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75th IEA-FBC Meeting

Skive, Denmark

23th-25th October 2017

H_2 Production from Biomass Feedstocks Utilising a Spout-Fluidised Bed Reactor

Peter Clough, Liya Zheng, Paul Fennell

p.t.clough@cranfield.ac.uk, p.fennell@imperial.ac.uk

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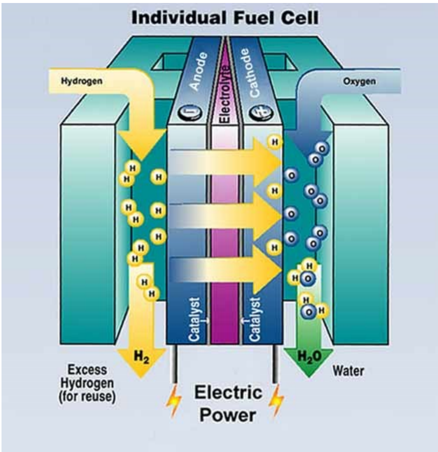
What are the uses of H_2?



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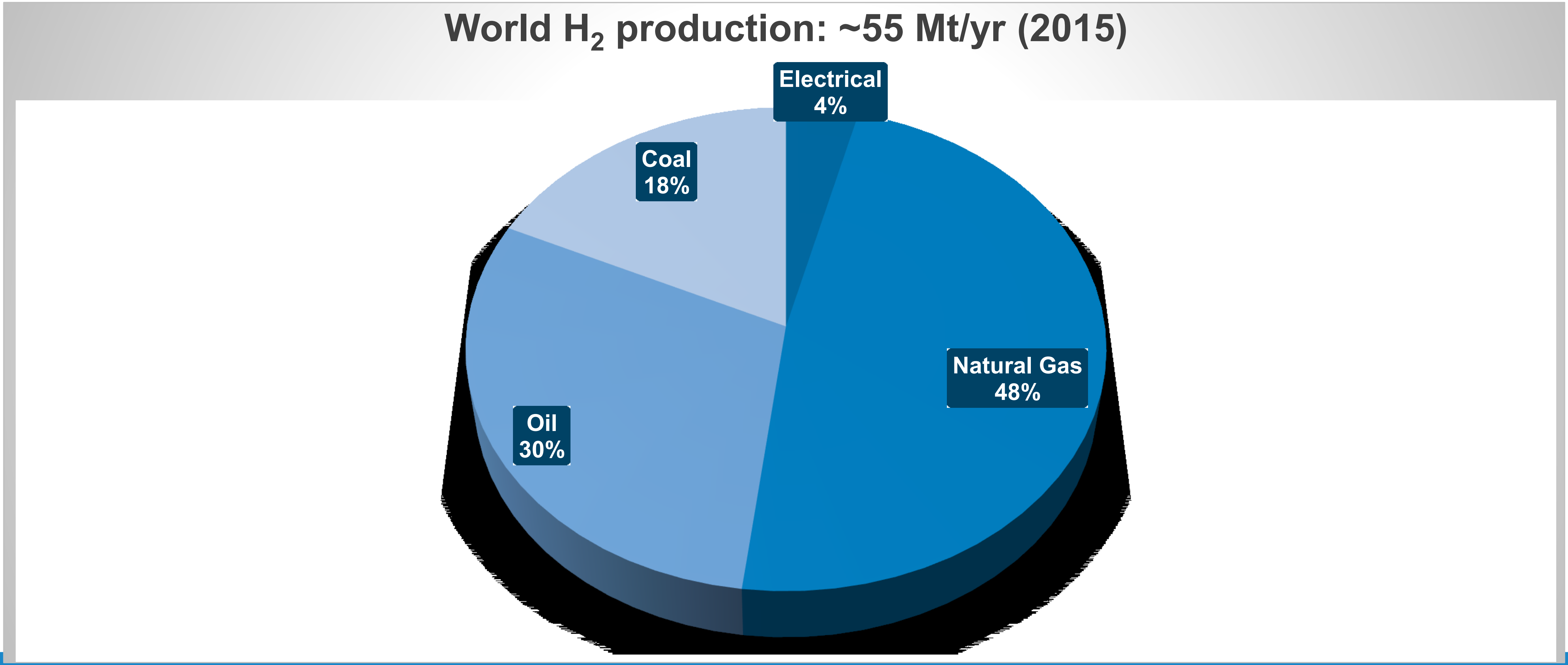
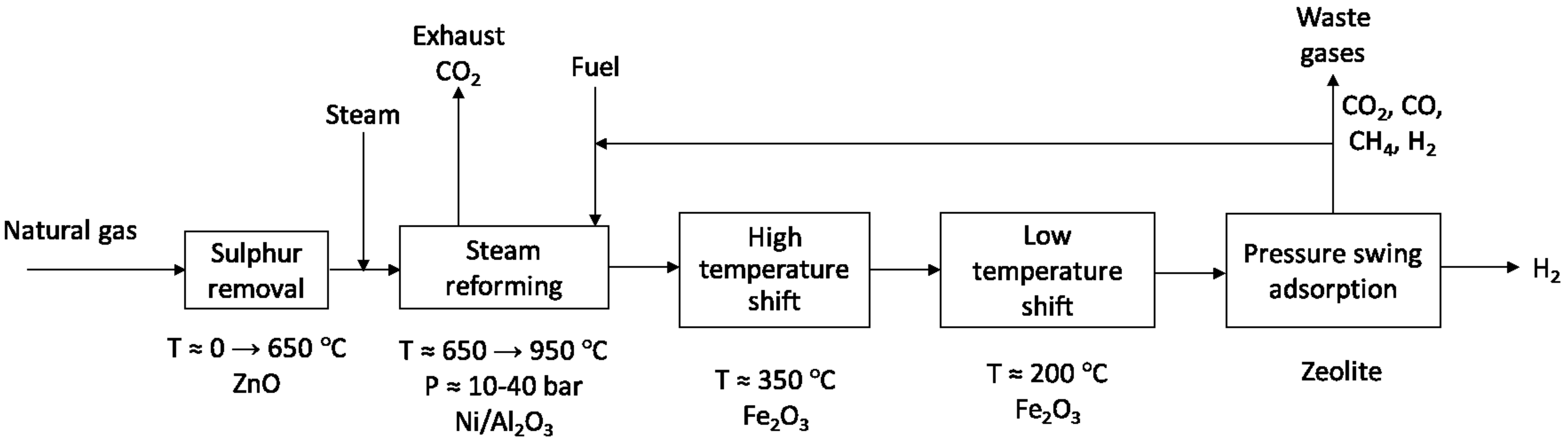
How is H_2 produced?



http://hydrogeneurope.eu/wp-content/uploads/2017/01/20170109-HYDROGEN-COUNCIL-Vision-document-FINAL-HR.pdf

SMR process description



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Better option

SMR + CaL = SER

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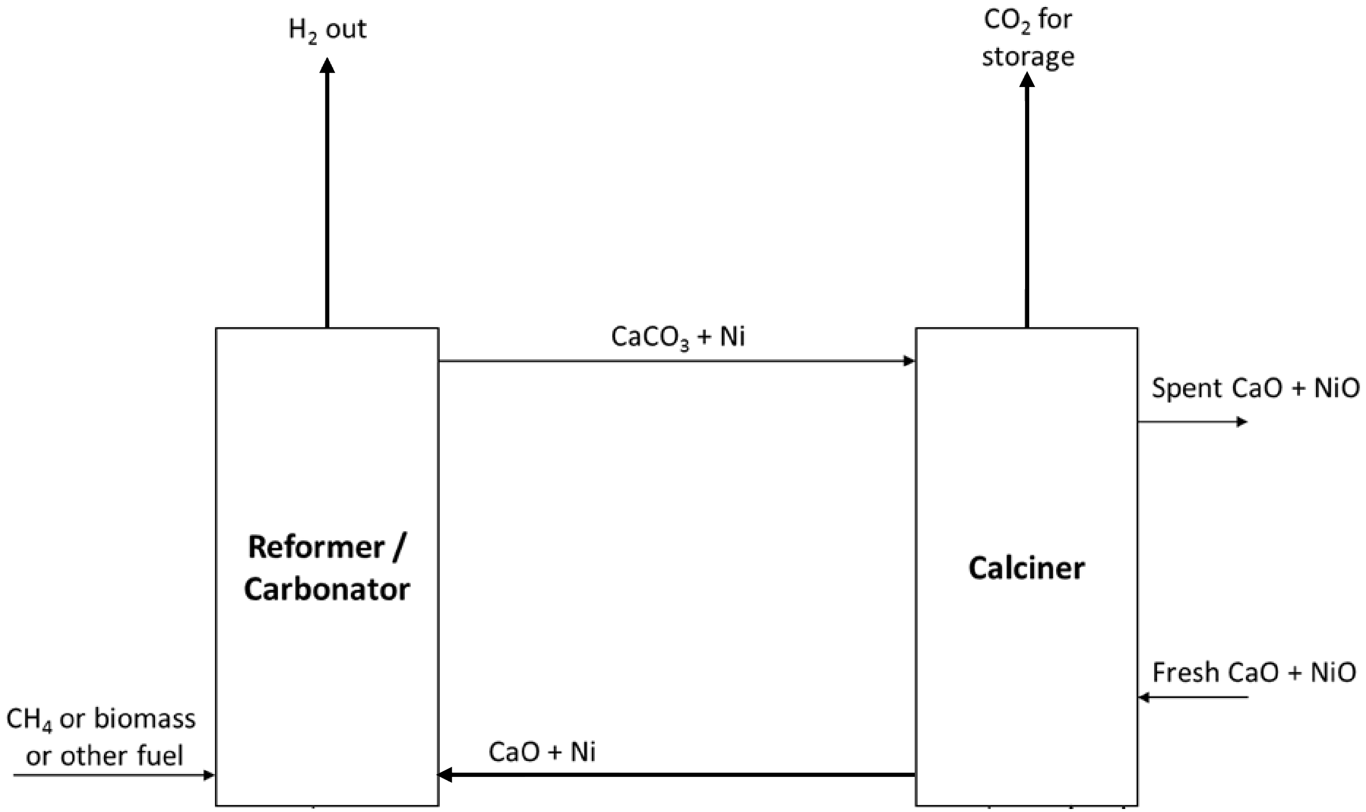
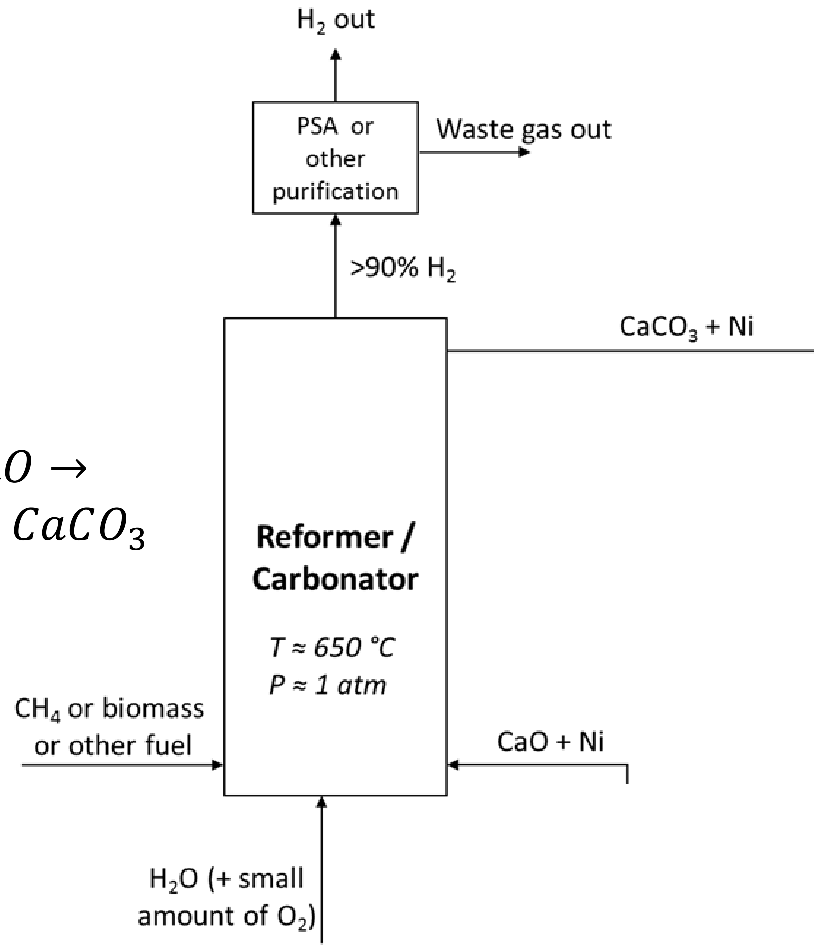
SER process description - Simplified



SER process description

$$CH_{1.6}O_{0.8} + 1.2H_2O + CaO \rightarrow 2H_2 + CaCO_3$$



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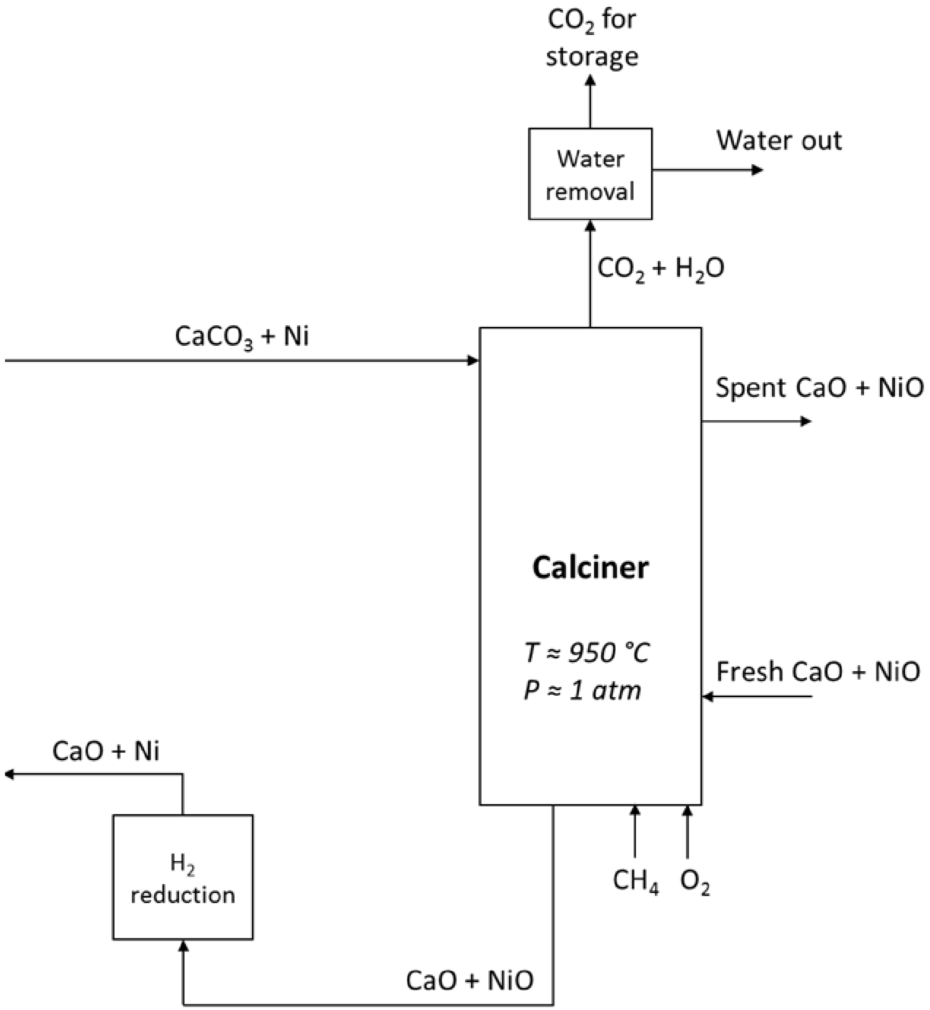

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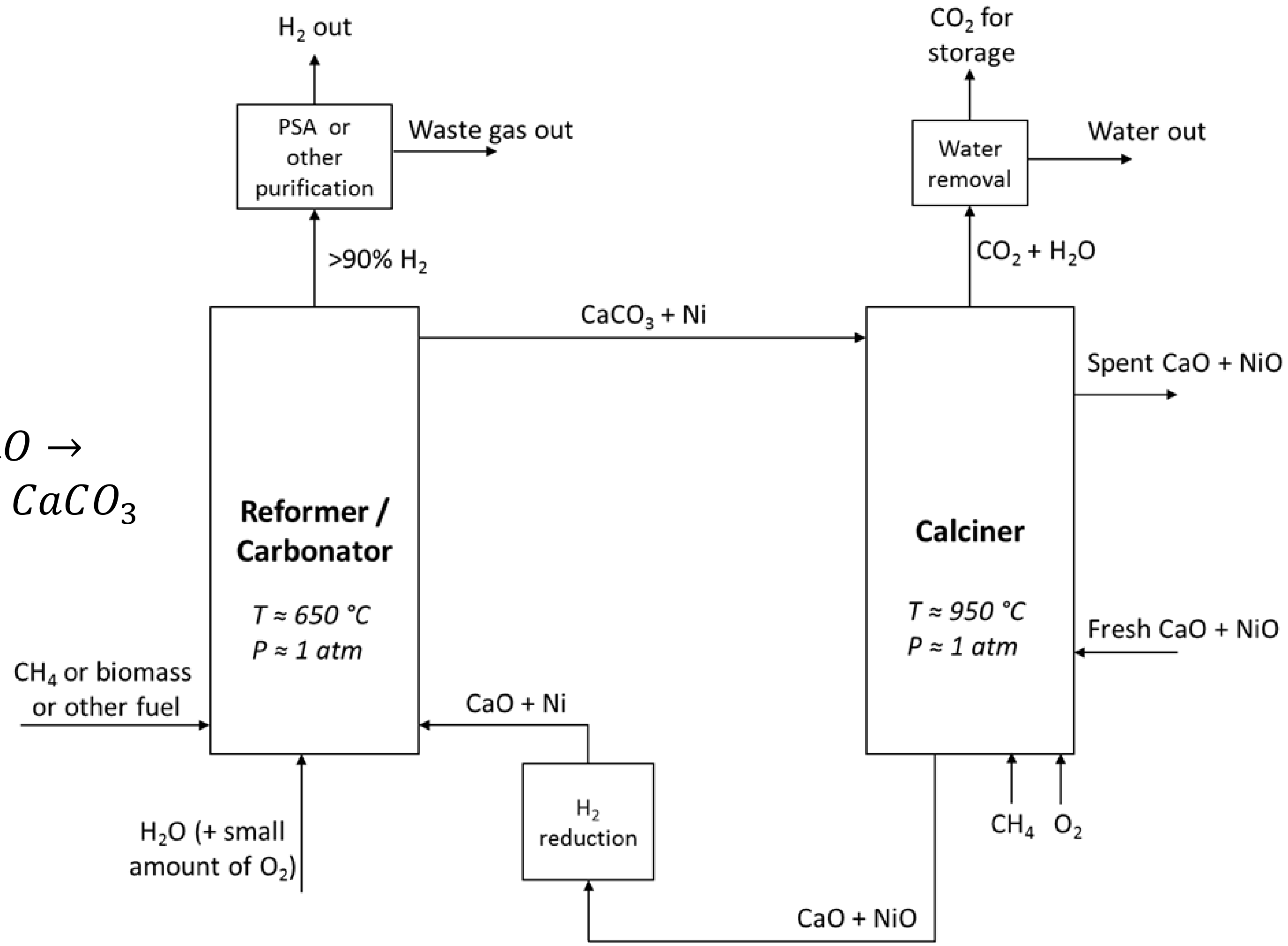

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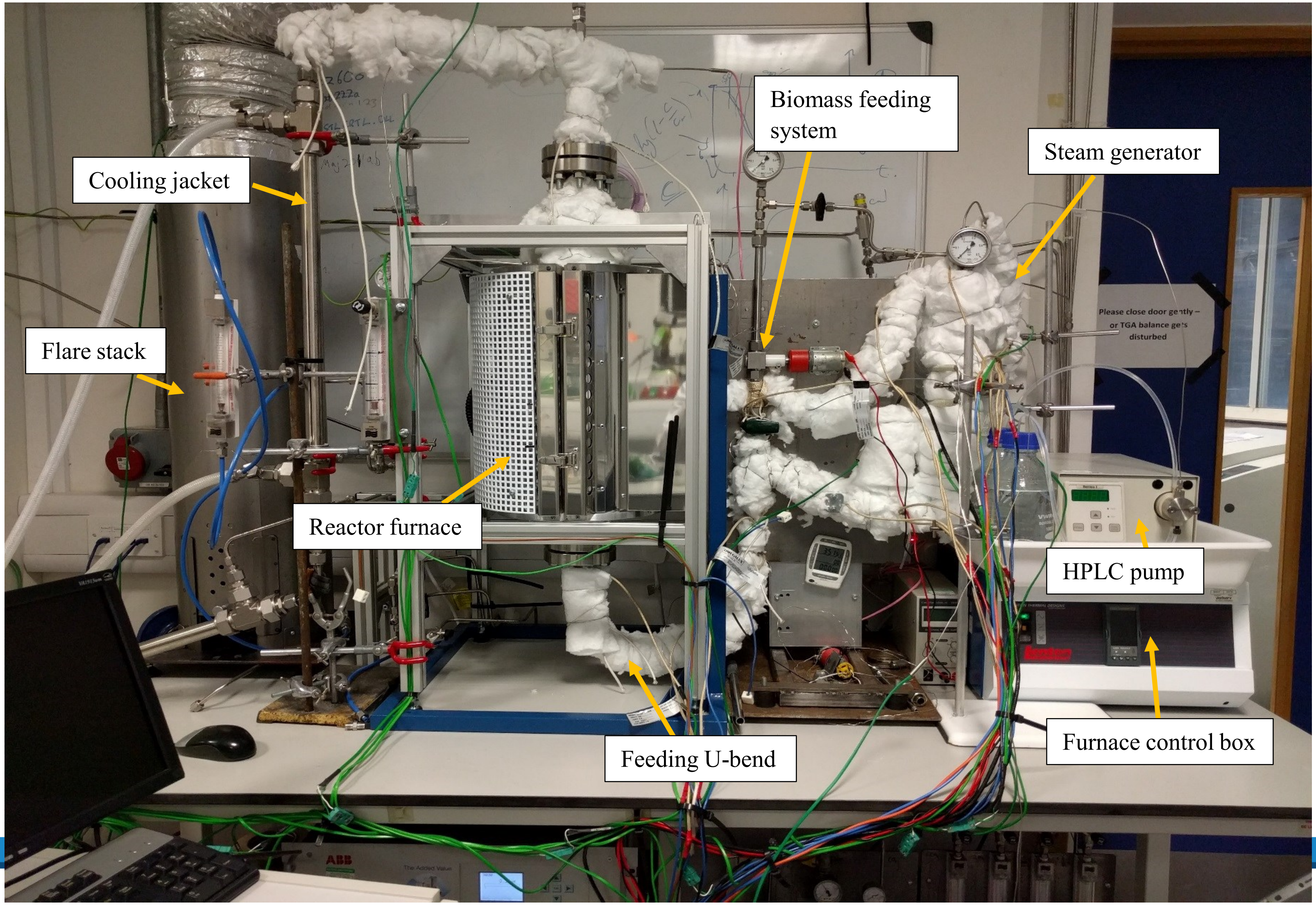
Reactor design



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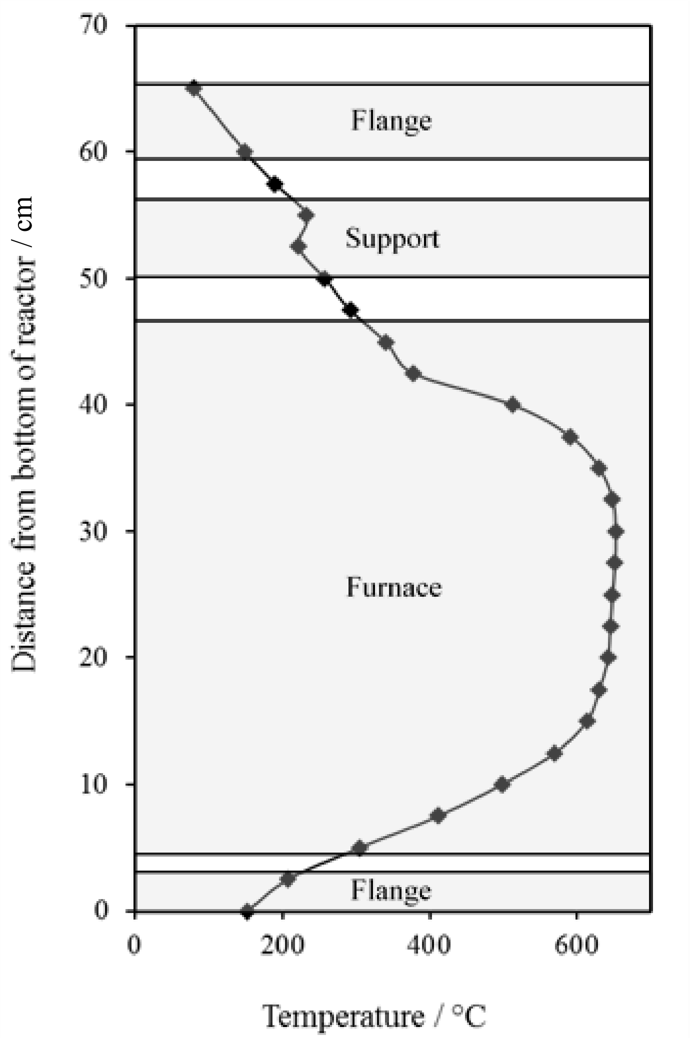
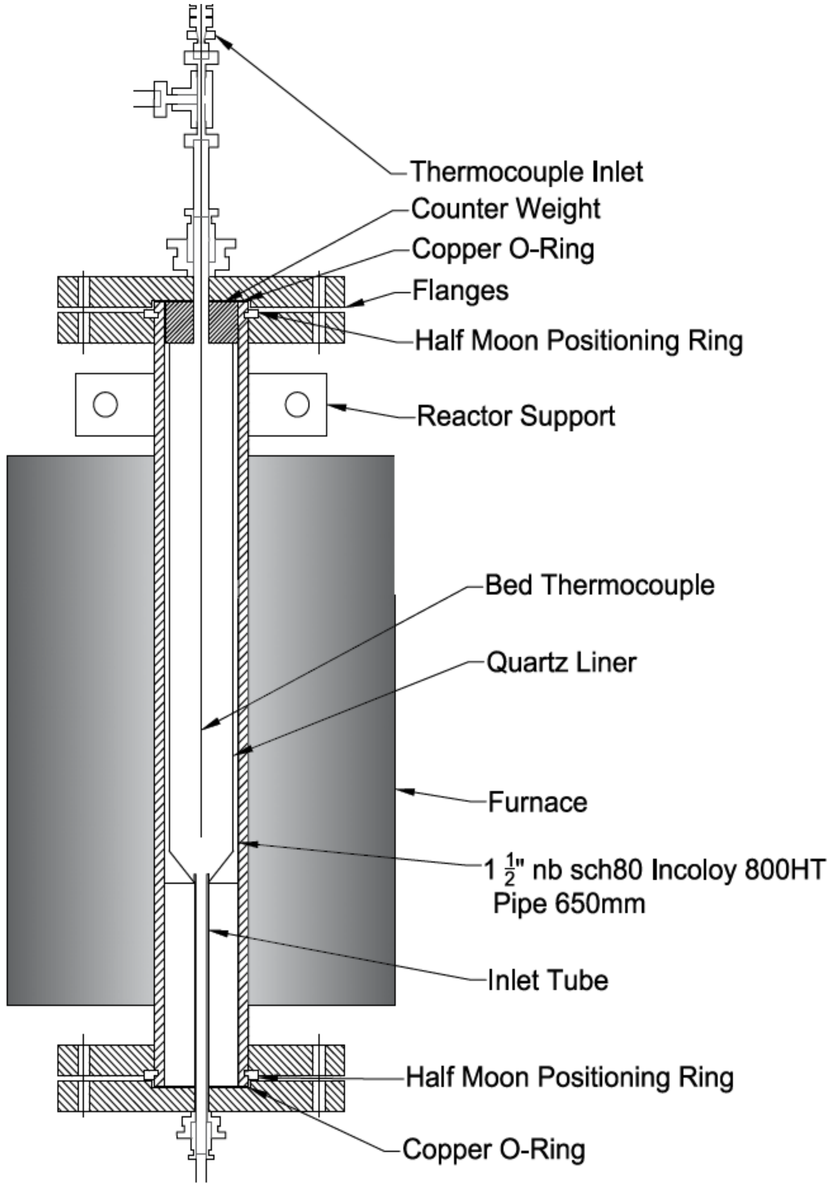
Reactor Design and Construction





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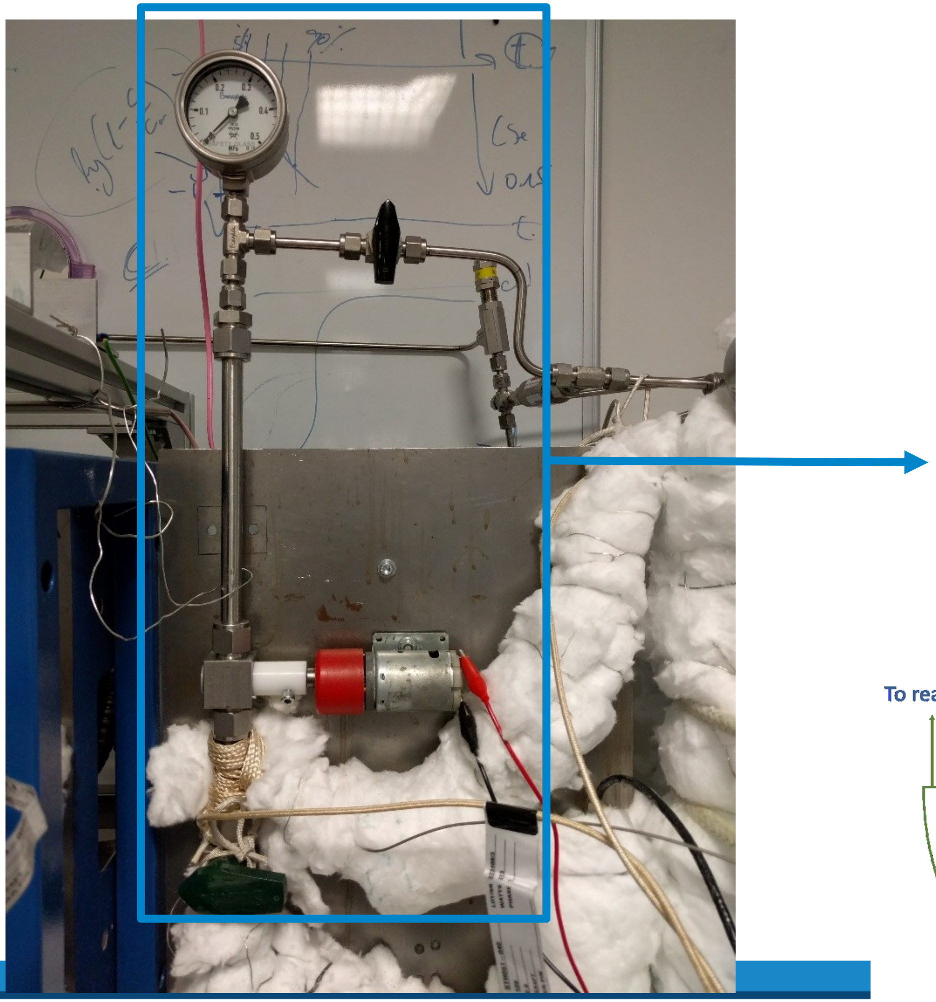
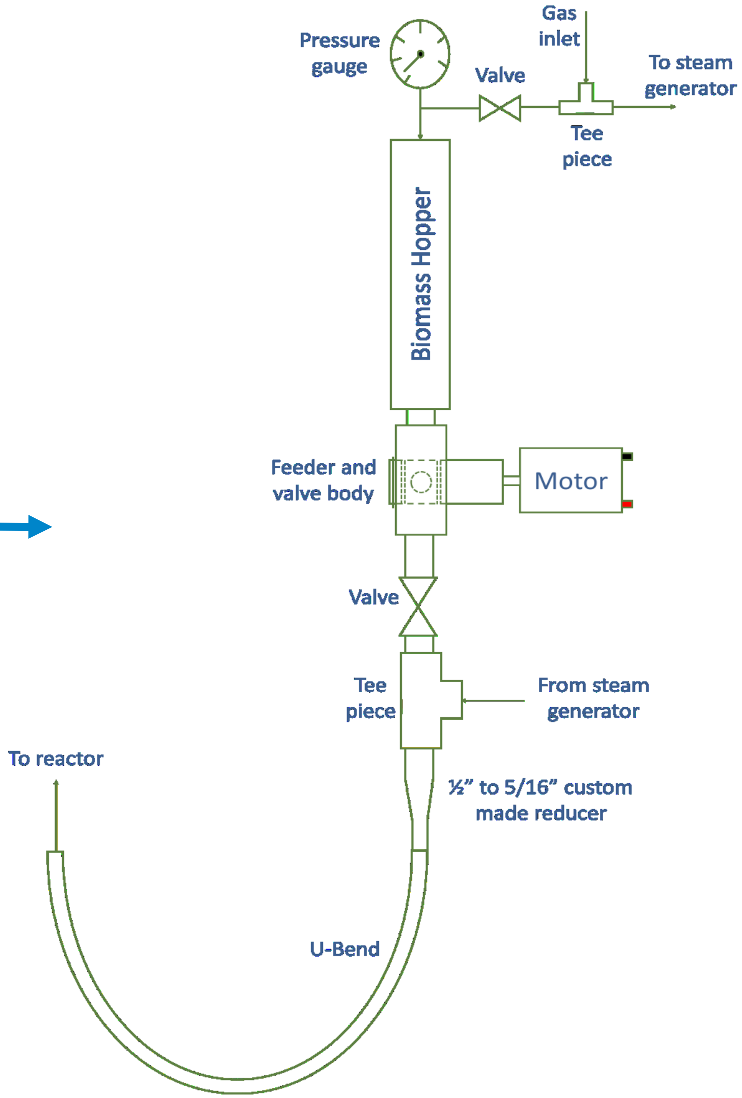
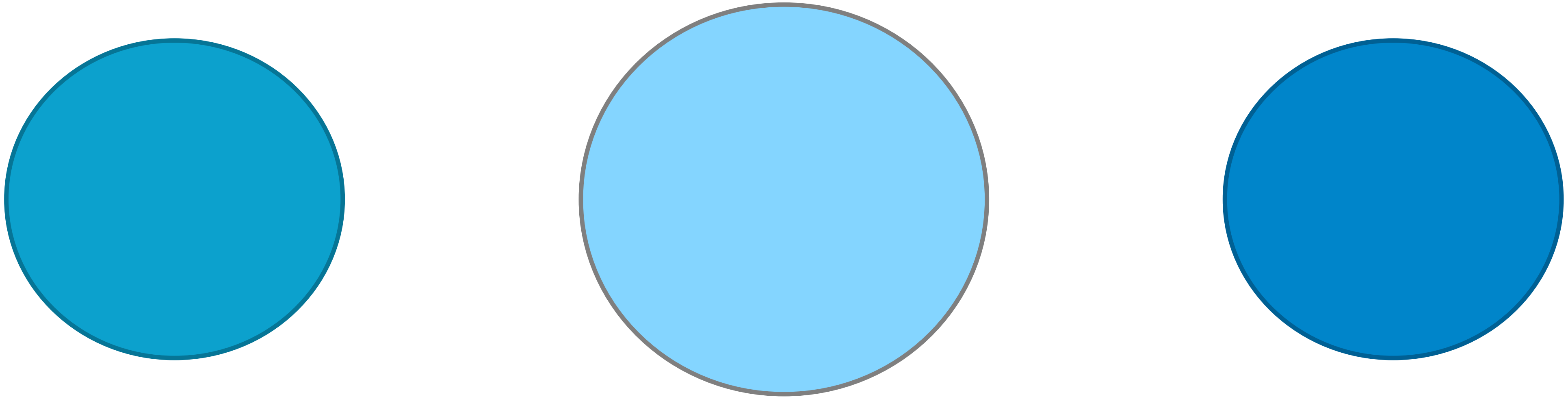
Biomass/Coal feeding system

Rotary hopper feeder





Combined Particles



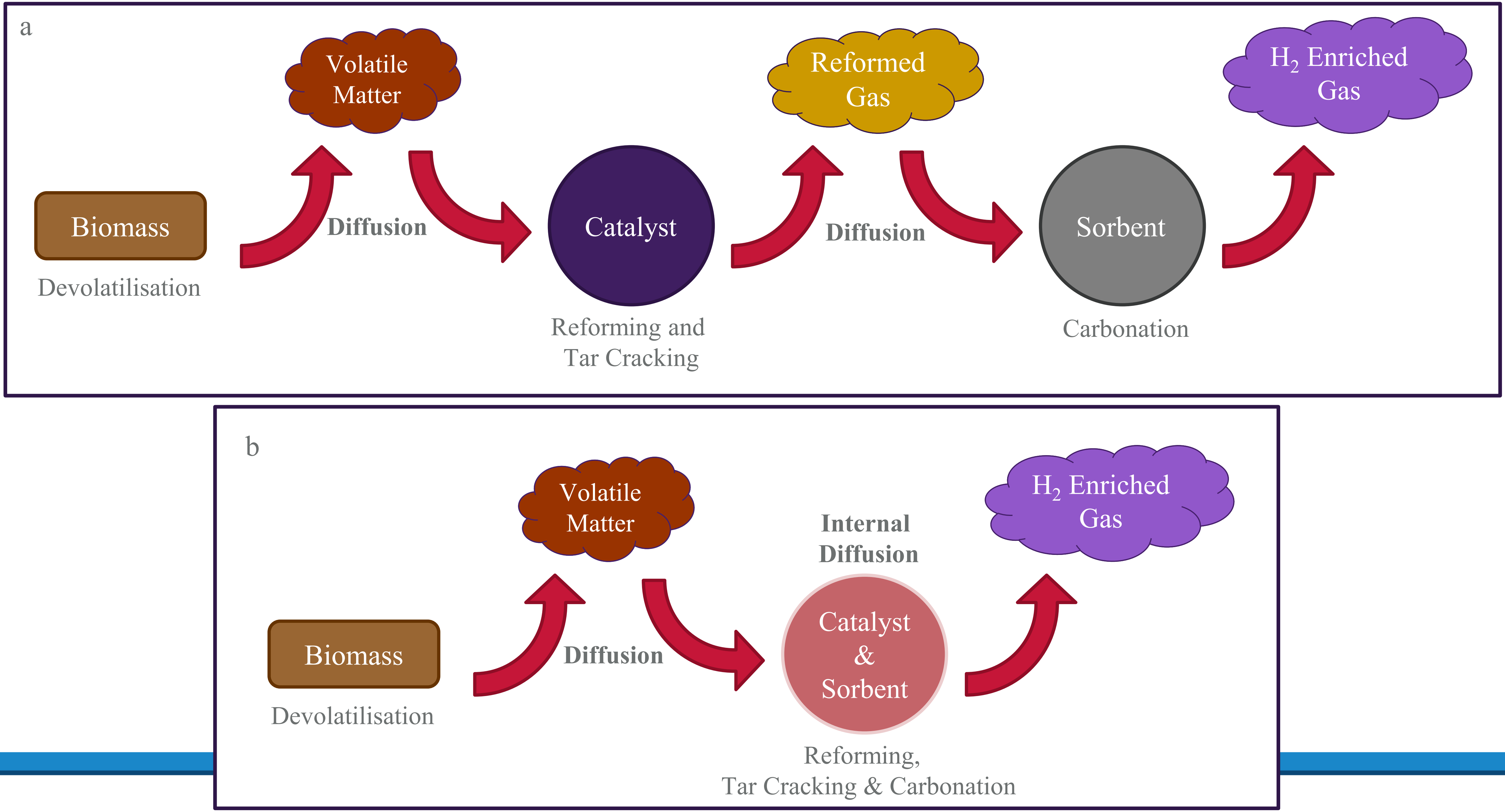
CaO

CO_2 sorbent

Combined sorbent and catalyst particle

Ni

Reforming catalyst


a
Volatile Matter
Reformed Gas
H_2 Enriched Gas
Biomass
Diffusion
Catalyst
Diffusion
Sorbent
Devolatilisation
Reforming and Tar Cracking
Carbonation
b
Volatile Matter
Internal Diffusion
H_2 Enriched Gas
Biomass
Diffusion
Catalyst & Sorbent
Devolatilisation
Reforming, Tar Cracking & Carbonation

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Sorbent and catalyst materials

	Materials preparation method
Low-engineered	*Wet granulation (mechanical mixing)*
	Hydrolysis
	Wet impregnation
	Spray drying / freeze drying
	Co-precipitation
Highly-engineered	*Sol-gel*

- **Maximise**
  - Particle porosity
  - **Similarity of reaction kinetics for carbonation and reforming**
  - **Sorbent carrying capacity**
  - Particle and individual component lifetime
  - Particle strength
  - **Resistance to attrition**
  - Ability to reuse/recycle spent material
- **Minimise**
  - Material sintering
  - Pore blocking/product layer resistances
  - Unintended inter-component interaction
  - **Expense, difficulty and time to manufacture**
  - The quantity of unreactive material

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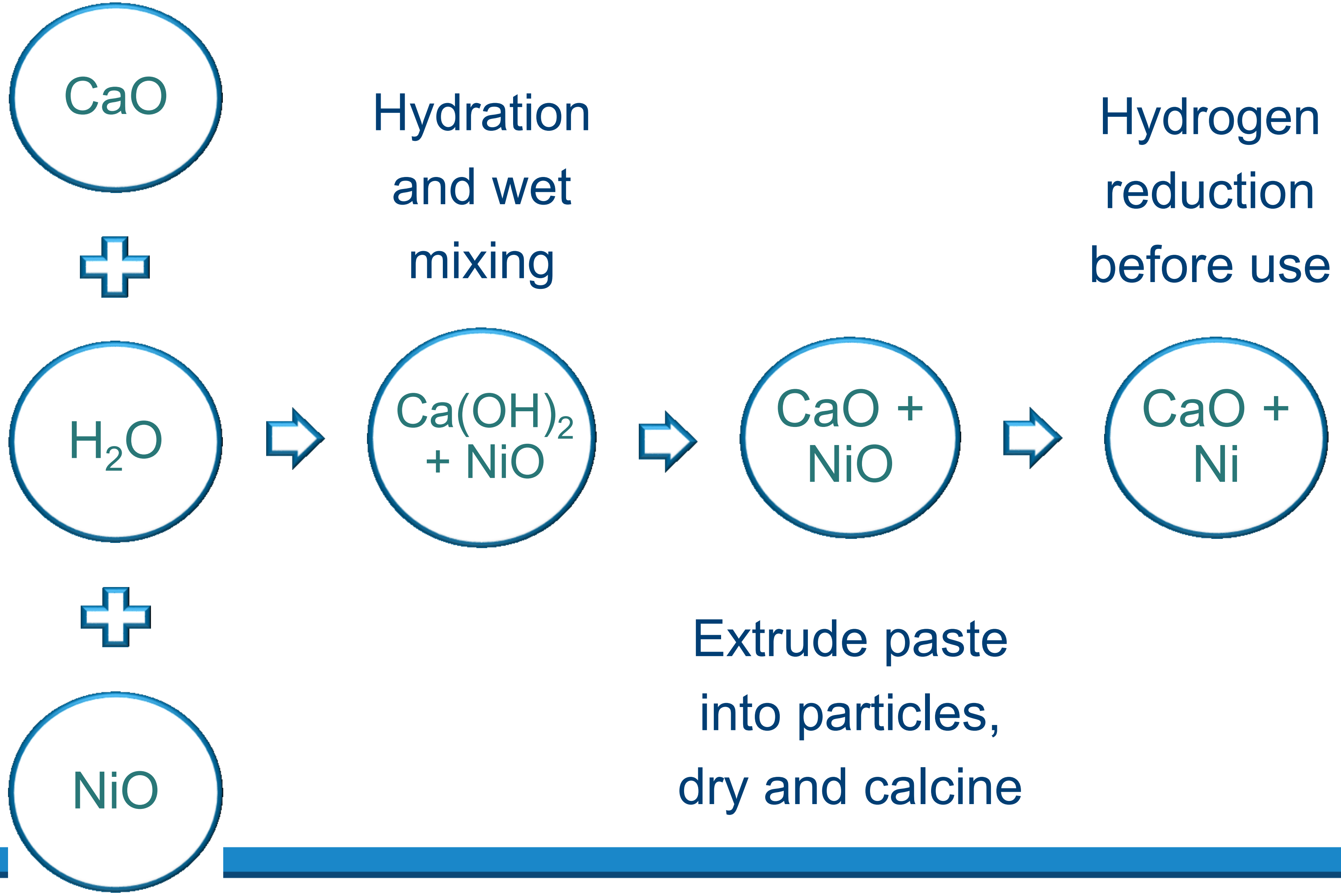
Unsupported material preparation method



Degradation study of a novel polymorphic sorbent under realistic post-combustion conditions
https://doi.org/10.1016/j.fuel.2016.08.098

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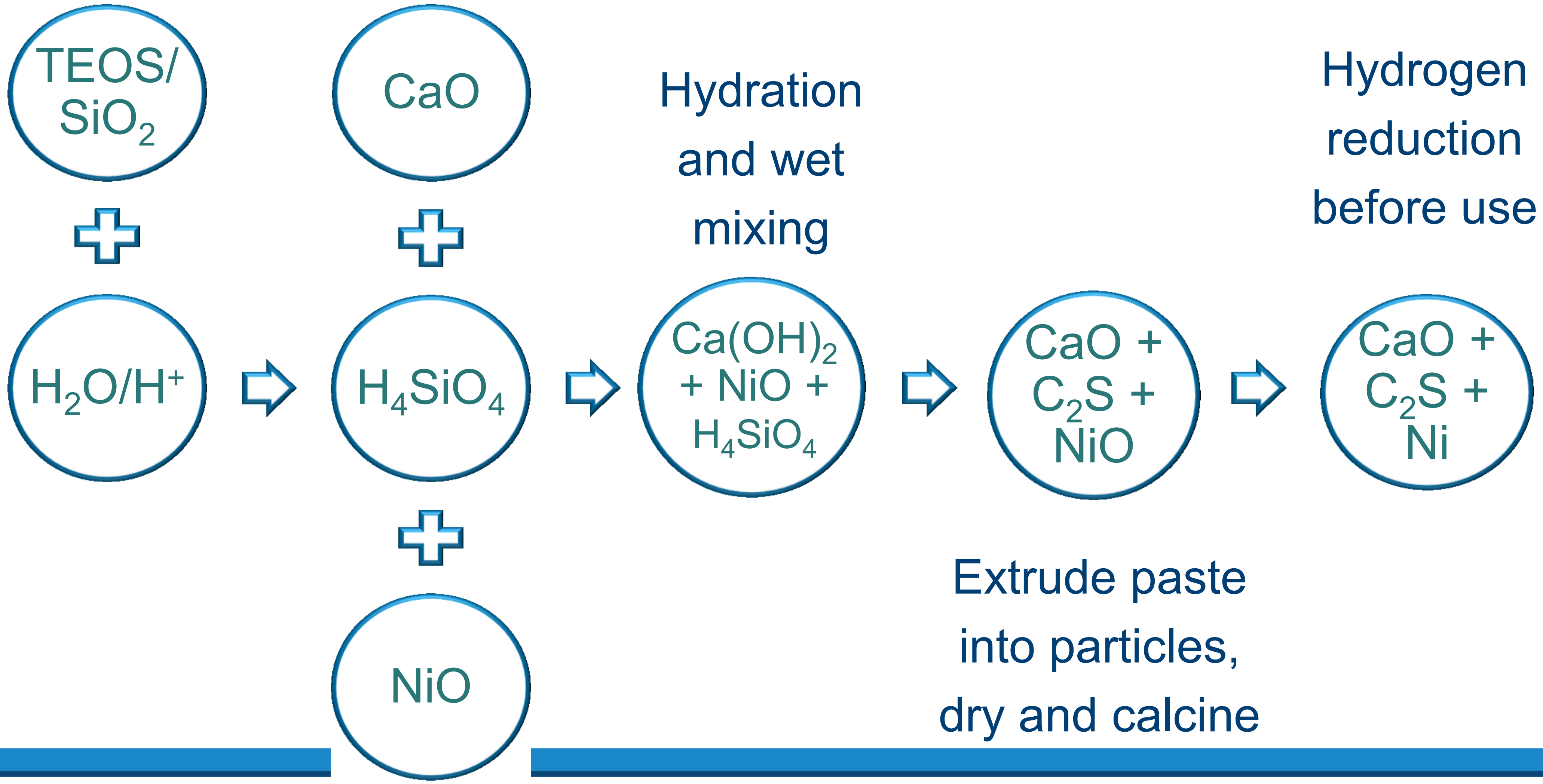
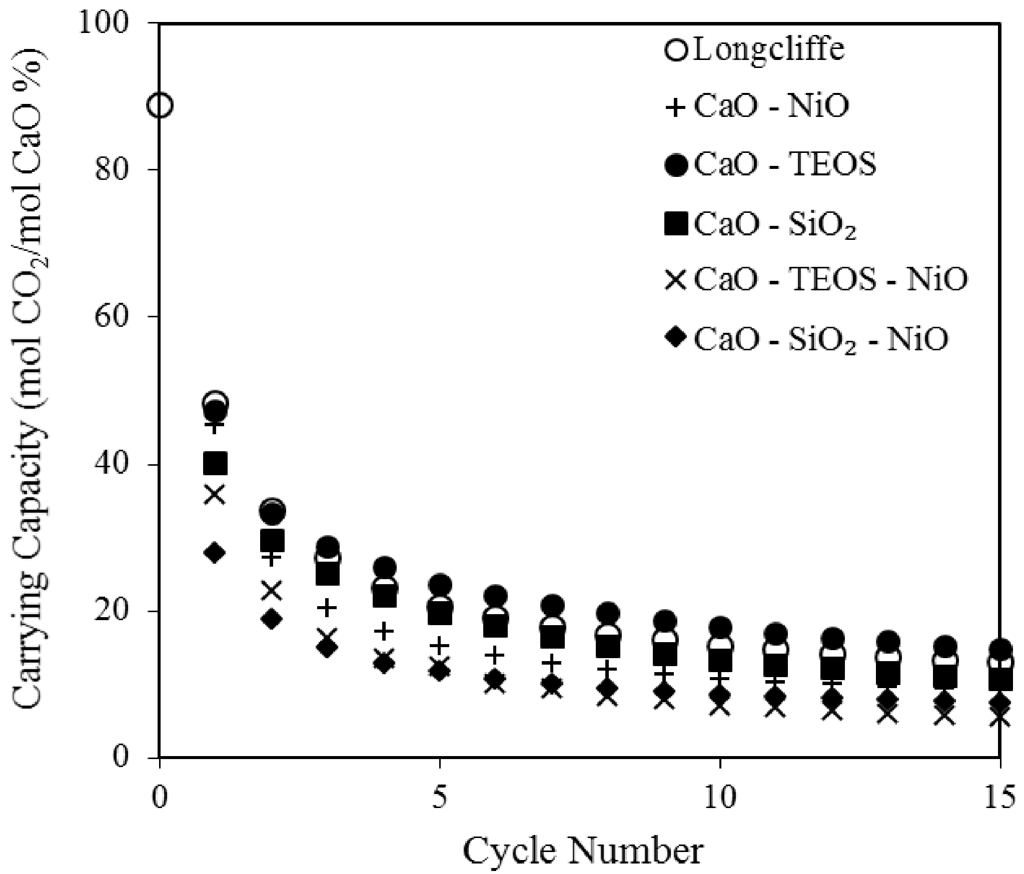
Supported material preparation method



Calcium looping carrying capacity supported and unsupported combined particles



Carbonation – 650 °C, 15 vol.% CO_2
N_2 balance, 5 minutes

Calcination – 950 °C, 100 vol.% CO_2,
1 minute

C_2S supported combined particle (CaO and NiO, 300 - 500 µm) CO_2 carrying capacity in moles of CO_2 absorbed per mole of CaO as a percentage.

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SER reaction conditions

Conditions:

- 650 °C ± 8 °C
- 1 atm
- Steam 20 vol.%, N_2 balance → S:C = 1.2 $$CH_{1.6}O_{0.8} + 1.2H_2O + CaO \rightarrow 2H_2 + CaCO_3$$
- $U/U_{mf} \approx 3$
- 80 cm^3/s @ 293 K
- Bed of sand, CaO and Ni (content and particle sizes varied)
- 0.9 g/min Oak biomass (212 - 300 µm)
- NiO → Ni reduction @ 650 °C for 30 minutes in 5 vol.% H_2
- Combined particles - 14, 26, 36 and 47 wt.% NiO = 11, 21, 28 and 37 wt.% Ni

Total amount of CO_2 that could be produced from 1 min of biomass feeding:

~0.04 moles CO_2 ∴ ≈ 1.9 g CaO

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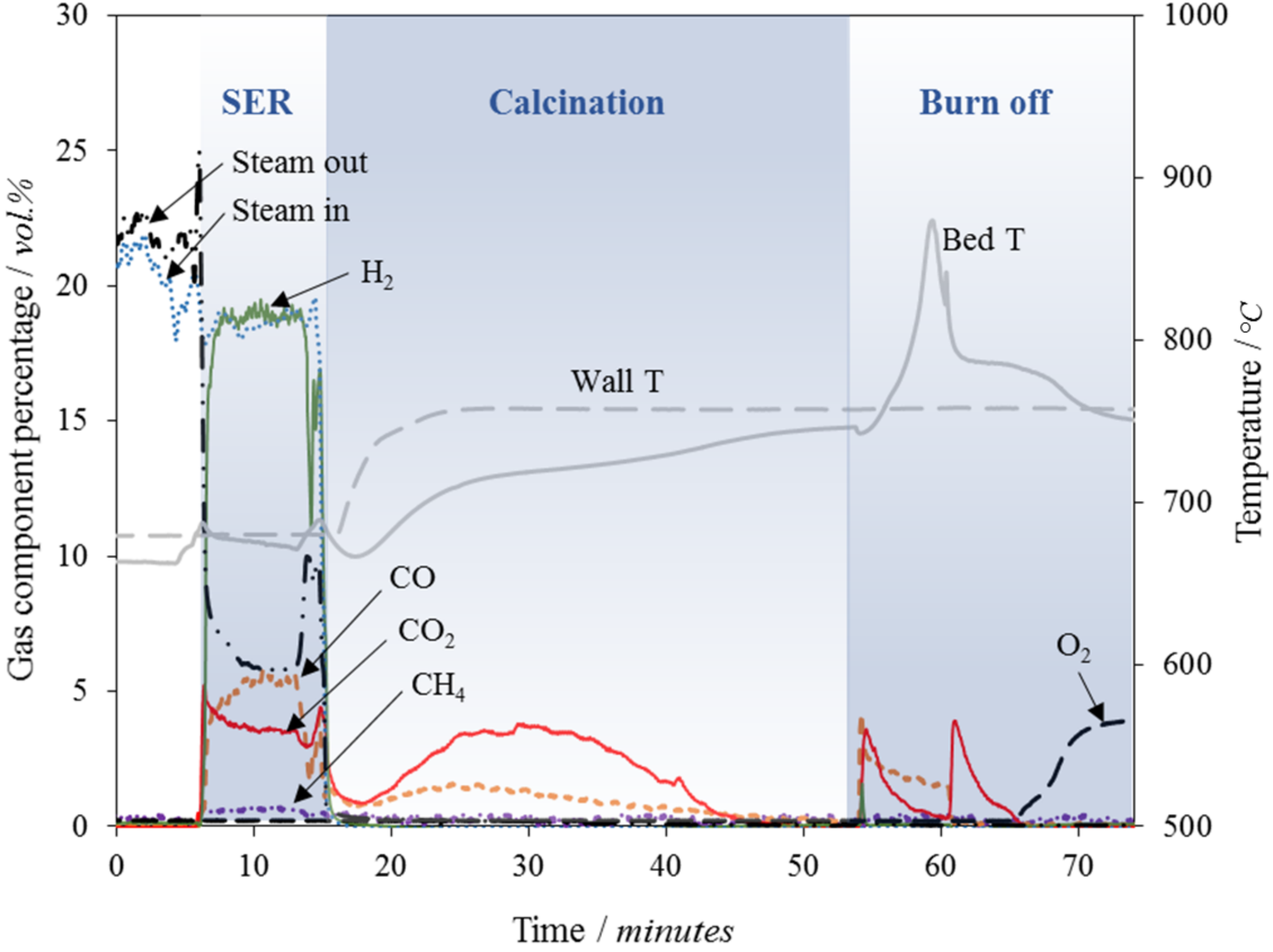
Typical experimental profile



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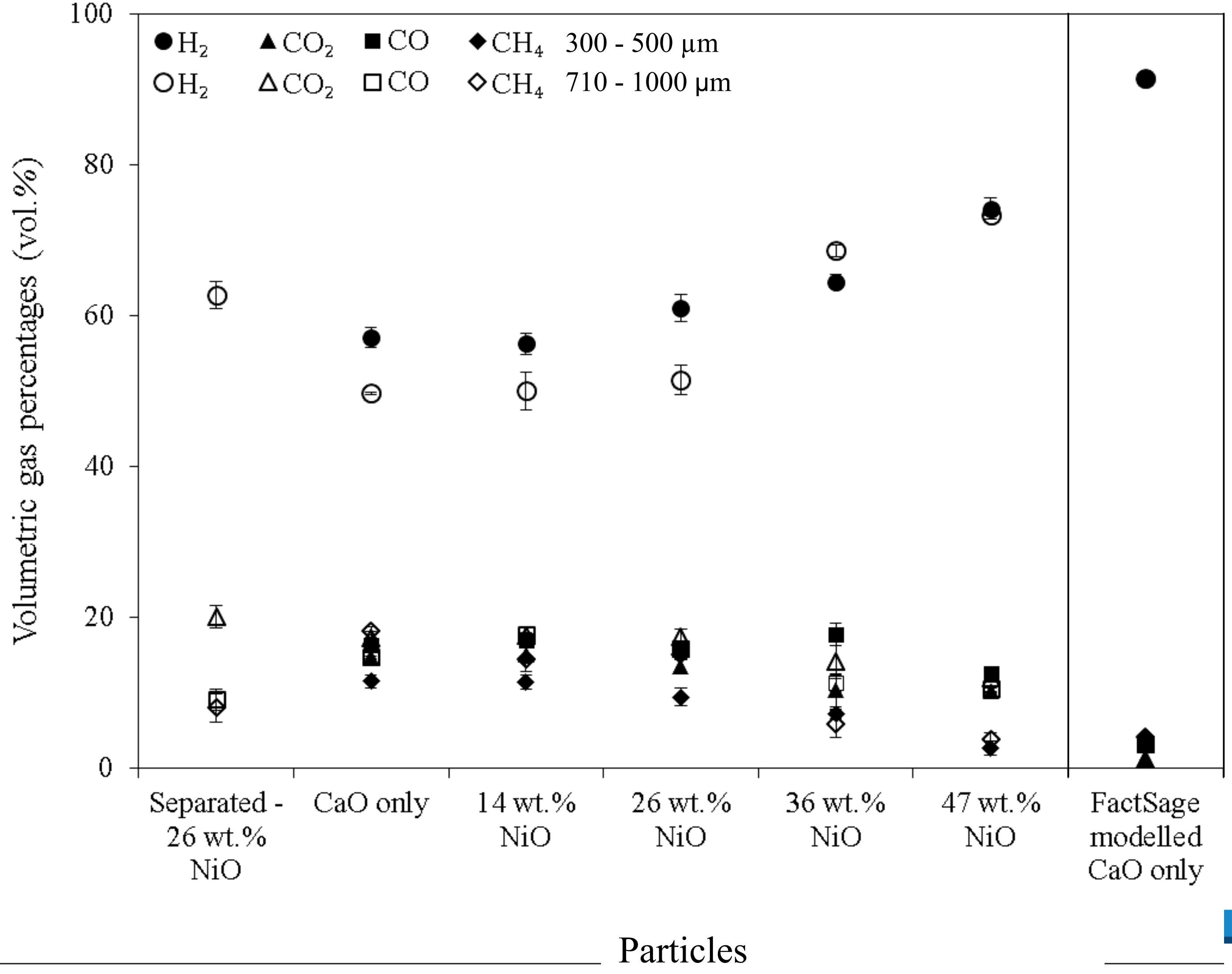
SER with unsupported combined particles



- Steady state period
- H_2 vol.% greater with more Ni
- H_2 vol.% greater with smaller particles
- Inefficient gasification or diffusional issues
- Approaches thermodynamic equilibrium
- FactSage – thermodynamic only

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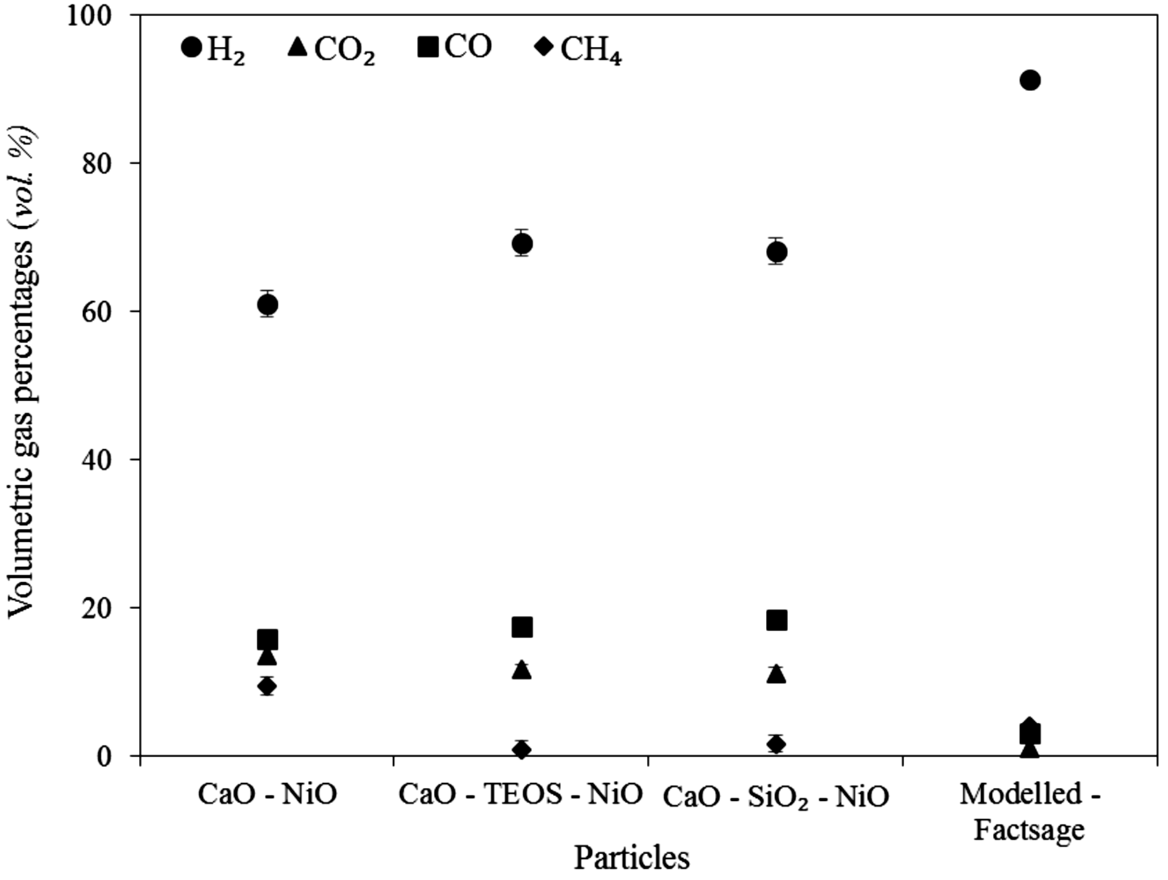
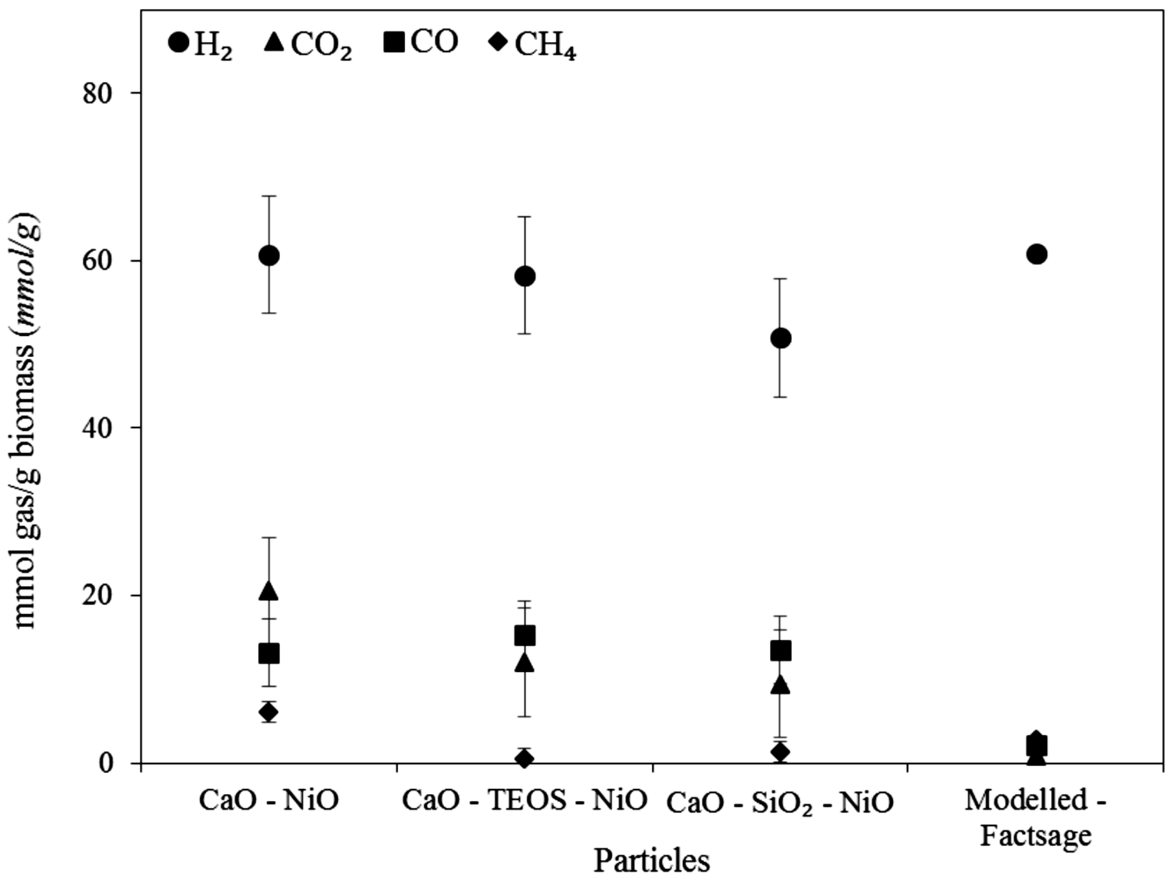
SER with 26 wt.% NiO C_2S supported combined particles

CH_4 decreased significantly with the addition of Si-based support





Gas purity / vol.%

Gas yield / mmol/g $_{biomass}$

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SER with combined particles

- Unsupported and C_2S supported 26 wt.% Ni produced 60 and 70 vol.% pure H_2, respectively
- 60 mmol H_2 / $g_{biomass}$ ≈ 120 g_{H_2} / $kg_{biomass}$
- Average closure of 100.4 ± 15.4 % for C, H and O – Unsupported particles
- Average closure of 115.0 ± 10.7 % for C, H and O – C_2S supported particles
- Average CO_2 capture of 32.8 % for 300 – 500 μm – Unsupported particles
- Average CO_2 capture of 55.7 % for 300 – 500 μm – C_2S supported particles

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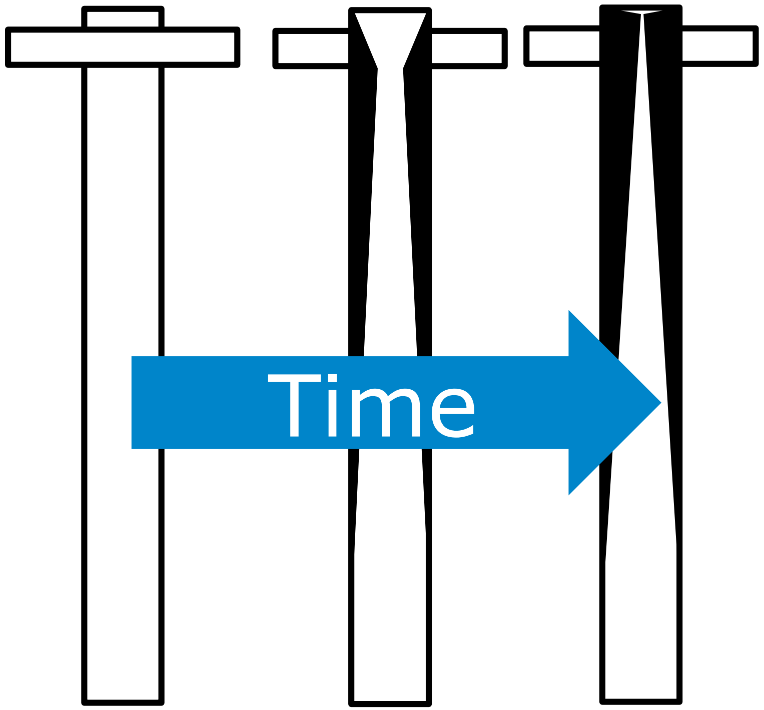
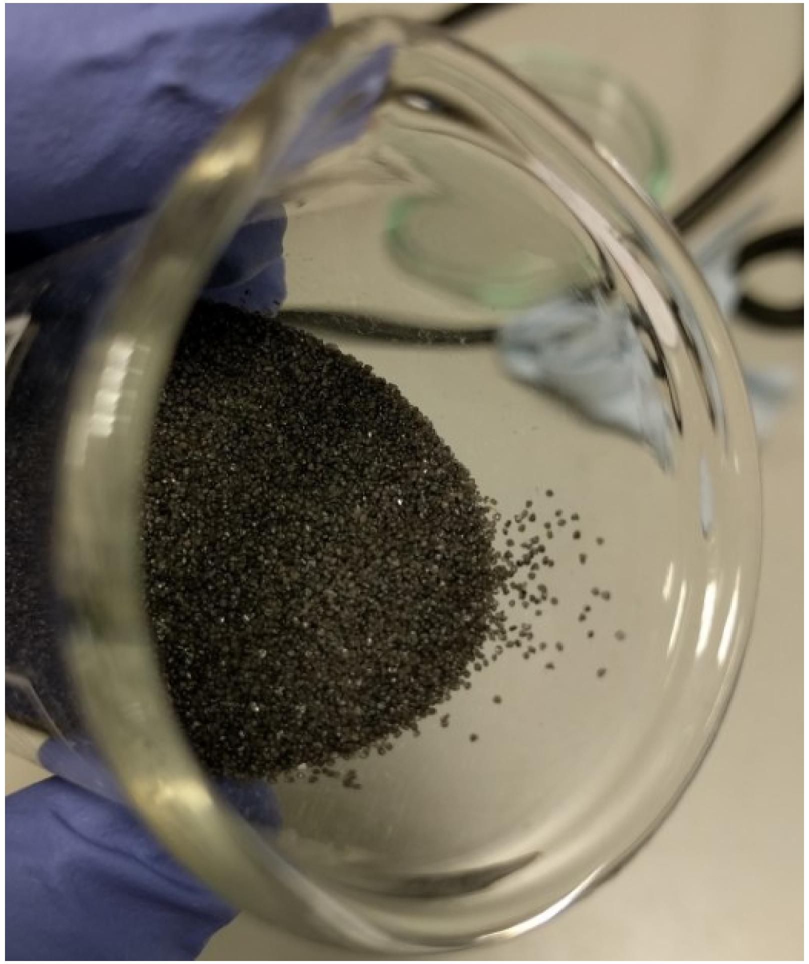
Operational issues

- Attrition of particles
- Coking on particles
- Coking within the reactor





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Conclusions

- Combined NiO and CaO particles produced (some with C_2S support)
- Tested SER within a fluidised bed reactor with solid biomass feeding
- Stoichiometric steam to carbon ratios
- H_2 purity and yield did approach equilibrium
- Si-based support dramatically affected CH_4 production
- Demonstrated ability to balance SER reactions with gasification
- Coking limited reactions and operation

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