Fast Pyrolysis Of Biomass With Catalytic Vapor Phase Upgrading: Process Design, Optimization, And Integration

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Outline

- Introduction and objective
- Catalytic vapor phase upgrading
- Experimental and results
- Modeling and integration
- Conclusion

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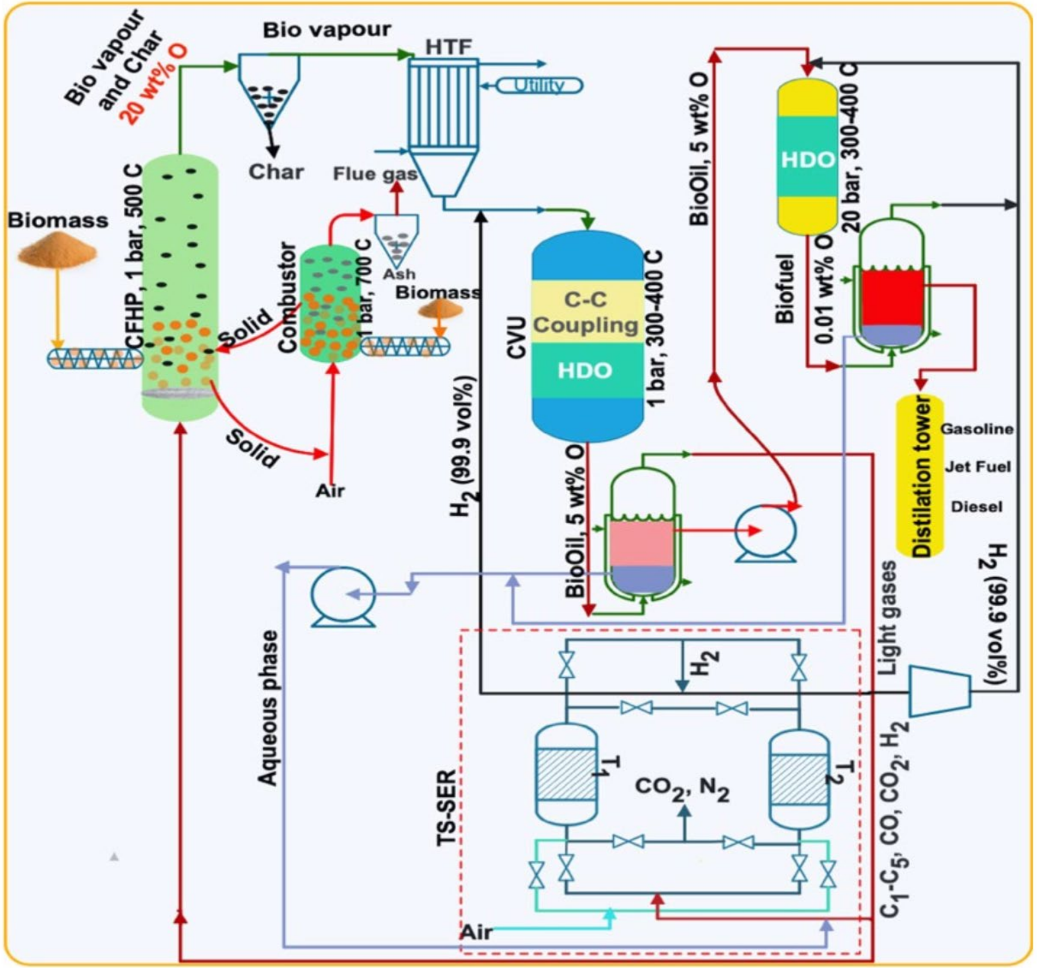
Objective

- Improve the pyrolysis and catalytic vapor phase upgrading part of the B2A process.
- Produce raw bio-oil with as little oxygen content as possible
- Start: 40 %
- Goal: 5 %
- Currently: 20 %



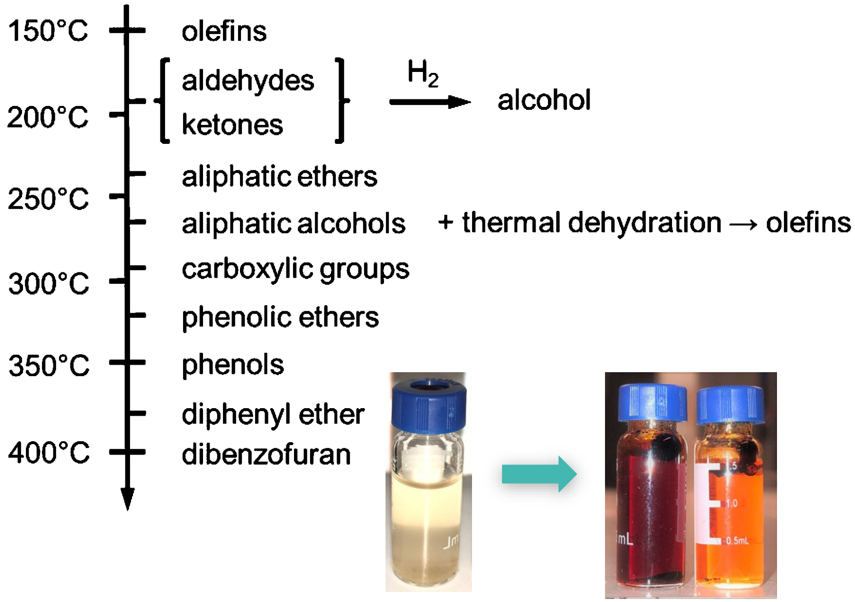
Objective

- Develop catalyst and process to increase the hydrocarbon oil yield for jet fuel production through incorporating vapor phase upgrading to fast pyrolysis.
  - Convert reactive oxygenates to hydrocarbons through carbon coupling reactions
  - Study the effect of reaction parameters and catalyst properties
- Develop model
  - Process design synthesis
  - Techno-economic evaluations
  - Test new technologies and sensitivity analyses

Why catalytic vapor phase upgrading?

- Pyrolysis vapor contains 100s of reactive oxygenates, soluble in the aqueous phase.
- Unstable compounds leads to polymerization and phase separation.
- Selected carbon coupling reactions will increase the yield for the oil phase
- Low pH of the liquid leads to corrosion issues and chemical instability.
- The compounds are thermodynamically unstable.

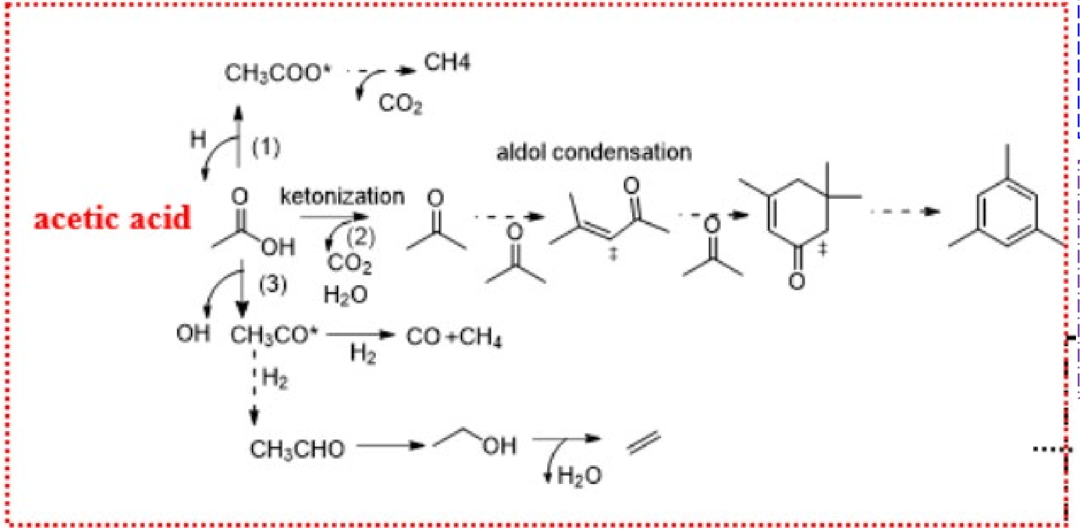
Carboxylic acid, alcohols, aldehydes, ketones +.

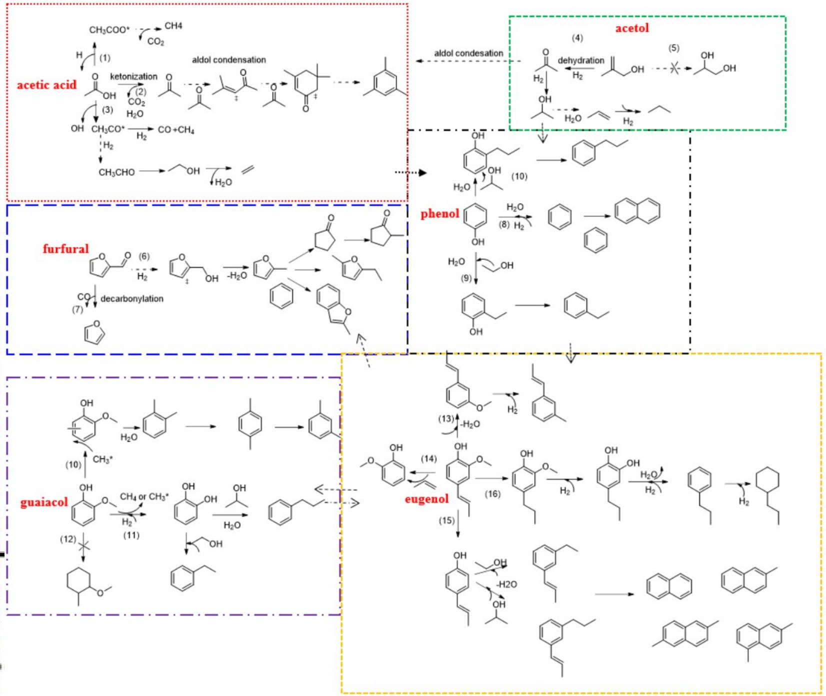


Green Chem., 2018, **20**, 567-582

Why catalytic vapor phase upgrading?

Incorporation of CVU improves the fuel carbon yield of the process. Oxygenates polymerize and does not end up in gas phase





The rig and experimental setups

- Online gas analysis
- Liquid sample collection
- Two-reactor setup
  - Fluidized bed
  - Fixed bed
  - 500 g/h capacity

Materials and methods

- Fluidization gas
  - 60 % H_2, 40 % N_2.
- In-house Catalyst pellets
  - Pt/TiO2, anatase, 1 wt% Pt, d_{Pellet}=3 mm
- Biomass feedstock
  - Beechwood sawdust mixture, 250 – 500 µm
  - Composition [wt%]: C 51.7, H 6.3, O 41.5, Ash 0.5
  - Bone dry

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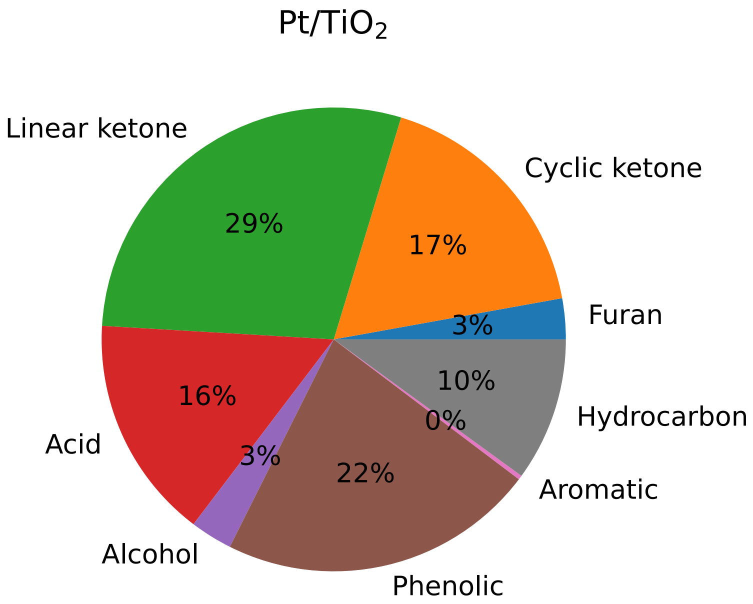
Results from the catalyst – yields

- Gas – 25 wt%
- Solid – 14 wt%
- Water – 11 wt%
- Oil – 50 wt%

- Oil properties:
  - C: 70 %, H: 10 %, O: 20 %



10 g/h Beechwood, 20 g catalyst, 1.5 l/min H_2, 1.0 l/min N_2. Pyrolysis reactor 500 °C, fixed-bed reactor 400 °C. duration 6 h.

From experimental to modeling

- The most efficient catalyst system was implemented in a ASPEN Plus model to scale the production.
- The plant was cost estimated and sensitivity analyses were run to pin-point the most sensitive areas.
- The plant was heat integrated using ASPEN Energy Analyzer
- Byproducts were studied.

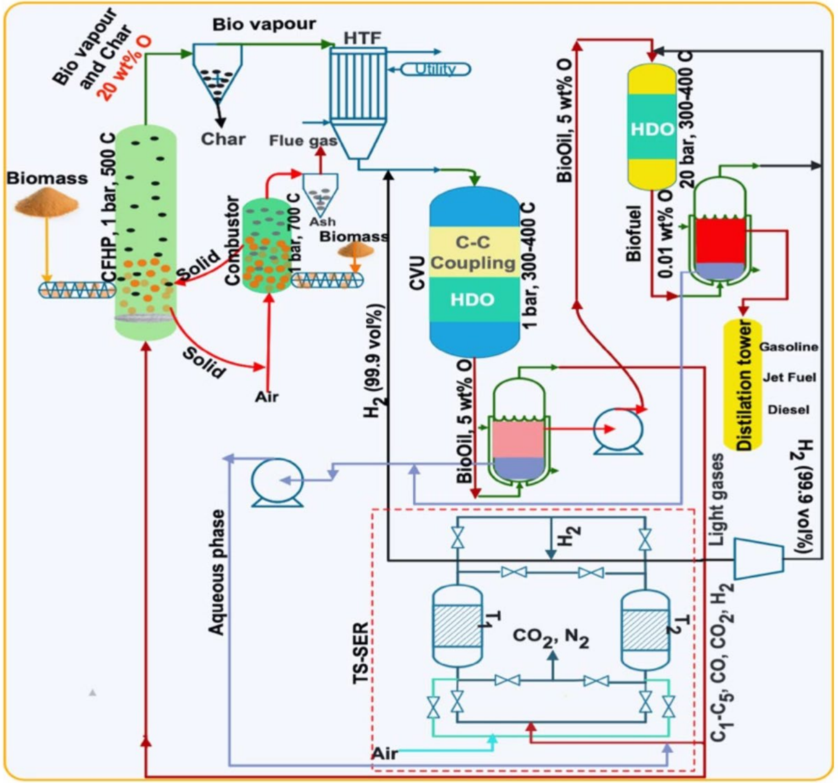
Model challenges

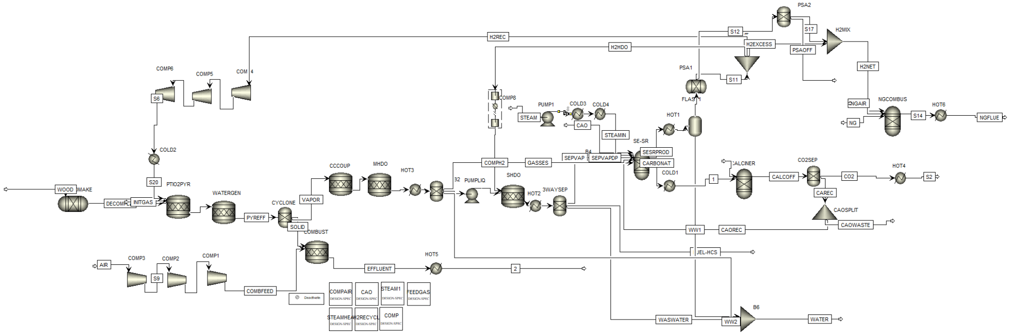
- Due to varied nature of pyrolysis, high resolution modeling is difficult
- The solid compounds are non-conventional materials. Ash, Char, coke and biomass
- Lack of thermodynamic fluid package to accurately describe the system.

Model development

- Modeled using Aspen PLUS and Aspen Energy Analyzer.
- The model has 45 conventional compounds and 3 non-conventional compounds.
- Beechwood was used as biomass feedstock
- Validated against experimental results from several groups.
- Scaled on 2 000 t/h biomass

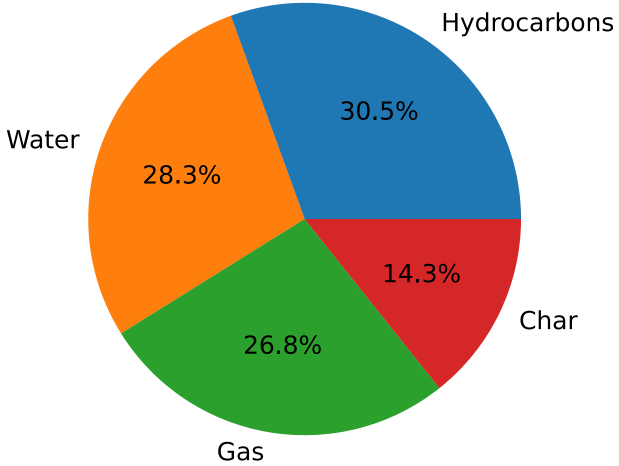
The model

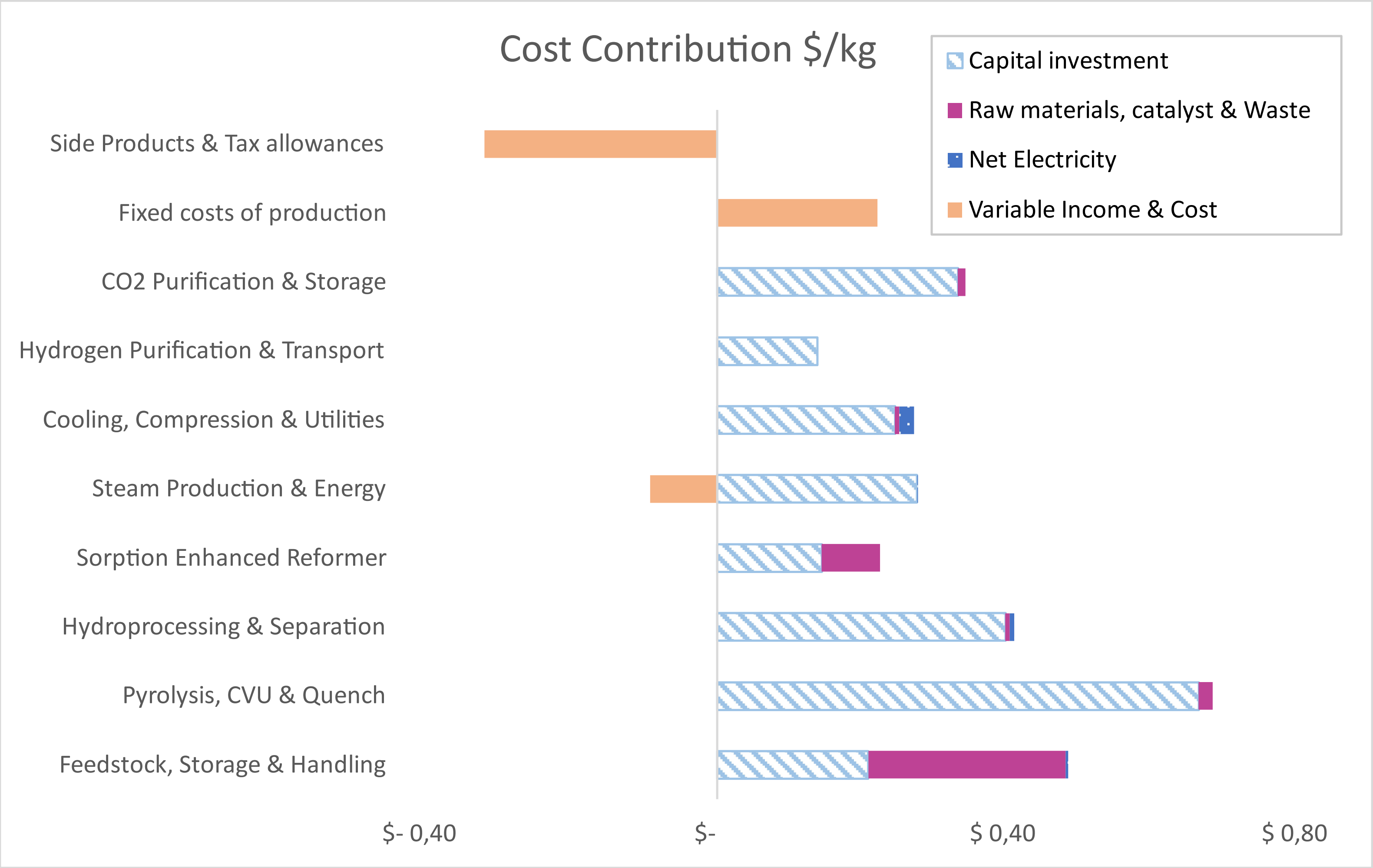

Bio vapour and Char
20 wt% O
Bio vapour
HTF
Utility
Char
Flue gas
Biomass
CFHP, 1 bar, 500 C
Combustor
1 bar, 700 C
Ash
Biomass
Solid
Solid
Air
C-C Coupling
HDO
CVU
1 bar, 300-400 C
BioOil, 5 wt% O
HDO
20 bar, 300-400 C
Biofuel
0.01 wt% O
BioOil, 5 wt% O
Distillation tower
Gasoline
Jet Fuel
Diesel
H2 (99.9 vol%)
H2 (99.9 vol%)
Aqueous phase
Light gases
C1-C5, CO, CO2, H2
TS-SER
H2
T1
T2
CO2, N2
Air



Efficiency and yield calculations

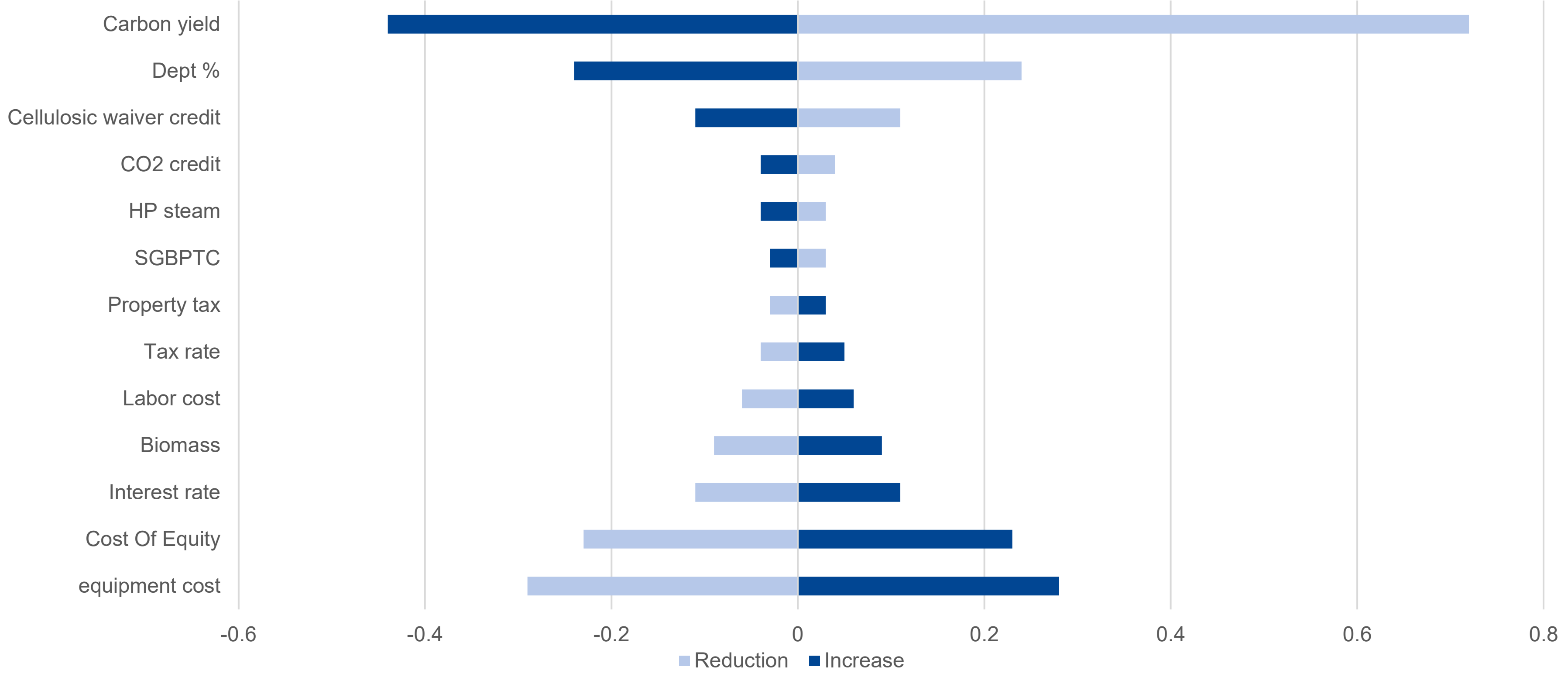
- $\eta_{Energy} = \frac{Q_{HC}+Q_{H_2}+Q_{Steam}}{Q_{Biomass}+Q_{Heat}+W}$
- $\eta_{Energy} = 87\ \%$
- $\eta_{Carbon} = 52\ \%$





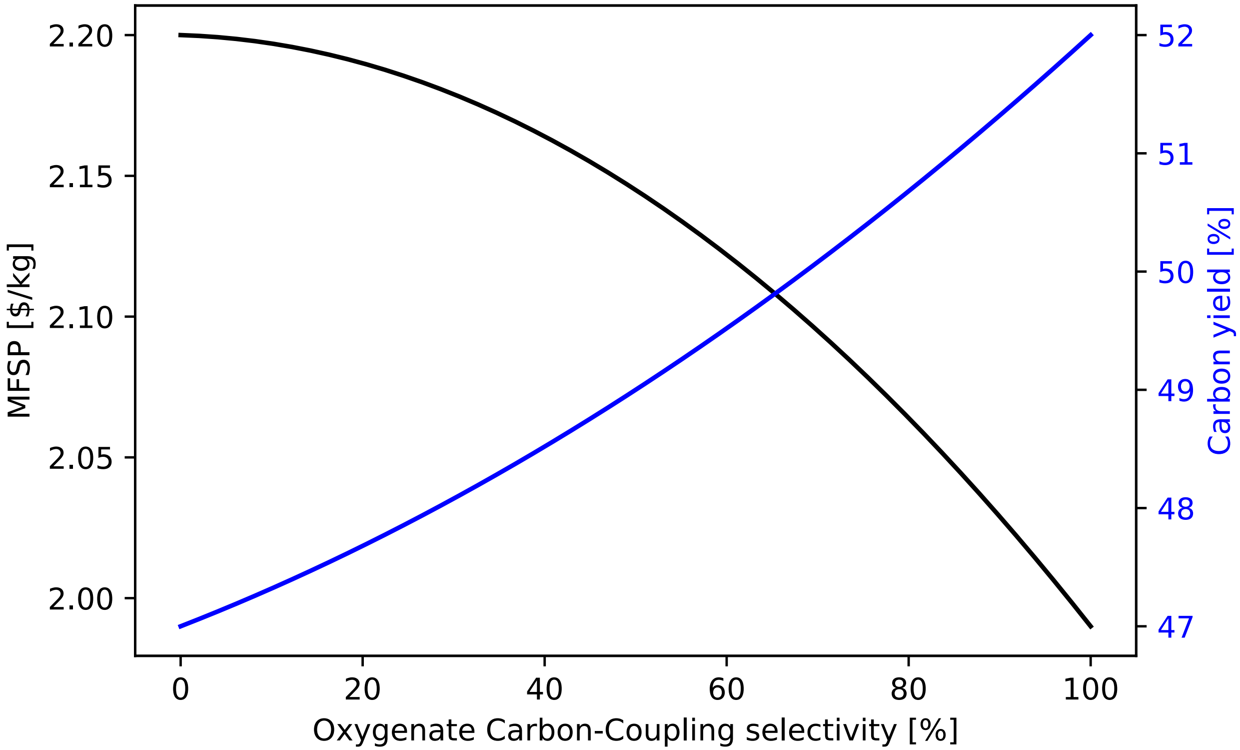
Cost Contribution $/kg
Capital investment
Raw materials, catalyst & Waste
Net Electricity
Variable Income & Cost
Side Products & Tax allowances
Fixed costs of production
CO2 Purification & Storage
Hydrogen Purification & Transport
Cooling, Compression & Utilities
Steam Production & Energy
Sorption Enhanced Reformer
Hydroprocessing & Separation
Pyrolysis, CVU & Quench
Feedstock, Storage & Handling
$- 0,40
$-
$ 0,40
$ 0,80

Cost sensitivity analysis

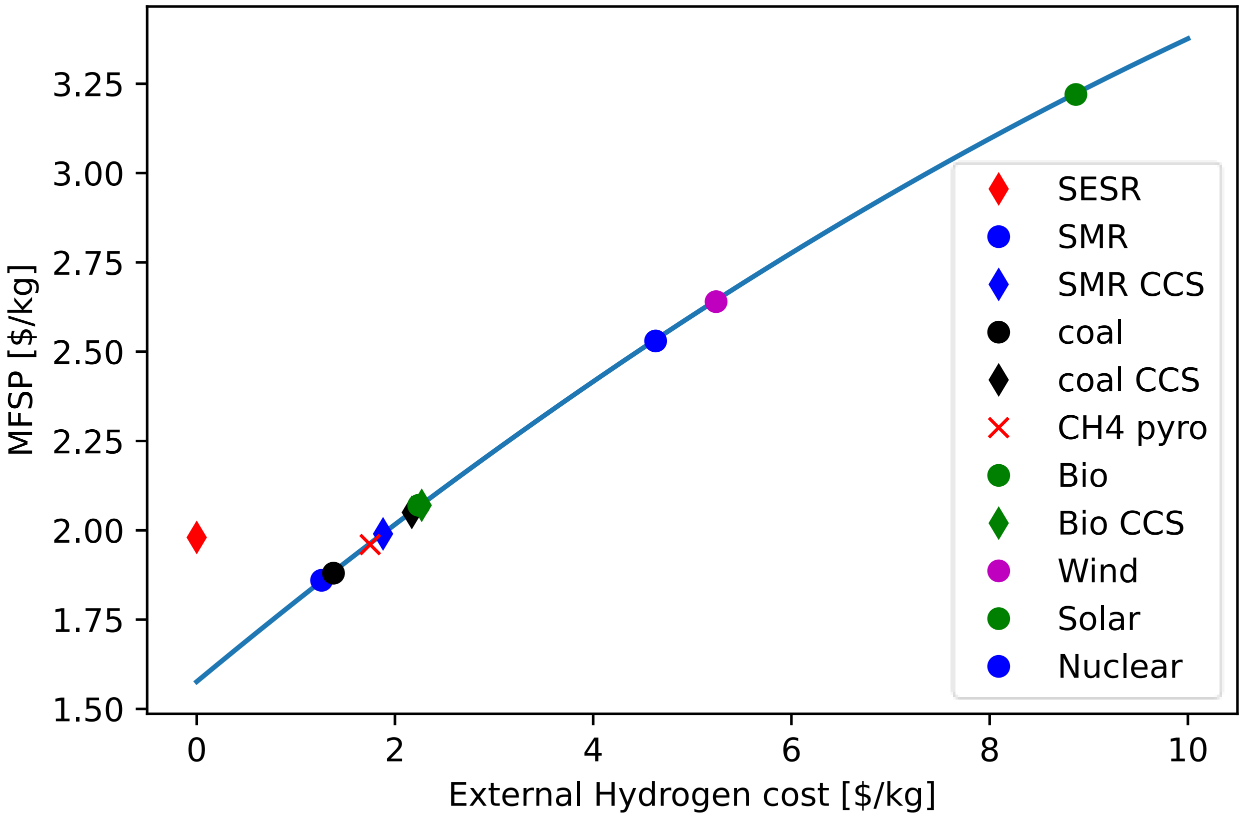


Sensitivity analysis for yield CVU

- MFSP = Minimum fuel selling price
- Complete conversion could reduce MFSP by 10 %
- Carbon yield can be improved by 5 %-points



Sensitivity of hydrogen cost



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Conclusion

- CVU can help increase the efficiency of the process and is crucial for upgrading the properties of the raw bio oil.
- CVU enables higher fuel carbon yields
- For a true Green process, the hydrogen has to be supplied by non-fossil sources.
- Sorption enhanced reforming is an attractive route for producing the necessary hydrogen.

Thank you for your attention – Questions?

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