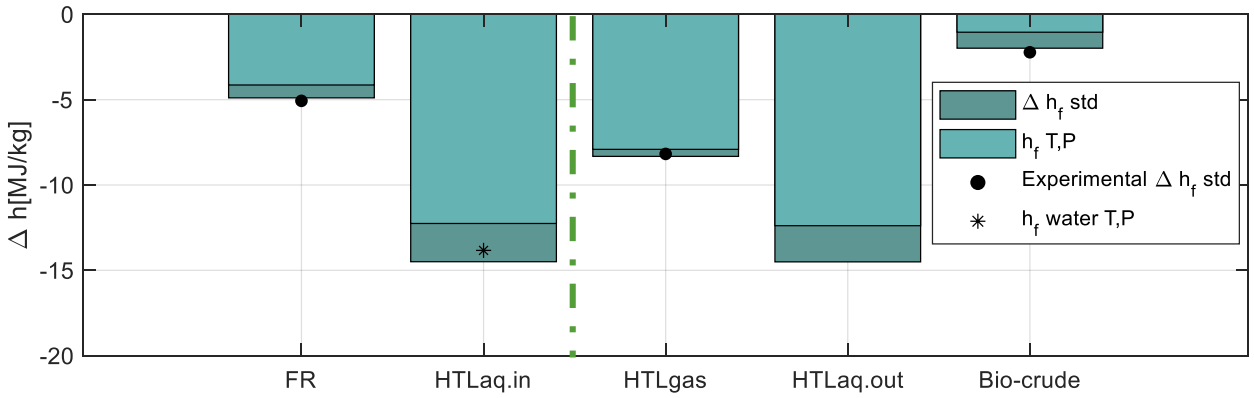
	Δh_f [MJ/kg]	HHV [MJ/kg]	C [wt.%] (daf)	H [wt.%] (daf)	O [wt.%] (daf)	Density [kg/m3]
Reference	-2.22	35.90	80.00	8.40	11.00	1050.67
Initial values	-2.69	34.04	72.46	9.15	18.38	1007.19
Relative error [%]	**20.99**	**5.18**	**9.42**	**8.95**	**67.12**	**4.14**
Optimized (equal weights)	-2.24	37.75	77.16	10.36	12.48	1051.63
Relative error [%]	**0.83**	**5.14**	**3.55**	**23.36**	**13.41**	**0.09**
Optimized (Δh_f hard constraint)	-2.22	37.39	76.39	10.28	13.34	1047.83
Relative error [%]	**0.00**	**4.15**	**4.52**	**22.37**	**21.23**	**0.27**

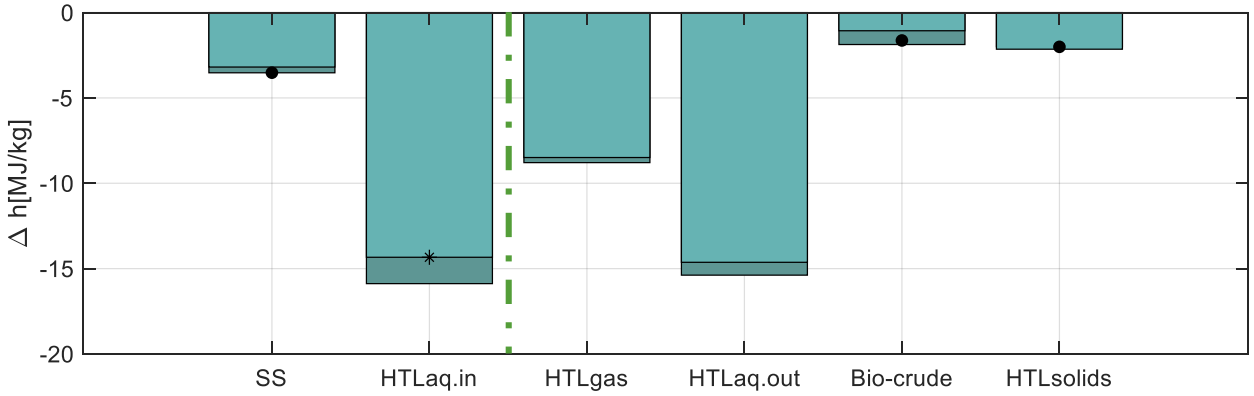
The optimization routine is freely available from the authors:

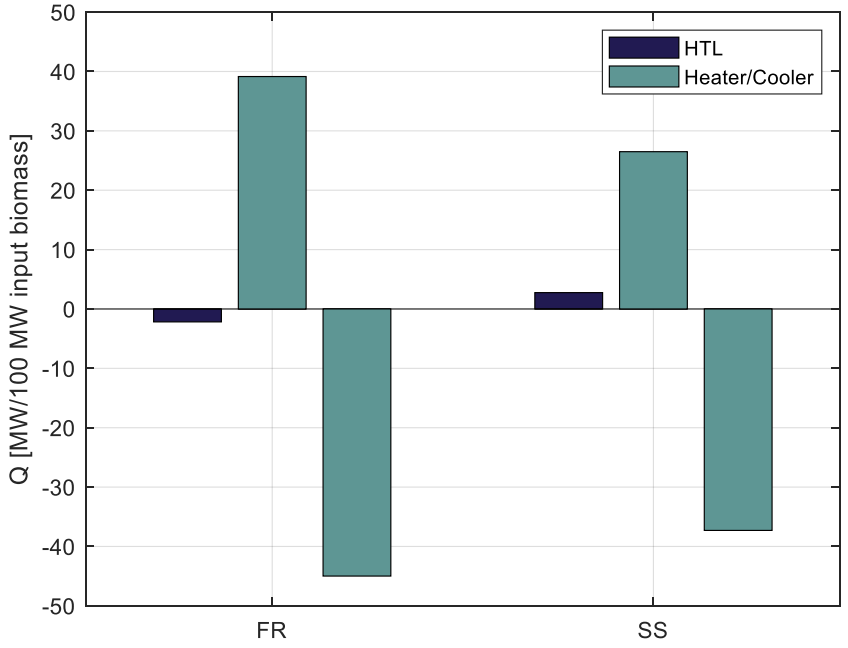
Sanchez, E. M. L., Rosendahl, L., & Pedersen, T. H. (2019). Modeling of thermochemically liquefied biomass products and heat of formation for process energy assessment. *Applied Energy*

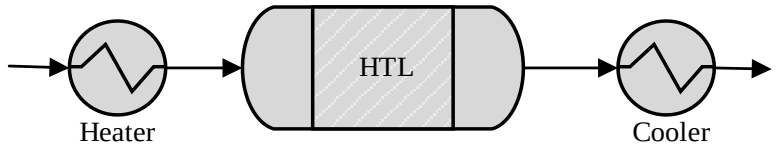
European Union's Horizon 2020 research and innovation programme, GA No. 727531

Some modelling results and considerations



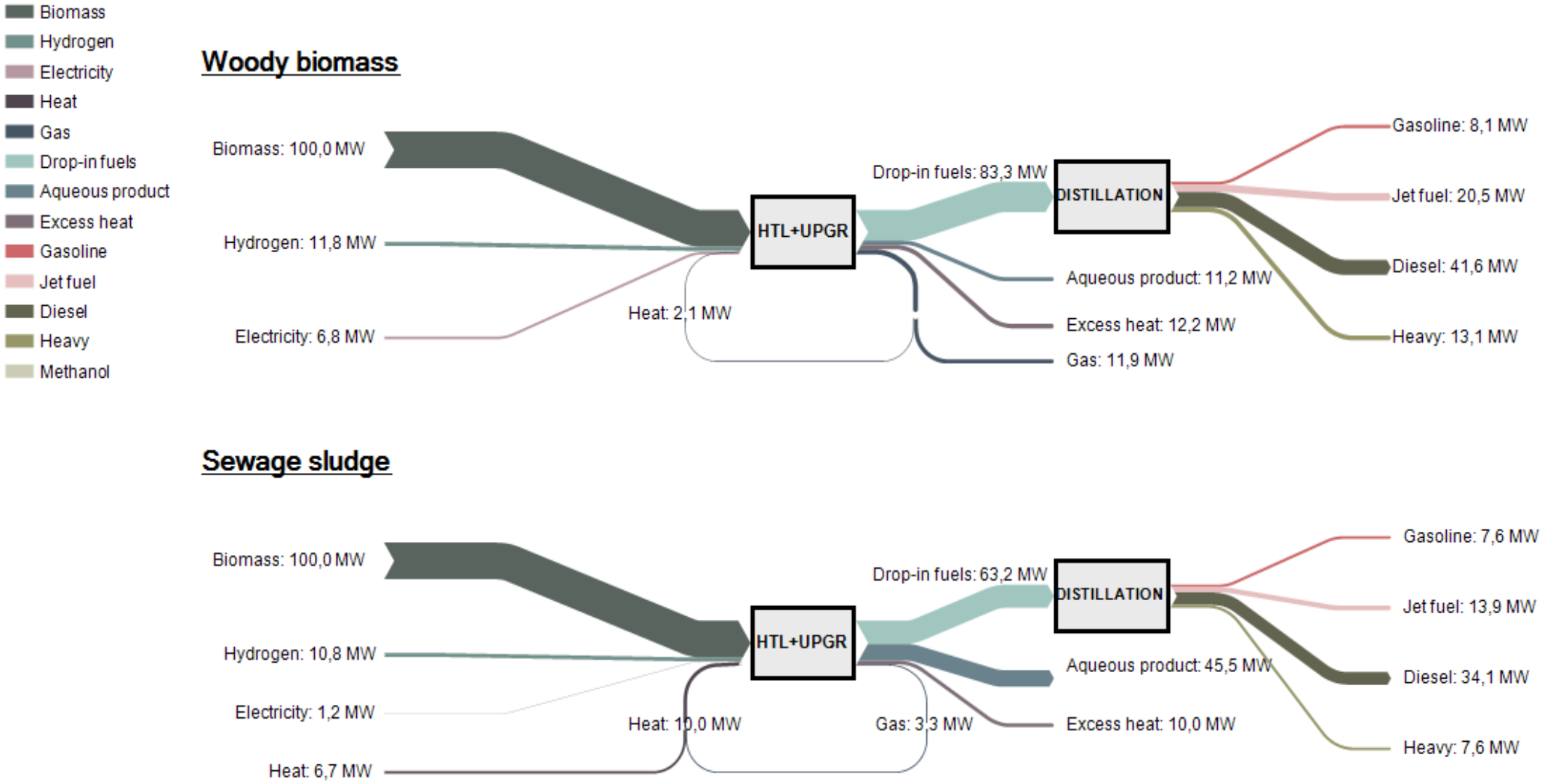






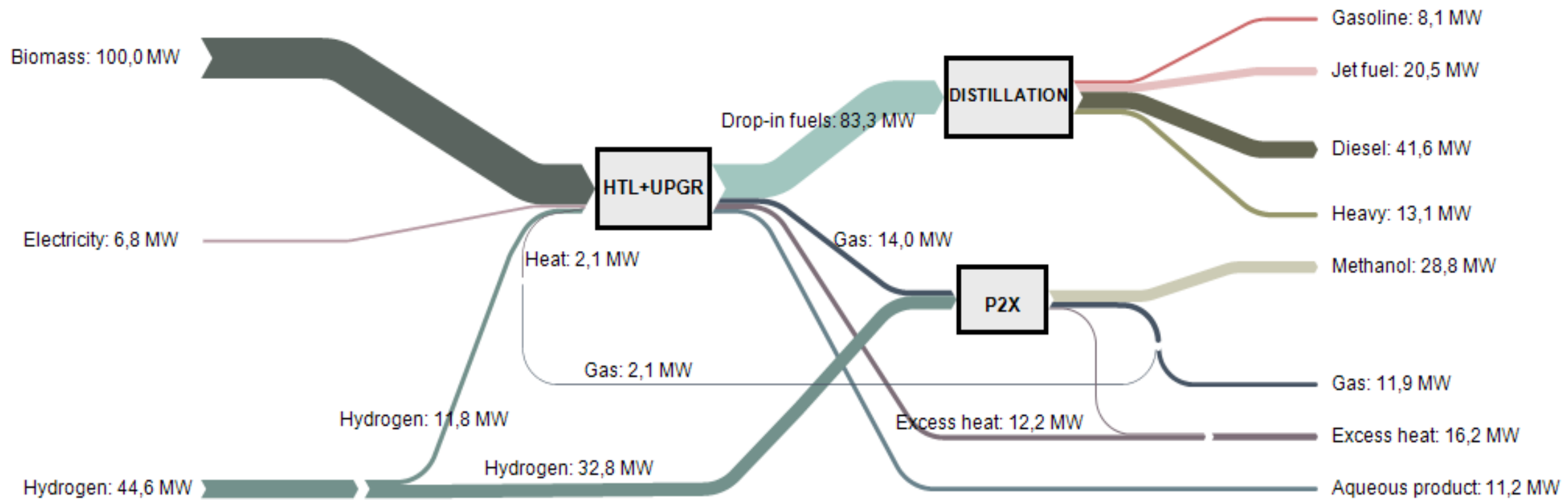
European Union's Horizon 2020 research and innovation programme, GA No. 727531

Case study: HTL integrated with refineries



Case study: HTL integrated with refineries

HTL + eFuels (woody biomass)



European Union's Horizon 2020 research and innovation programme, GA No. 727531

Wrapping up

- The *non-conventional solid* approach is feasible for biomass modelling with fitted correlation parameters.
- Accurate enthalpy of formation calculations are of high importance.
- Cp correlations should be used with care. Always verify with experimental data.
- The *model compounds* approach with optimized bio-crude composition can accurately model bio-crude properties.
- Also be critical to your model results. ☺

European Union's Horizon 2020 research and innovation programme, GA No. 727531

Thank you for your attention!

Contact: thp@et.aau.dk

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 727531.