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Science and Technology

Hydrogen Potential Role in Decarbonizing Heavy Industry

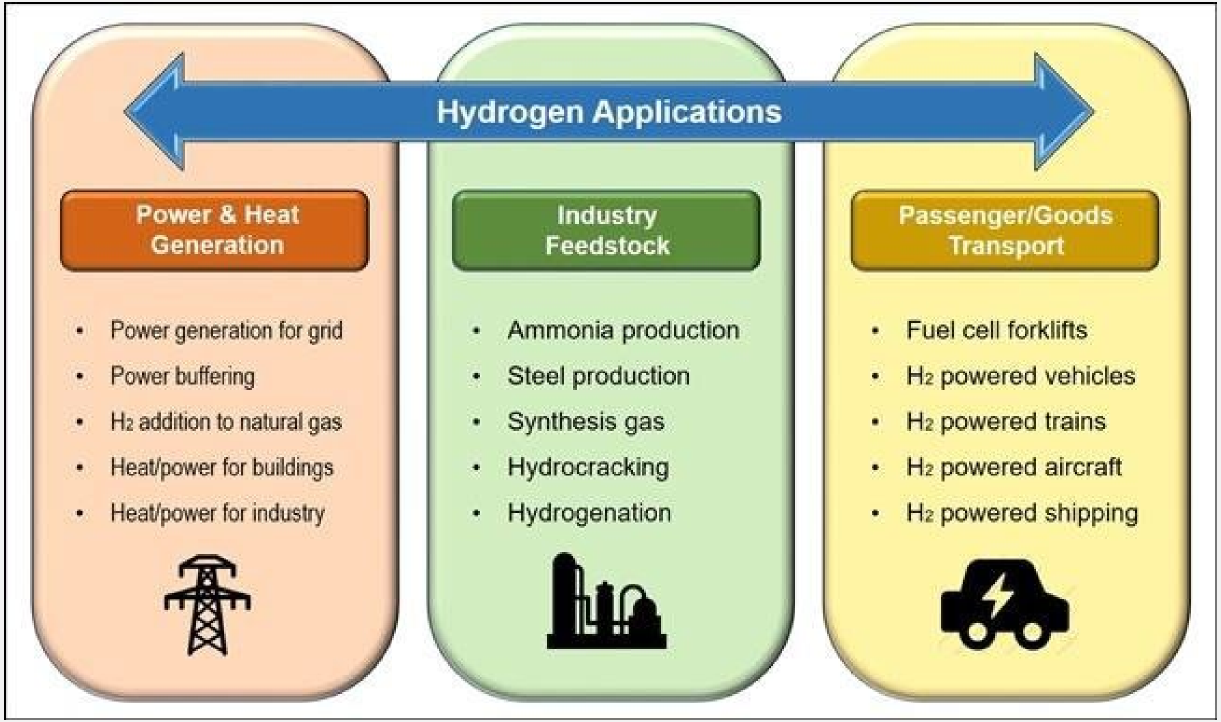
Bassam Dally

Clean Combustion Research Center (CCRC)

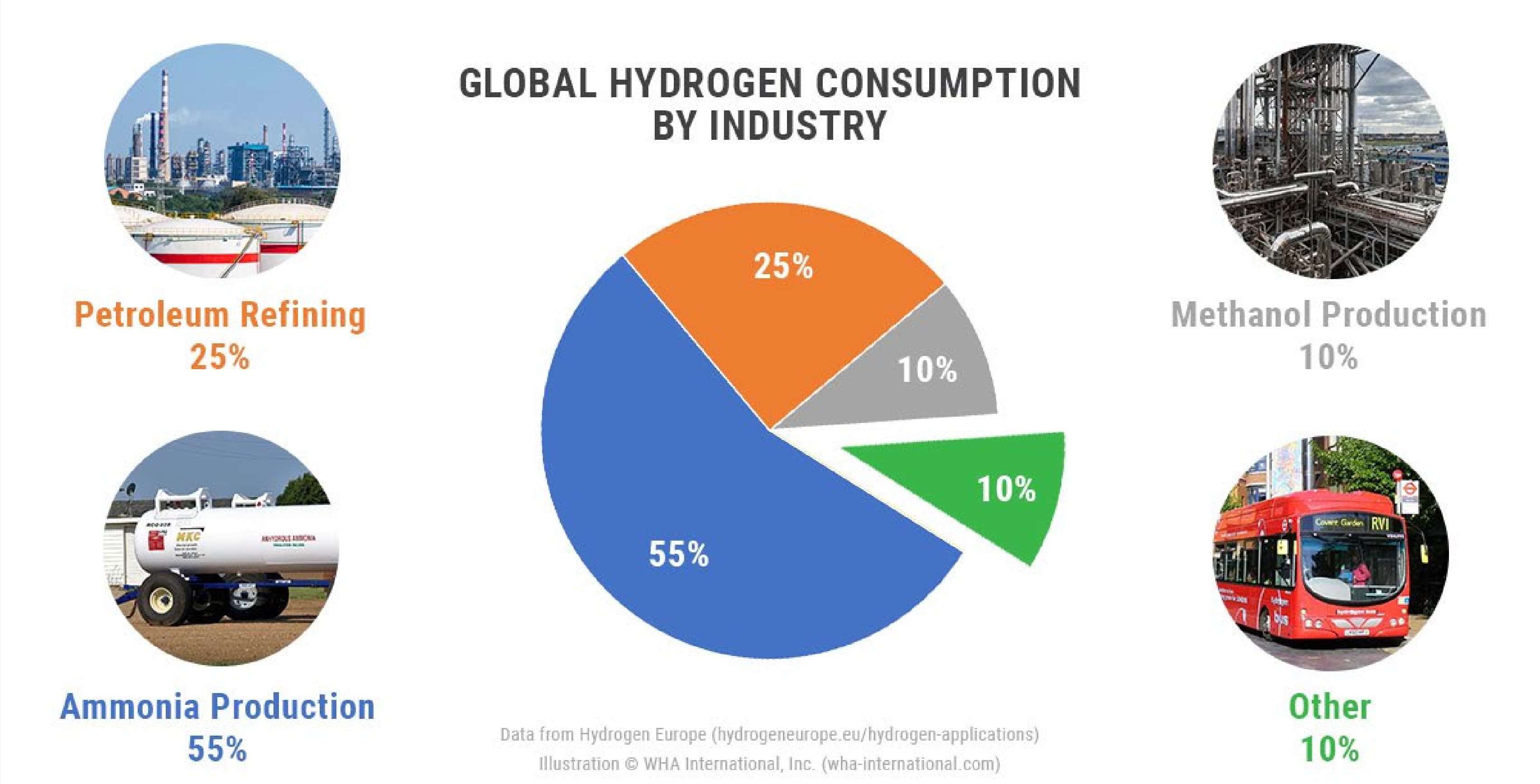
Talk Content

- Hydrogen versatility
- Hydrogen for energy storage
- Hydrogen use in Iron/Steel production
- Hydrogen use in cement production
- Hydrogen use in fertilizers production
- Final thoughts and future trends

Hydrogen Versatility

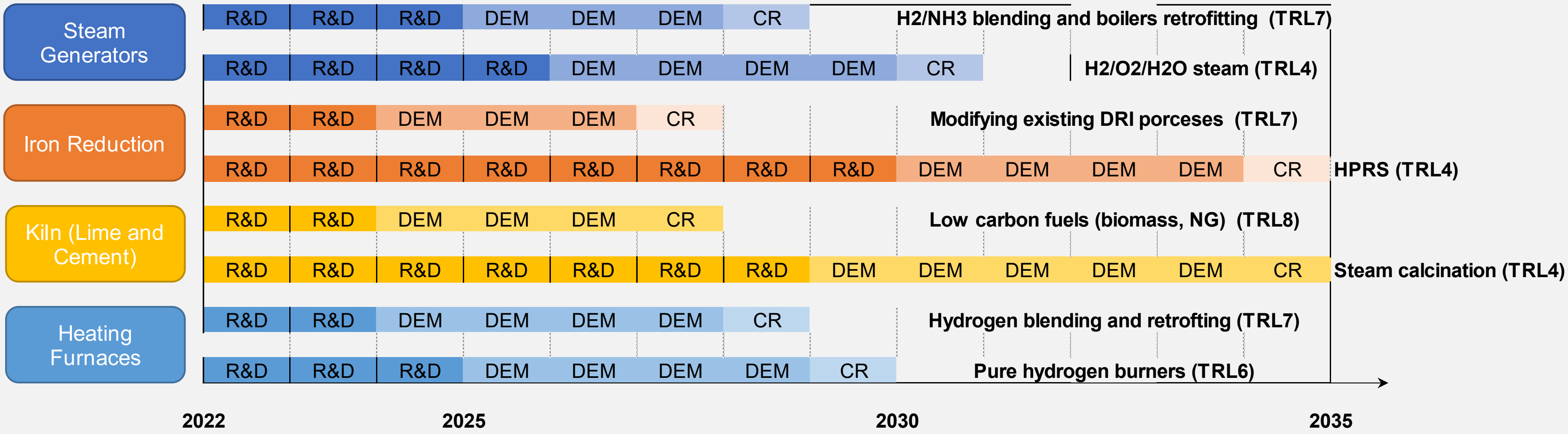


Hydrogen Versatility



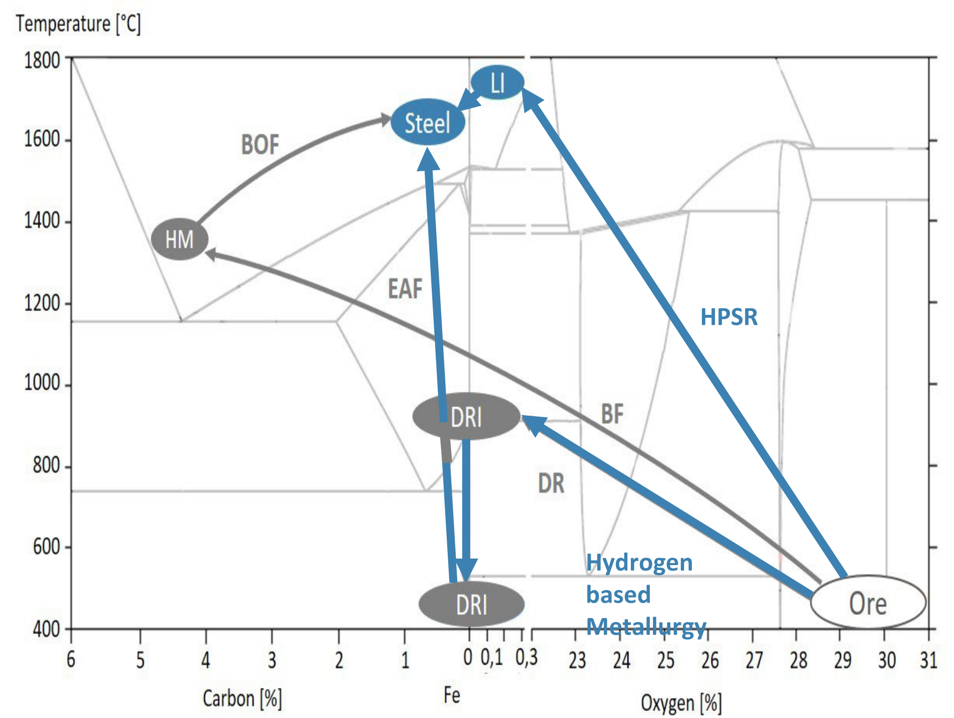
Hydrogen Other Use

- **Food**
  To turn unsaturated fats into to saturated oils and fats, including hydrogenated vegetable oils like margarine and butter spreads.
- **Metalworking**
  Hydrogen is used in multiple applications including metal alloying and iron flashmaking.
- **Welding**
  Atomic hydrogen welding (AHW) is a type of arc welding which utilizes hydrogen stream.
- **Flat Glass Production**
  H2/N2 mixture is used to prevent oxidation and defects during manufacturing.
- **Electronics Manufacturing**
  As an efficient reducing and etching agent, hydrogen is used to create semiconductors, LEDs, displays, photovoltaic segments, and other electronics.
- **Medical**
  Hydrogen is used to create hydrogen peroxide (H_2O_2). Recently, hydrogen gas has also been studied as a therapeutic gas for a number of different diseases.

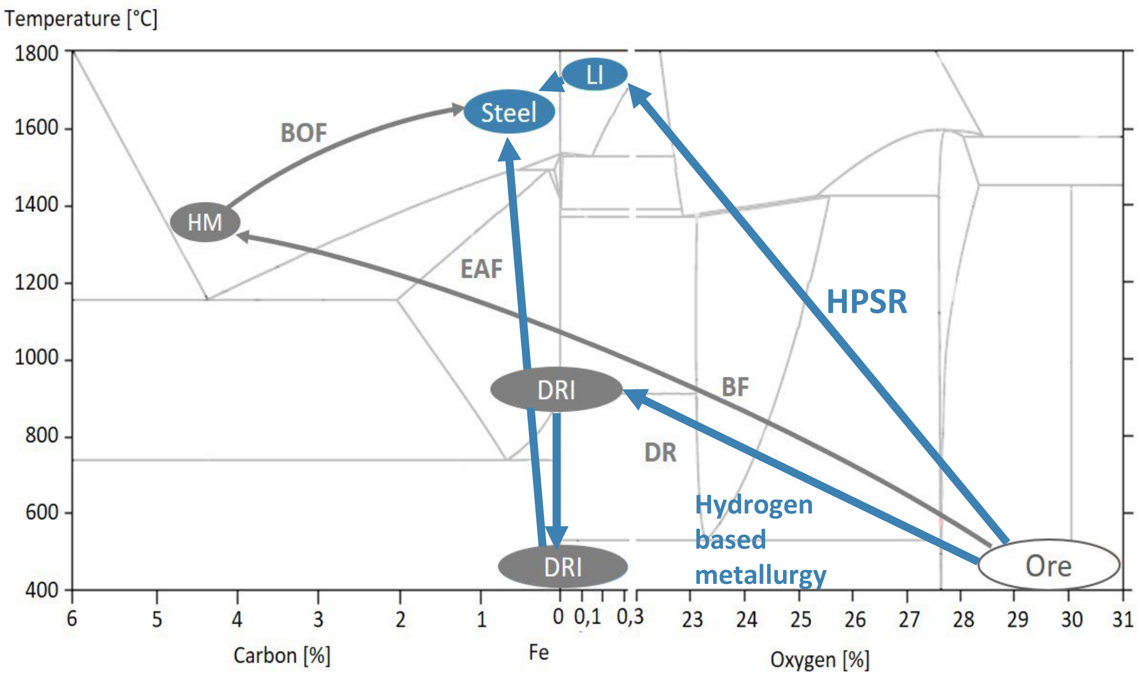

Steam Generators
R&D R&D R&D DEM DEM DEM CR
H2/NH3 blending and boilers retrofitting (TRL7)
R&D R&D R&D R&D DEM DEM DEM DEM CR
H2/O2/H2O steam (TRL4)
Iron Reduction
R&D R&D DEM DEM DEM CR
Modifying existing DRI porcesses (TRL7)
R&D R&D R&D R&D R&D R&D R&D R&D DEM DEM DEM DEM CR
HPRS (TRL4)
Kiln (Lime and Cement)
R&D R&D DEM DEM DEM CR
Low carbon fuels (biomass, NG) (TRL8)
R&D R&D R&D R&D R&D R&D R&D DEM DEM DEM DEM DEM CR
Steam calcination (TRL4)
Heating Furnaces
R&D R&D DEM DEM DEM DEM CR
Hydrogen blending and retrofting (TRL7)
R&D R&D R&D DEM DEM DEM DEM CR
Pure hydrogen burners (TRL6)
2022
2025
2030
2035

Strategies to Decarbonize HI

	Direct Electrification	Solar Thermal	Hydrogen	Ammonia	Bio-fuels
Iron and Steel	Electric furnaces (9) Direct Reduction Iron (9) Plasma reduction (3)	Heat source (5)	Reductant (9) Heat source (7)	Reductant (4) Heat source (4)	Heat source (4)
Cement	Electric kilns (3)	Direct calcination (3)	Heat source (4) Steam calcination (3)	Heat source (4)	Heat source (9)
Alumina	Electric heating (4)	Indirect Bauxite calcination (6)	Heat source (6) Steam calcination (5)	Heat source (4)	Heat source (4)
Petrochemicals	Electric furnaces (3)	Heat source (4)	Heat source (6) Chemical (9)	Heat source (4)	Heat source (4)


Temperature [°C]
1800
1600
1400
1200
1000
800
600
400
LI
Steel
BOF
HM
EAF
HPSR
DRI
BF
DR
Hydrogen
based
Metallurgy
DRI
Ore
6
5
4
3
2
1
0
0,1
0,3
23
24
25
26
27
28
29
30
31
Carbon [%]
Fe
Oxygen [%]

Single Step versus Two-Steps Reduction



Process routes for steel production

BF - Blast Furnace, BOF - Basic Oxygen Furnace, EAF - Electric Arc Furnace, HM - Hot Metal, DRI - Direct Reduced Iron, HPSR - Hydrogen Plasma Smelting Reduction, LI - Liquid Iron

- Single-step process
- No need for preprocessing, sintering, or pelletization of the iron ore
- Energy reduction of **54.77%** in comparison with the BF
- Low-grade iron ore <69%
- Zero CO_2 emission

Direct Reduced Iron (DRI) – Electric Arc Furnace (EAF)

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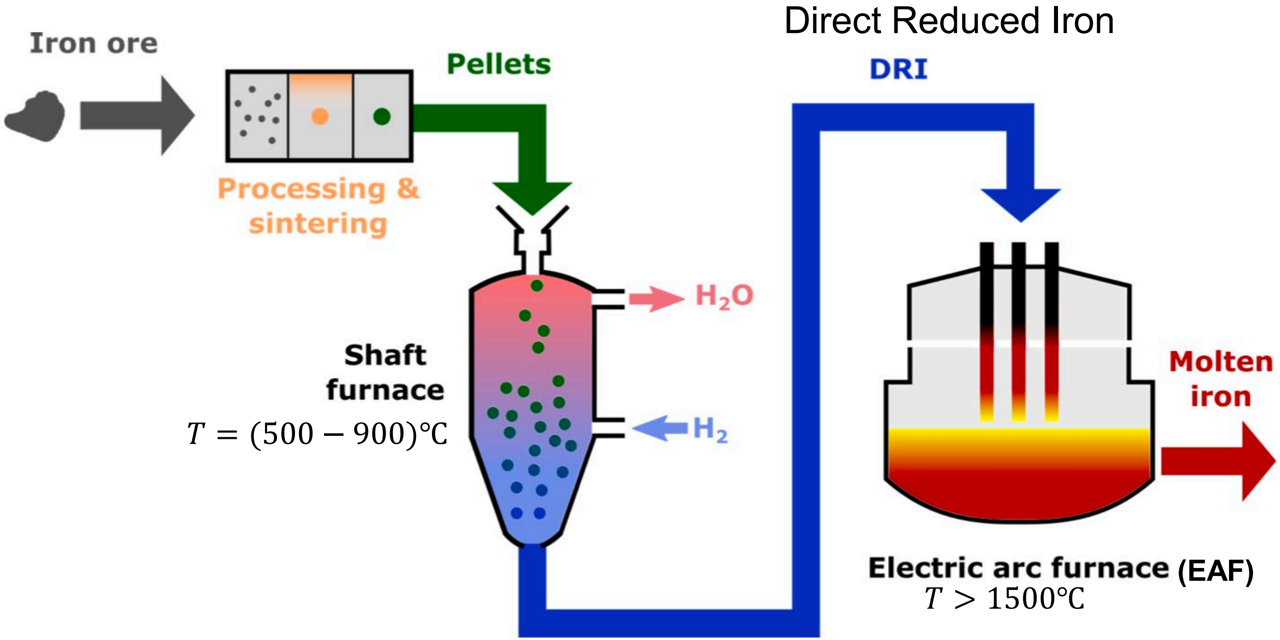
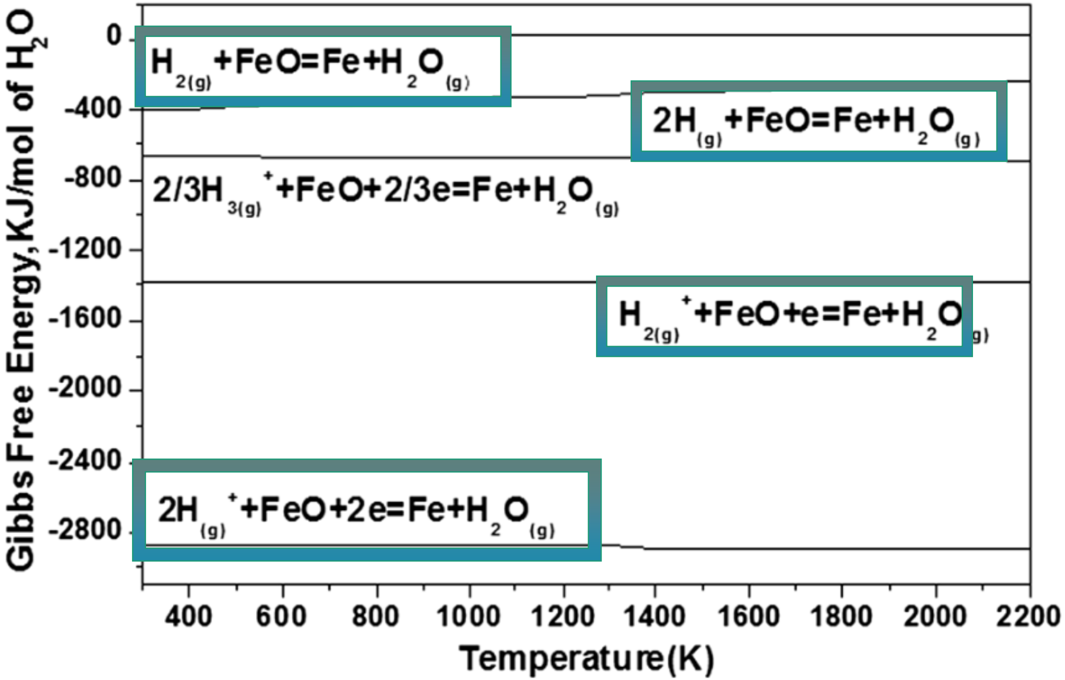


- Processing & Sintering requires a large amount of energy
- It requires a high-grade iron (>69%). The iron grade in many countries is below 40%
- Two-step process

Brännberg Fogelstr¨om, J., Experimental Study of the Temperature Profile in an Iron Ore Pellet During Reduction Using Hydrogen Gas, Master's thesis, KTH Royal Institute of Technology, 2020.

Hydrogen Plasma Smelting Reduction (HPSR)



- Negative Gibbs free energy
- Temperature obtained in an H_2 - plasma medium is greater than the melting point of oxide ore.

Y. Zhang, W. Ding, and X. Lu: Shanghai Met., 2009, vol. 31 (4), pp. 15–20.

Reduction Methods

In Flight Reduction

- Small moving particles being reduced while in movement and bring to rest in a collector;
- 25-150 micrometers;
- Seconds or milliseconds.

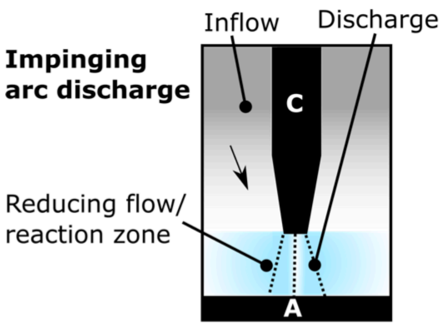
Direct Reduction

- The iron oxide stays stationary in a reductant flow.
- 1000-6000 micrometers;
- Minutes or hours;
- Higher degree of reduction and lower energy intensity.

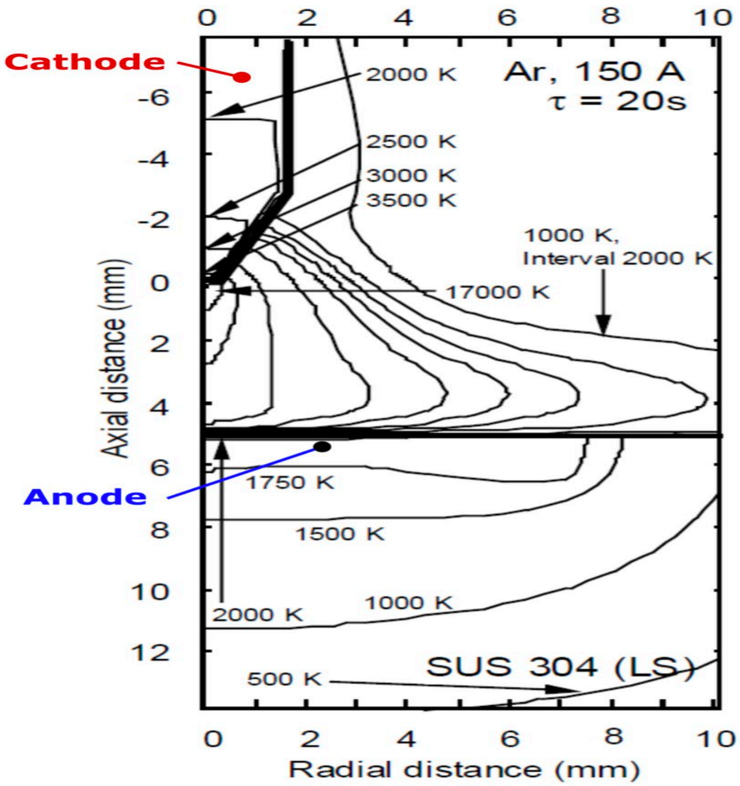
Combined

- Pulverized particles of moving iron oxide are reduced and the process finishes with further reduction in plasma volume.

Plasma Generators for HPSR- Arc Heated Flow (EAF)



Advantages	Disadvantages
+ Simple to construct	- Susceptible to working gas degradation
+ Extensive Literature	- Degradation through arc attachment
+ High efficiency	- Degradation can alter operational stability and reducing flow chemistry



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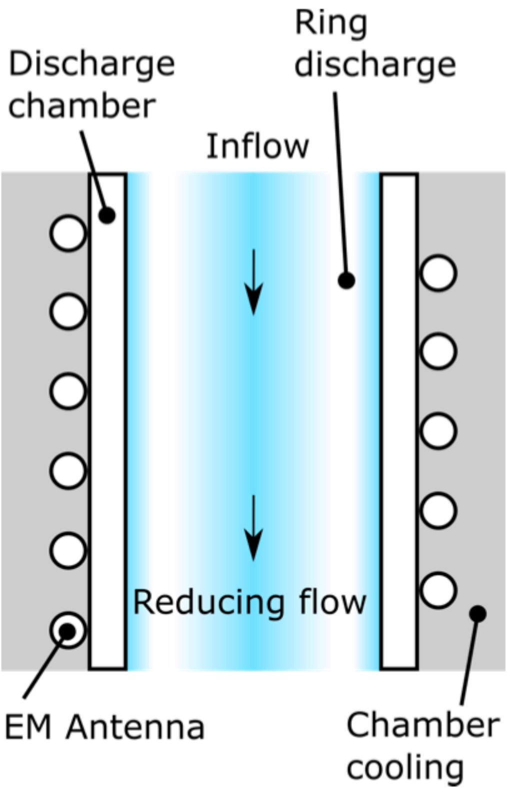
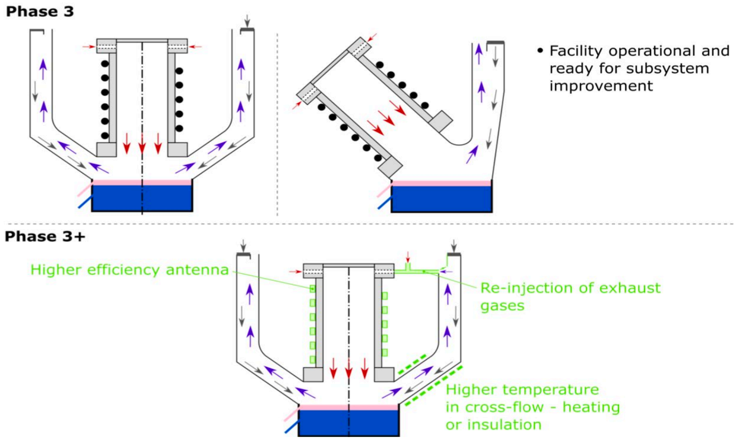
Plasma Generators for HPSR- Microwave Inductive Reactor





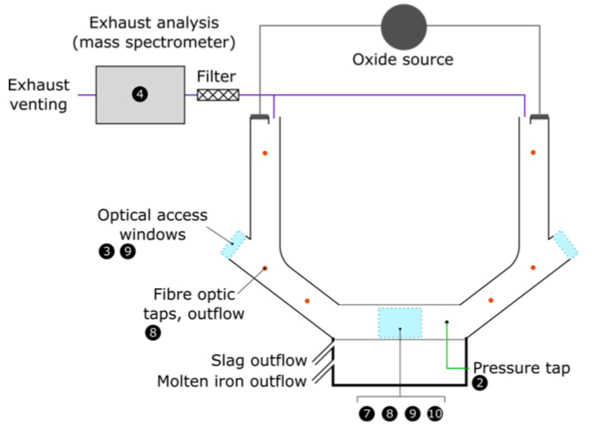
Advantages	Disadvantages
+ Gas Flexible	- More complicated to construct and operate
+ Pure flow	- Lower thermal efficiency
	- More difficult to ignite at high pressure

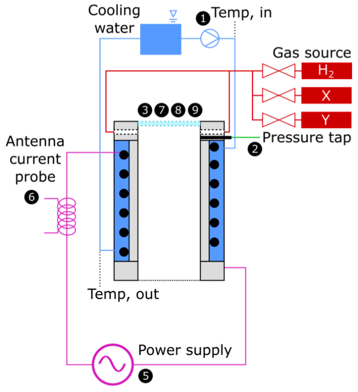
Jordan Figueiredo and Prof Deanna Lacoste

King Abdullah University of Science and Technology

Planned Diagnostics

	Measurement	Technique
Pre/post-process	Oxide/reduced iron compositon Oxide size and shape Oxide size distribution Oxide/reduced ore mass	• X-ray diffraction • Wet chemical analysis • Atom Probe tomography Scanning Electron microscopy Granulometer Scales
Process	Absorbed plasma power (1) Chamber pressure (2) Surface temperatures (3) Hydrogen utilization (4)	Calorimetry Pressure gauge Pyrometry • Mass spectrometry and water mass measurement • Infrared analyser for water content • Calculations from oxygen removal
Plasma Source	Input voltage (5) Antenna current & frequency (6) Discharge shape and movement (7) Plasma chemistry (8) Specific species distribution (9) Specific species temperature/velocity (10)	Voltmeter HOKA probe CCD camera and photodiode array Mass spectrometry Monochromater/narrow bandwidth filter Fabry-Perto spectroscopy





Simulations of electron-impact reactions

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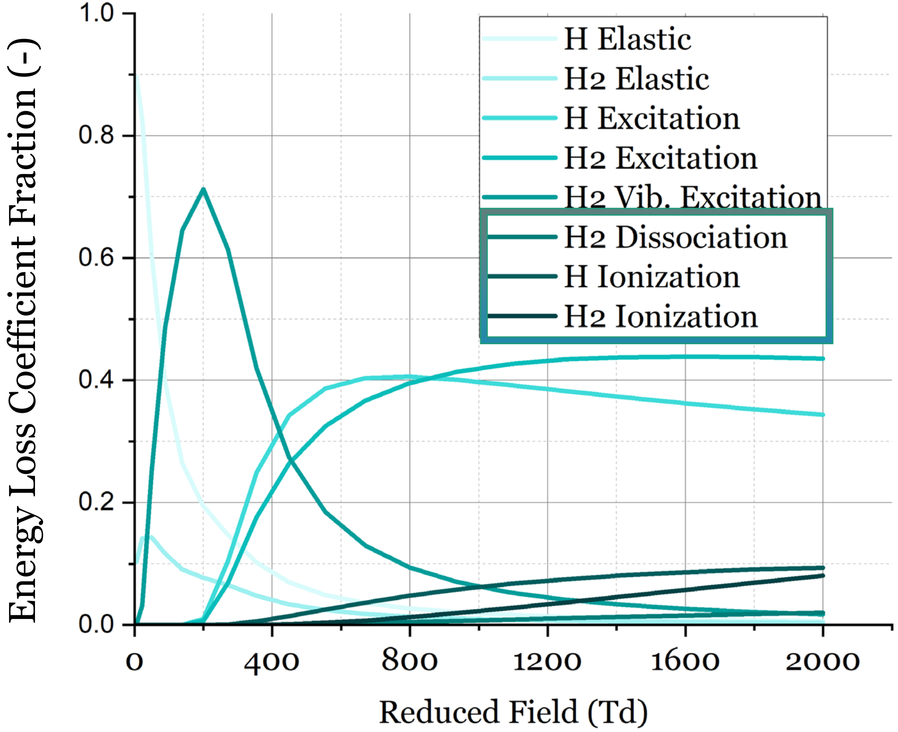


$H + e^- \rightarrow H + e^-$
$H_2 + e^- \rightarrow H_2 + e^-$
$H + e^- \rightarrow H^* + e^-$
$H_2 + e^- \rightarrow H_2^* + e^-$
$H_{2\,(v-1)} + e^- \rightarrow H^*_{2\,(v)} + e^-$
$H_2 + e^- \rightarrow 2H + e^-$
$H + e^- \rightarrow H^+ + 2e^-$
$H_2 + e^- \rightarrow H_2^+ + 2e^-$

R&D Questions

- What are the reaction rates of key steps in the reduction process?
- Can we probe the reduction process to better understand the mechanism of reduction and the interdependence of plasma-particles?
- What is the best hydrogen plasma actuation strategy to increase the efficiency of the process?
- Is it possible to scale up the process to an industrial scale maintaining the energy cost of conversion (GJ/T)?

Ammonia Iron Reduction

- In the temperature range from 793 to 863 K, hematite can be directly reduced to magnetite by ammonia:

$$1/2Fe_2O_3 + 1/9NH_3 \rightarrow 1/3Fe_3O_4 + 1/6H_2O + 1/18N_2)$$

- At temperatures above 873 K, ammonia causes the generation of *α-Fe (alpha iron)*. X-ray diffraction (XRD) measurements showed that *α-Fe* was immediately nitrided to an ε-$Fe_{3-x}N$ ($0 \le x \le 1$) phase, and the N/Fe atomic ratio decreased gradually with increasing temperatures.

- Magnetite was reduced mainly to iron by hydrogen generated from the decomposition of ammonia

$$1/3Fe_3O_4 + 4/3H_2 \rightarrow Fe + 4/3H_2O$$

More work is needed to resolve process and technical challenges of using ammonia as a reductant

ISIJ International, Vol. 55 (2015), No. 4, pp. 736–741

R&D - Iron and Steel

Steel Slag Carbonation

- Iron reduction produces large quantity of slag ~20% of the mass of iron produced;
- Tenova HYL DRI process uses Hydrogen currently produced from the reforming of methane;
- The process produces a stream of pure CO2 that is vented to the atmosphere;
- Carbonation is a process which binds CO2 into a solid (slag);
- Research shows that we can store CO2 equivalent to 7.5%-34% by mass of slag produced depending of CaO content;
- Research also shows that the carbonated slag yield strength increases by ~20%;
- Potentially we can store all CO2 and make iron carbon free.

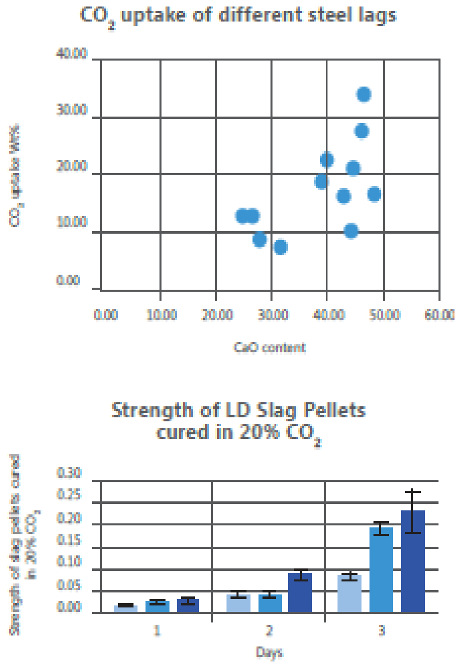
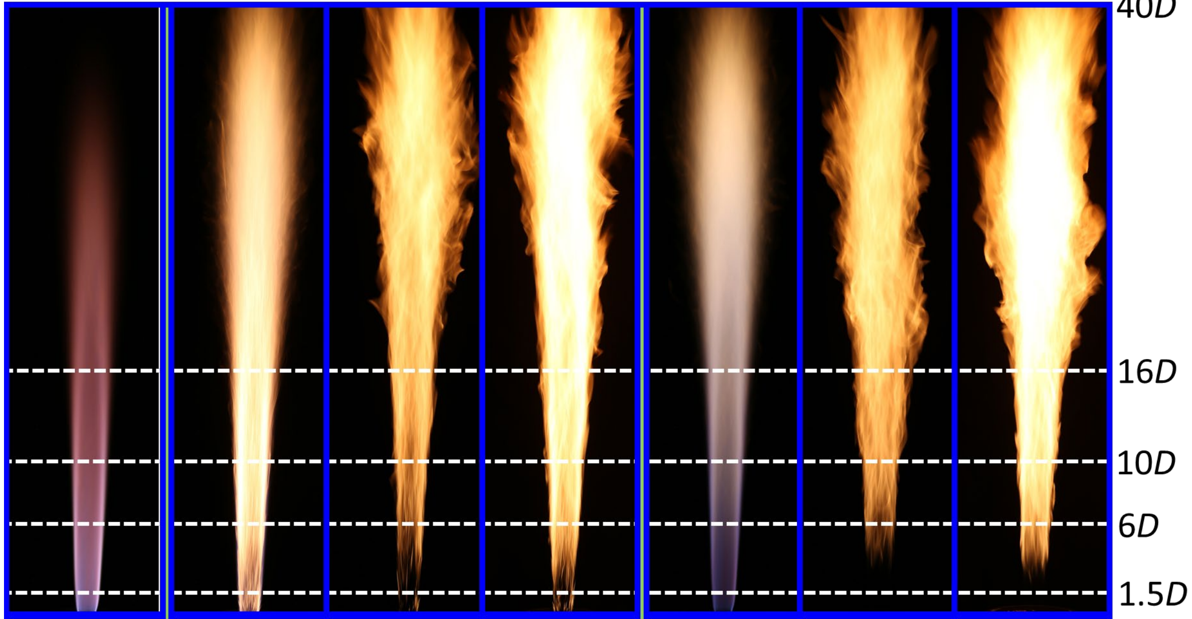


Figure 1 Percentage of CO2 by weight that can be bonded with slag as function of CaO content (top), and impact of carbonation on strength of slag (bottom). (Carbon8 Systems 2020)

Hydrogen for Reheat Furnaces

- Thermal radiation from H2 flames is very low
- Many industrial applications requires enhanced radiation, furnaces, boilers, kilns, etc
- Doping hydrogen flames with aromatics will help increase radiation
- Radiation lower flame temperature and reduces NOx.
- Bio-oils can be used



HT0	HT1-S	HT3-S	HT5-S	HT1-V	HT3-V	HT5-V
30 s f/8	30 s f/16	0.2 s f/16	0.2 s f/16	30 s f/16	0.2 s f/16	0.2 s f/16

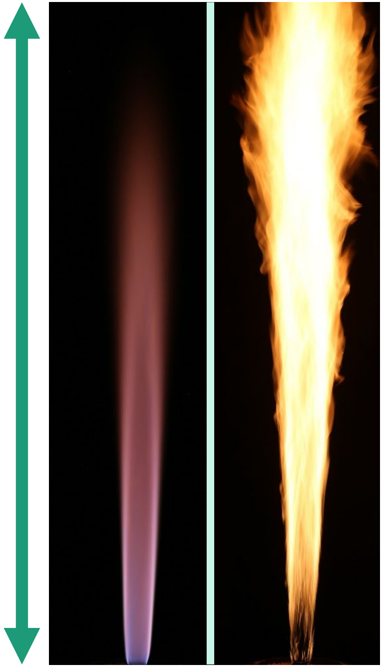
Hydrogen for Reheat Furnaces

- 1:1 H_2/N_2 jet flames in air coflow
  - D_{jet} = 20 mm
  - Re_D = 5k
  - D_{coflow} = 110 mm, v = 0.33 m/s

- **Toluene** added as percent mole of H_2
  - vapour (V)
  - droplets (S) → dilute spray

  - negligible heat added (≤ 0.35%)
  - Z_{st} shift: 0.30 (H_2) → 0.20 (5% tol.)

Case	***toluene (% H_2)***	***phase***
HT0	0	-
HT1-S	1	
HT3-S	3	droplets (40 μm)
HT5-S	5	
HT1-V	1	
HT3-V	3	vapour
HT5-V	5	



HT0 30s exp

HT5-S 0.2s exp

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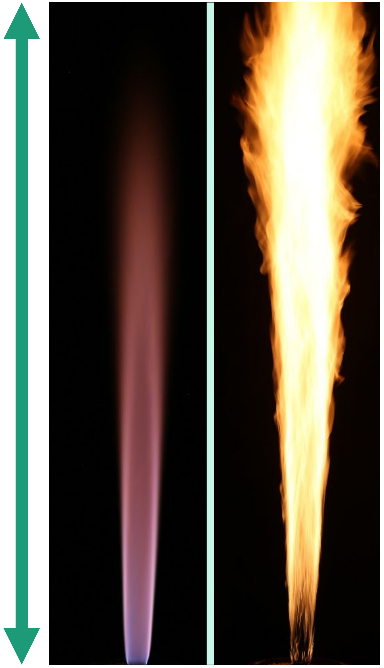
Case	***toluene (% H_2)***	***phase***
HT0	0	-
HT1-S	1	droplets (40 µm)
HT3-S	3	
HT5-S	5	
HT1-V	1	vapour
HT3-V	3	
HT5-V	5	

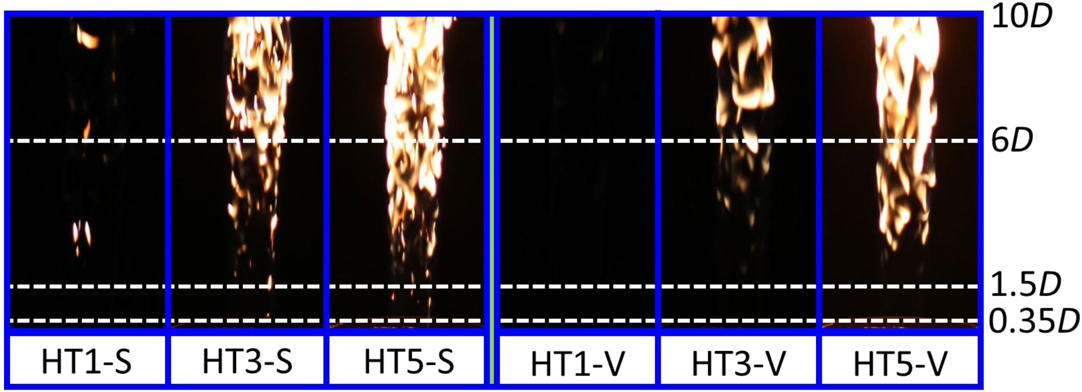


HT0 30s exp

HT5-S 0.2s exp

Soot Sheets Vapor versus Spray

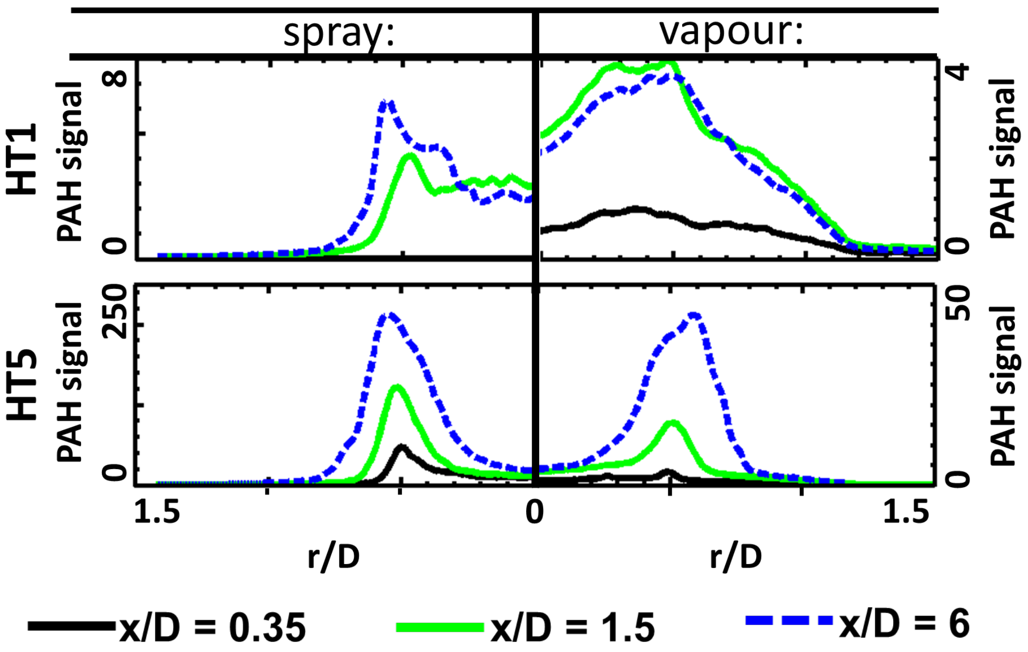
- Distinct regions of soot in all flames except lowest concentration of doping by vapour
- Heterogeneous combustion around droplets evident in spray flames
- Soot around droplets similar to soot kernels, upstream of soot sheets



f/2, 1 ms exposure

PAH PLIF Formation

- 1% (mol_{H_2}) toluene
  - very little PAH from dilute spray in near-field
  - similar signal at *x/D* = 1.5
  - greater signal from dilute spray further downstream
- 5% (mol_{H_2}) toluene
  - qualitatively similar profiles
  - 5× higher in dilute spray



Fate of carbon in doped flames

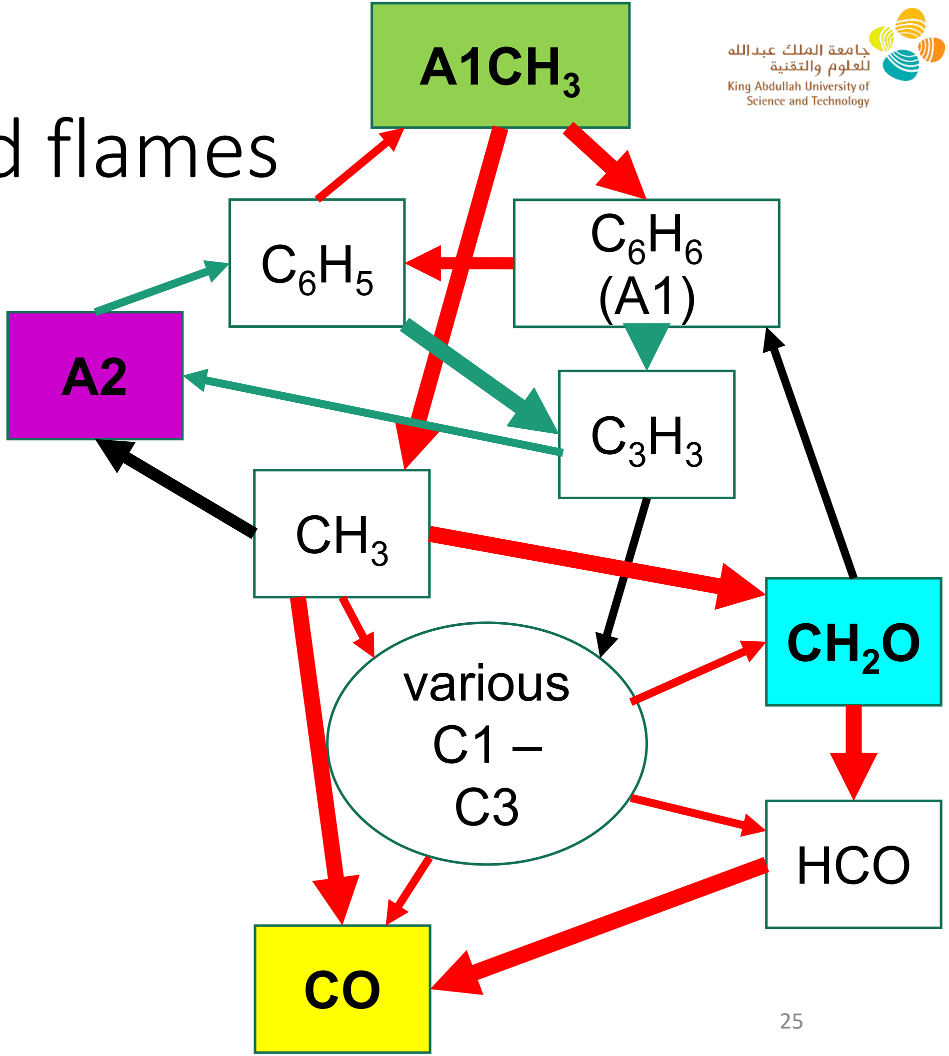
- Pathway to soot via PAH, via A2
  - mostly endothermic

  → pyrolysis

- Pathway to CO predominantly via CH_2O
  - mostly exothermic

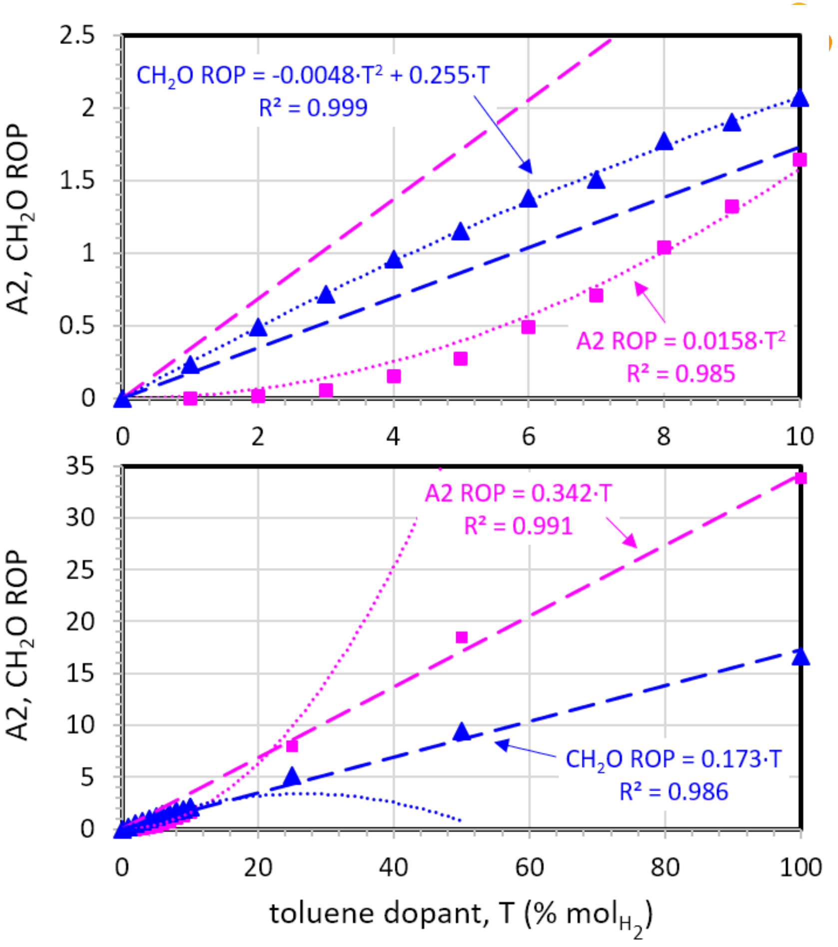
  → oxidation

- Consider peak rate of production of both A2 and CH_2O



Trends with toluene additi

- Different trends for the two ranges of toluene addition:
  - 0-10% (quadratic)
  - 10-100% (linear)
- PAH, and soot, formation favoured for high toluene concentrations (blending)
- CH_2O formation favoured for low toluene concentrations (doping)
  - not adequately represented by linear fits
- Toluene addition via vapour is doping, blending occurs locally around evaporating droplets



Peak rate of production of CH_2O and A2 as a function of toluene addition

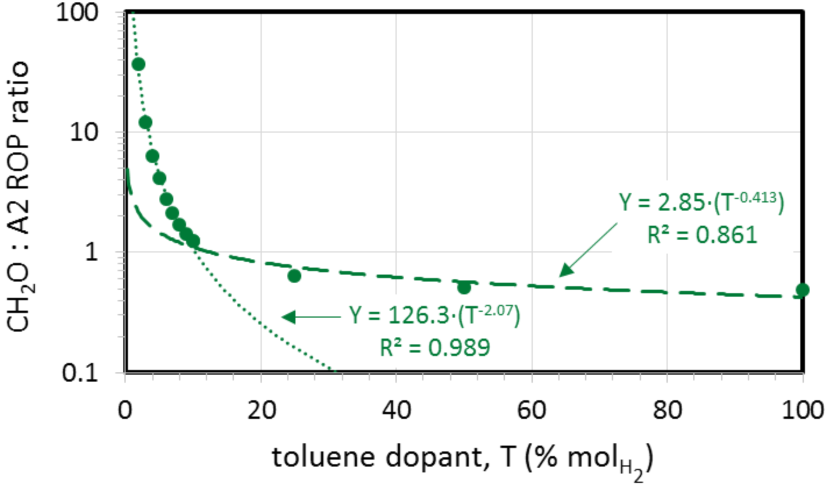
Trends with toluene addition

- Two regimes also seen from taking a ratio of peak CH_2O and A2 production rates

- Blending regime
  - $A1CH_3$ decomposes to C_6H_5, C_5H_5 and C_2H_2 directly
  - C_6H_5 forms monocyclic aromatics and C_9H_7 (A2 precursor)
  - C_5H_5 forms C_2H_2 and C_3H_3 (A2 precursor)

  →favours PAH formation and growth

- Dopant regime
  - C_6H_5, C_5H_5 and C_2H_2 formation are all suppressed



Ratio of peak rate of production of CH_2O and A2 as a function of toluene addition

Finding from Hydrogen Doping

- Experimental measurements show soot volume fraction increases non-linearly with small concentrations of toluene (A1CH3) added to turbulent H2/N2 jet flames
- Addition of toluene to 3-5% (molH2) result in significant soot loading with little change in OH concentration
- Explained by rate of production and pathway analyses of CH2O and A2
- Combined results suggest that a non-linear hydrocarbon doping regime should be considered separately to blending fuels in H2 flames

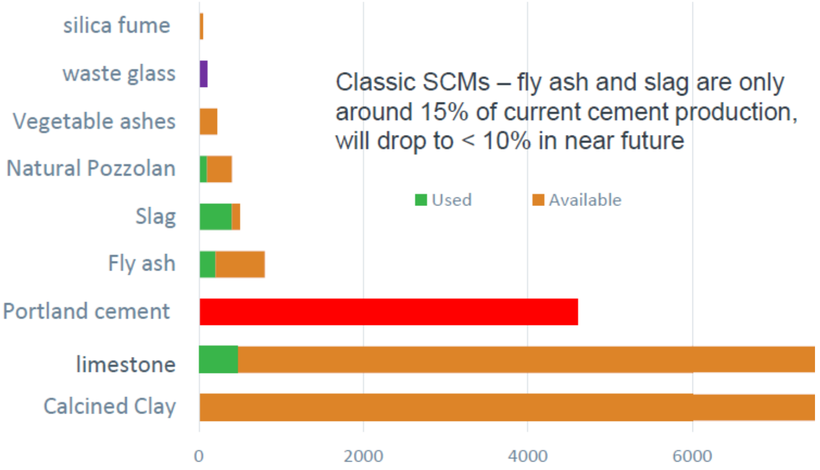
Cement Industry - Decarbonization

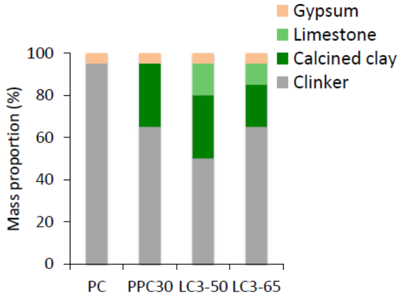
	SCOPE OF EMISSIONS	DECARBONIZATION PATHWAY	POTENTIAL TECH
MATERIAL	**60%**	**Efficiency:** use less binder to achieve the same strength material **Substitution:** use more binder (less CO2 intensive than Ordinary Portland Cement) **Waste:** reduce wasted cement material	• New generation SCMs • Binder efficiency • Alternative CaO sources
ENERGY	**40%**	**Reduction:** optimize / change industrial processes to be more energy efficient **Substitution:** replace energy with renewable or waste-derived sources	• New generation process controls • Next gen biogenic fuels • Electrification
CAPTURE	**80%**	**Post-combustion:** capture CO2 without affecting the production process **Process-specific:** modify the production process to emit less or capture more CO2 **Use-focused:** use waste products as a CO2 sink; use CO2 to make building materials	• Process capture • Post-combustion capture • Mineralization

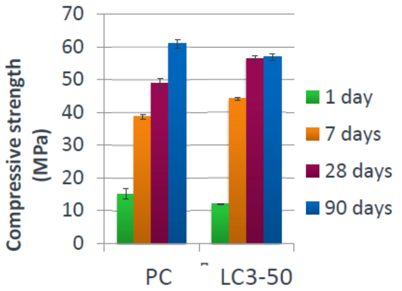
Cement Industry – Supp. Cement Material

Limestone Calcined Clay Cement – LC^3

- A blend developed by EPFL in Switzerland and made it public for anyone to use;
- It uses 50% less clinker and emits 40% less CO2;
- Kaolinite clay 40-60% is ideal;
- Similar strength as Portland Cement;
- Better chloride and alkali reaction resistance;
- Potential reduction of 400 Mt/year of CO2 if LC^3 is used;
- Challenges
  - Changing standards and codes
  - Finding the right clay in close proximity
  - Willingness to change







New Section

Cement Industry – Energy Reduction

Calcination of Limestone and Cement

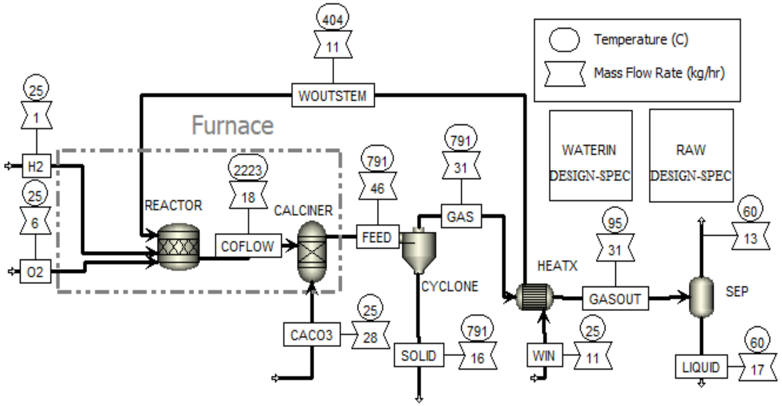
- Limestone calcination requires heat at 800 – 950 °C

$$CaCO_3 + Heat \rightarrow CaO + CO_2$$

- Burning fossil fuels to generate the heat required will produce more CO_2 that requires calcination at a higher temperature
- Capturing the CO_2 from the exhaust gases (mostly separating CO_2 and N_2) is expensive and can reach $100 a ton.
- One option is to use Oxy-Fuel which eliminates the N_2. However, the cost of the O_2 production and the need to blend CO_2 from the exhaust (up to 30%) which again requires higher temperatures makes it less attractive
- Steam can provide the heat needed, has catalytic effects and can be condensed in the exhaust and recycled.

Steam Calcination of Limestone and Cement

- Steam can be generated from $H_2/O_2/H_2O$ combustion;
- Using steam requires lower temperature and hence reduces energy per ton of lime;
- Hydrogen and oxygen can be produced by electrolysis using renewable electricity;
- Condensing the steam will leave a pure stream of CO_2 to be capture, stored or used;
- More than 90% of the water is recycled and 94% of the CO_2 is captured;
- Technology is financially competitive with natural gas+capture, when hydrogen cost reaches USD $2.2/kg.
- Note that this process also applies to



Steam Calcination Process Modeling

Commercially Confidential

Parity price of H2 as a function of the NG price

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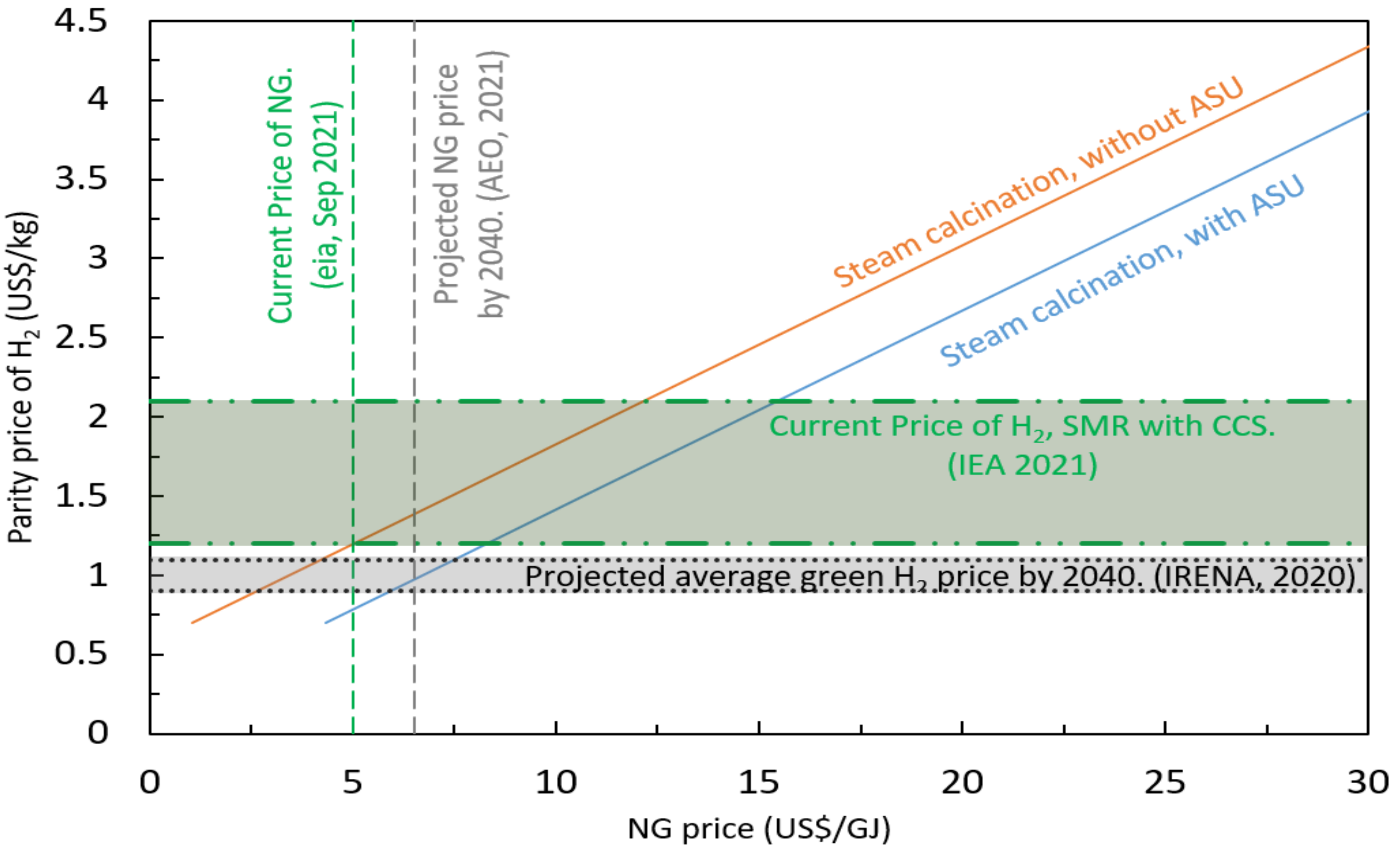

Cost of Lime as function of fuel cost

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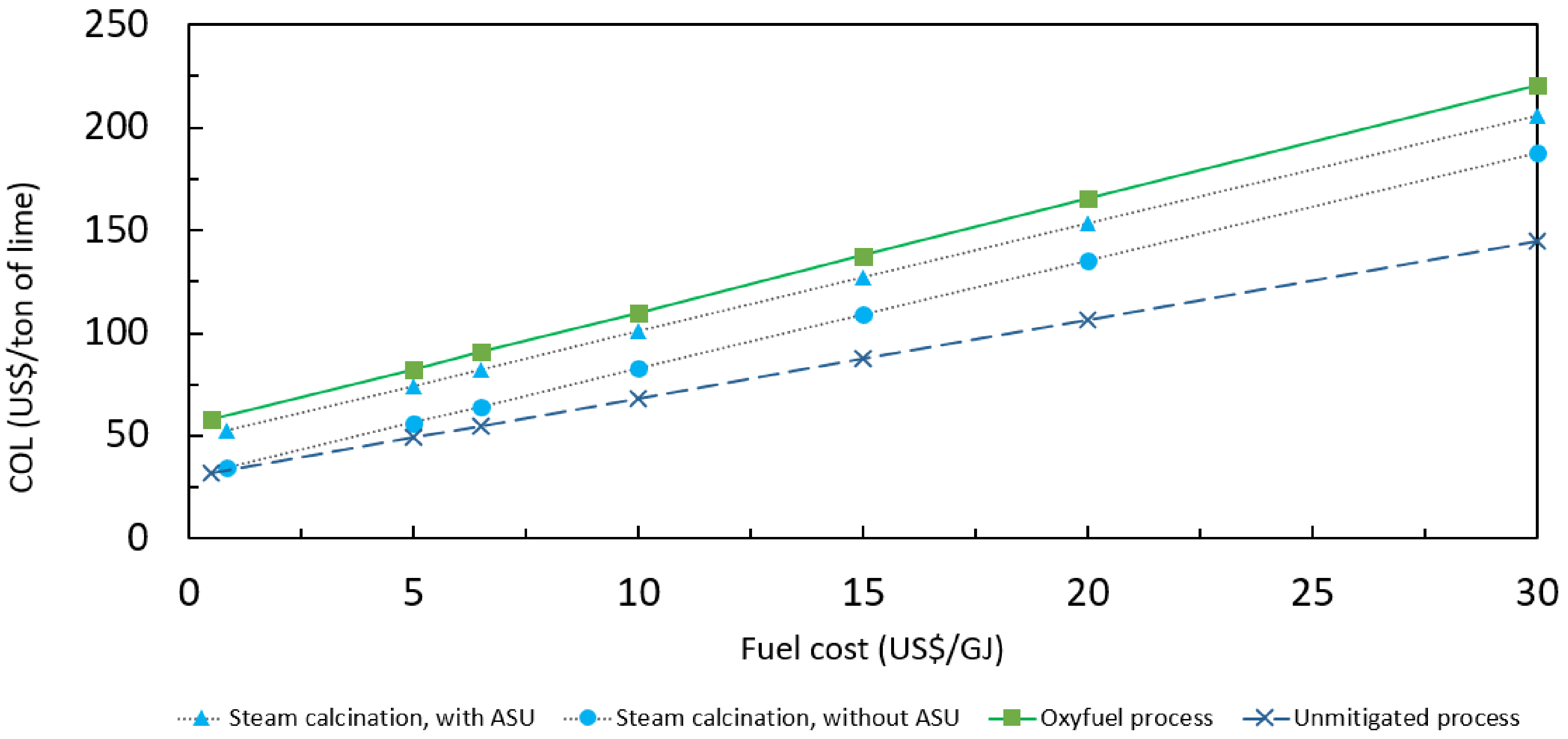
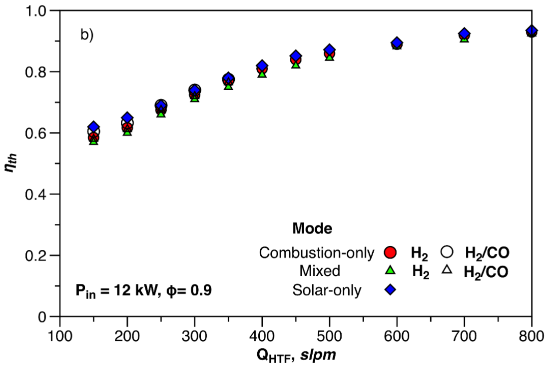


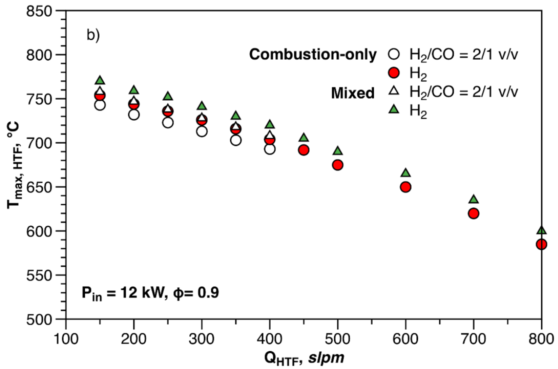
Solar Hydrogen Combustion Hybridization

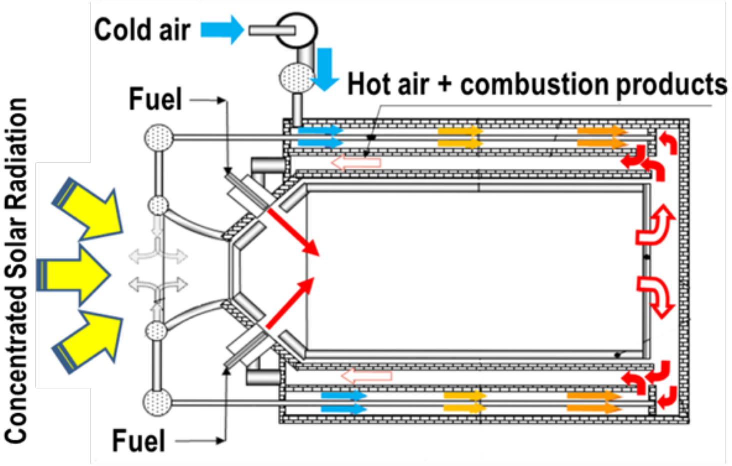
Hybrid Solar Receiver Combustor

Thermal Efficiency



Maximum HTF Temperature





Nathan, Dally, Ashman, Steinfeld (2013). *PCT Patent App* #PCT/AU2013/000326

Key findings from demonstration

- Efficient operation in the three modes: **h_{th} up to 90%, T_{HTF} > 750 ^oC**
- Low solar fluxes can be used to supplement combustion
- Convective losses through aperture < 50% of radiative (no wind)

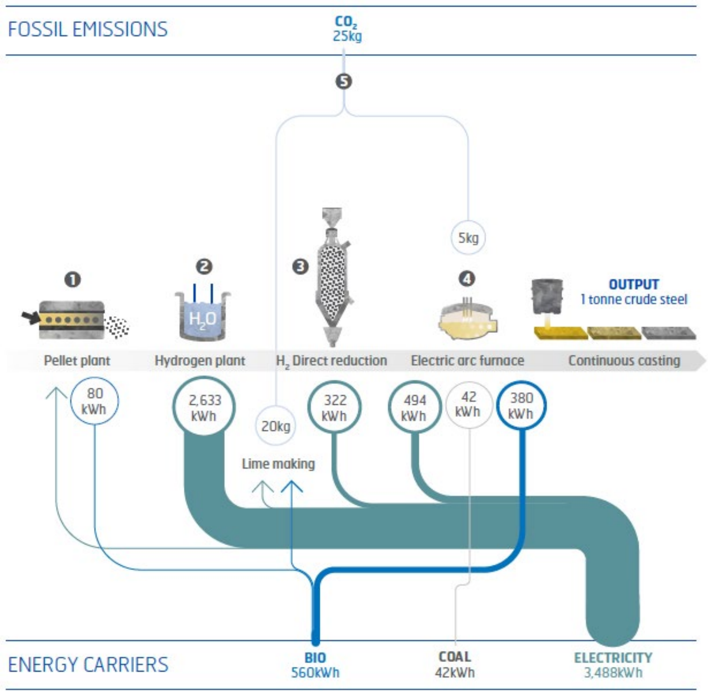
		Technology readiness	Years until plateau of productivity	Development costs[1]	CAPEX requirements[2]	Operating costs[3]	Public acceptance	Possibility to transform brownfield plant
CCUS	Carbon capture, use and/or storage	◕	5-10	◑	◔	◕	◔	◕
	Carbon capture, use and/or storage with biomass	◑	5-10	◕	◑	◔	○	◕
Alternative reductant agent	H_2-based direct reduced iron – Shaft furnace	◕	0-3	◔	◔	◔	◕	◕
	H_2-based direct reduced iron – Fluidized bed	◕	5-15	◔	◔	◔	◕	◕
	Suspension ironmaking technology	◔	17-22	◕	◔	◔	◕	◔
	Plasma direct steel production	◔	20-25	◕	◔	◔	◕	◔
	Electrolytic processes	◔	20-30	◕	◔	◔	◕	◔

● High ○ Low

[1] Compared to the other presented carbon neutral technologies [2] Compared to CAPEX of BF-BOF greenfield plant in 2040-2050
[3] Compared to BF-BOF plant in 2040-2050 (incl. carbon tax)

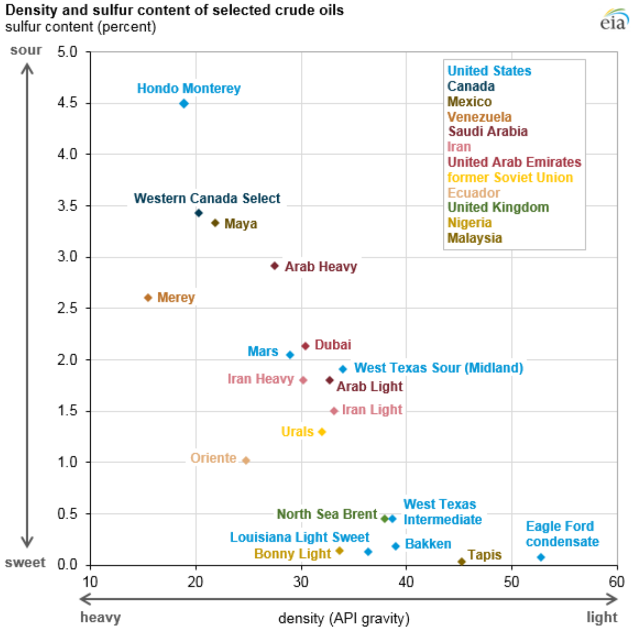
Source: Roland Berger

Hybrit



FOSSIL EMISSIONS
CO_2
25kg
5
5kg
1
2
3
4
H_2O
OUTPUT
1 tonne crude steel
Pellet plant
Hydrogen plant
H_2 Direct reduction
Electric arc furnace
Continuous casting
80 kWh
2,633 kWh
20kg
322 kWh
494 kWh
42 kWh
380 kWh
Lime making
ENERGY CARRIERS
BIO
560kWh
COAL
42kWh
ELECTRICITY
3,488kWh

Crude to Hydrogen opportunity



Source: U.S. Energy Information Administration, 2017

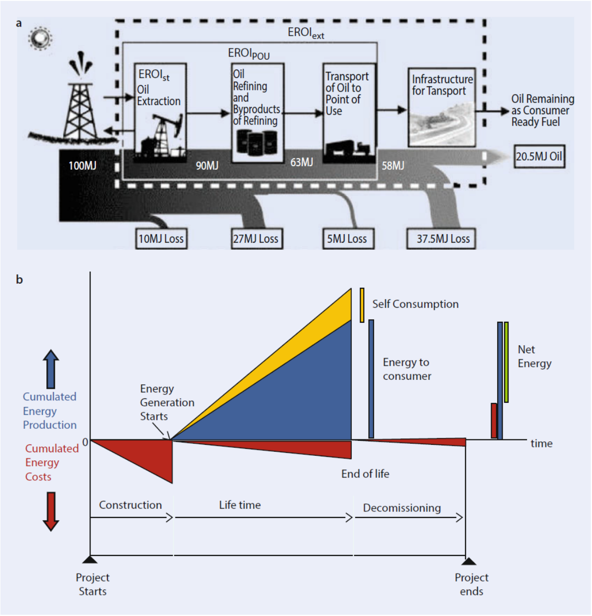


Fig. 18.2 a Diagram of energy losses between the well-head and use for petroleum (from [16]). b Schematic for the energy used and gains over time of an energy project. The EROI would be the final value of the blue triangle on top divided by the sum of the final values for the three brown triangles on bottom. These are represented by bars on right

Source: Energy and the wealth of nations: An introduction to biophysical economics. Vol. 511. Springer International Publishing, 2018.

- Crude oil to Hydrogen: Avoids energy & carbon footprint of refining processes; low-or-no CO_2 as a byproduct; Valorization of solid carbon
- Gasification to syngas to hydrogen: Valorization of petroleum residues; Minimal pre-processing needed

Molten metal pyrolysis of heavy oils

جامعة الملك عبدالله
للعلوم والتقنية
King Abdullah University of
Science and Technology

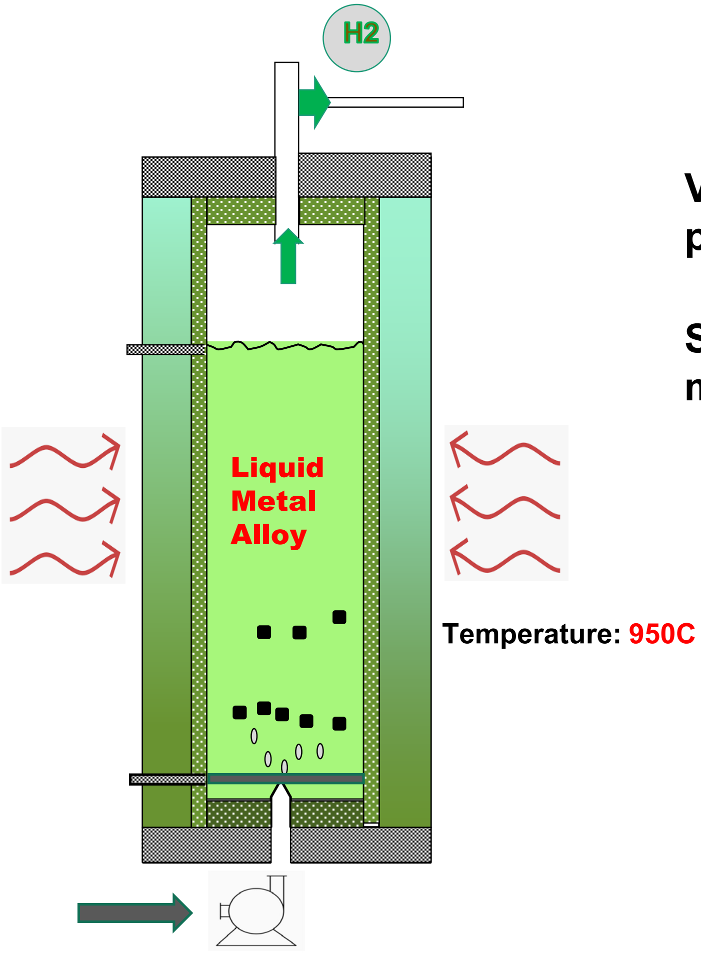
Simpler downstream process for VRO and GFO

100% H_2 selectivity at 950C

Only H_2 and C products

Catalyst regenerates itself

No prior treatment required to remove Sulphur
Sulphur collected at downstream cooling process



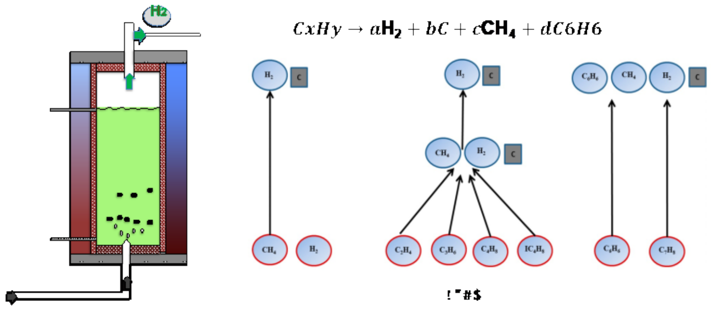
Viscosity check on the feed pump

Strainer to collect heavy metal impurities

Modeling to develop scaled–up reactors

King Abdullah University of Science and Technology

Realistic gas-phase kinetics



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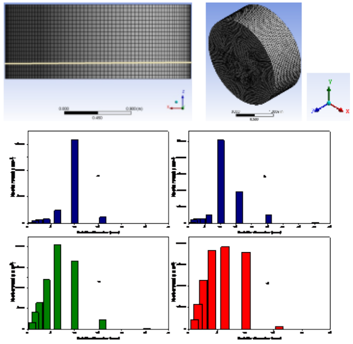
Multiphase flow physics

Modeling tool	Ansys Fluent V17
Dimensionality and type of grid	3D with Adaptive Mesh Refinement
Turbulence model	RNG k-ε;
Phase Interaction models	Breakup: KH-RT Drag-law: Universal Lift: Tomiyama Dispersion: Sato
Time step	Variable time step
Multiphase model	PPM (Population Balance model) - 10 bins Aggregation: Luo Breakage: Luo



Hydrodynamics and catalysis kinetics

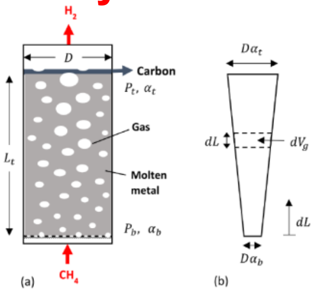
+

Hydrodynamics

$$j_g^+ \equiv \frac{j_g}{\left(\sigma g \Delta\rho/\rho_f^2\right)^{1/}} \quad \alpha = \frac{j_g^+}{C_0 j_g^+ + V_{gj}^+}$$

$$N_{\mu f} \equiv \frac{\mu_f}{\left(\rho_f \sigma \sqrt{\sigma/(g\Delta\rho)}\right)^{1/2}}$$

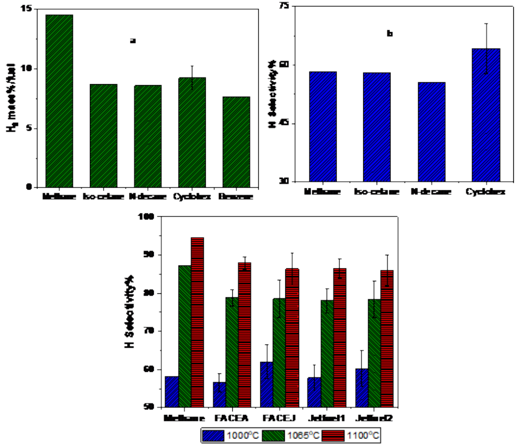
$$\frac{dP}{dL} = -\left[\rho_f(1-\alpha) + \rho_g \alpha\right] g = -(\rho_f - \alpha\Delta\rho) g$$



$$V_{gj}^+ = 0.030\left(\rho_g/\rho_f\right)^{-0.157} N_{\mu f}^{-0.562} \text{ for } D_H^* \geq 30$$

→

Accurate Prediction for H2 from real oils



Microwave based deasphalting and thermo-cracking

Gasification

Supercritical water gasification (SCWG)