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Low carbon hydrogen production via the advanced reforming of bio-oil

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1. Introduction

H_2 production & project scope

2. Conventional SR of bio-oil

Process modelling

3. CCS in bio-oil reforming

Preliminary study

4. Advanced reforming

Improving H_2 production from bio-oil

5. Summary

The role of hydrogen

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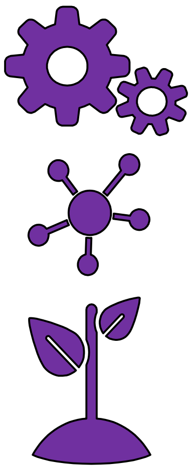
Now

7.2×10^{18} joules per year[1]
(UK total energy = 8.1×10^{18} J per year[2])

98% from fossil fuel steam reforming[3]

1.4% of emissions from fossil fuels & industry[1,4]



Future

Population growth
Unconventional oils
New applications

Steam reforming

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$$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$$

$$\Delta H_r = +165 \text{ kJ mol}_{CH4}^{-1}$$

10 kg CO_2 per kg H_2[5,6]

First patent in 1912[7]
Efficiencies over 80%[8]
Lowest cost route to H_2[9]

Bio-oil steam reforming

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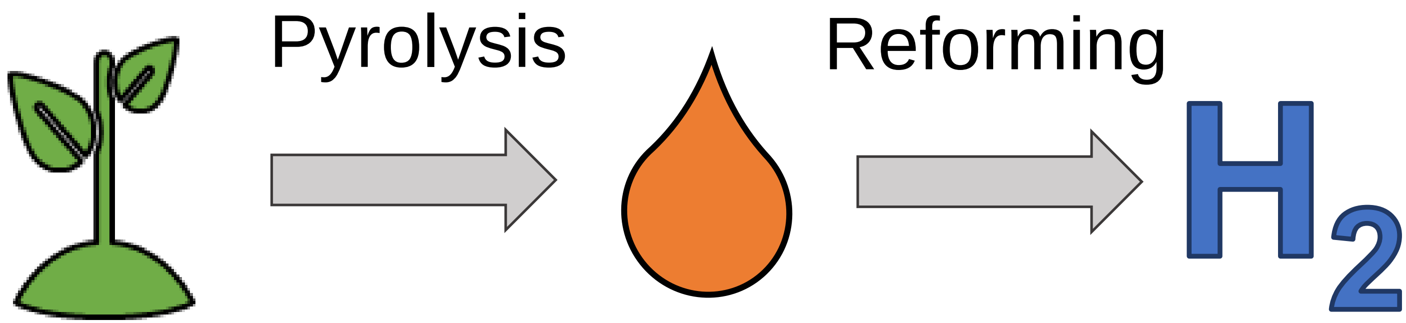

Biomass
Waste plastics
MSW

Acids
Ketones
Aldehydes
Phenolics

Energy
Bio-oil refining
Fischer-Tropsch

Research question

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How does bio-oil perform in a steam reforming process?

How do advanced steam reforming techniques enhance this performance?

Key performance indicators are:

- Hydrogen yield
- CO_2 emissions
- Thermal efficiency
- Cost

2. Conventional SR of bio-oil

Process modelling

Process modelling

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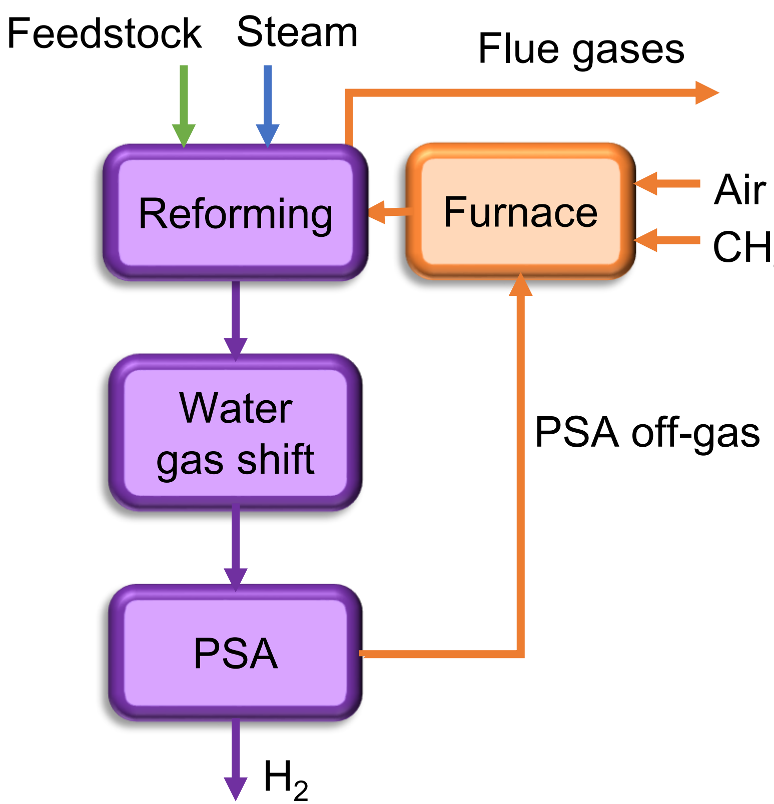

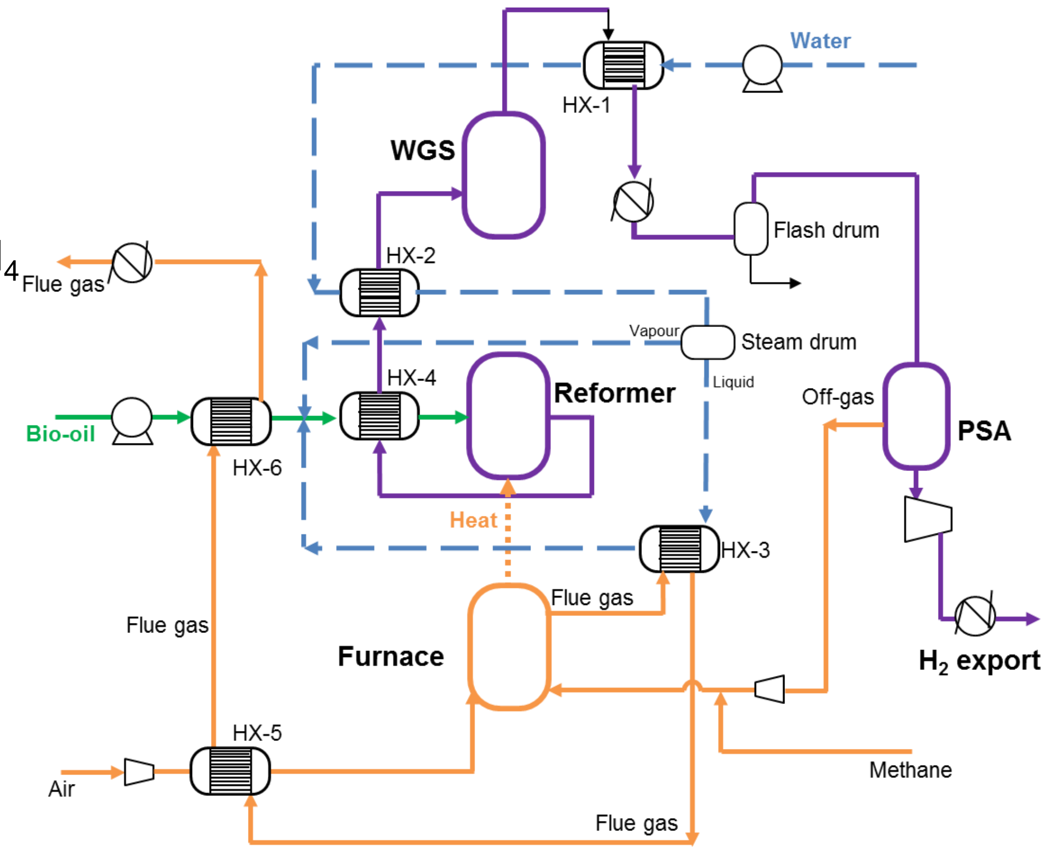

- Bio-oil modelled as surrogate mixture
- Industrial pressure (30 bar) & scale (10-100,000 Nm^3/h)

Process performance at 30 bar

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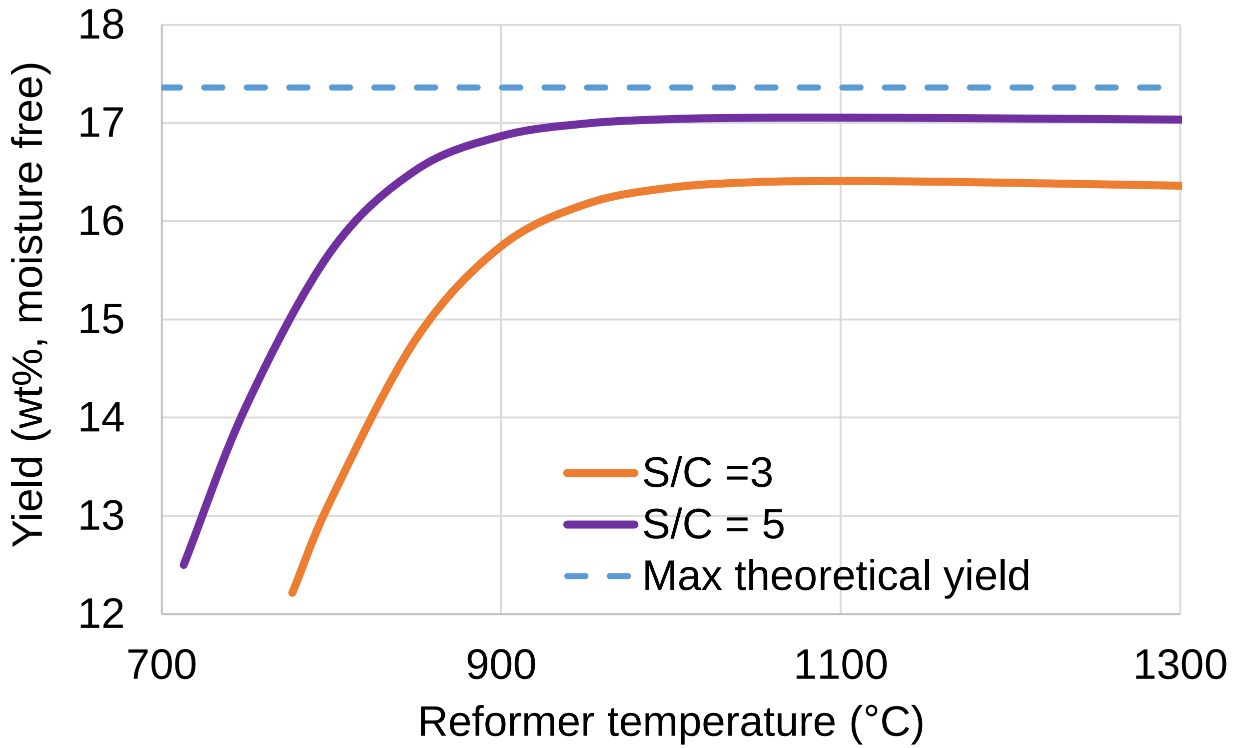

S/C = steam to carbon ratio

Process performance at 30 bar

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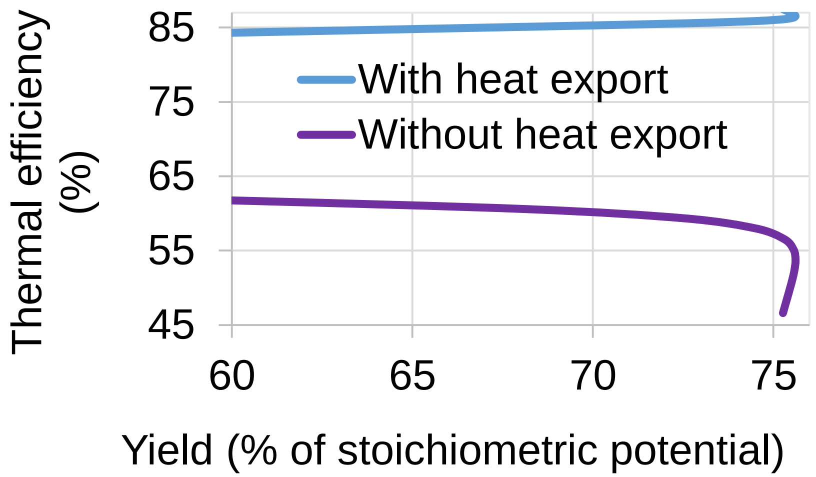
Without heat export:

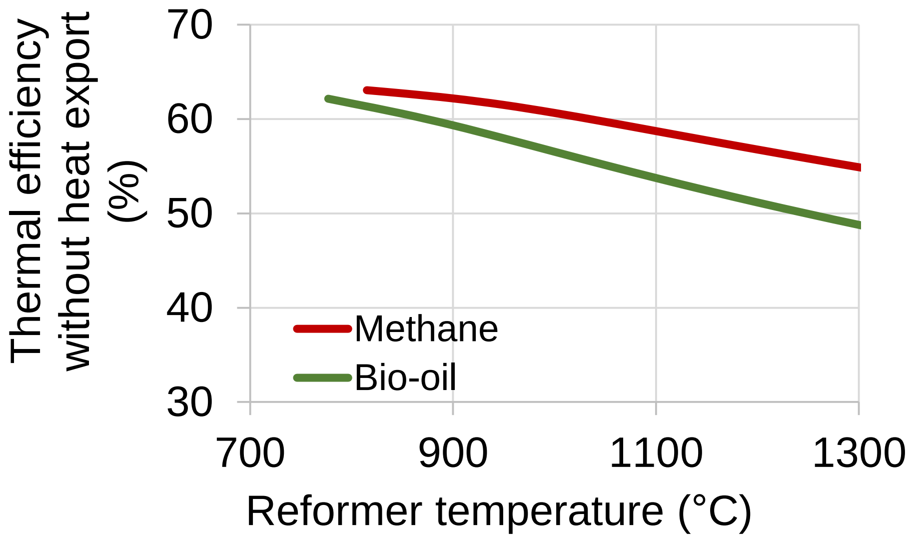
$$\eta_{thermal} = \frac{\dot{Q}_{H2}}{\dot{Q}_{bio-oil} + \dot{Q}_{methane} + P^{+}_{electrical}}$$

With heat export:

$$\eta_{thermal} = \frac{\dot{Q}_{H2} + \dot{Q}^{-}_{heat}}{\dot{Q}_{bio-oil} + \dot{Q}_{methane} + P^{+}_{electrical}}$$

where '+' and '-' signify import or export of utilities





CO_2 emissions

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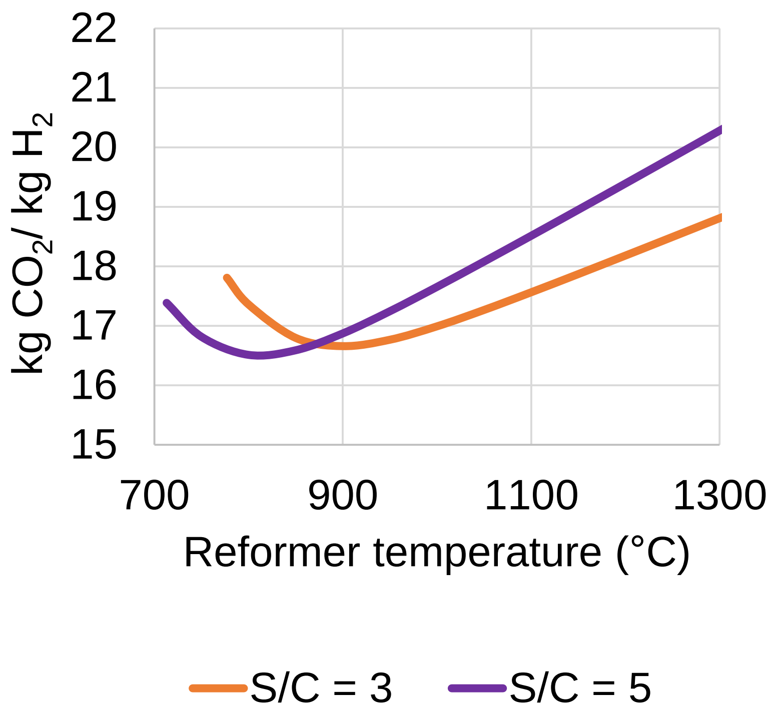

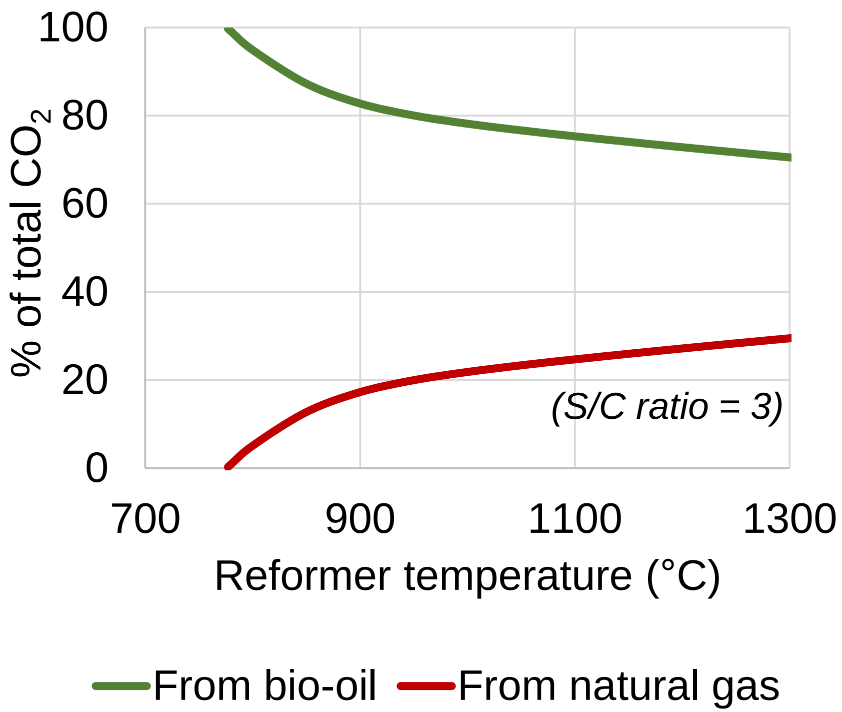

$$C_nH_mO_k + (2n - k)H_2O \leftrightarrow nCO_2 + (2n + \frac{m}{2} - k)H_2$$

CO_2 emissions (kg CO_2/kg H_2) = $\frac{n}{2n+\frac{m}{2}-k}$ + *CO_2 from furnace*

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3. CCS in bio-oil reforming

Preliminary study

CCS in steam reforming

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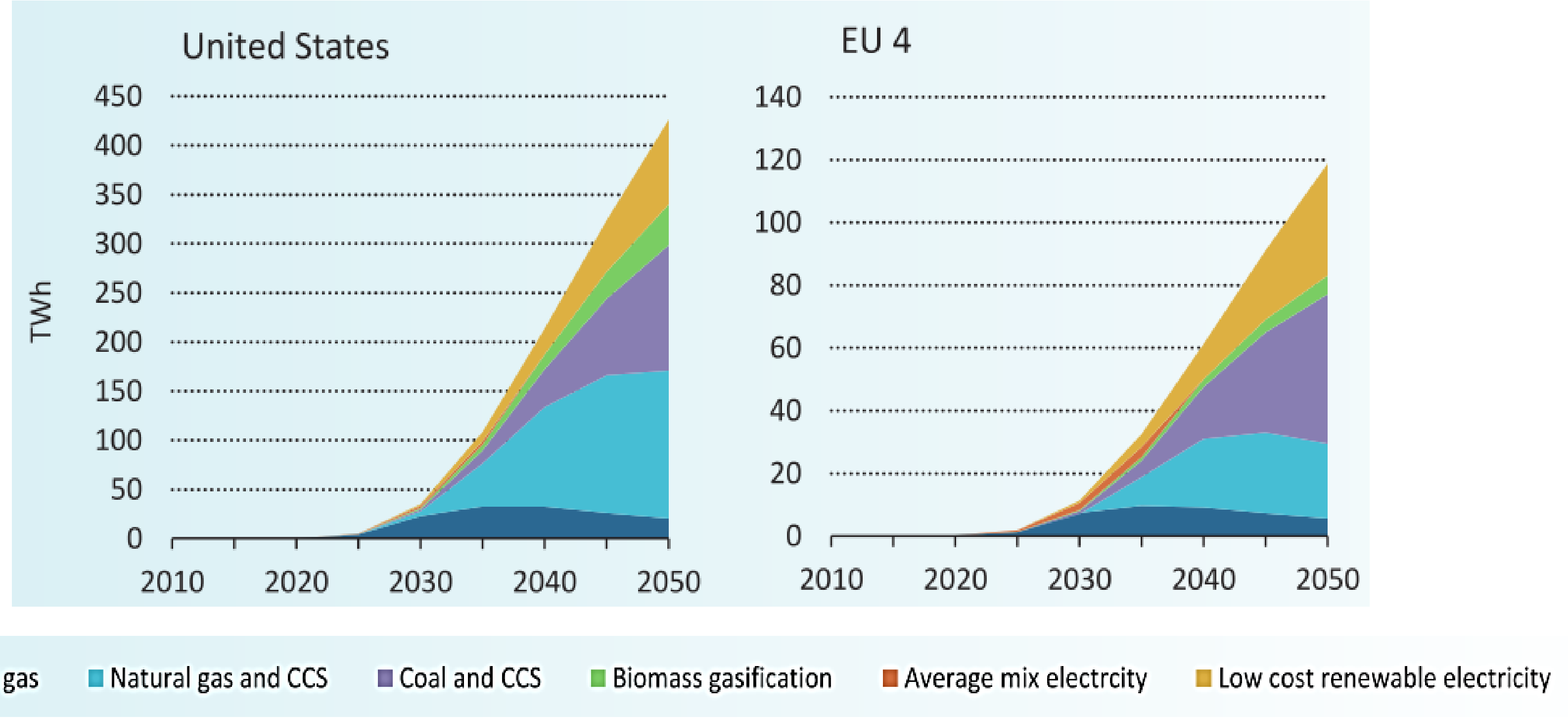
Hydrogen generation in the IEA 2°C high H2 scenario



From IEA, 2015 [1]

CCS: locations

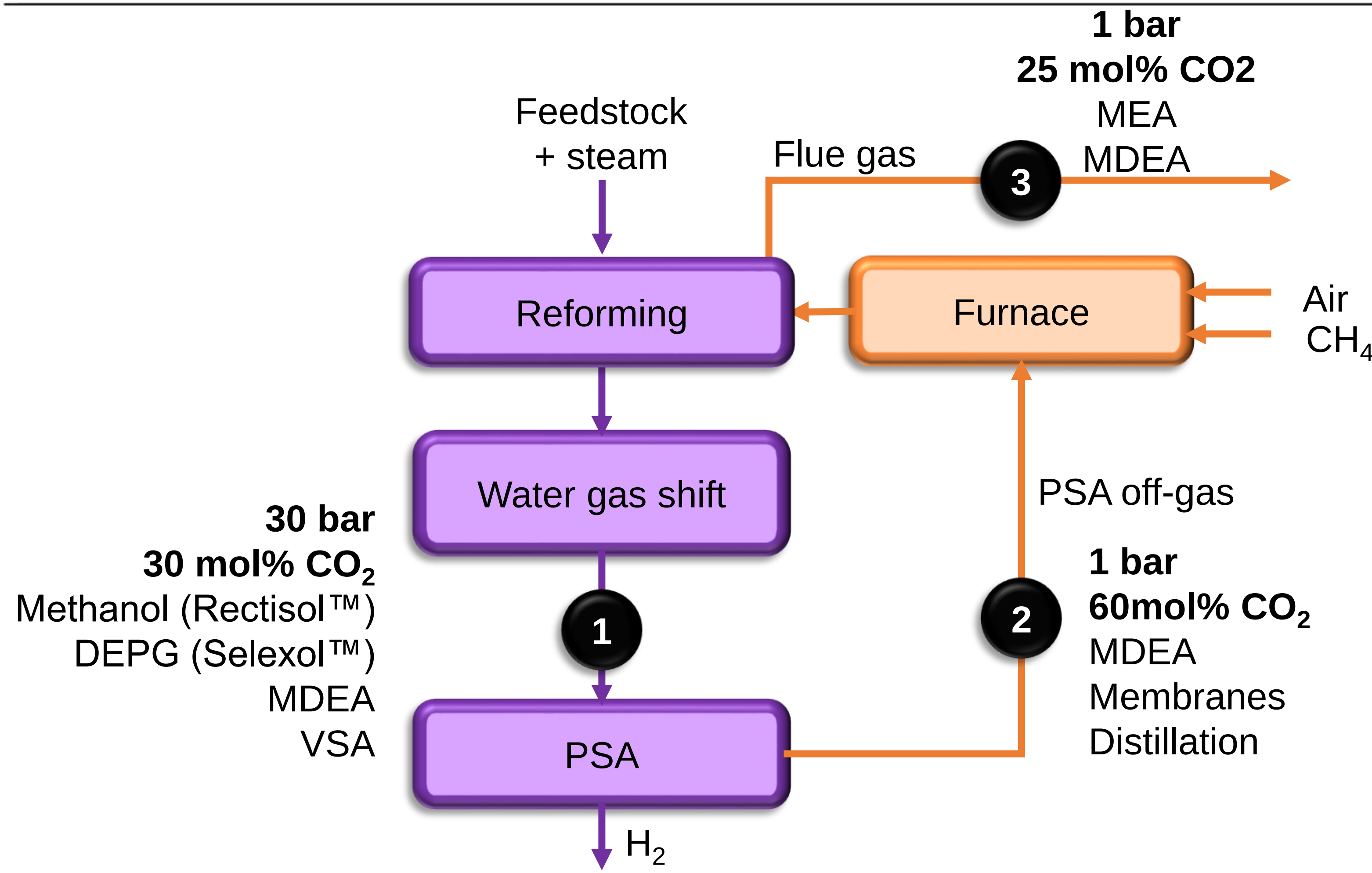
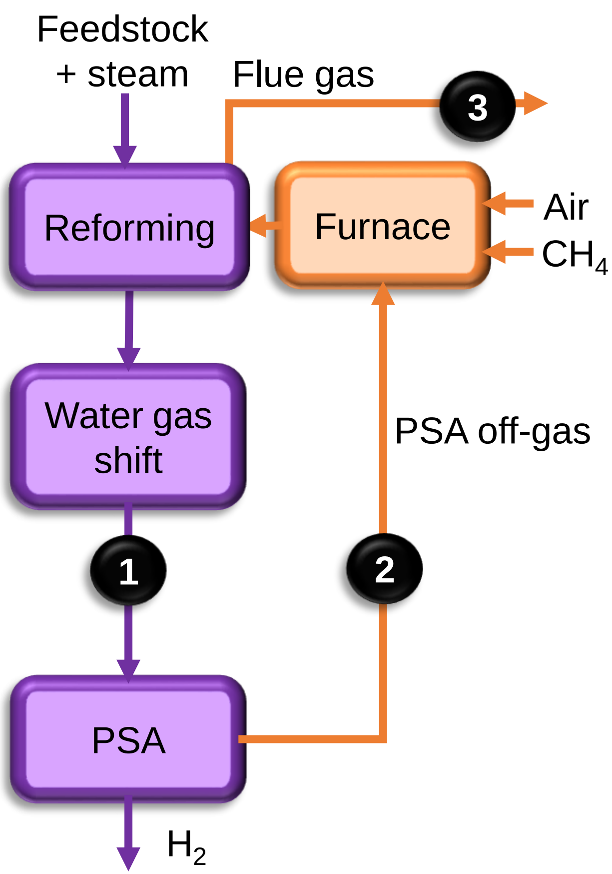


Diagram adapted from Soltani et al. [10]
Technology selections based on Im et al. [11]

CCS: impact of location



Capacity: 50,000 $Nm^3\ h^{-1}$
Bio-oil feed: 34500 kg h^{-1}

	Base case	**1 and 2**	**3**
CCS location	-	Syngas or off-gas	Flue
% of total CO_2	-	81%	100%
CO_2 capture rate			
From stream	0%	95%	90%
Process total	0%	77%	90%
Emissions (kg CO_2/kg H_2)			
Captured			
Biogenic	0.0	10.3	12.0
Fossil	0.0	2.4	2.8
Emitted			
Biogenic	13.4	3.1	1.3
Fossil	3.1	0.7	0.3

CCS: process net emissions

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Process net emissions
= fossil emissions released - biogenic emissions captured

	Bio-oil no CCS	**Bio-oil with CCS (1 or 2)**	**Bio-oil with CCS (3)**
Process net kg CO_2/kg H_2	3.1	-9.6	-11.7

Simplified analysis - direct emissions from the process.

It does not represent a full LCA, but provides a benchmark:

Bio-oil SR with CCS has net negative emissions if:

- Total other life cycle emissions < 9.6 kg CO_2/kg H_2
- Bio-oil production << 1.2 kg CO_2/kg bio-oil

CCS: modelling Rectisol™

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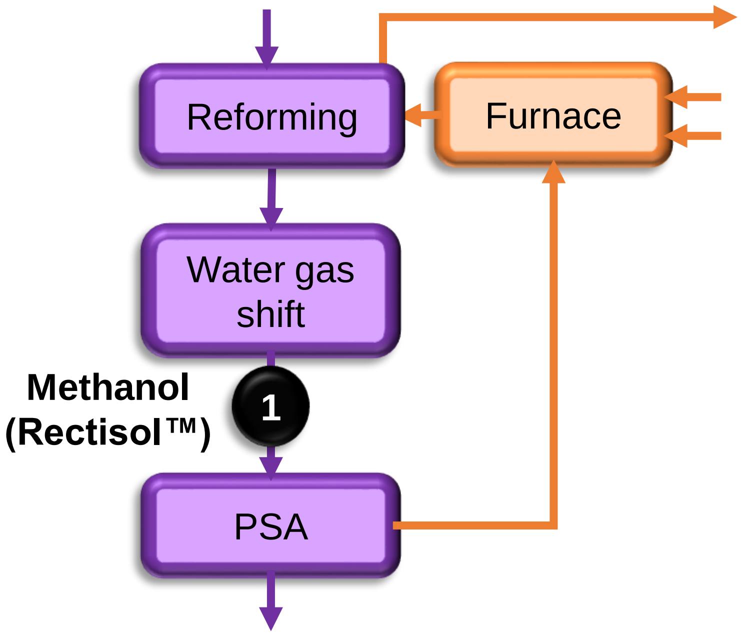

	Theoretical	Actual
CO_2 capture rate		
From stream	95%	95%
Process total	77%	79%
Emissions (kg CO_2/kg H_2)		
Process net	-9.6	-10.0

Assumes PSA recovery = 80%

Thermal efficiency (with heat export):

No CCS: 78%

With CCS: 64%

4. Advanced reforming

Improving H_2 production from bio-oil

Sorption-enhanced chemical looping

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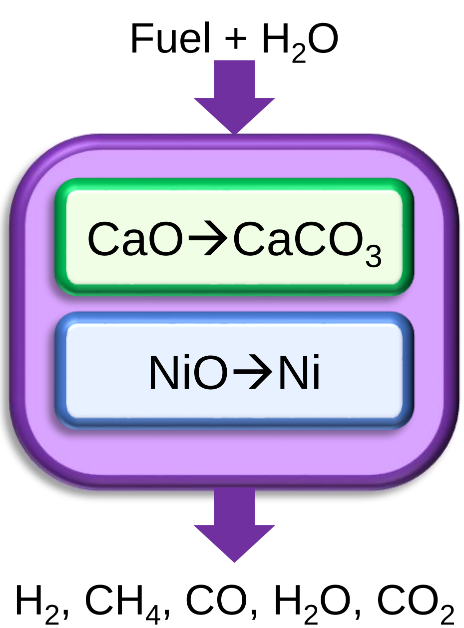
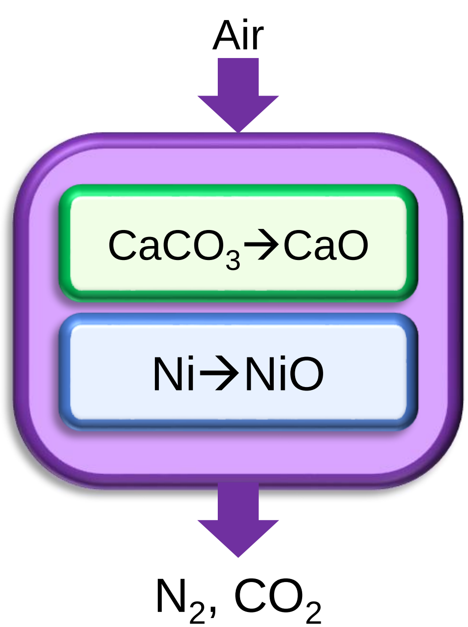
Sorption enhancement	Enhanced purity	In situ CO_2 capture	Heat from sorption	Enhanced yield
Chemical looping	Autothermal	Scalable	Efficient	

STAGE 1
Reduction, reforming, sorption



STAGE 2
Regeneration, oxidation



Thermodynamic analysis

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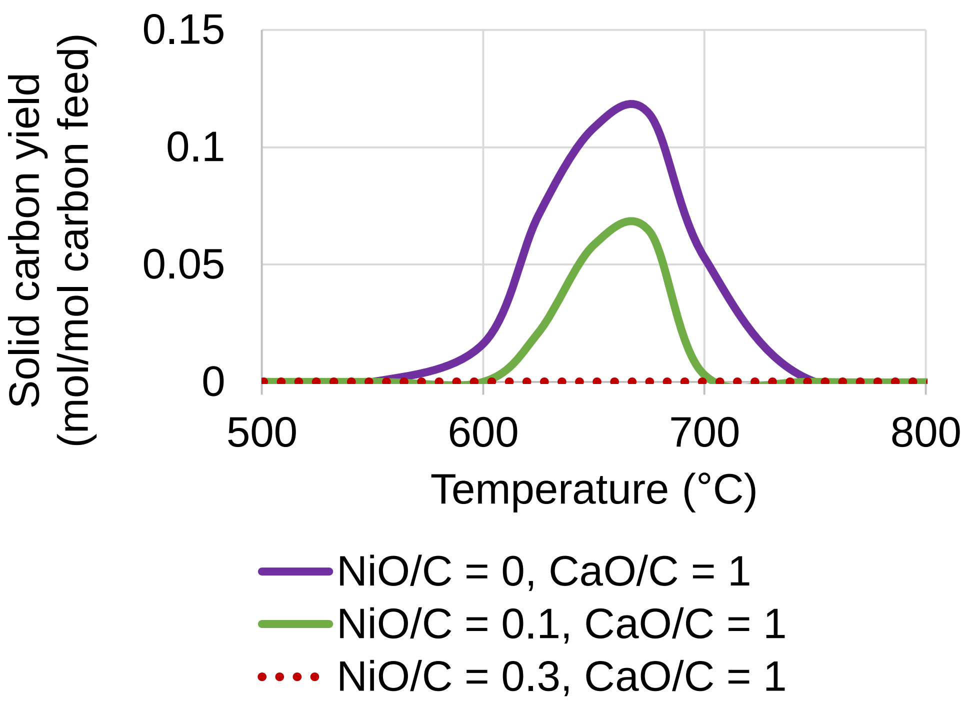
Autothermal operation at industrial pressures

Pressure (bar)	Temp (K)	Yield (wt% m.f.)	H_2 purity (mol%)
1.013	723	13.6	99.5
30	973	11.8	96.9

(S/C ratio = 2)

Carbon deposition
(S/C ratio = 1)



Next steps

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Modelling of sorption-enhanced chemical looping:

- kinetic data
- rigorous reactor modelling
- whole process modelling

Economic assessment

Techno-economic comparison of processes

Summary

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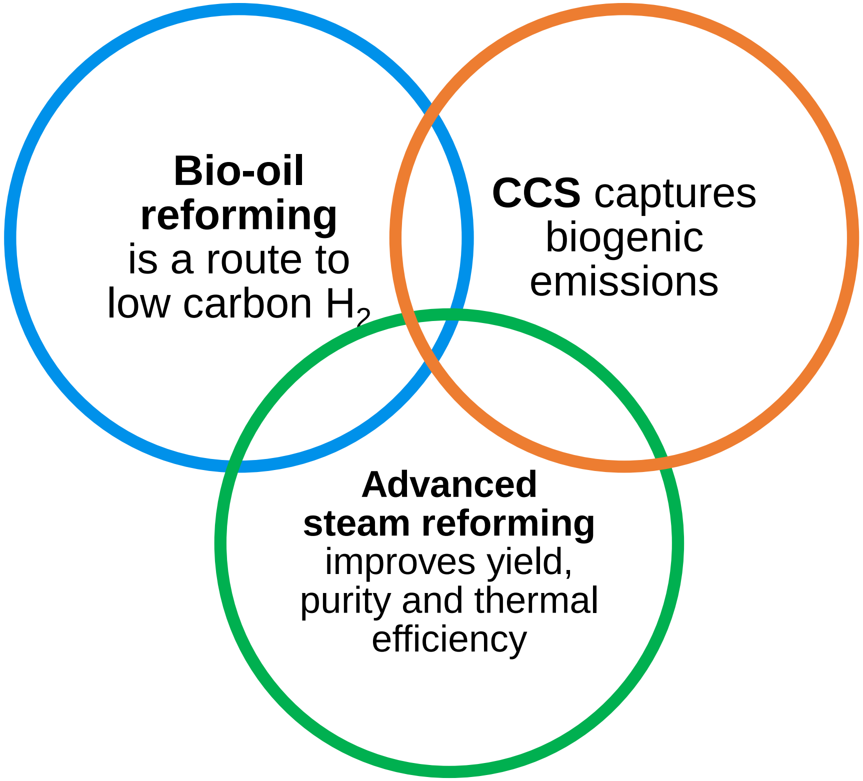
The challenge:

New methods to produce low carbon H_2 on a large scale.

A solution?



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Reformer image from ThyssenKrup: https://www.thyssenkrupp-industrial-solutions.com/en/products-and-services/chemical-plants-and-processes/organic-chemicals-and-petrochemicals/dehydrogenation-plants/overview/