Technologies Making Hydrogen Happen

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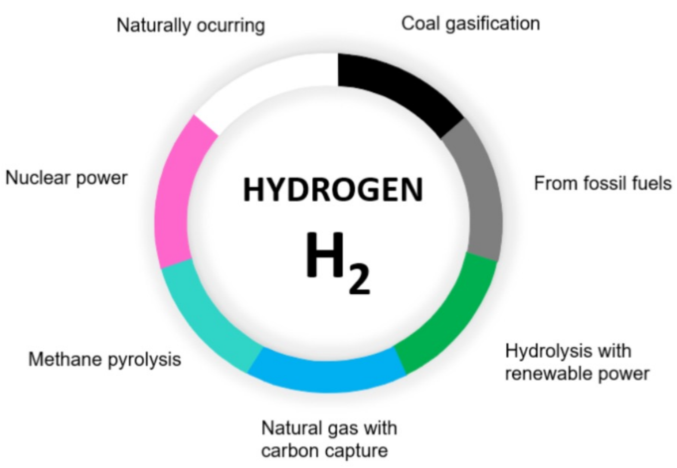
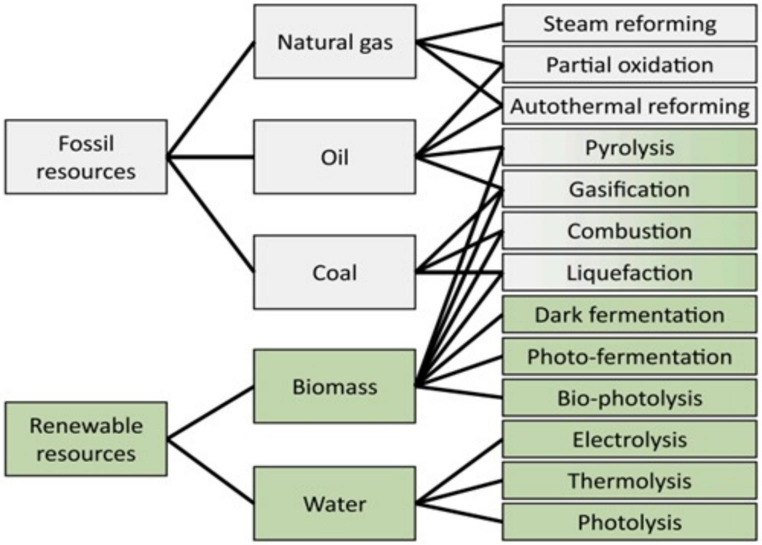
LEADERS IN IDEAS AND SOLUTIONS

Hydrogen Colours





Classification of hydrogen production technologies with regard to the use of fossil (grey) and renewable (green) resources.

	H_2 type	Production cost, \$/kg	CO_2 emissions	Ref.
⬛	Black/Brown	1.2- 2.2	830 million tonnes/ year	[30]
▨	Grey	1.0	9-12 tonnes CO_2/ every tonne H_2	[31]
🟩	Green	6	none	[32]
🟦	Blue	1.5-2.5	none	[33]
▢	Turquoise	1.5-6	None/negative	[23]

Research Areas

- ✓ Catalytic Pyrolysis & Gasification
- ✓ Hydrogenation & Hydrotreating
- ✓ High Pressure & Membrane Reactors

- ✓ Materials Development & Characterisation
- ✓ High Temperature CO2 Capture
- ✓ BECCS

Modelling (R Ocone)
Experiments (A Sanna)

Current Relevant Projects

2022-2024 KTP, Innovate UK, In collaboration with Alpha Solway (Globus Group), £200k (PI: A Sanna)

2022-2025 Production of Blue H2, Petronas, ~£1M (PI: R Ocone)

PETRONAS Global Technology Centre (PGTC)

PACESET

A new technology and research centre has been established by PETRONAS, with the Institute of GeoEnergy Engineering (IGE) at Heriot-Watt University UK campus, to pursue cleaner energy solutions.

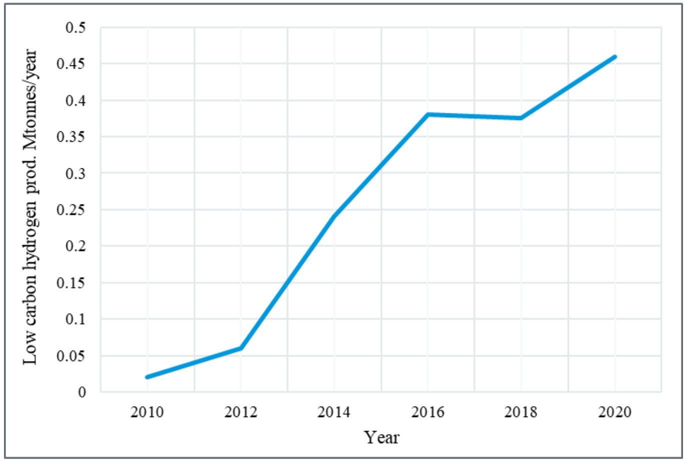
The long-term commitment will focus on research and development projects that look into solutions to reduce carbon footprint while optimising hydrocarbon resources though technological advancements and digitalisation.

NINE Projects Ongoing

Setting up ELEVEN New Projects

First project on Blue H2 ... more on the way ..

Low Carbon H2 Production



IEA, "Hydrogen - Fuels & Technologies - IEA," December 21, 2021

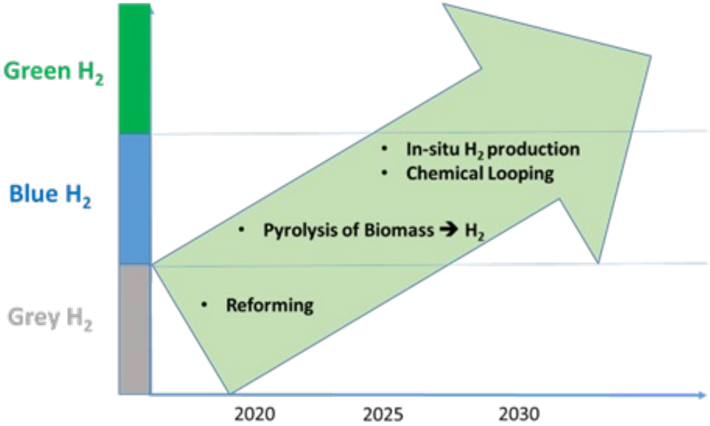
Blue Hydrogen Production via Thermochemical Routes for Application both Downhole and Topside

PETRONAS

Evolution of Thermochemical Production of H2

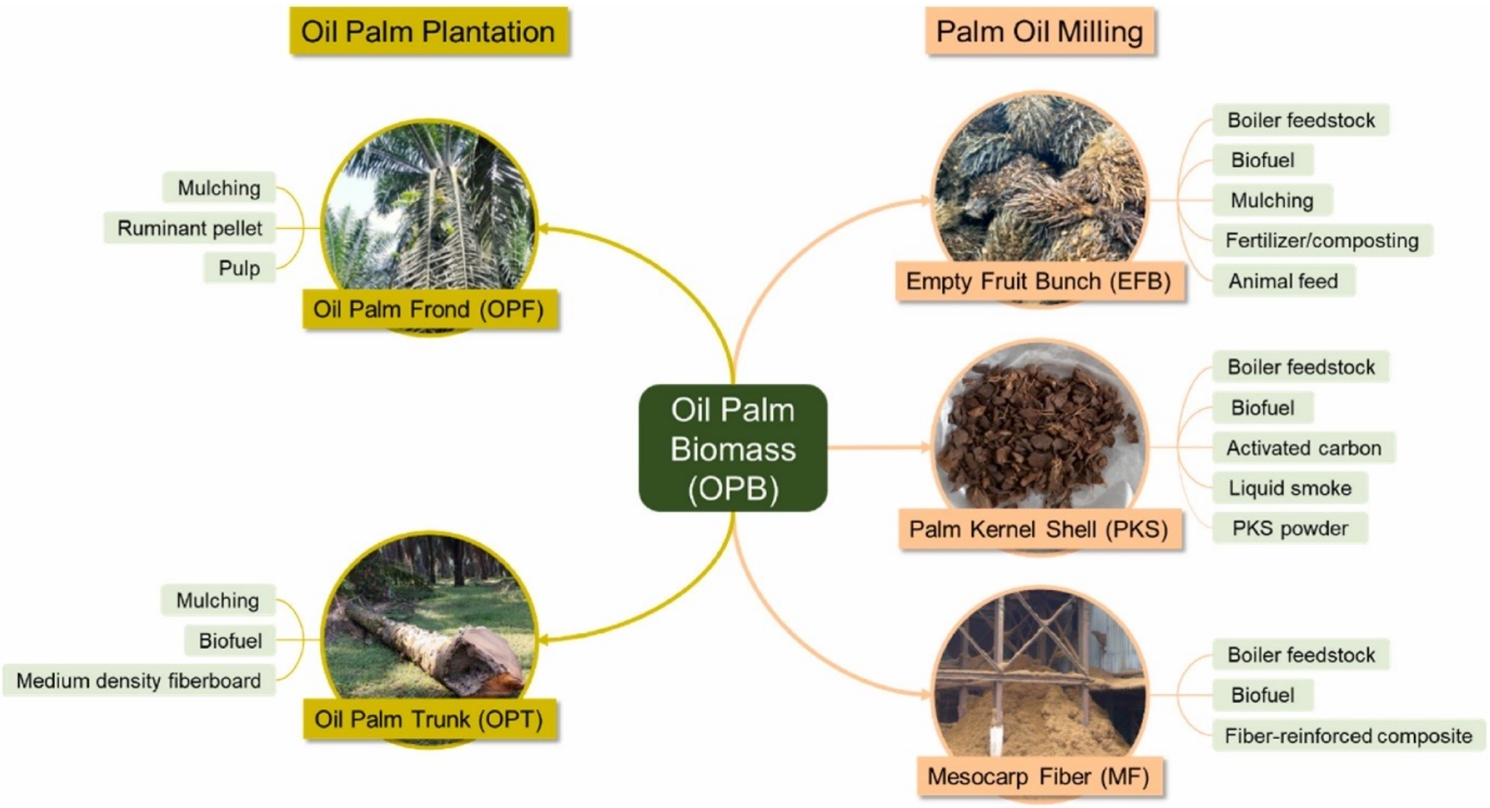
Pyrolysis of Biomass (Ocone, Sanna, Salem)

In-situ pyrolysis (Maes, Egya)



- In-situ H_2 production
- Chemical Looping
- Pyrolysis of Biomass → H_2
- Reforming

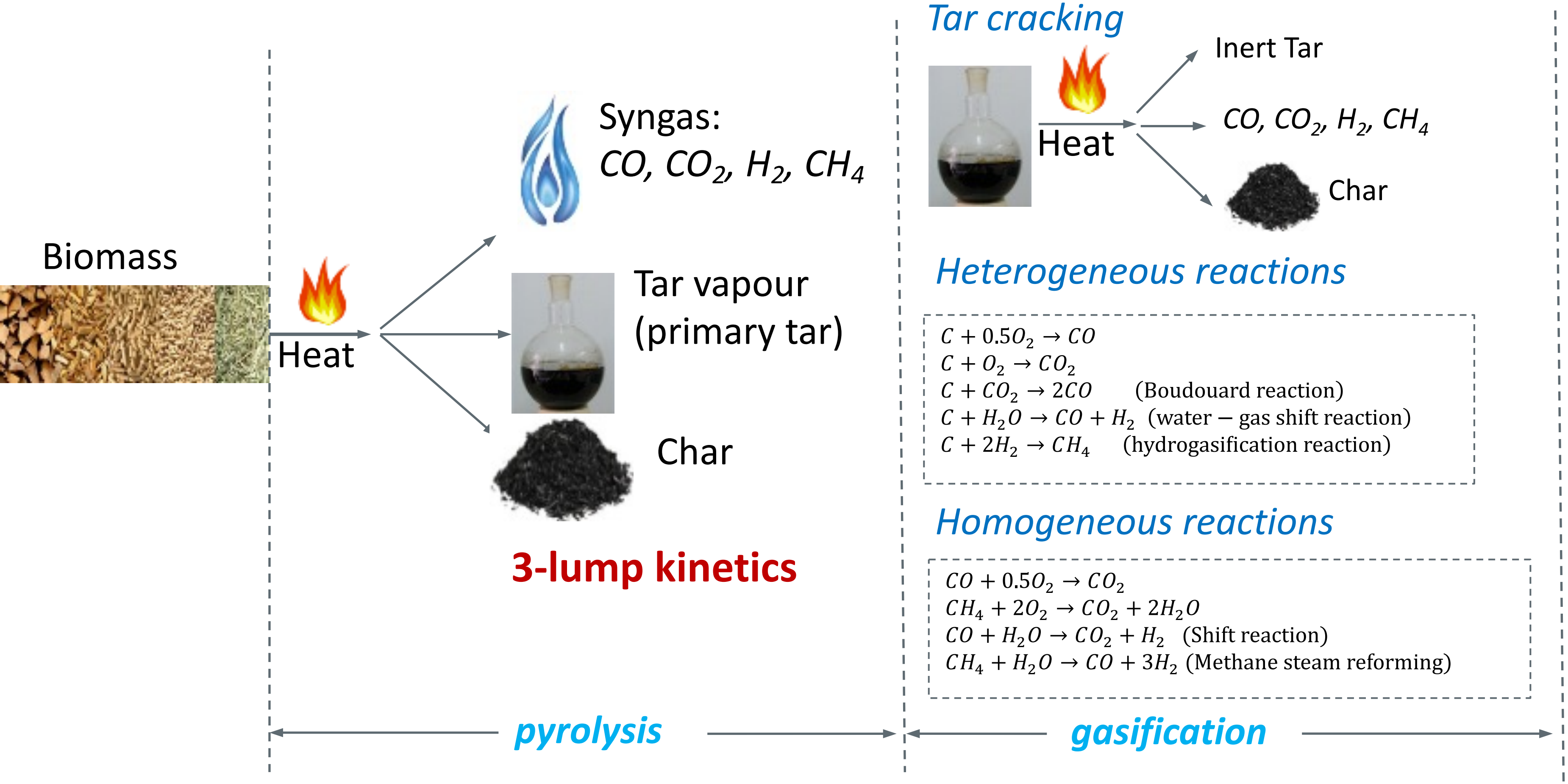
Palm oil wastes, source of bioenergy



One of the largest biomass resources is the palm products/wastes. Palm oil wastes is a promising feedstock for biohydrogen production. Palm oil demands are expected to rise to 240 Mt by 2050, resulting in massive amounts of by-products and wastes. Among bio-oil by products and wastes are empty and fresh fruit bunch, oil palm frond, palm kernel shell, seed shells, palm pressed fibre, …etc. Additionally, ***the palm oil accounts only for 10% of the total biomass, while the residual wastes are estimated by 90%***

Our selection considered a number of properties in a decision matrix based on annual production, chemical composition, minerals distribution, ash content, etc.

Pyrolysis of Biomass



Biomass

Heat

Syngas:
CO, CO_2, H_2, CH_4

Tar vapour
(primary tar)

Char

3-lump kinetics

Tar cracking

Heat

Inert Tar

CO, CO_2, H_2, CH_4

Char

Heterogeneous reactions

$C + 0.5O_2 \rightarrow CO$
$C + O_2 \rightarrow CO_2$
$C + CO_2 \rightarrow 2CO$ (Boudouard reaction)
$C + H_2O \rightarrow CO + H_2$ (water – gas shift reaction)
$C + 2H_2 \rightarrow CH_4$ (hydrogasification reaction)

Homogeneous reactions

$CO + 0.5O_2 \rightarrow CO_2$
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
$CO + H_2O \rightarrow CO_2 + H_2$ (Shift reaction)
$CH_4 + H_2O \rightarrow CO + 3H_2$ (Methane steam reforming)

pyrolysis

gasification

Methodology

- ✓ **Pyrolysis of biomass (Blue H_2)**
  - Feedstock Characterisation
  - Catalyst Screening

- ✓ **In-situ (downhole) pyrolysis** optimised for Blue H_2 production
  - In-situ challenges: comparison/differences with in-situ combustion
  - Chemical re-optimisation for Blue H_2 production

- ✓ **Modelling**

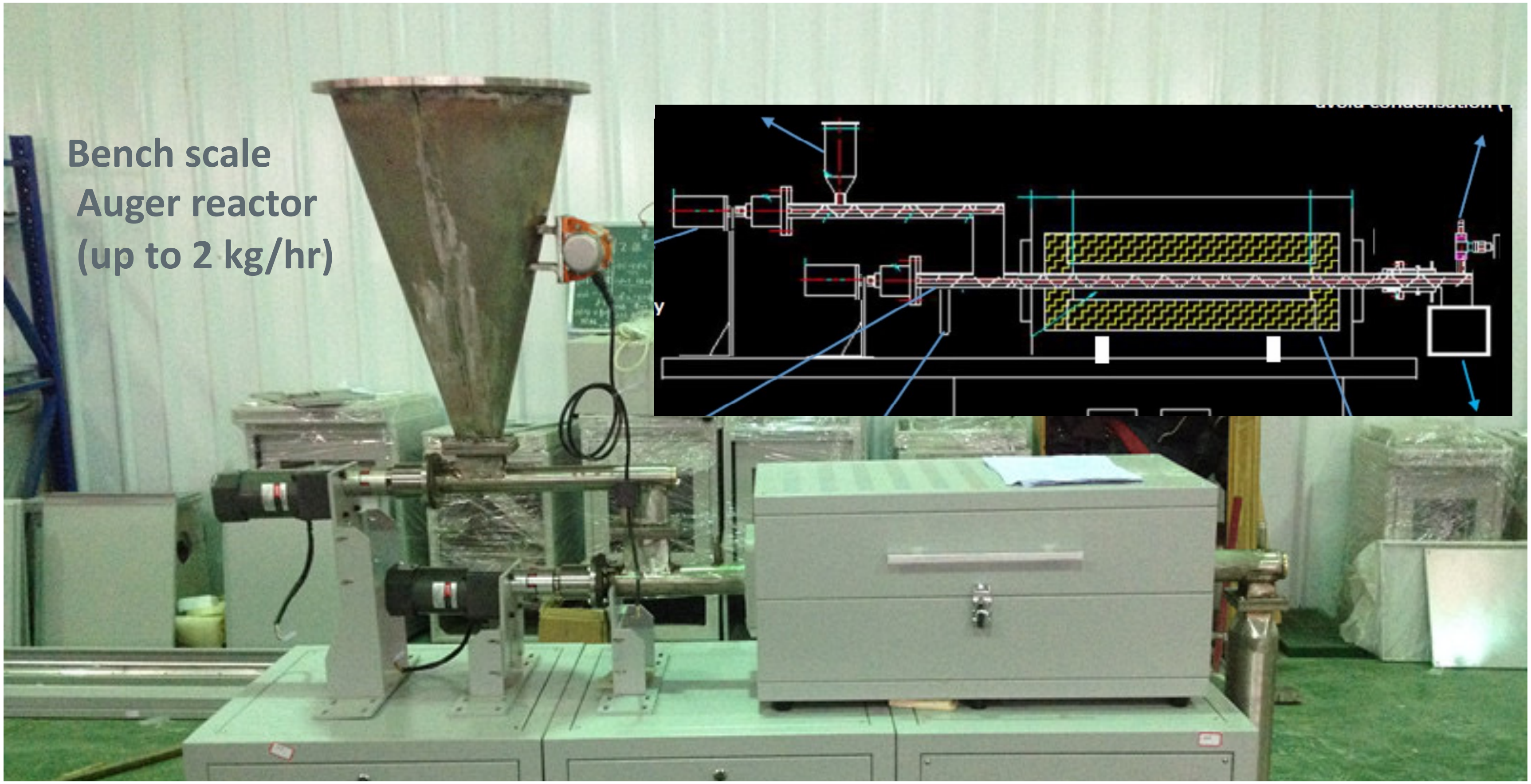
Current Interests

Lignin, plastic, catalyst development/evaluation, chemicals and **hydrogen** production, scale-up, TEA

Biomass Pyrolysis/Gasification

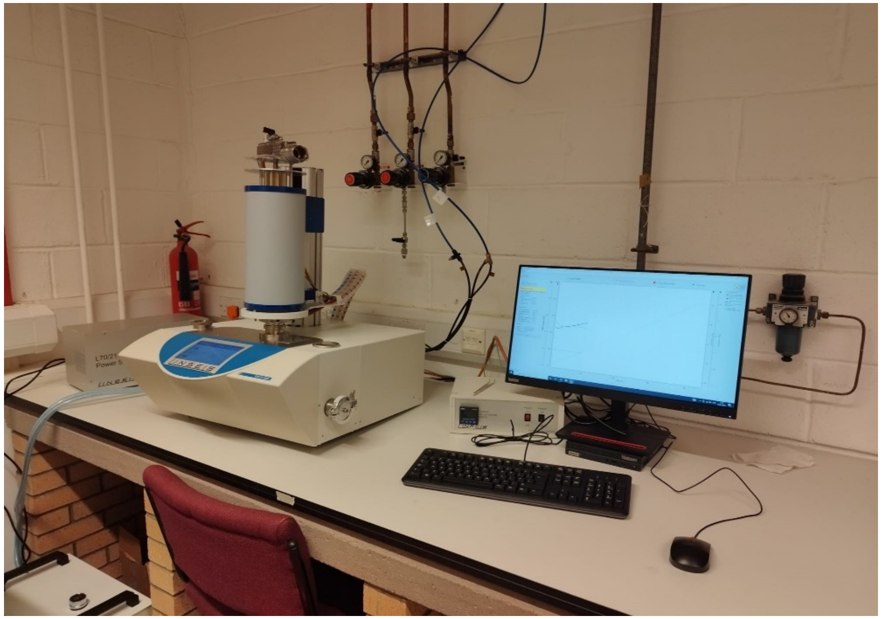
Small scale
fixed bed reactor
(up to 10 g)

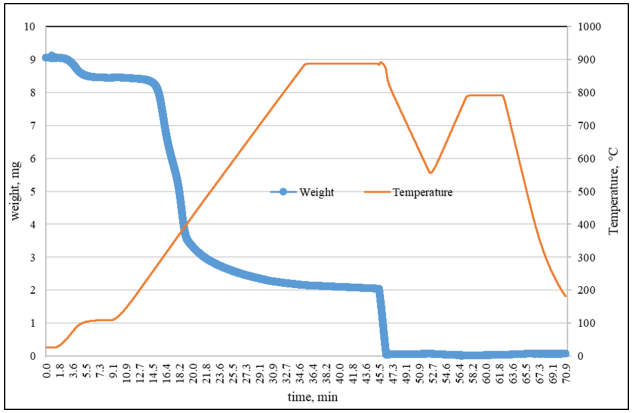
Biomass Pyrolysis/Gasification



Bench scale
Auger reactor
(up to 2 kg/hr)

Thermogravimetric analysis (TGA)





- ✓ Linseis STA PT 1600 is used for the analysis.
- ✓ 5 different heating rates are used; (1,5,10,20,&30 °C /min).
- ✓ Temperature range (up to 900 °C)
- ✓ Mixtures of (N_2 and CO_2) are used during pyrolysis and reforming of the samples.
- ✓ Data are used for calculating the kinetic parameters of the samples (A, E, R^2).
- ✓ Collected data (T, gas flowrate, time, heat flow, enthalpy of reaction, mass loss, HDSC signal (µV), ….etc)

Model

Continuity equation:

Gas phase:

$$\frac{\partial(\alpha_g \rho_g)}{\partial t} + \nabla(\alpha_g \rho_g \vec{u}_g) = R_g$$

Solid phase:

$$\frac{\partial(\alpha_{s_i} \rho_{s_i})}{\partial t} + \nabla(\alpha_{s_i} \rho_{s_i} \vec{u}_{s_i}) = R_{s_i}$$

$$\sum_{i=1}^{2} \alpha_{s_i} + \alpha_g = 1$$

Momentum equation :

Gas phase:

$$\frac{\partial(\alpha_g \rho_g \vec{u}_g)}{\partial t} + \nabla(\alpha_g \rho_g \vec{u}_g \vec{u}_g) = -\alpha_g \nabla P + \nabla \bar{\bar{\tau}}_g - \sum_{i=1}^{2} \beta_{gs_i}(\vec{u}_g - \vec{u}_{s_i}) + \alpha_g \rho_g \vec{g} + \vec{R}_{s_2 g} + \dot{m}_{s_2 g} \vec{u}_{s_2 g}$$

Sand phase:

$$\frac{\partial(\alpha_{s_1} \rho_{s_1} \vec{u}_{s_1})}{\partial t} + \nabla(\alpha_{s_1} \rho_{s_1} \vec{u}_{s_1} \vec{u}_{s_1}) = -\alpha_{s_1} \nabla P - \nabla P_{s_1} + \nabla \bar{\bar{\tau}}_{s_1} + \beta_{gs_1}(\vec{u}_g - \vec{u}_{s_1}) + \beta_{s_1 s_2}(\vec{u}_{s_2} - \vec{u}_{s_1}) + \alpha_{s_1} \rho_{s_1} \vec{g}$$

Biomass phase:

$$\frac{\partial(\alpha_{s_2} \rho_{s_2} \vec{u}_{s_2})}{\partial t} + \nabla(\alpha_{s_2} \rho_{s_2} \vec{u}_{s_2} \vec{u}_{s_2})$$
$$= -\alpha_{s_2} \nabla P - \nabla P_{s_2} + \nabla \bar{\bar{\tau}}_{s_2} + \beta_{gs_2}(\vec{u}_g - \vec{u}_{s_2}) + \beta_{s_2 s_1}(\vec{u}_{s_1} - \vec{u}_{s_2}) + \alpha_{s_2} \rho_{s_2} \vec{g} + \vec{R}_{gs_2} - \dot{m}_{s_2 g} \vec{u}_{s_2 g}$$

Granular temperature:

Solid phase:

$$\frac{3}{2}\left[\frac{\partial(\alpha_{s_i} \rho_s \Theta_{s_i})}{\partial t} + \nabla(\alpha_{s_i} \rho_s \Theta_{s_i}) \vec{u}_{s_i}\right] = \left(-P_{s_i} \bar{\bar{I}} + \bar{\bar{\tau}}_{s_i}\right) : \nabla \vec{u}_{s_i} + \nabla\left(\kappa_{\Theta_{s_i}} \nabla \Theta_{s_i}\right) - \gamma_{\Theta_{s_i}} + \sum_{k=1}^{2} \phi_{ks_i}$$

X. Yu, Y. Makkawi, R. Ocone, M. Huard, C. Briens, F. BerrutiFuel Proc Tech, 126, 366-382, 2014

Model

Gas species conservation

$$\frac{\partial(\alpha_g \rho_g Y_{i,g})}{\partial t} + \nabla(\alpha_g \rho_g \vec{u}_g Y_{i,g}) = -\nabla \cdot \alpha_g \vec{J}_{i,g} + (\dot{m}_{i,gs_2} - \dot{m}_{i,s_2 g}) + R_{i,g}$$

diffusion flux of species i

$$\vec{J}_{i,g} = -\left(\rho_g D_{i,g} + \frac{\mu_t}{Sc_t}\right)\nabla Y_{i,g} - D_{T,i,g}\frac{\nabla T}{T}$$

Energy equation

Gas phase:

$$\frac{\partial(\alpha_g \rho_g h_g)}{\partial t} + \nabla(\alpha_g \rho_g \vec{u}_g h_g) = \alpha_g \frac{\partial P_g}{\partial t} + \bar{\bar{\tau}}_g : \nabla \vec{u}_g - \vec{q}_g + S_g + Q_{gs_1} + Q_{gs_2} + (\dot{m}_{s_2 g} h_{s_2 g} - \dot{m}_{gs_2} h_{gs_2})$$

Sand phase:

$$\frac{\partial(\alpha_{s_1} \rho_{s_1} h_{s_1})}{\partial t} + \nabla(\alpha_{s_1} \rho_{s_1} \vec{u}_{s_1} h_{s_1}) = \alpha_{s_1} \frac{\partial P_{s_1}}{\partial t} + \bar{\bar{\tau}}_{s_1} : \nabla \vec{u}_{s_1} - \vec{q}_{s_1} + Q_{s_1 g}$$

Biomass phase:

$$\frac{\partial(\alpha_{s_2} \rho_{s_2} h_{s_2})}{\partial t} + \nabla(\alpha_{s_2} \rho_{s_2} \vec{u}_{s_2} h_{s_2}) = \alpha_{s_2} \frac{\partial P_{s_2}}{\partial t} + \bar{\bar{\tau}}_{s_2} : \nabla \vec{u}_{s_2} - \vec{q}_{s_2} - S_g + Q_{s_2 g} + (\dot{m}_{gs_2} h_{gs_2} - \dot{m}_{s_2 g} h_{s_2 g})$$

The intensity of the heat exchange between the gas and solid phase

$$Q_{s_i g} = h'_{s_i g} A_i (T_{s_i} - T_g)$$

The heat transfer coefficient

$$h'_{s_i g} = \frac{\kappa_g Nu_{s_i}}{d_{s_i}}$$

Nusselt number

$$Nu_{s_i} = (7 - 10\alpha_g + 5\alpha_g^2)\,(1 + 0.7 Re_{s_i}^{0.2} Pr^{1/3}) + (1.33 - 2.4\alpha_g + 1.2\alpha_g^2) Re_{s_i}^{0.7} Pr^{1/3}$$

Closure Equations

Chemical composition of switch grass

	Fixed carbon	Moisture	Volatile	Ash
Proximate analysis (wt%)	13.81	2.65	81.20	2.54
	C	H	O	N
Ultimate analysis (wt%)	48.8	6.99	43.68	0.53

Drying

$$m_{lv} = k_m \times \alpha_l \rho_l \frac{(T_l - T_{sat})}{T_{sat}}$$

A one-global reaction scheme is used to for the formation of various pyrolysis products as follows (*Boateng and Mtui, 2012*)

$$\boldsymbol{BIOMASS \rightarrow \alpha_1 CHAR + \alpha_2 BIO.OIL + \alpha_3 H_2O + \alpha_4 H_2 + \alpha_5 CO + \alpha_6 CO_2 + \alpha_7 CH_4}$$

Stoichiometric coefficient used in the pyrolysis reaction (*Boateng and Mtui, 2012*)

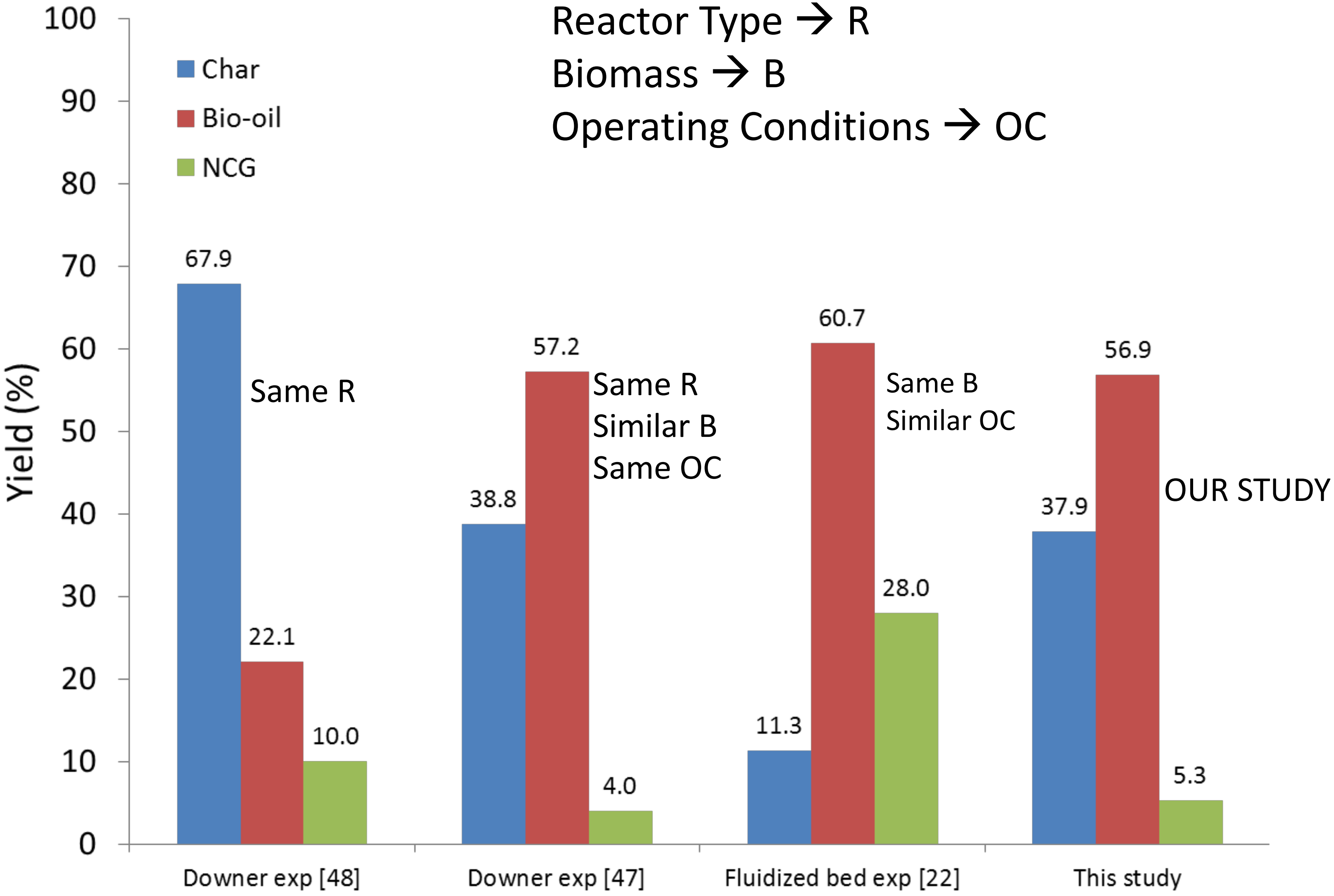
α_1	α_2	α_3	α_4	α_5	α_6	α_7
0.138	0.805	0.15	0.003	0.035	0.018	0.008

Pasangulapati,2012

$$r = k\alpha_{s_2} [C_{vol}]^{0.67} \qquad k = Aexp[-E/RT]$$

Pre-exponential factor A and the activation energy E used are 2.16× 10^7 s^{-1} and 1.037 × 10^8 J/Kmol

Results



Reactor Type → R
Biomass → B
Operating Conditions → OC

Same R

Same R
Similar B
Same OC

Same B
Similar OC

OUR STUDY

Comparison of the predictions and experimental data from the literature for the mass fraction of the pyrolysis products at steady state condition (a) Overall products (b) non- condensable gases. See further details on the operating conditions in the comments table.

Comments

(1) Reactor (Ding et al, 2012) [48] : 0.1 m diameter and 1.1 m height; biomass: Palm shell of 280 µm diameter; pyrolysis temperature of 520 °C; heated section of 0.2 m.

(2) Reactor (Punsuwan and Tangsathitkulchai, 2014) [47]: 0.039 m diameter and 3 m height; biomass: acid treated wheat straw of 180~280 µm diameter; pyrolysis temperature of 400 °C.

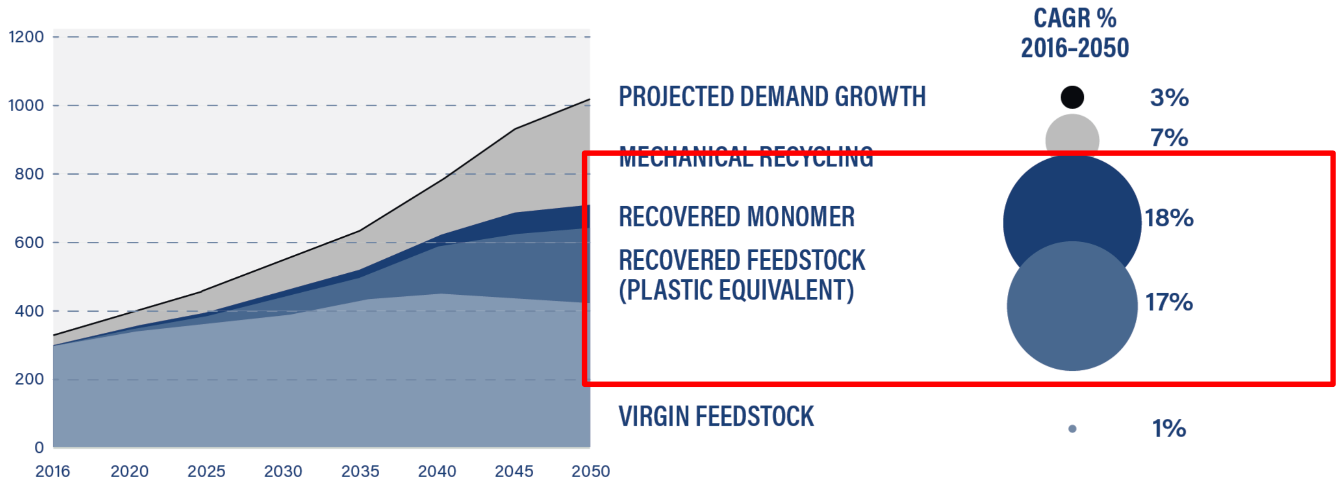
(3) Reactor (Boateng and Mtui, 2012) [22]: 0.075 m diameter and 0.5 m height; material: Switch grass of 500 µm size; wall temperature 480-550 °C.

PPE Waste Pyrolysis

- Pyrolysis offers an effective means for recovering energy and chemicals through carbon rearrangement, eradicate waste management problems
- It does not need earlier separation of dissimilar waste plastics; hence a mix of plastics can also be converted into crude bio-oil
- It is not affected by bio-contamination since operates at high temperature and without need of sorting

Market Opportunity

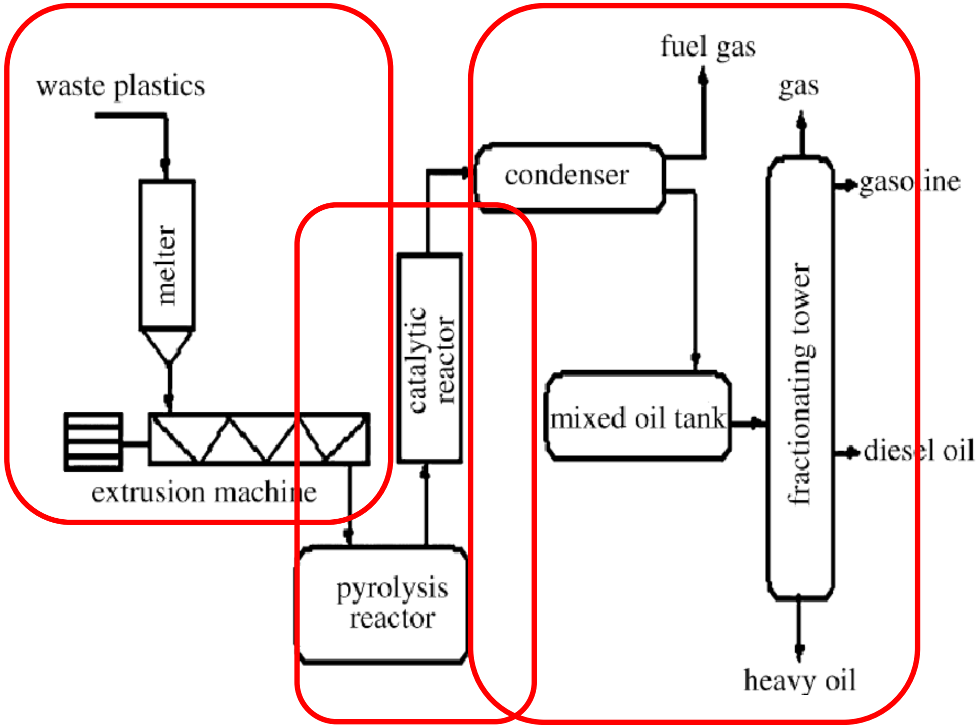
McKinsey & Company has predicted that chemical recycling will contribute to a 60 billion USD growth in the profit pool of the petrochemical and plastics sectors between 2016 and 2030.



GLOBAL POLYMER DEMAND AND HOW IT COULD BE RECOVERED, MILLIONS OF METRIC TONS

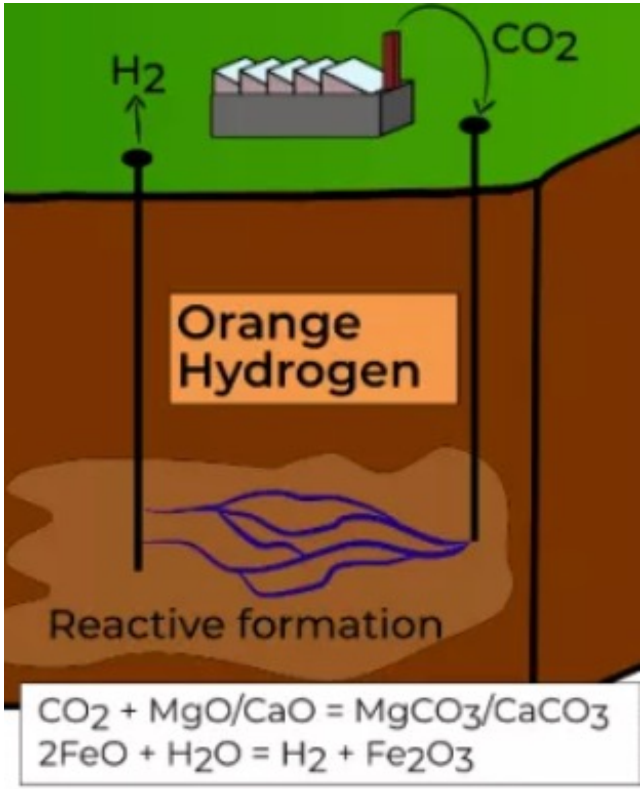
Source: How plastics waste recycling could transform the chemical industry. DECEMBER 2018, MCKINSEY ON CHEMICALS

Pyrolysis Option

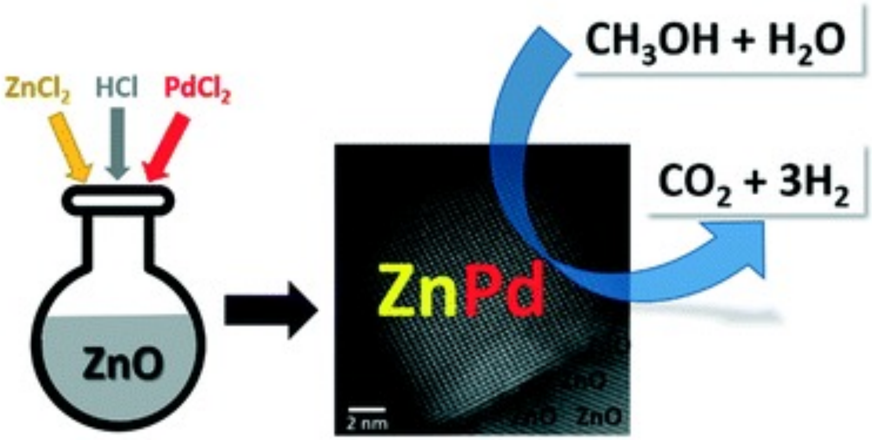


- ✓ High flexibility and modularity
- ✓ Lower capex and operating issues than gasification
- ✓ Potential for recovering metal
- ✓ Pyrolysis particularly attractive for PP/PE for absence of O_2 and low char yield
- ✓ Carbon distribution into products is controllable by altering the operational parameters and adopting catalysts

Future Work



Orange H2 production



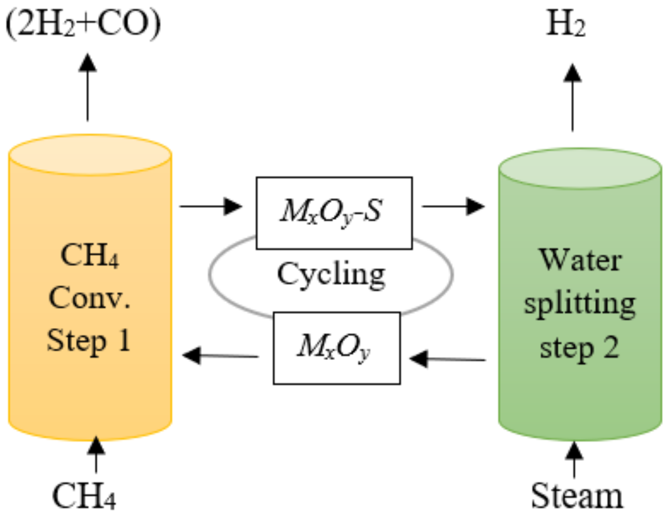
Methanol SR

There are approximately 100 trillion tonnes of hydrogen that could be extracted from the subsurface within 1020 kg of peridotites in the upper surface (~ 7km) – **COMBINING H2 PRODUCTION with CO2 STORAGE**

Future Work

Chemical looping SMR

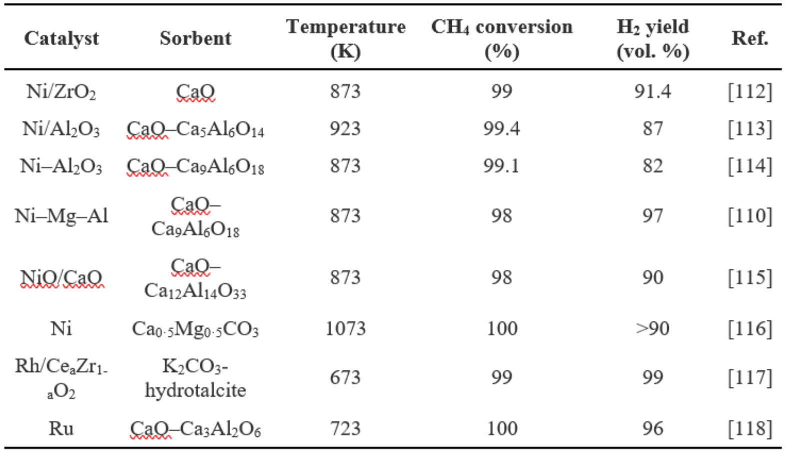
The technology could be easily integrated with gasification or pyrolysis.



Sorbent enhanced SMR

CO2 sorbents are added during the SMR process. The equilibrium drives the shift of the WGS and SMR reactions towards hydrogen production. The process shows higher performance with potential to reduce the reactor volume.

Table 8: Representative catalysts for sorbent enhanced SMR process.



Catalyst	Sorbent	Temperature (K)	CH_4 conversion (%)	H_2 yield (vol. %)	Ref.
Ni/ZrO_2	CaO	873	99	91.4	[112]
Ni/Al_2O_3	$CaO–Ca_5Al_6O_{14}$	923	99.4	87	[113]
$Ni–Al_2O_3$	$CaO–Ca_9Al_6O_{18}$	873	99.1	82	[114]
Ni–Mg–Al	$CaO–Ca_9Al_6O_{18}$	873	98	97	[110]
NiO/CaO	$CaO–Ca_{12}Al_{14}O_{33}$	873	98	90	[115]
Ni	$Ca_{0.5}Mg_{0.5}CO_3$	1073	100	>90	[116]
$Rh/Ce_aZr_{1-a}O_2$	K_2CO_3-hydrotalcite	673	99	99	[117]
Ru	$CaO–Ca_3Al_2O_6$	723	100	96	[118]