Thermochemical conversion of biomass to hydrogen

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Biomass to Green hydrogen

S. Dasappa
Indian Institute of Science
Bangalore, India

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Conceived in 1896 by the inspired vision of the pioneering industrialist Jamsetji Tata

- Established in1909 as a Trust (Charitable Endowments Act 1890)
- Deemed University from 1957
- Funded by MHRD since 1993

Vision

Founder’s mandate: Institute designed to promote original investigations in all branches of learning and to utilise them for the benefit of India.

21st century: to be among the world’s foremost academic institutions through the pursuit of excellence and the promotion of innovation.

Brief history on the gasification technology at IISc

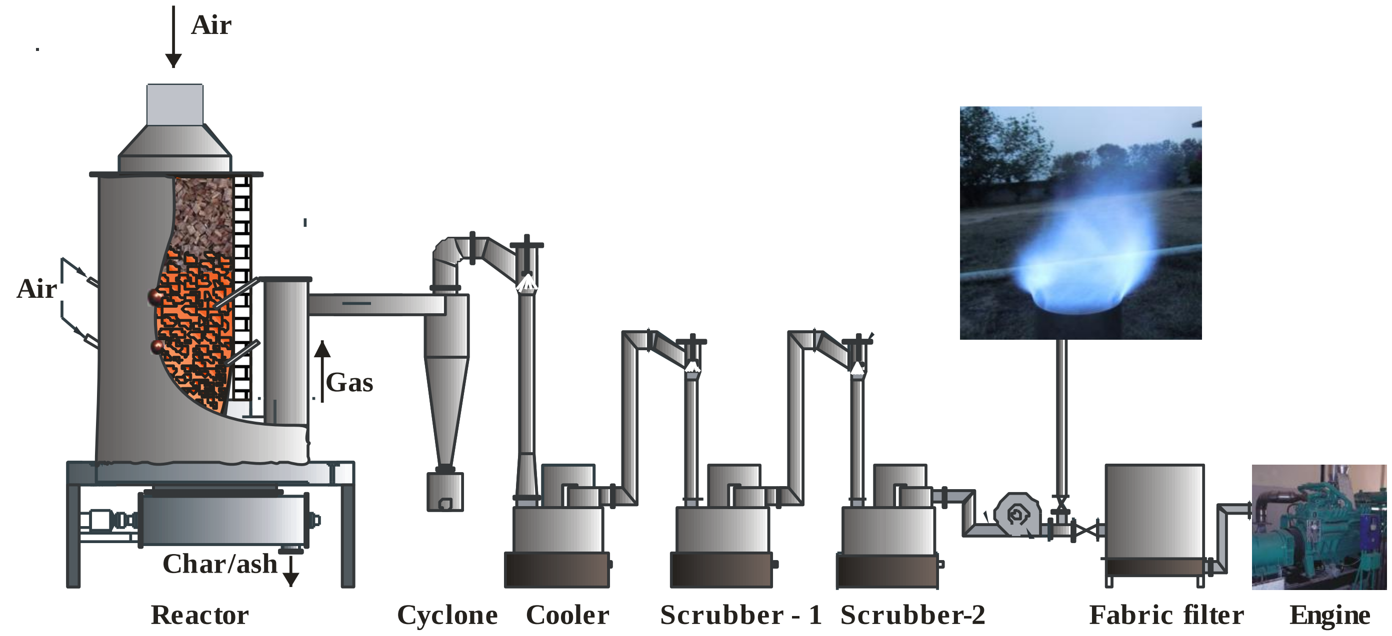
- Gasification research commenced in 1980's
  - Emphasis was on 5 hp diesel pump sets
- Evolved **State-of-the art** technology
- Undergone critical third party evaluation – by various groups
- Commercial applications
- Ten manufacturers in the field (India and abroad)

- At IISc (Open top down draft technology - distinctly different from other designs)
  - Technology package for **agro residue** as the fuel
  - Power range 5 – 1000 kWe
  - Both power and high quality thermal applications
  - Over **500,000** hours of operational experience
  - Gas cleaning system for **turbo-charged engines**

- High pressure gasification for micro-turbine

Open top Dual air down draft – The IISc design

- Integration of over 10,000 component



- ➢ Gasification research commenced Emphasis was on 5 hp diesel pump sets
- ➢ **State-of-the art** technology
- ➢ Undergone critical third party evaluation – by various groups
- ➢ Commercial applications
  - ➢ Both power and high quality thermal applications
- ➢ Technology transfers across the globe (Japan, US, Europe, ..)
- ➢ Technology package for agro residue as the fuel
- ➢ High pressure gasification for micro-turbine

Availability of prime movers

- ➢ Diesel engine – Dual fuel
- ➢ Gas engine – not available

Power generation – few examples


400 kWe Grid connected – Wila Switzerland

1000 kWe Grid connected – Thailand

Univ of Florence - Italy

1000 kWe, San Francisco, USA


250 kWe, Hiroshima, Japan

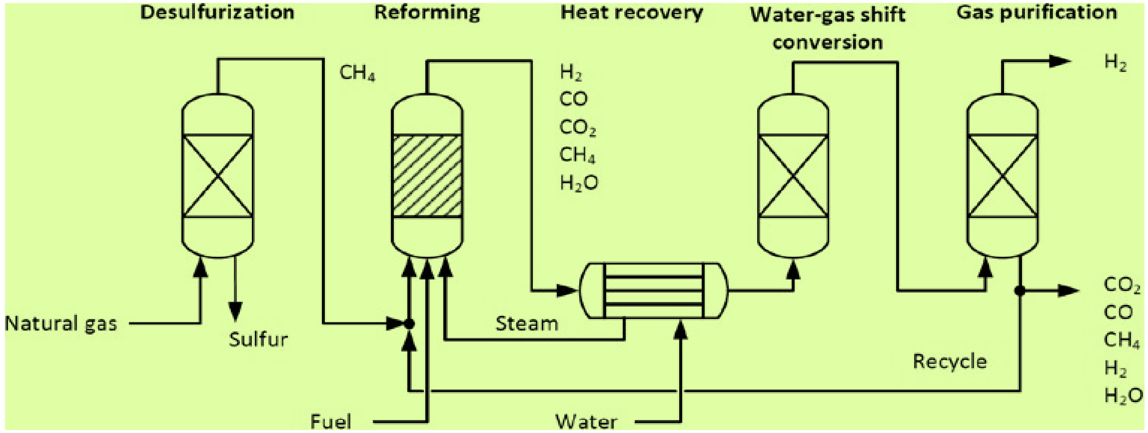


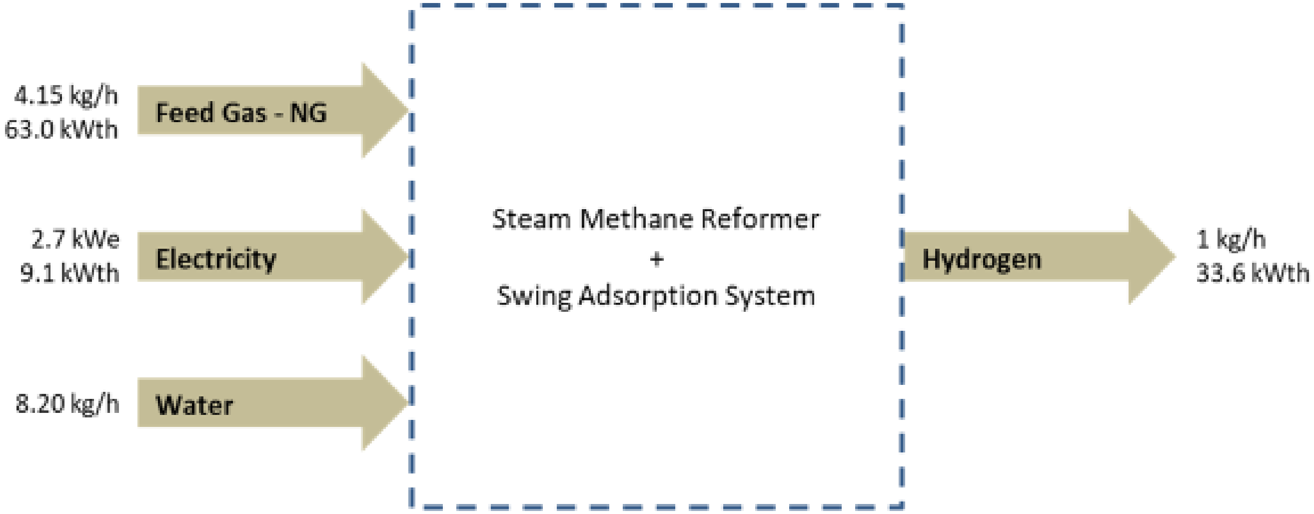
50 kWe Cocodrilo - Cuba

- Potential use for distributed power generation as a **firm power producer** with a potential to **hybrid with other renewables** for continuous generation of **green electricity**

Background

- The worldwide hydrogen production is mainly used by four consumers: ammonia production 50%, refinery applications 22%, methanol production 14%, and various reduction processes 7%. The rest of 7% is spread to other consumers





The typical overall in generating hydrogen from natural gas by the SR process is approximately

- 50% on a LHV basis in the 0.15-15 MW range and
- up to 85 % in the 150-300 MW capacity range. (Körner, 2015)

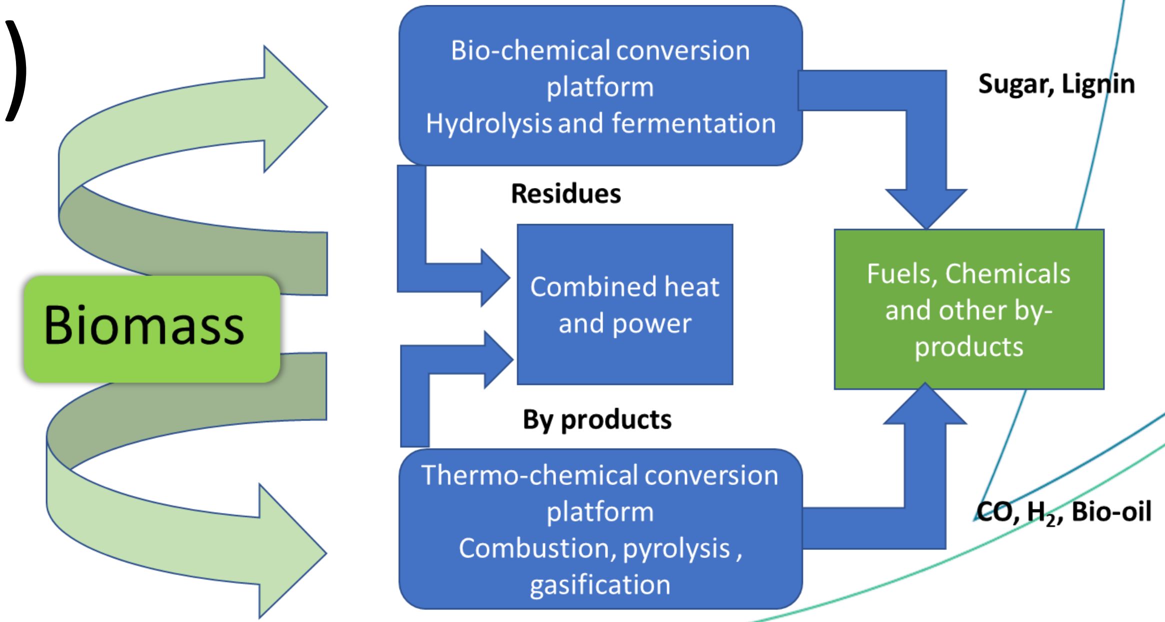
About 3.2 to 4.5 kg of natural gas is required to generated one kg of hydrogen and the other 0.95 to 2.25 kg is towards the energy purpose depending upon the size of the plant

Natural available substances with Hydrogen as an element

- Water (H_2O)
  - Electrolysers
    - $2H_2O \rightarrow 2H_2 + O_2$
    - Theoretical H_2 yield is about 100 g/kg of water

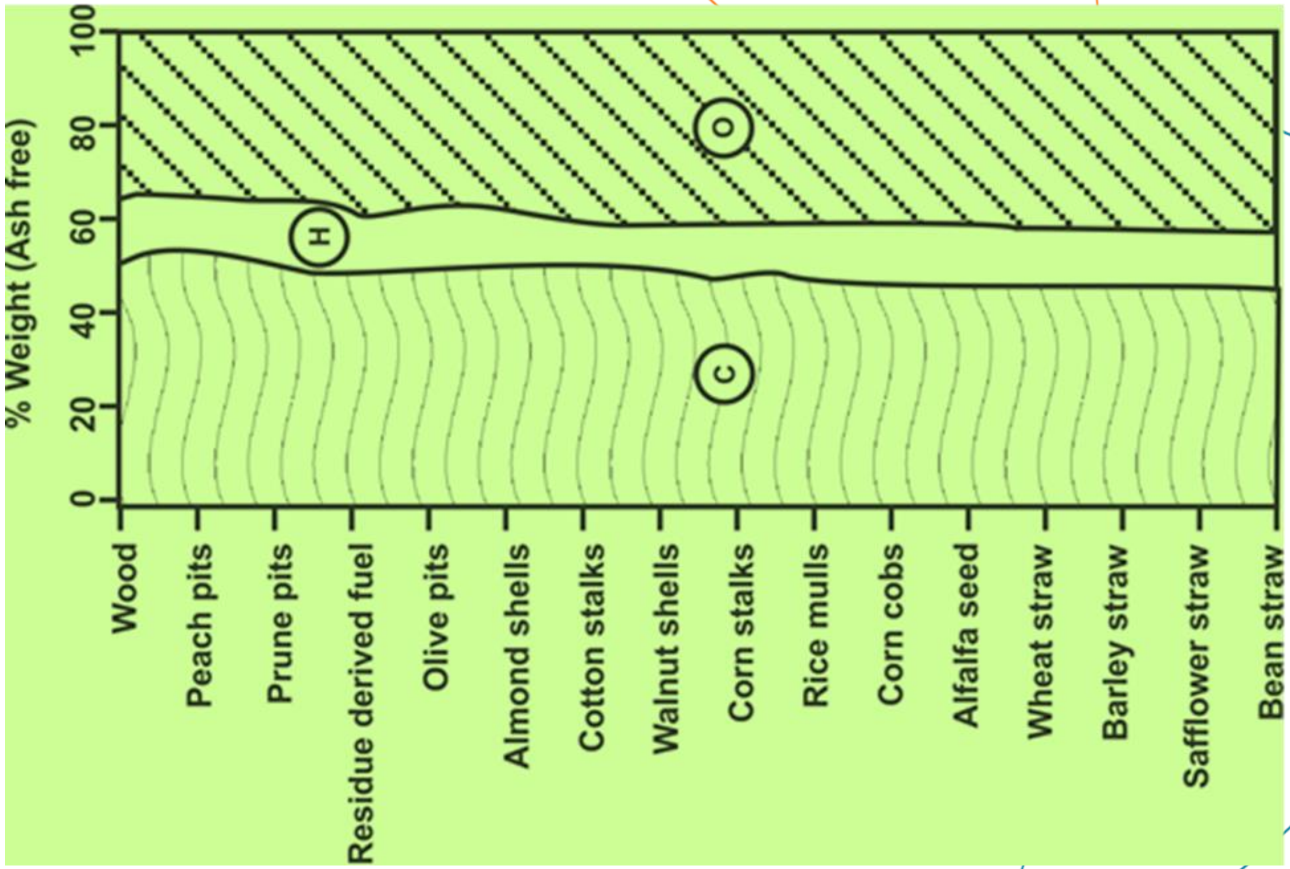
> - Energy required to break the stable molecule ~ 60 kW electricity
> - Major research to reduce the input power

- Biomass ($C_{1.0}$ $0.7(H_2O)$)
  - Bio-chemical and
  - Thermo-chemical



Composition of biomass

Element	Mass fraction (%)
Carbon	52.02
Nitrogen	0.12
Sulphur	0.42
Hydrogen	6.55
Oxygen	41.43
Chemical Composition	$CH_{1.4}O_{0.6}$
Molecular weight	27.89 kg $kmol^{-1}$



Water has hydrogen about 11 % mass fraction

Gasification to hydrogen conversion

- Biomass to mixture of gas and separating hydrogen
- $C_{1.0}\ 0.7(H_2O) + 0.2\ O_2 + H_2O \rightarrow 1.7H_2 + CO_2$
  - Theoretical limit → 150 g of H_2/kg of biomass
- Air gasification
  - $C_{1.0}\ 0.7(H_2O) + 0_2 + 3.76\ N_2 \rightarrow 0.2\ H_2 + 0.2\ CO + 0.02\ CH_4 + 0.12CO_2 + 0.46N_2$
  - Here about 40 – 45 g of hydrogen per kg of biomass
- Oxy-steam
  - $C_{1.0}\ 0.7(H_2O) + \mathbf{x}\ 0_2 + \mathbf{y}\ H_2O \rightarrow 0.25 - 0.50\ H_2 + 0.12 - 0.25\ CO + 0.04 - 0.05CH_4 + 0.15 - 0.25CO_2$
  - Up to 100 g of hydrogen per kg of biomass

Research at IISc on thermo-chemical conversion

- For the first time a fixed bed system is used for oxy-steam gasification to generate hydrogen rich syngas in an allothermal mode
  - Novel design of the open-top downdraft gasifier developed in Indian Institute of Science (IISc) delivers product gas with tar less than 2 mg/Nm^3 in cold gas.
    - The principle used in the design of the reactor increases the residence time of gas inside the reactor, by establishing a high temperature environment in the char bed, thus improving the conversion efficiency and reducing the higher molecular weight compounds.
  - 100 kg/h capacity of open top downdraft gasifier design has been adopted for the oxy-steam gasification with few modifications.

Sandeep K and Dasappa S, Oxy–steam gasification of biomass for hydrogen rich syngas production using downdraft reactor configuration, International Journal Energy Res. (2013), DOI: 10.1002/er.3019.

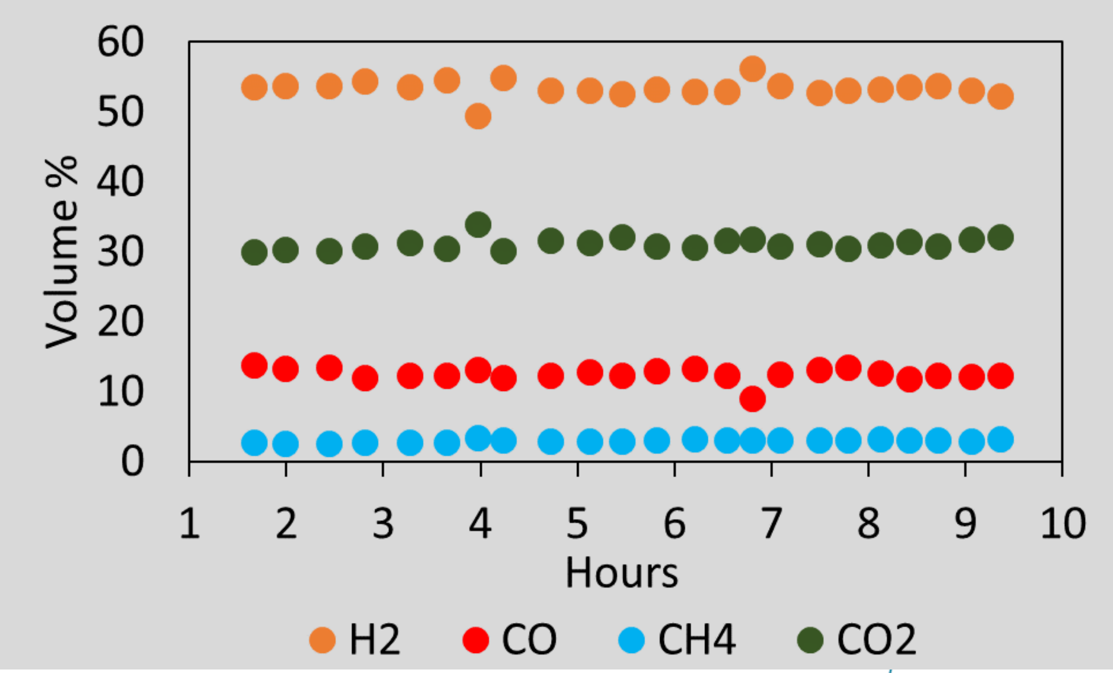
Air gasification – Oxy-steam gasification

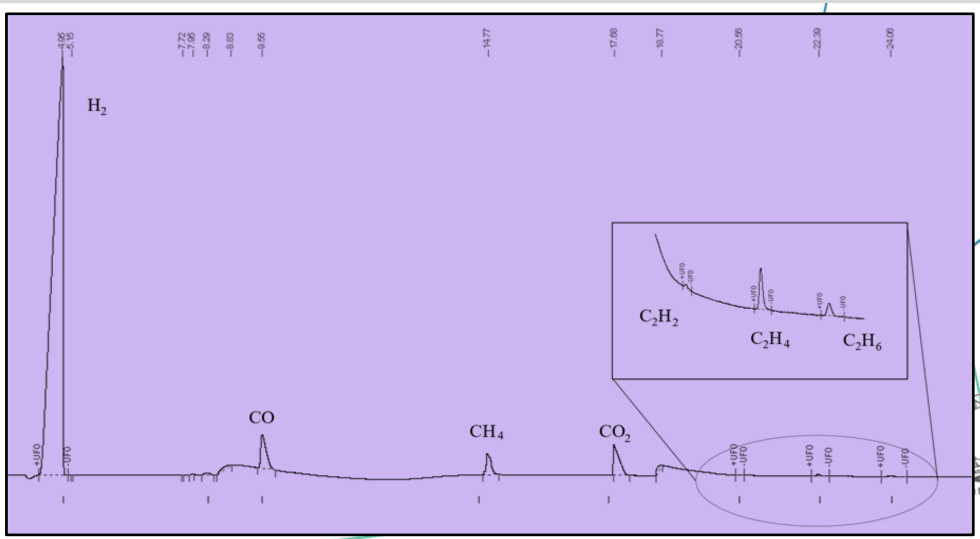
Gasification

↓

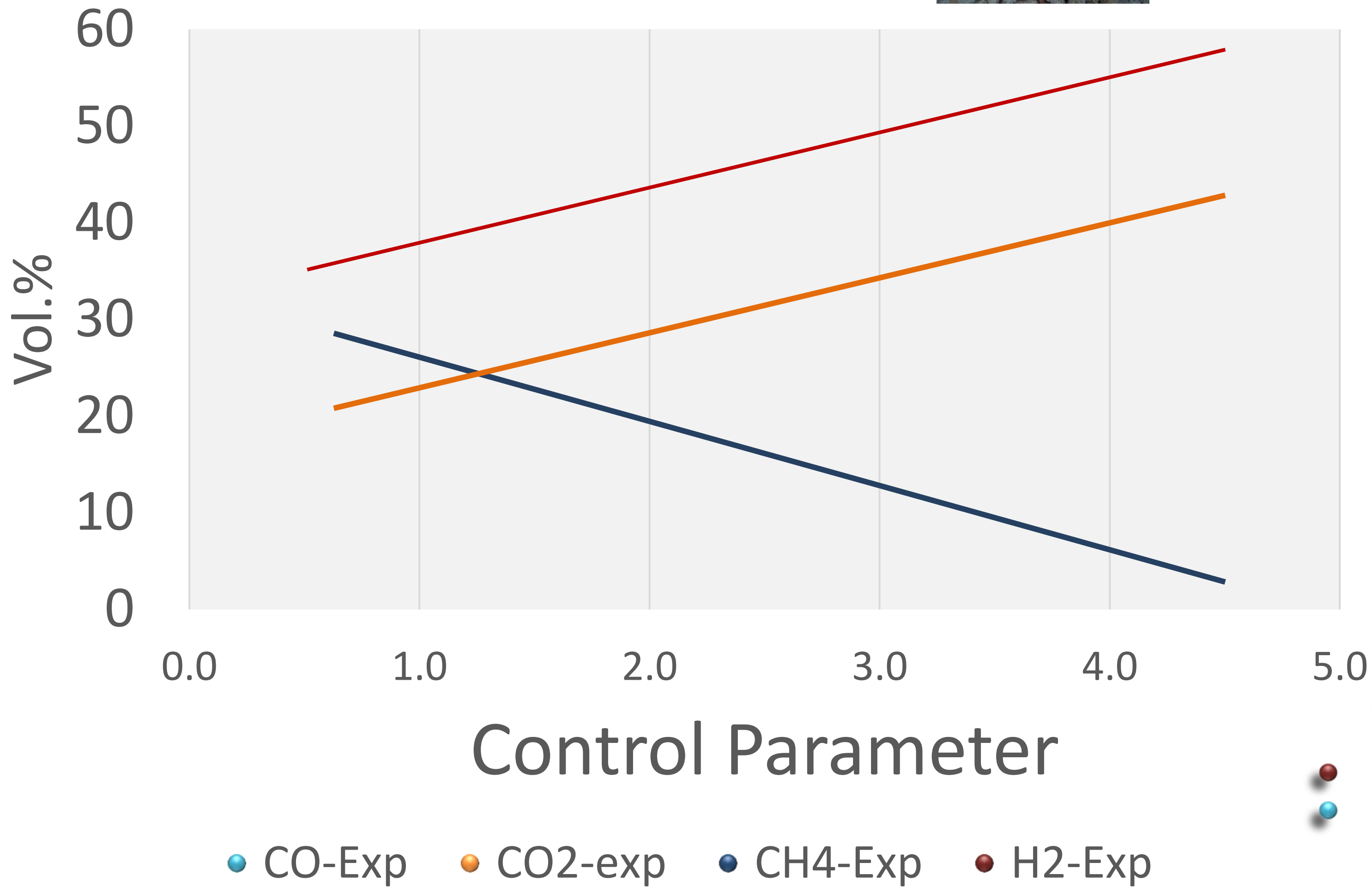
Single stage process

Air gasification	Oxy-Steam gasification
Yield limited by H2 content in biomass ~ 60 g/kg of biomass	H2 yield enhanced by using H2O as a reactant
Low volume fraction (~20% H2, ~45% N2) makes it economically non-viable for separation	Use of O2 instead of air enhances the H2 yield to 45-55%





Oxy-steam gasification results



	Casuarina (CP 1.9)	Coconut shells (CP 1.8)
H_2	48.9± 2	44.1
CO	20.2± 1.5	23.2
CH_4	4.4± 0.8	3.6
CO_2	26.5± 2.1	29

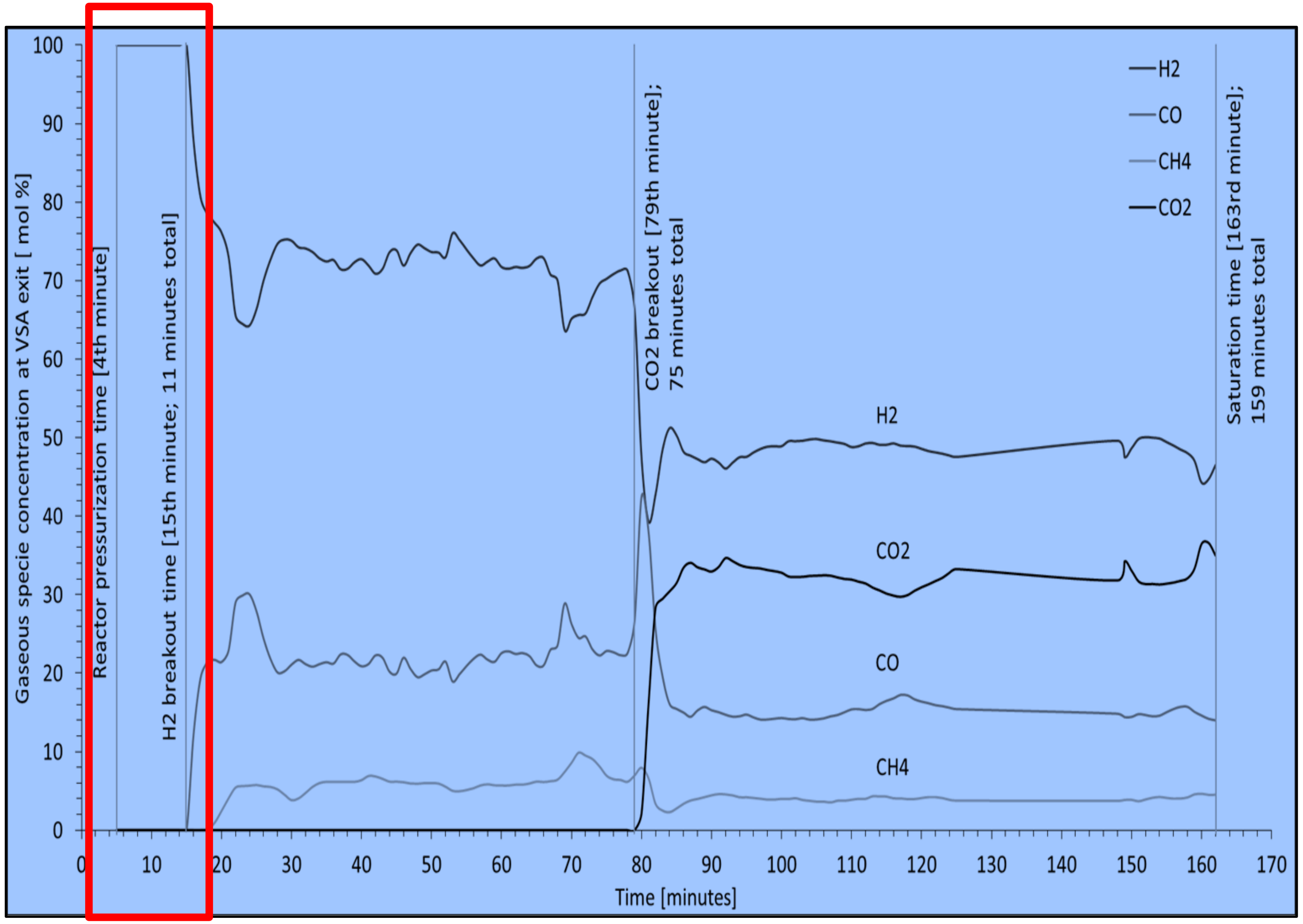
	Casuarin a (CP 1.9)	Casuarina (CP – 2.8)	Casuarina (CP - 3.8)
H_2	48.9	50.7	55.2
CO	20.2	15.3	10.1
CH_4	4.4	3.3	2.7
CO_2	26.5	30.7	31.9

- Sandeep K and S. Dasappa,. Applied Thermal Engineering.:12: pp.1382-1395, 2017.

Results from Oxy-steam gasification

SBR	0.75	1	1.4	1.5	1.8	2.4	2.7
ER	0.21	0.18	0.21	0.23	0.27	0.28	0.3
H_2 yield (g kg^{-1} of biomass)	66	68	71	73	94	99	104
H_2 yield (volume fraction, %) on dry basis	41.8	45.2	43.1	45.2	49.6	51.6	50.5
CO yield (volume fraction, %) on dry basis	27.6	24.9	26.5	24.9	17	12.4	13
H_2/CO	1.5	1.8	1.6	1.8	2.9	3.8	3.9
LHV (MJ Nm^{-3})	8.9	8.6	8.8	8.7	8	7.4	7.4
Hydrogen efficiency (%)	73.7	63.2	67.2	63.5	70.5	61	63.7
Gasification efficiency (%)	85.8	76.8	80.8	77	79.5	70.5	71.5

Gas separation



H_2	CO	CH_4	CO_2	Remarks
46.9	13.9	3.9	35.3	VPSA input
~100.0	0.0	0.0	0.0	VPSA exit

Specifications of the final product gas as per PEM requirements

Standard reference	ISO-DIS14687-2	Status
Characteristics (assay)	Type I, Type II,Grade D	
Hydrogen fuel index (minimum mole fraction)	>99.97%	Achieved
Maximum concentration of Impurities		
Total non-hydrogen gases	<300 µmol/mol	Achieved
Helium (He)	<300 µmol/mol	
Nitrogen (N2), Argon (Ar)	<100 µmol/mol	
Carbon dioxide (CO2)	<2 µmol/mol	<10 ppm
Carbon monoxide (CO)	<0.2 µmol/mol	<10 ppm
Water (liquid)	<5 µmol/mol	14 mg/l
Water (Vapor)	-	
Total hydrocarbons b (C1 basis)	<2 µmol/mol	<3
Oxygen (O2)	<5 µmol/mol	<5 ppm
Total sulfur compounds c	<0.004 µmol/mol	<0.1 ppm (H2S)
Formaldehyde (HCHO)	<0.01 µmol/mol	Being Measured
Formic acid (HCOOH)	<0.2 µmol/mol	< 1
Ammonia (NH3)	<0.1 µmol/mol	<6.0
Total halogenated compounds	<0.05 µmol/mol	<1.0
Maximum particulates concentration	<1 mg/kg	<3 ppm
Max Particulate size	<10µm	Achieved
Conductivity due to Max Inorganic Content	< 5 mS	
Max Inorganic Convent	< 0.01 % ash	Being measured
Na Concentration	<0.05 mg/liter	
K Concentration	<0.08 mg/liter	

Challenges – Gasification Island

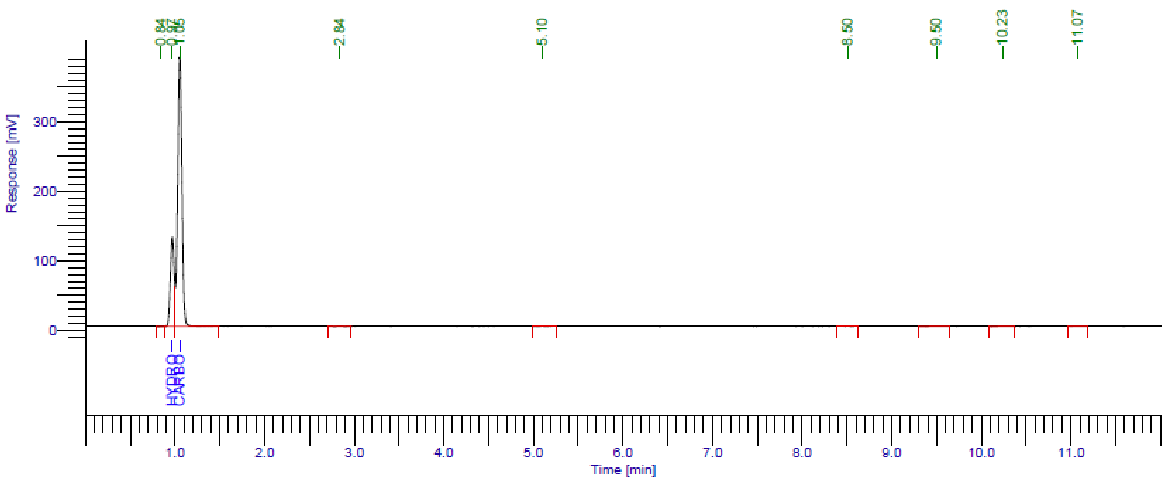
- Establishing the syngas quality and process conditions for PEM fuel cell quality
- Fine tuning the gas composition as per the process requirements
- Ensuring overall energy balance to ensure minimizing in-house power consumption

Analytical systems for quantification of contaminants specified under ISO

Analysers to quantify contaminants

- **GC with Thermal Conductivity Conductor (TCD)** – to analyze Hydrogen and Helium content
- **GC with methanizer, Discharge Ionization Detector (DID) and Flame Ionization Detector (FID)** – to analyze N_2, O_2/Argon, CO, CO_2 & total hydrocarbon
- **GC with Sulphur Chemiluminescence detector (SCD)** – to analyze total sulphur compounds including H_2S, COS, CS_2 and mercaptans
- **FTIR with Mercury-Cadmium-Telluride (MCT) detector and Deuterated triglycine sulfate (DTGS) detector** – to analyze organic compounds
- **Diluter** – to dilute standards to ppb levels

Syngas/H2 Characterization – Sulfur CD



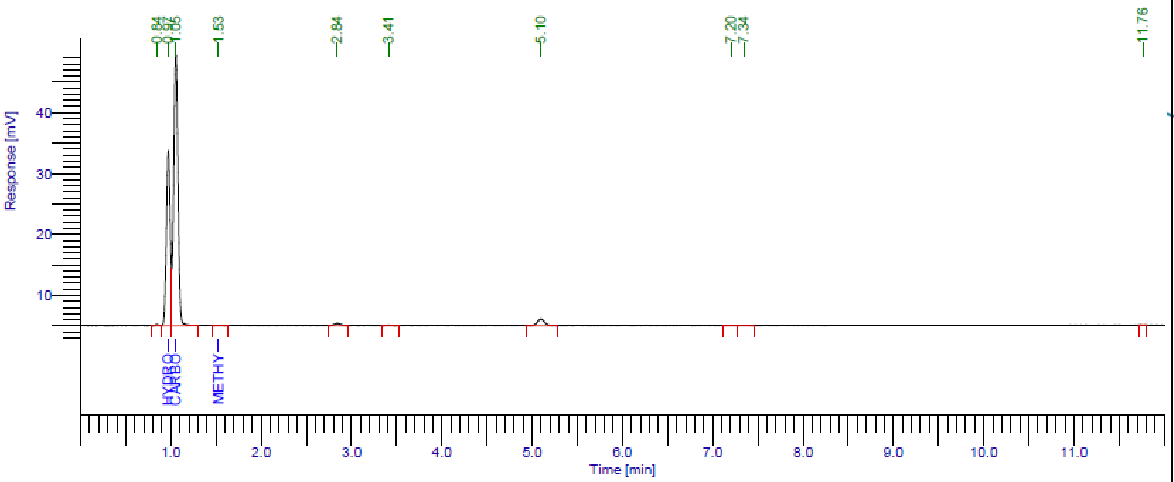
DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	Adjusted Amount in PPM
2	Hydrogen Sulfide	0.970	381110.79	128809.24	22.68	22.68	14.1487
3	Carboxyl Sulfide / S	1.052	1299511.17	388273.03	77.32	77.32	98.8467
			1680621.96	517082.26	100.00	100.00	112.9955

Missing Component Report

Component	Expected Retention (Calibration File)
Methyl Mercaptan	1.527
Ethyl Mercaptan	2.306
Dimethyl Sulfide	2.522

Syngas Characterization



DEFAULT REPORT

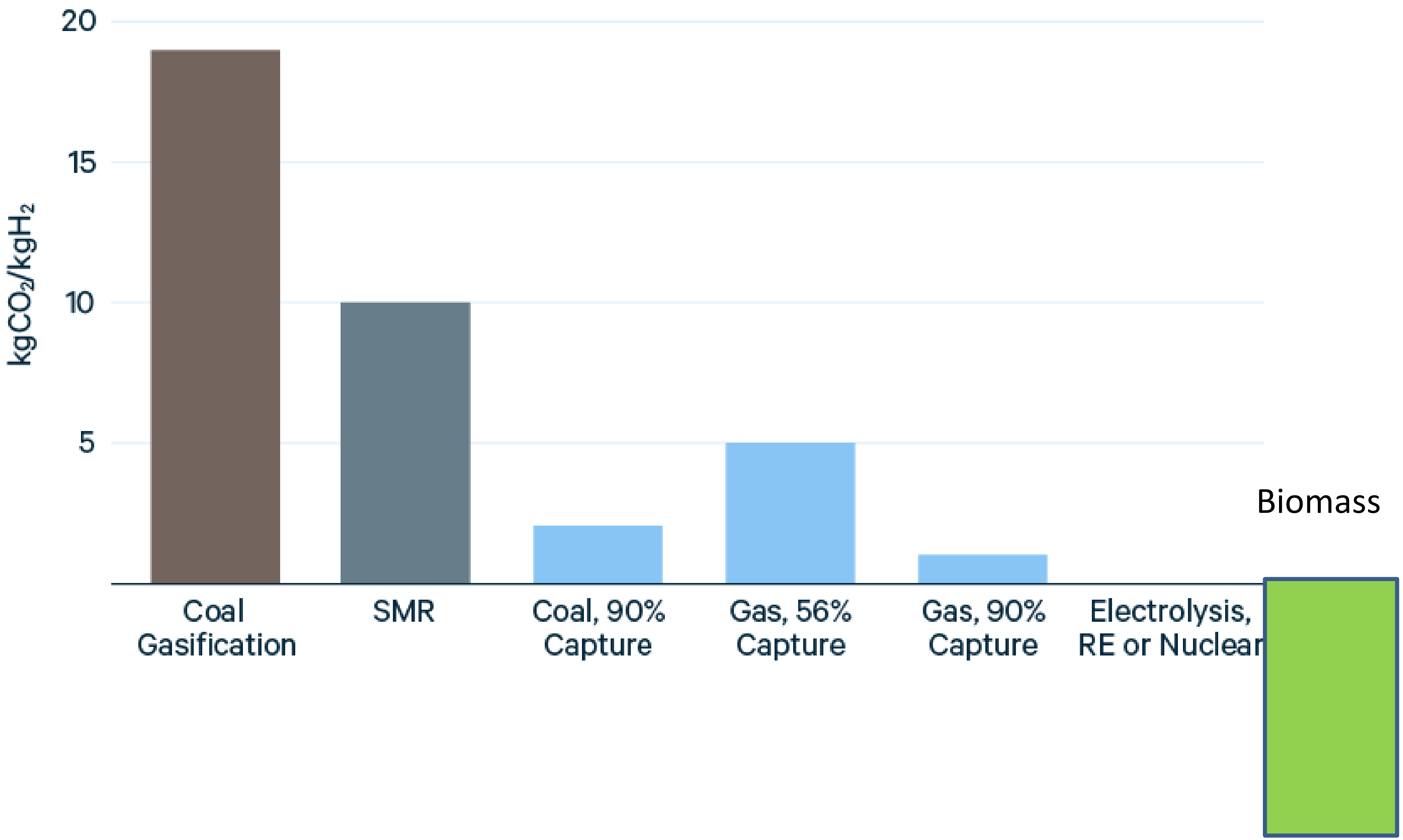
Peak #	Component Name	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	Adjusted Amount in PPM
2	Hydrogen Sulfide	0.971	86076.38	28683.01	37.02	37.02	-10.1797
3	Carboxyl Sulfide / S	1.054	146263.00	44521.70	62.90	62.90	-47.7487
4	Methyl Mercaptan	1.527	194.85	43.67	0.08	0.08	-9.6880
			232534.23	73248.38	100.00	100.00	-67.6165

Missing Component Report

Component	Expected Retention (Calibration File)
Ethyl Mercaptan	2.306
Dimethyl Sulfide	2.522

Hydrogen Characterization

Opportunity for sustainable future



Way forward

- PEM single and stack level testing in progress
- Range of biomass to be tested
- Major initiative by IOCL to setup a 10 kg/hr hydrogen generation is being setup at their Faridabad plant for generation and utilization in the bus
  - The complete package from biomass gasification to separation and purification is planned for implementation

- Opportunities decarbonizing
  - Steel, fertilizers, etc
- High potential for MSW as a fuel for hydrogen production
  - Focused development required

……………….Thank you

dasappa@iisc.ac.in