



BIOHYDROGEN PRODUCTION VIA STEAM REFORMING OF PYROLYSIS BIO-OIL

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Introduction

Biohydrogen production from fast pyrolysis of biomass is becoming increasingly attractive as a convenient path to produce clean hydrogen at affordable costs. Bio-oil can be converted to hydrogen via reforming or gasification processes. Catalytic steam reforming is the best alternative to produce high quality biohydrogen at lower reaction temperature. The combined fast pyrolysis/steam reforming process for biohydrogen production is analysed from a variety of perspectives.

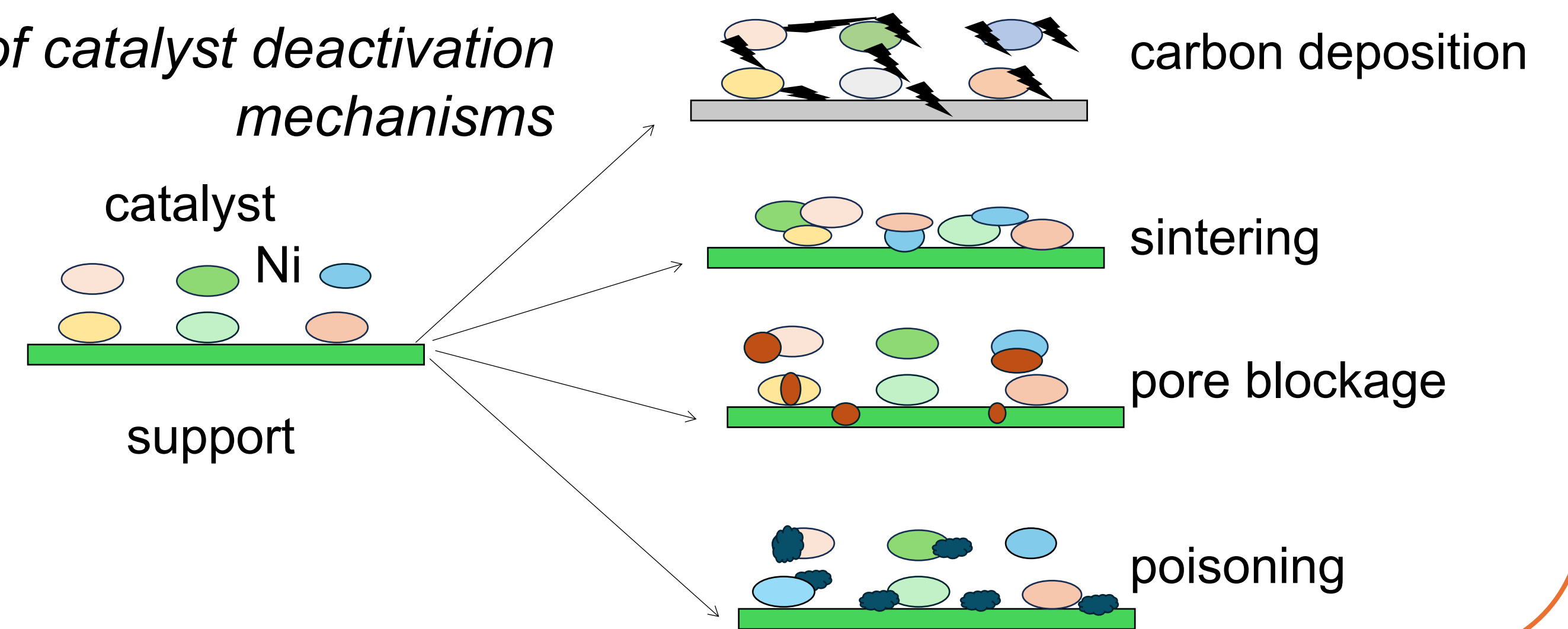
Steam reforming of pyrolytic bio oil: the challenges

The main drawback of steam reforming of bio-oil is low hydrogen yield and fast catalysts deactivation.

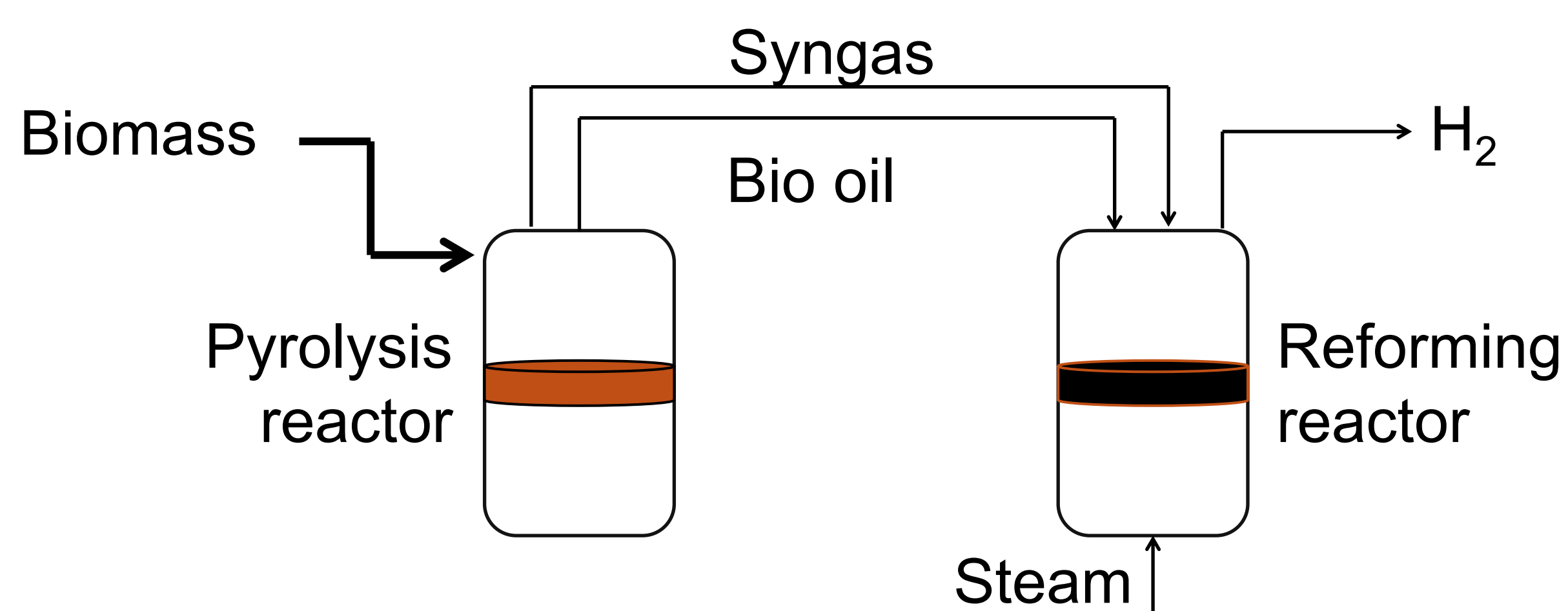
Causes of low hydrogen yield and fast catalysts deactivation

- Feedstock characteristics
- Catalysts type
- Type of reactor and feeding process
- Operating parameters

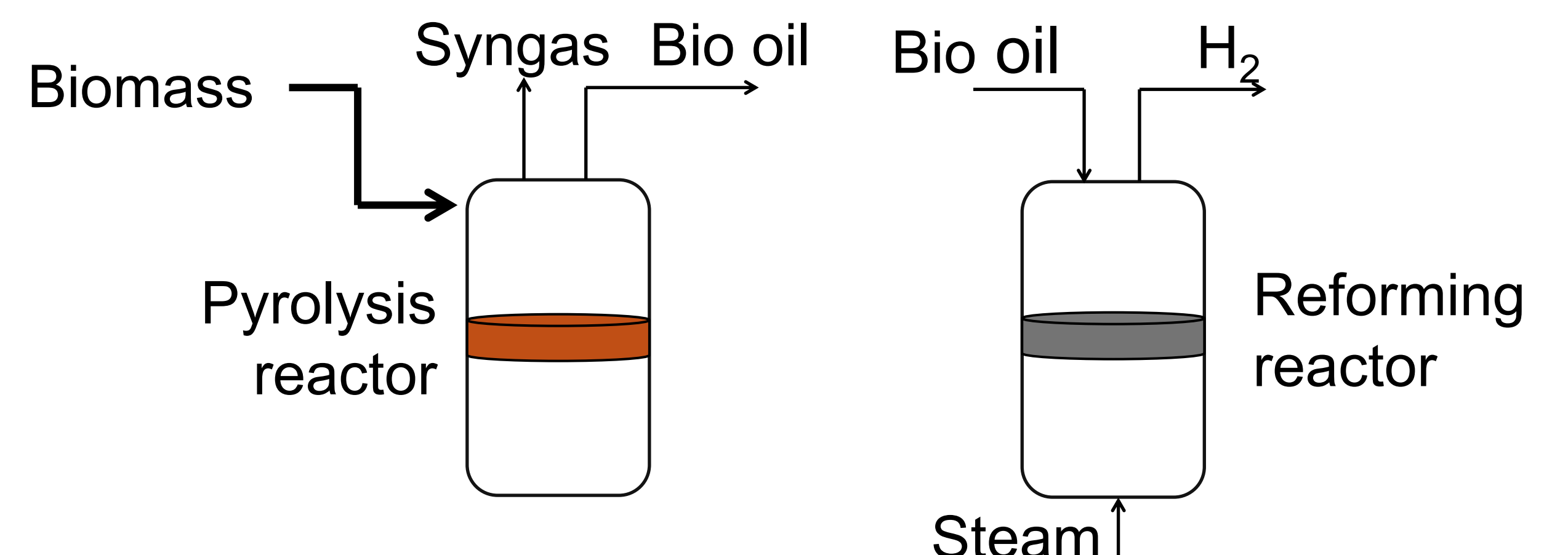
Outline of catalyst deactivation mechanisms



Process layout: in-line or off-line combination of the pyrolytic and reforming stages



In-line



Off-line

Process layout	Benefits	Drawbacks
In-line	<ul style="list-style-type: none"> • avoids using condensation and volatilization • cost effective 	<ul style="list-style-type: none"> • possible operational problems at reforming stage • difficult to control the stability of the intermediate product
Offline	<ul style="list-style-type: none"> • flexibility with respect to operation parameters of either stage • suited for hybrid delocalized/centralized biomass exploitation schemes 	<ul style="list-style-type: none"> • uses condensation and volatilization steps that negatively impact the economics of the process

Proposed areas of focus

Off-line process layout:

- suitable for hybrid delocalized/centralized biomass exploitation schemes.
- flexible as to the choice of processing bio-oil as a whole, or selected fractions of it resulting from simple fractionation stages.

Design and operation of the steam reformer: Fluidized bed as reference technology:

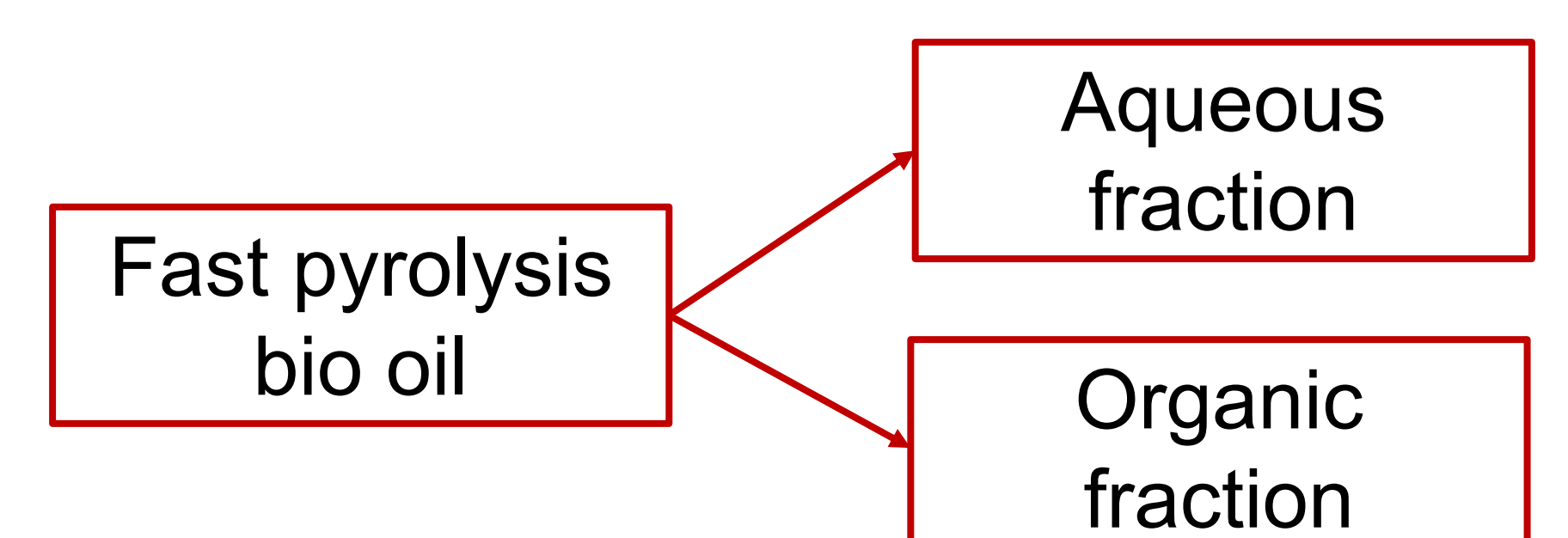
- excellent thermal performance;
- favourable multiphase contacting patterns.

Key issues to be addressed:

- dispersion/mixing pattern of highly viscous & unstable bio-oil upon feeding to a fluidized bed;
- reactor design and control of fluidization patterns to ensure effective contact between bio-oil vapours and the catalyst and overcome gas phase segregation and inefficient vapour/catalyst contact.

Catalyst formulation: Optimization of catalyst formulation with reference to the specific feedstock/ process layout to ensure:

- maximum hydrogen yield and productivity;
- maximum stability and minimal deactivation due to bio-oil contaminants that lead to loss of active sites of catalysts.



Preliminary process design

Reforming temperature (°C)	600 – 800
S/C (-)	5 – 10
τ_{cat} (g h g _{vol} ⁻¹)	0.1 – 0.3
Gas velocity (m/s)	0.4 – 0.8
Reactor diameter (m)	~ 0.08
H ₂ max production (%wt)	~ 10

References

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- Olazar, M., Santamaria, L., Lopez, G., Fernandez, E., Cortazar, M., Arregi, A., & Bilbao, J. (2021). Progress on catalyst development for the steam reforming of biomass and waste plastics pyrolysis volatiles: A review. *Energy and Fuels*, 35(21), 17051–17084.