Hydrogen Production – Thermochemical Approaches for India

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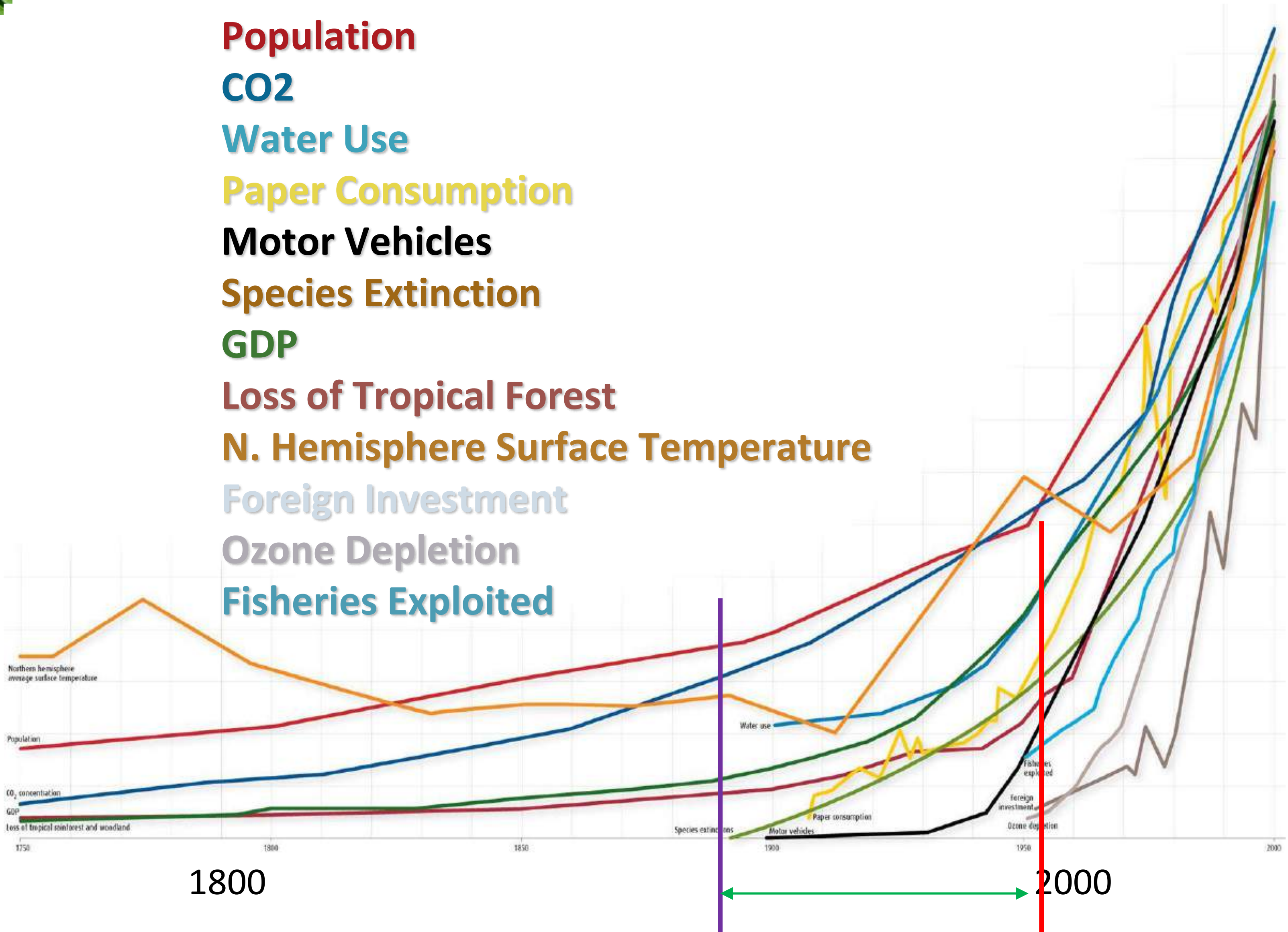
Anjan Ray
Independent Consultant (Sustainable Energy, Chemicals and Infrastructure)
Former Director, CSIR-Indian Institute of Petroleum
Inputs:Dr S Srikanth, Former Director, CSIR-National Metallurgical Laboratory

250 Years of “Progress”



Population
CO2
Water Use
Paper Consumption
Motor Vehicles
Species Extinction
GDP
Loss of Tropical Forest
N. Hemisphere Surface Temperature
Foreign Investment
Ozone Depletion
Fisheries Exploited

1800

2000

Rules of Thumb for Sustainability

- ***INPUT** RULE*

RENEWABLES: Harvest rates of resources must be within the regenerative capacity of systems that produce them.

NON-RENEWABLES: Rates of depletion must not exceed the rate at which ecologically sound, long-term resource substitutes are developed.

- ***OUTPUT** RULE*

Waste and pollution from a community must not exceed the assimilative capacity of its bioregion and must not degrade future absorptive capacity or any other important ecological services. (Note: residuals exported beyond the bioregion must be accounted for)

Source: Ismail Serageldin, 1993

India’s Energy Scenario: Carbon Atom Imports

Commodity	Import MMT, 2022	% C, approx.	Imported C atoms, MMT/yr
Crude Oil	212	85%	180
Coal incl. Pet. Coke	180	75%	135
Natural Gas	20	77%	15

Demand Side Response

- Reduce energy requirement (enhance efficiency)
- Reduce carbon requirement (non-carbon energy e.g. solar, wind, geothermal)

Supply Side Response

- Find ~330 MMT of domestic carbon atoms to replace our fuel carbon imports

India's Energy Scenario: Available Carbon Sources

Carbon Source	Scope, MMT/yr	% C, approx.	Potential C, MT/yr
Agri-residue (surplus)	120	40%	48
Forest residue	150	42%	63
Sewage / dairy / distillery (biogas)	400	45%	180
MSW	60	25%	15
UCO	5	85%	4
Industrial / Urban emissions	500+	25-70%	150

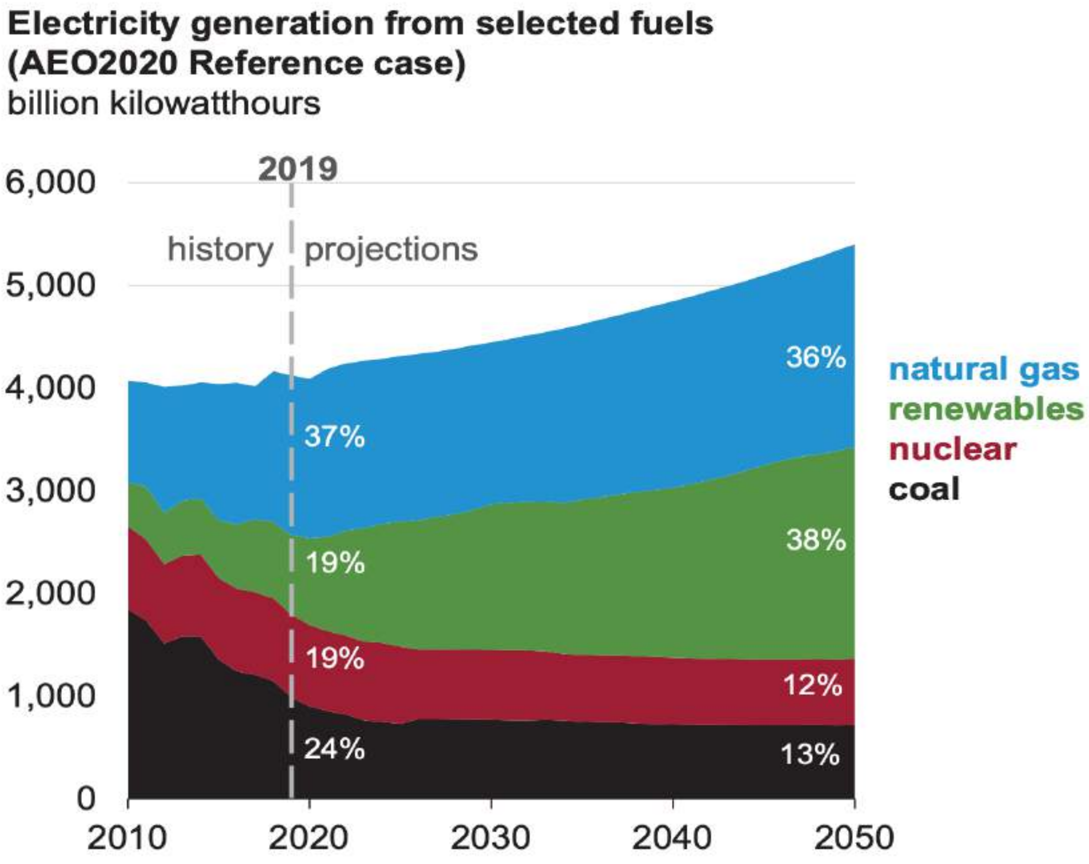
- Carbon atoms discarded by each person add up
- 460+ MMT of domestic recyclable / renewable carbon excluding purpose-grown crops
- Imports ~330 MMT of C-atoms annually; theoretically could be self-sufficient!
- All the carbon we need is available within our borders – but supply chains are immature
- But Repurposing Carbon needs Water, Energy, Catalysts, Equipment, Labour

Energy Transition to Alternate and Low-Carbon Fuels

A Basket of Possibilities: but can H replace C?

INCUMBENT	REPLACEMENT	TECHNOLOGY	CHALLENGES
Diesel	Biodiesel, Green Diesel, Bio-based alcohols and Ethers	Esterification, Hydroprocessing, Fermentation, Syngas-derived	Scalable Feedstock Supply
Gasoline	Bio-based alcohols and ethers, green gasoline	F-T, Fermentation, Alcohol-to-gasoline, Hydroprocessing, Pyrolysis/FCC, Catalytic Pyrolysis Bio-coking	Handling and blending infrastructure, feedstock variation
Aviation Fuel	Bio-jet (SAF)	Hydroprocessing, Sugar conversion, alcohol-to-jet, F-T	Scalable Feedstock Supply
CNG / PNG	Bio-CNG/Bio-PNG, HCNG, Bio-H2	Fermentation	Purification, Supply chains
LPG	DME (via Biomass gasification / Dry-reforming)	Catalytic conversion of bio-gas and producer gas	Economies of scale
Low-sulfur Bunker Fuel	Green marine distillate, biomass-derived pyrolysis oils	Hydroprocessing, Pyrolysis/FCC, HTL, MSW-thermochemical processing	Economic value relative to alternatives

Can Hydrogen Generation be Carbon Neutral?



Projected Energy Mix for US by 2050

US Energy Information Administration (EIA) Annual Energy Outlook 2020 report

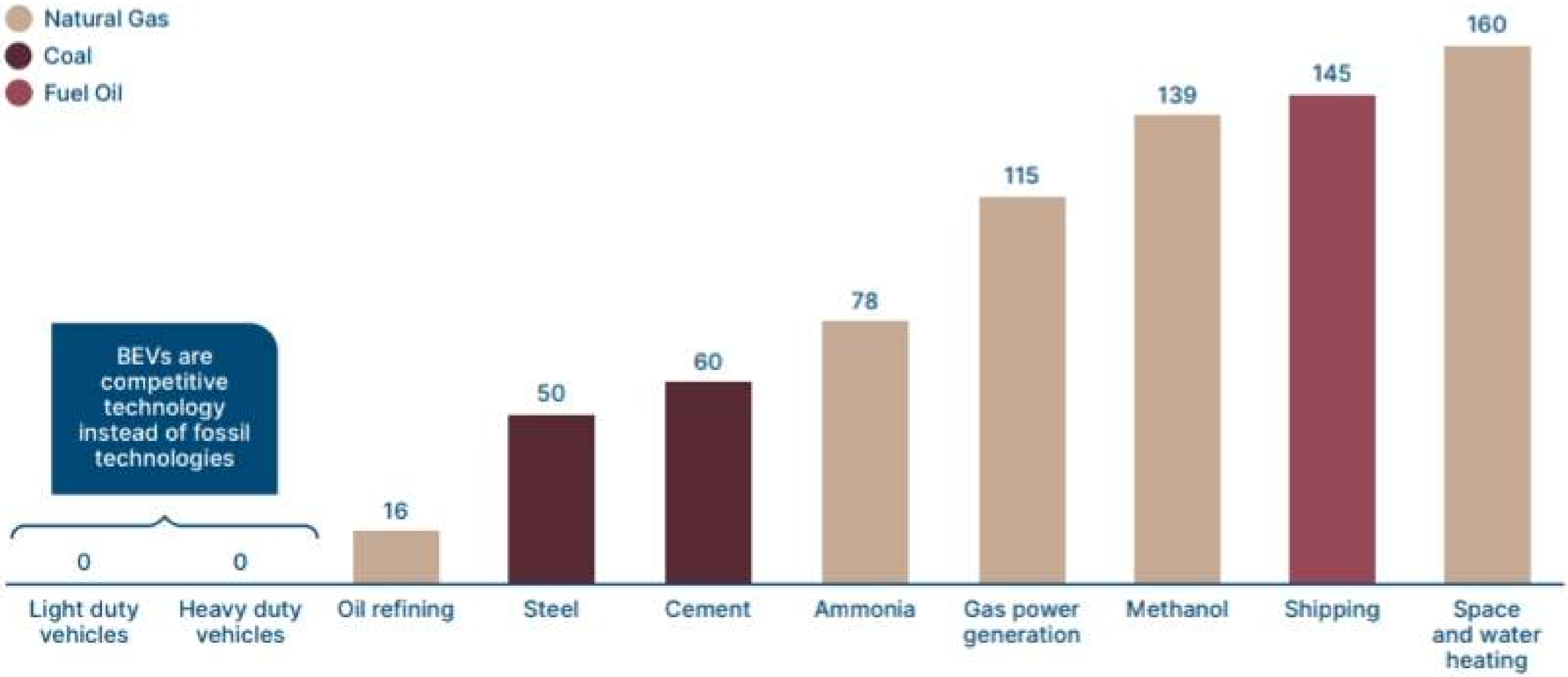
The process of electricity generation through Hydrogen consumes about 4 times the electricity that it generates. ***Therefore, as long as fossil fuels contribute to more than 20% electricity generation,*** *Hydrogen generation cannot become Carbon neutral.*

While a highly optimistic outlook of 80% electricity generation from renewables by 2050 exists, ***geo-politically realistic estimates*** *with suggest around 40% electricity from renewables and share of electricity in energy mix ~35%.*

Can Hydrogen Generation be economically viable?

Even at $1/kg further support will be required to make clean hydrogen use competitive in end-use applications

Carbon prices required for hydrogen to compete with the cheapest fossil fuel in each use-case (2050)
$/ton CO_{2eq}



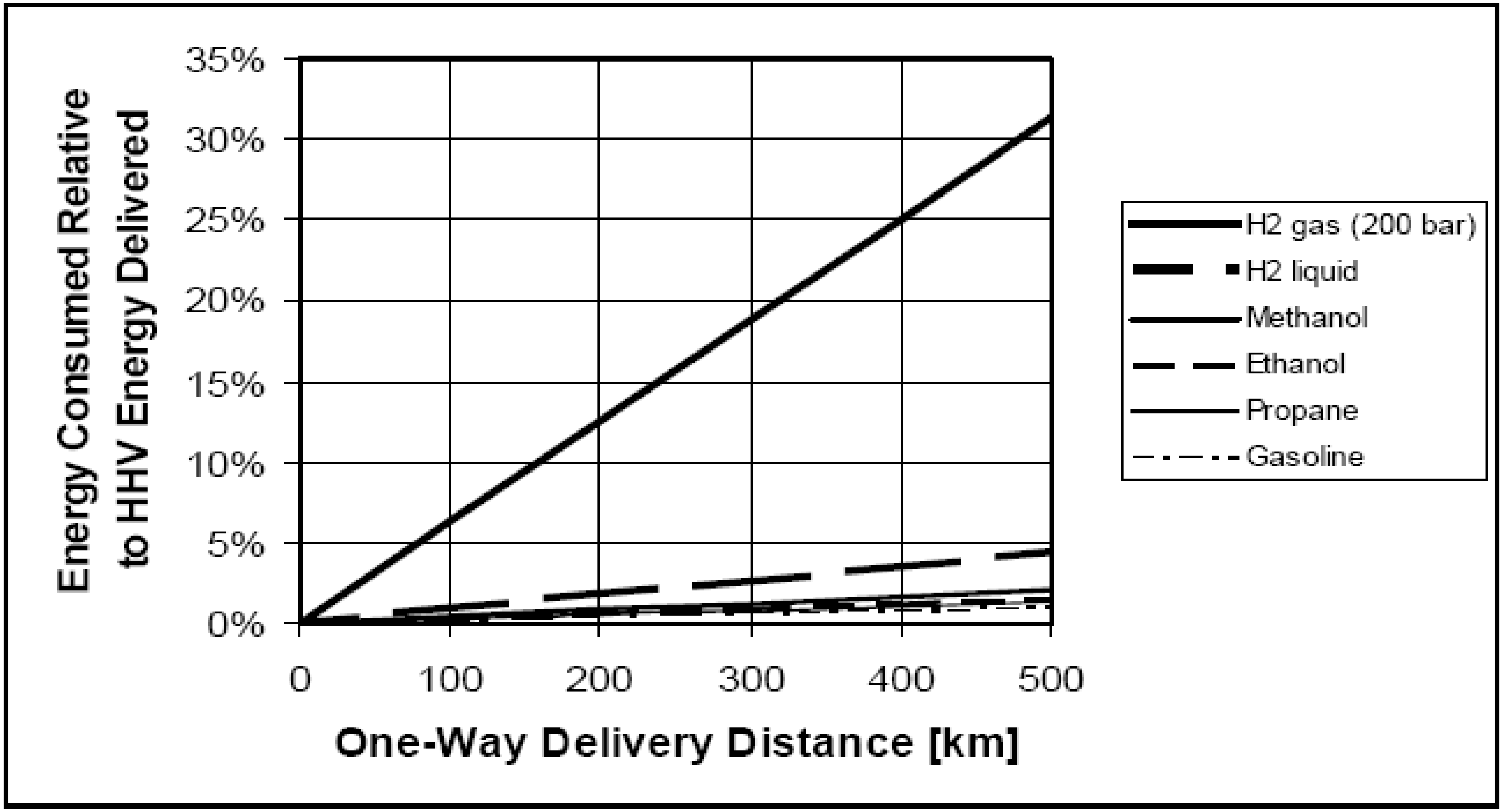
SOURCE: BloombergNEF (2020), *Hydrogen Economy Outlook*

"Making the Hydrogen Economy Possible; April 2021; Report of the Energy Transitions Commission; www.energy-transitions.org

What does 5 Million Tonnes/Year of electrolyser-dependent H_2 Imply?

- Additional investment of ~US$ 1 trillion
- More than 0.1 M (1 lakh) square kilometre of land with solar radiation
- ~0.7 billion tonnes of additional fresh water
- Additional electricity of 3,200 TWh purely for production of H_2 (Electricity generated by 5 MMT H_2 is ~900 TWh)
  - *Present electricity generation is 1719 TWh/year (2021-22)*
- Total hydrogen pipeline length in excess of 300,000 km – *present natural gas pipeline length is about 17000 kilometres*
- We may therefore wish to consider augmenting electrolyser capacity with a **relatively decentralized approach** for green hydrogen in India**: biomass, nuclear, thermochemical, photochemical** – AND **use of impure-water resources** rather than pure-water resources

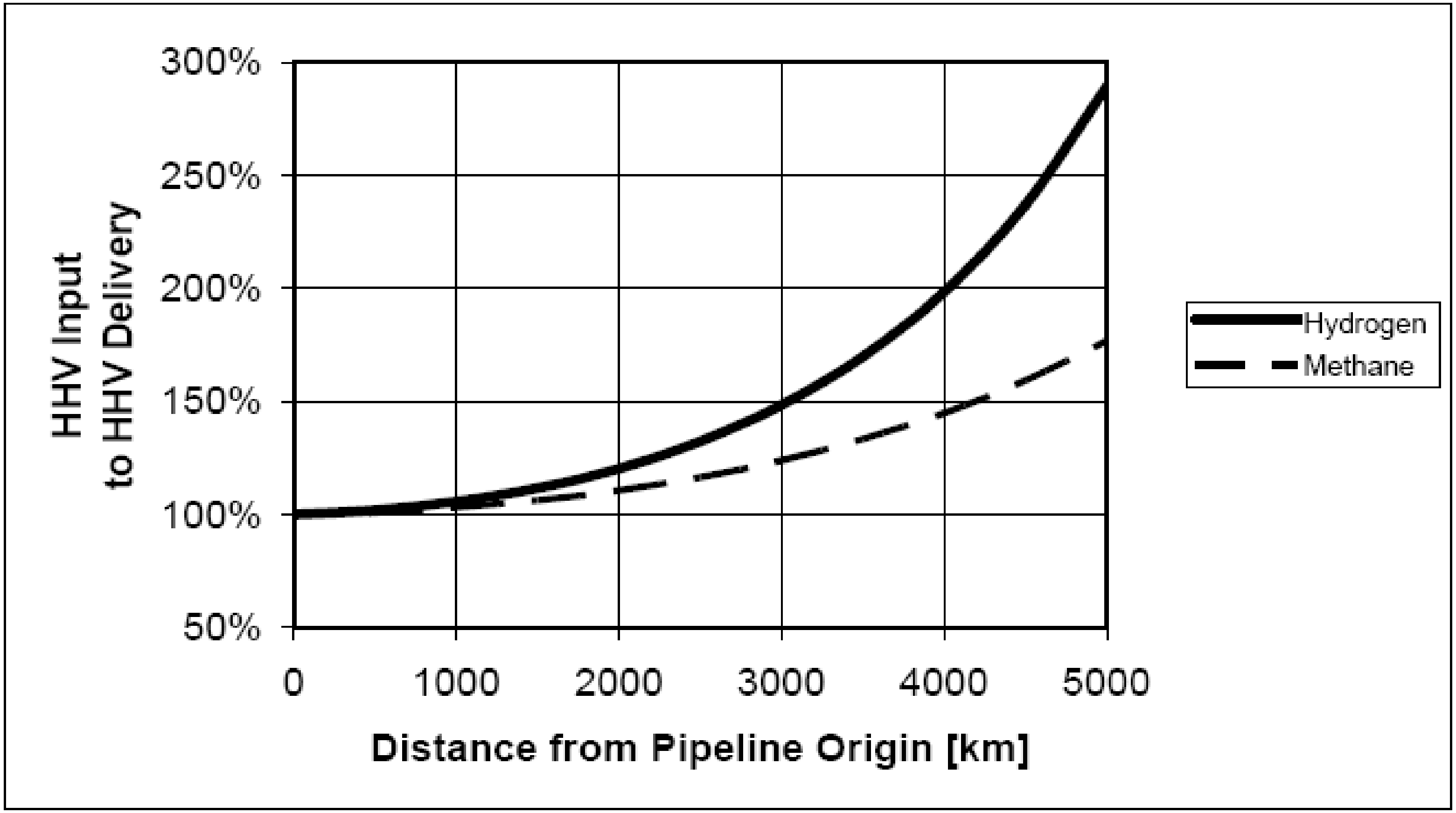
Energy Needed for Road Delivery of Hydrogen



Energy needed for the road delivery of fuels relative to their HHV energy content

Reproduced from: U.Bossel, B.Eliasson & G.Taylor, www.efcf.com/reports, 2005

Energy Needed for Pipeline Transportation of Hydrogen



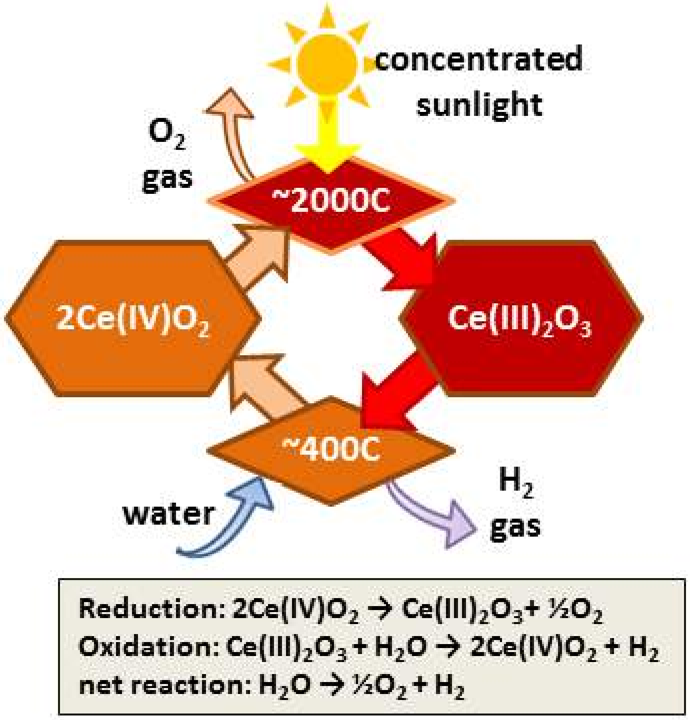
HHV hydrogen energy fed into the pipeline inlet compared to HHV hydrogen energy delivered at the pipeline outlet

Reproduced from: U.Bossel, B.Eliasson & G.Taylor, www.efcf.com/reports, 2005

Thermochemical cycles

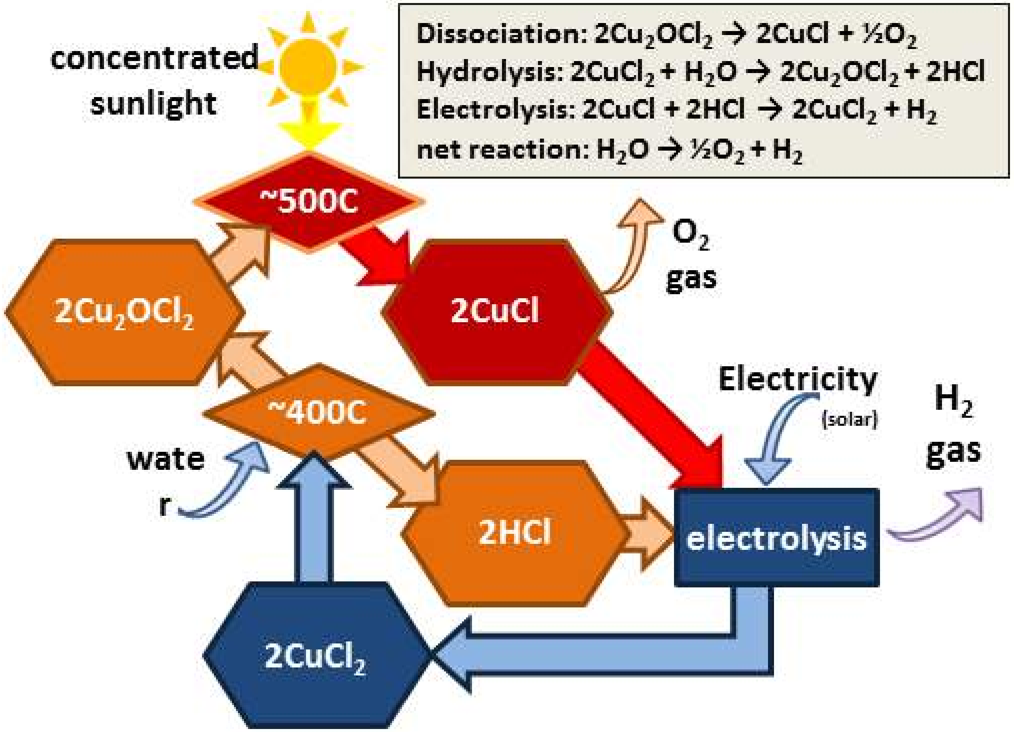
- High heat (500°–2,000°C) drives a series of reactions to produce H_2
- Chemicals used in the process are reused within each cycle.
- Net outcome: consume only water; produce hydrogen and oxygen
- High temperature / heat flux could come from:
  - ➢ Concentrated sunlight via heliostats
  - ➢ Using waste heat from large nuclear reactors or sensible heat from SMRs

cerium oxide two step cycle



Reduction: 2Ce(IV)O_2 → Ce(III)$_2O_3$+ ½O_2
Oxidation: Ce(III)$_2O_3$ + H_2O → 2Ce(IV)O_2 + H_2
net reaction: H_2O → ½O_2 + H_2

copper chloride hybrid cycle



Dissociation: 2Cu_2OCl_2 → 2CuCl + ½O_2
Hydrolysis: 2$CuCl_2$ + H_2O → 2Cu_2OCl_2 + 2HCl
Electrolysis: 2CuCl + 2HCl → 2$CuCl_2$ + H_2
net reaction: H_2O → ½O_2 + H_2

Other than water, what hydrogen sources exist in India?

Production of waste by various branches of chemical industry

Industry	**Product scale (t/year)**	**Kg waste / Kg product (*E* factor)**
Oil refining	10^6-10^8	<<0.1
Bulk chemicals	10^4 - 10^6	1-5
Fine chemicals	10- 10^4	5 - 50
Pharma	1- 10^3	25 - > 100

Sheldon R.A., Green Chemistry, 2007, 9, 1273-1283

Some abundant H-rich wastes in India and their theoretical H_2 potential:

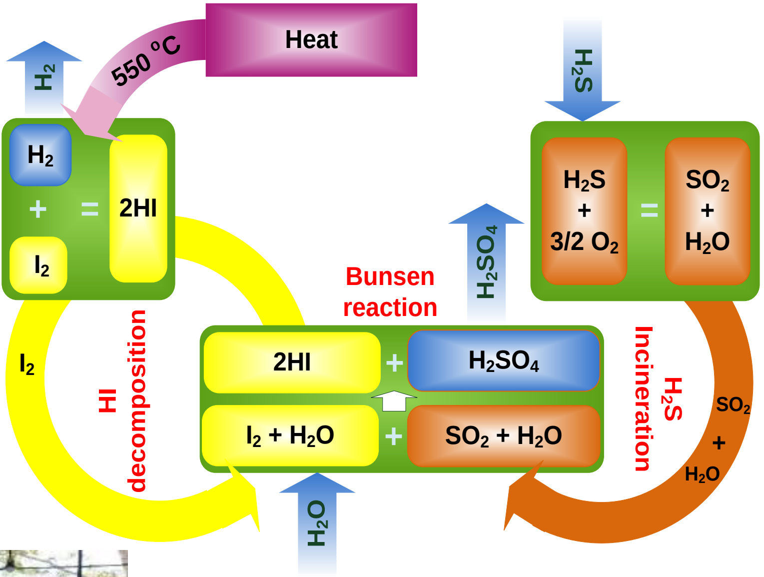
Hydrogen sulfide (refinery sour gas streams) – 54000 TPA

End-of-life Plastics (especially polyolefins) – 300,000 TPA

Methane (e.g. stranded gas) and flared hydrocarbon streams – *to be quantified*

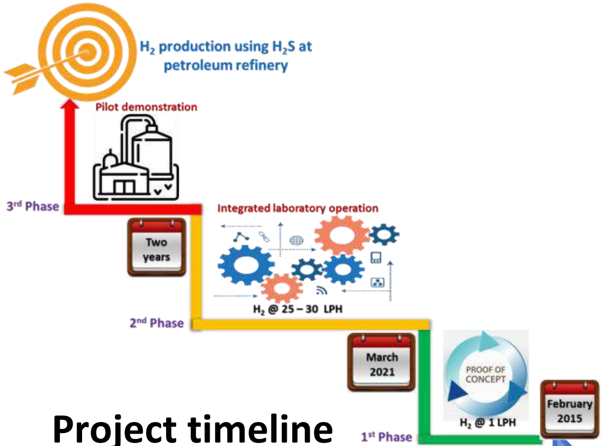
Open loop thermochemical S-I cycle

HI distillation and decomposition



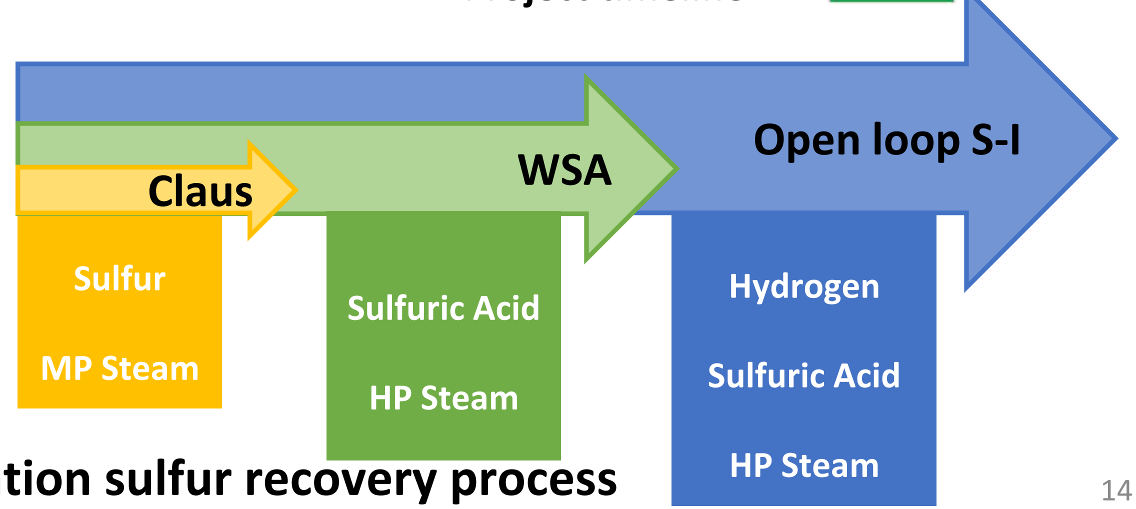
Process principle

H_2S incinerator



Project timeline

Bunsen reaction set-up



Process benefit: Next generation sulfur recovery process

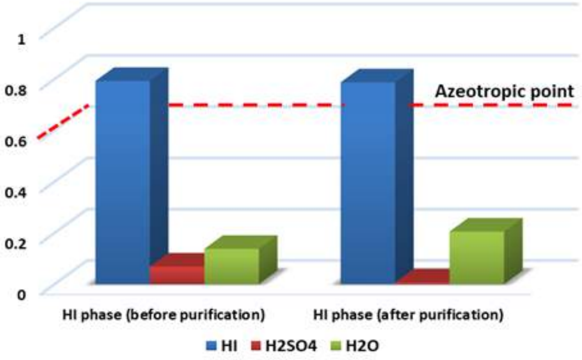
Open loop thermochemical S-I cycle

Objective: **Hydrogen production through partially open loop S-I cycle at refineries; optimized conditions to achieve better economics of the process**

Proof of concept and optimized parameters for 1 LPH H_2 production completed

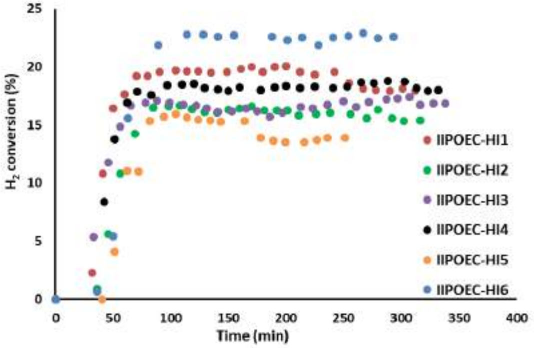
H_2S incineration

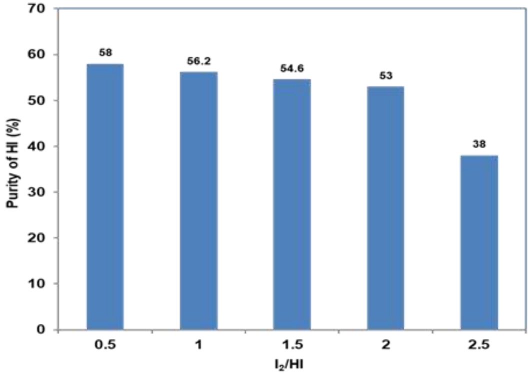
- Design of laboratory scale incinerator with 50 KW burner
- Complete combustion of H2S to SO2 without using excess air



Bunsen reaction

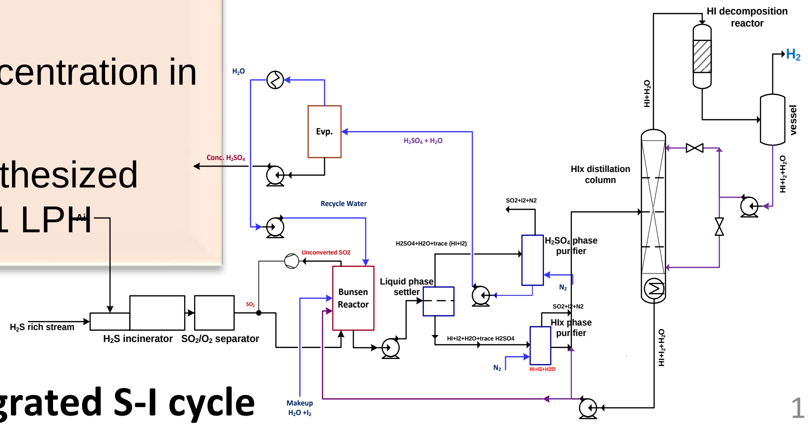
- Optimized feed composition
- Separation and purification of H_2SO_4 and HIx phases
- Achieving over-azeotropic HIx phase





HIx distillation and decomposition

- Distillation of purified HIx obtained from Bunsen reaction
- Optimization of iodine concentration in distillate
- HI decomposition with synthesized catalyst to produce H_2 @ 1 LPH



Schematic of integrated S-I cycle

Hydrogen from Plastic

Technology Would Help Enhance Plastics Sustainability and Use of Renewable Energy

Image by Edwin L. Aguirre

Assoc. Prof. Juan Pablo Trelles, right, and Ph.D. student Benard Tabu with their nonthermal atmospheric plasma reactor setup for producing hydrogen from low-density polyethylene (LDPE) waste.

03/15/2023

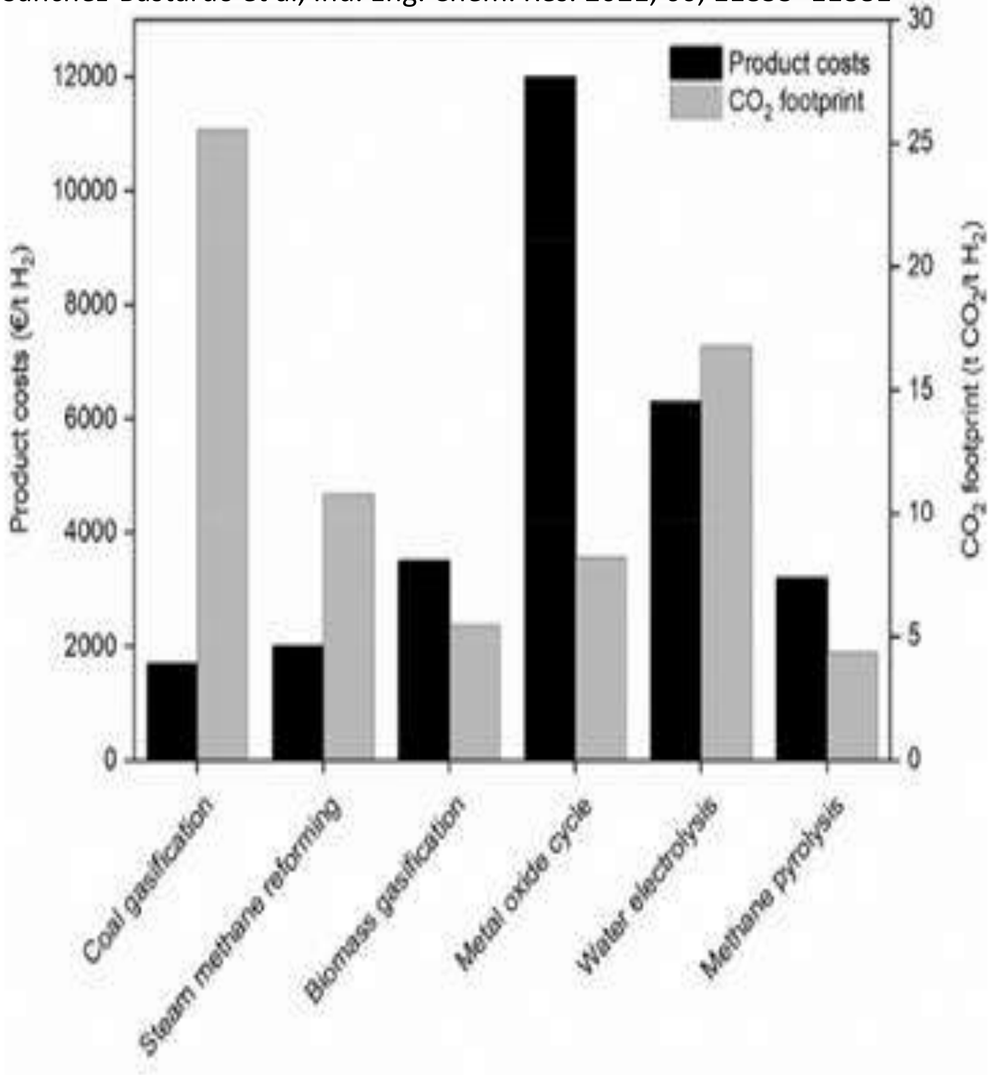
By Edwin L. Aguirre

A team of university and U.S. Army researchers, led by UML Mechanical and Industrial Engineering Assoc. Prof. Juan Pablo Trelles, has developed a way to extract hydrogen from plastic waste that can be used as fuel for transportation as well as to produce electricity in fuel cells.

- Plastic litter containing contaminated food packaging, styrofoam and plastic bags is challenging to recycle and is currently incinerated or buried in landfills, leading to both water and ground pollution.
- Scientists from **Nanyang Technological University, Singapore** can now convert plastic litter via pyrolysis into two main products, hydrogen and carbon nanotubes – a high value material used in biomedical and industrial applications.
- This waste-to-hydrogen project used marine litter collected from local waters in collaboration with NGO **Ocean Purpose Project,** together with industrial partner **Bluefield Renewable Energy**

Hydrogen from Methane

Sanchez-Bastardo et al, Ind. Eng. Chem. Res. 2021, 60, 11855−11881



Methane cracking: Endothermic reaction

- T>300°C is theoretical decomposition temperature (C + H_2) without catalyst
- Conversion remains limited <1200°C due to kinetic factors
- Catalytic cracking is constrained by coke deposition on catalyst surface

Catalyst options

- Metal / Metal Oxide

e.g. Ni on Magnesia, Silica

- Metal on C-support
- Second metal as promoter

e.g. Ni with Pd or Cu

Metal systems typically offer good kinetics but deactivate easily and require regen

- Carbonaceous

e.g. Biochar, Coal fines, graphite, CNT

Slower rates of pyrolysis, variability control

In Conclusion...

- We need to look beyond electrolysis for green hydrogen acceleration in India
- Thermochemical cycles and pyrolysis systems that use hydrogen-rich wastes and low-value resources offer promise
- Decentralized models of generation, along with make-and-use systems, can be valuable for adoption in the MSME sector
- All proposed solutions must be rigorously evaluated for Life cycle costs, life cycle GHG emissions and impact on water resources

THANK YOU