Supplementary Material

Comparative analysis of hydrogen production pathways for emethanol synthesis to decarbonise industry

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Modelling Context and Input Data:

Hydrogen Pathways

The following provides modelling considerations for the three hydrogen pathways.

Blue Hydrogen



In Methane Reforming, Methane reacts with steam in the presence of catalyst to produce Hydrogen and Carbon Monoxide/Dioxide with heat supplied from combustion of natural gas. Autothermal Reforming is similar but utilises a pure oxygen stream to react with steam and methane directly instead methane with air reacting in isolation in the burner compartment of the reformer.

CO2 is therefore generated both in the conversion process and in the combustion of methane. It is currently not viable to electrify the process at scale, however, research is being done to develop an electrified version of this technology.

To reduce the CO2 intensity of the process, the CO2 produced needs to be captured and stored or utilised. Hydrogen generated from Methane Reforming with Carbon Capture/Utilisation is known as Blue Hydrogen.



*includes balance of plant (BOP) but excludes the air separation unit (ASU) energy demand additional energy of 2.66 kWh/kg-H2 which is considered separately.

Table: Reforming Technologies Comparison

Description	SMR NG fired	CR	ATR	
Capacity (single train)	Downfired high capacity approaching 400kNm3/h	400kNm3/h	Approx. 400kNm3/h	
	Others low <200kNm3/h			
Carbon Capture	85 - 90%	Max 95%	95-97%	
Efficiency (HHV incl. power import)	70 - 75%	75%	75 – 79%	
Cost	High	High	Low	
Power Import	High	Low	Low	

Note: SMR stands for Steam Methane Reforming, CR stands for Combined Reformer, ATR stands for Autothermal reforming. Heat Exchanger reformers have not been included in above table. ATR are suitable for large scale facilities, however, for this analysis only ATRs have been considered due to time constraints in developing additional models.

As illustrated above, blue hydrogen under an ATR process requires an air separation unit to supply oxygen for the autothermal reaction, along with water/steam and methane. An air separation unit is required to supply the oxygen, with the by-product nitrogen either being sold or vented. No valorisation of the Nitrogen is considered in this study.

The CO2 from the autothermal steam reforming process is typically utilised in the downstream methanol plant, which is how most of the methanol is currently produced globally. However, this does not allow for decarbonisation of other industries as the CO2 from other industries is not required. Furthermore, if the Methanol is used as a fuel then net fossil CO2 will continue to be released into the atmosphere. CO2 captured from the Blue Hydrogen facility will consider compression to around 130 barg.

There are several methane reforming technologies available in the market, though Steam Methane Reforming (SMRs) are the most common. The below table compares the various technologies.

Green Hydrogen



Hydrogen is produced from Water Electrolysis (dissociation of Water into Hydrogen and Oxygen using electricity). When this electricity is sourced from a renewable supply it is termed as Green Hydrogen. The main model parameters used for this study are shown in the figures below.



* Inclusive of BOP loads and excluding additional compression loads for storage.

The below figure illustrates the key block components of the process value chain for the Green Hydrogen Route to Methanol.



Electrolysis requires treated water supplied from an RO plant and a Demin plant, RO water is also utilised as a cooling medium. The oxygen by-product from electrolysis can be sold, however, for this study it is ignored.

There are several technologies for Water Electrolysis, these are compared in the table below.

Table: Electrolysis Technologies Comparison

Parameter	AWE	PEM	SOEC
Technology Maturity	TRL 9/CRI 4	TRL 9/CRI 3	TRL 7/CRI 1
Annual Degradation (%/yr)	1-1.5	1-2.3	04-Aug
Stack Material	Zirfon, Nickle	Nafion, Plt, Iridium	Ceramic materials
Flexible Operation	High	Very High	Low
Req Demin Quality (µS/cm)	<5	<1	01-May
Efficiency %	70-80	68-75	99
Energy Demand (kWh/kg-H2)	49-56	52-58	39
Turndown *	10%	40%*	unknown
Module Size	20 MW	20 M W	20MW
Operating Temperature	Higher	Lower	Very High
CAPEX	Lower (1)	Higher (>+30%)	Unknown at large scale
SUSEX	Lower (1)	Higher stack replacement less frequently $(>+6\%)$	Unknown at large scale
Other Advantages	 Well Established Large scale Long term stability Pressurised Alkaline version available 	 High Current Density Compact System Dynamic Operations High Imp potential 	 Potentially higher Efficiencies Integrated with Exothermic Process Non-noble materials
Other Disadvantages	 Low Current Density Corrosive electrolyte Slow dynamics Gas permeation 	 High degradation High membrane & electrode cost Noble materials Low Efficiency 	 Demo Small Scale Unstable Electrodes Brittle ceramics Sealing issues

SOEC is a promising new development for electrolysis, however, it has not been considered in this study as there are no commercial operating examples and carries uncertainty in costing. While AWE is modelled in this study owing to its mature economics and lower costs and higher efficiency compared to PEM.

Turquoise Hydrogen



Involves heating Methane to high temperatures in the absence of oxygen, causing dissociation into hydrogen gas and solid carbon. The energy/heat input for the reaction is provided conventionally from fossil fuels such as natural gas and the hydrogen generated is of lower carbon intensity than conventional hydrogen from Methane reforming. This hydrogen is termed Turquoise Hydrogen. When the power for

this is also supplied from renewable sources, feasible with some nascent pyrolysis technologies, then the Hydrogen product could be considered of low emission standard.



The below figure illustrates the supply chain for Turquoise Hydrogen:



There are several developing pyrolysis technologies which differ primarily in the method of heat transfer, these are categorised as follows:

- Thermal Pyrolysis, which subdivided into:
 - Non-catalytic: conventional pyrolysis involving fossil fuel heat source to dissociate natural gas at very high temperatures (>1100 °C).
 - Catalytic: reduced activation energy and heat transfer in presence of metal or carbonaceous catalyst and occurs at reduced temperatures (400-1200 °C).
- Plasma, where electrically ionised gas/radicals and free electrons are formed in a reactor with natural gas. The energised electrons transfer energy for the dissociation of methane. This technology is also subdivided into:
 - \circ Thermal Plasma: the plasma energises the radical molecules as well as the electrons resulting in very high temperatures (1100 2000 °C).
 - Non-Thermal Plasma: apply technologies like microwaves to excite electrons to higher temperatures than the surrounding ionised gas molecules, allowing the overall temperatures to be lower (800-1100 °C). There is also potential for non-thermal plasma to be combined with catalyst with further technological development.

The below table provides a comparison of these pyrolysis technology routes.

Parameter	Thermal		Plasma		
~ .	Non-Catalytic		Catalytic	Thermal Plasma	Non-Thermal Plasma
Sub-set technologies	No Catalyst - high temperature dissociation of methane.	Solid Catalyst (can be metal or carbon based)	Molten Metal/Salt	Thermal Plasma – entire plasma is at very high temperature.	Non-Thermal Plasma (Microwave/gliding arc/dielectric barrier discharge)
Advantages / Disadvantages	 > No catalyst for upkeep or risk of deactivation/no catalyst cost > High conversion due to high temperature process > Scalable and can operate at elevated pressures if separation of carbon is managed. > High purity Hydrogen and Carbon product at high temperatures > utilises natural gas or recycled hydrogen for heat, which is either carbon intensive of less effient respectively. 	 > Low temperature operation thanks to lower activiation energy from catalyst > Lower temperature reactor allows for cheper material of construction > High quality carbon products (nanotudes) thanks to metal solid catalsyst surface > utilises natural gas or recycled hydrogen for heat, which is either carbon intensive of less effient respectively. > more sensitive to feedstock purity than non-catalytic pyrolysis 	 > Low temperature operation thanks to lower activiation energy but trade off with type of molten metal used which requires high temperature to maintain in liquid form. > Lower temperature reactor allows for cheper material of construction > No blocking/clogging of reactor and longer catalyst function but still deactivation can occur and contamination of carbon product. > Excellent heat transfer, but still utilises natural gas or recycled hydrogen for heat, which is either carbon intensive of less effient respectively. > more sensitive to feedstock purity than non-catalytic pyrolysis 	 > Flexible and responsible - on/off, however, high temperature requires maintaining and longer ramp up if cooled > Can utilise Renewable Energy supply on intermittent basis > No catalyst to maintain/manage > high conversion rate and single pass purity at high temperatures > High conversion rate but low energy effiency 	 > Flexible and responsible - on/off, > Low temperature > Can utilise Renewable Energy supply on intermittent basis > No catalyst to maintain/manage > High energy efficiency but low conversion rate. > Microwave process can be used to generate hydrogen and acetylene also to reduce solid carbon production.
Reaction Temp (C)	>1100 (High)	400-800 (Ni based) 600-900 (Fe based) 700 - 1200 (Carbon based)	700-1100	>1100-2000+ (very high)	<1100
Leading Developers	BASE	Hazer Group Ltd	TNO-EMBER	<u>Monolith</u> / <u>Graforce</u> / <u>Plenesys</u> / <u>SyngergenMet</u>	<u>Transform Materials / Atlantic</u> <u>Hydrogen / Gazprom / Aurora</u>
Efficiency	Low	High	High	Low	High
Conversion Rate	High	Low	Moderate	High	Low
Scalability	Good	Poor	Poor	Good	Good
Relative Cost	Low 1	Moderate 2	Moderate/high 3/4	High 4/3	High 5
Upkeep	Moderate, management of carbon deposition in reactor, but no catalyst management/regen or replacement required	Catalyst graduate deactivation requiring replacement or regen.Regeneration, potentially environmental concerns with CO2 release and comtamination of metal compounds in carbon product.	Loss of molten metal/salt over time, requirement top up and regeneration, potentially environmental concerns with CO2 release and comtamination of metal compounds in carbon product. High intensity for high purity carbon separation and corrosion risks.	Replacement of electrodes to compensate carbon deposition.	Replacement of electrodes to compensate carbon deposition.
Ramp up/Down	Moderate, temperature control and non-uniform temperature in reactor are an issue.	Moderate, catalyst to be kept at optimal condition and and non- uniform temperature in reactor can be an issue.	Poor – catalyst must be kept in optimal condition, molten metal if used must be kept liquid.	Good – fast switching on and off of the system. However, maintaining gas velocity is required for adequate evacuation of carbon black to avoid deposition in reactor.	Good – fast switching on and off of the system. However, maintaining gas velocity is required for adequate evacuation of carbon black to avoid deposition in reactor.
Carbon Product Quality	Moderate/Low - inhomogenous/ generally of graphite or carbon black quality	High - forming nanotubes/filaments and plates with metal catalyst and graphite with carbon based, better control of type of carbon by-product, however, carbon can be contaminated with impurities	Moderate/low - Carbon is soluble in molten metal and prevents, in most instances, formation of graphite and nanotubes structures. Carbon products contaminated with impurities.	Moderate/low - broad quality, typically graphite and carbon black and inadequate for high commericial products. Carbon black though of low value can have a large market in use in typre strengtening as observed with Monolith marketing their carbon black for tyre use.	Moderate/low - broad quality, typically amorphous/graphite and carbon black. Carbon Nanotudes can be formed if catalyst is also used because can operate at lower temperatures with non thermal plasma.

Technology/ Commercial Maturity	TRL 4-5/CRI 1	TRL 5/CRI 1	TRL 3/CRI 2	TRL 8-9 / CRI 2	TRL 4-5 / CRI 1
Development Status	Challenges with carbon deposition and clogging, development of carbon management. Pilot plant by BASF is under construction with commericial plant planned for 2030 (BASF 2022)	<u>Commercial demonstration plant</u> <u>constructed and planned</u> <u>commissioning in late 2023</u> – plant to prove challenges of catalyst management at scale. Regeneration of catalyst is considered but leads to gradual oxidation of active sites and/or release of CO2. Continued issue with carbon clogging of the reactor is also an issue as with the non catalytic approach.	Required to prove feasibility to resolve challenges of molten metal contamination and metal catalyst poisoning or deactivation even when utilisation carbon catlyst. Molten metal offers potential particularly in separating carbon and avoiding clogging of the reactor but results in gradual loss of the molten metal, which has been compensated partially by use of molten salt layer. Also molten metal still results in deactivation of the catalyst and toxic metal contamination of carbon product is a concerns which can lead to intensive additional separation steps. Regeneration of catalyst still leads to gradual oxidation of active sites and/or release of CO2.	Based on SINTEF/Kvaerner Thermal Plasma torch, was developed further and comericialised by Monolith. It's commericial Olive Creek Plant in Nebraska, US, is the only comericially operational Methane Pyrolysis plant in the world. Further technology development on heat management and efficiency is required and scaling up of operation is currently planned by Monolith as well as handling carbon deposition in reactor as facility is further scaled up.	Transform materials has successful carried out testing at a pilot plant. Technology requires further development to address low conversion rate concern and carbon deposition in reactor and electrode.

Table: Pyrolysis Technologies Comparison

The following table compares the most appropriate technologies from each of the three hydrogen production routes in terms of their technical parameters.

Comparison of H2 Technologies	Units	Green Hydrogen	Blue Hydrogen	Turquoise
Technical Parameters				
Power Sourcing	-	Electrical via Renewable Energy	Fossil Fuel + Grid Electricity	Electrical via Renewable Energy Thermal Plasma
Technology Approach Selection	-	Alkaline Water Electrolysis	Steam Methane Reforming	Pyrolysis
Operational Flexibility	-	Moderate	High	Moderate
Reactor Temperature	oC	80	1000	1200
Turn Down Ratio ³	%	30%	50%	30%
Availability	%	96-98%	96%	96-98%
H2 Product Purity	%	99%	99%	99%
Discharge Pressure	barg	0.2	0.2	0.2
Reaction Energy	kJ/mol-H2	286	41	37.8
	kWh/kg-H2	39.3	5.7	5.20
Reaction Efficiency	%	0.70	0.75	0.50
Energy Efficiency (with CCS)	%	N/A	0.56	N/A
(inc eff with CC)	kWh/kg-H2	56.3	10.1	10.5
Net Energy Imported from Electrical Source ²	kWh/kg-H2	60.75	1.17	9.00
Waste Heat Recovery	kWh/kg-H2	N/A	Go-Gen considered	Go-Gen considered
Methane Feedstock Required	kgCH4/kg-H2	N/A	2	4
Total Methane Required (inc fuel gas)	kgCH4/kg-H2	N/A	3.18	4
By Product (X)	-	Oxygen (O2)	Carbon Dioxide (CO2)	Carbon (C)
By Product (X) Production Rate	kgX/kg-H2	7.9	8.46	3.0
Cooling Water top up	kgH2O/kg-H2	26	9.39	5.7
Demin Water Rate/top up	kgH2O/kg-H2	10.0	4.2	0.3
Direct CO2 Captured/Sequestered	kgCO2/kg-H2	0	8.04	-
%CO2 Capture Rate	%	N/A	95	N/A
CO2 released direct to atmosphere	kgCO2/kg-H2	Note 1	0.42	Note 1
Nebraska ¹	kgCO2/kg-H2	Note 1	0.3	Note 1
CO2 Intensity of Methane Supply Chain	kgCO2/kg-H2			
Total CI (Scope 1 & 2) ¹	Н2	0.00	0.73	0.00
Note:				

Table: Hydrogen Technology Routes Technical Parameters.

1 - Electricity CI reported as 0.17kg-CO2eq/kWhe in Nebraska from general grid and 0 kg-CO2eq/kWh if from 100% renewables.

2 - Includes BOP and utilities, site requirements and considers power recovery from WHRU if applicable - but excluding H2 Compression for Transport & Storage - fuel gas considered within methane supply if required.

3 – Electrolysis and Pyrolysis achieve lower turndowns via use of smaller modular facilities and operating several in parallel.

Methanol Plant

Almost all methanol currently produced is from the reforming of fossil fuels in a two-step process. Step one is catalytic methane reforming to produce hydrogen (H2) and carbon monoxide (CO), aka syngas. In step two the syngas is reacted under high temperature and moderate pressure in the methanol synthesis reactor to produce methanol. Step one can also include the water gas shift reaction to obtain additional hydrogen and convert a portion of the carbon monoxide to carbon dioxide to obtain optimal blend of H2/CO/CO2 for methanol synthesis.

Under the conventional route, 3rd party CO2 for methanol production is not required because Carbon Monoxide and Carbon Dioxide, known as syngas is generated already in step one. However, in this study, the reforming facility will produce Blue Hydrogen only, the convert CO to CO2 for injection and storage underground. Blue hydrogen will then be supplied to the methanol plant separately from the biogenic CO2 for the ethanol plant.



The hydrogen to methanol overall value chain modelled in this study is depicted below.

The hydrogen plant and the methanol plant will be modelled as standalone facilities, with hydrogen supplied from the external source via an interconnecting pipeline. The pipeline is not modelled as a dynamic storage component itself and supplies hydrogen to the methanol plant at 7 barg while CO2 is supplied at 1.8 barg from the biogenic source (such as an ethanol plant) at an assumed cost of 10 USD/t-CO2, paid to the ethanol producer. Further compression of CO2 and Hydrogen is carried out within the Methanol plant to a feed gas pressure of 90 barg before undergoing conversion to methanol in the synthesis reactor. Following which methanol is distilled as a pure product and stored at 3 barg. In the case of a hydrogen plant supplied by renewable intermittent power, the hydrogen plant shall include storage bullets, wherein hydrogen is stored at a maximum pressure of 250 barg. The methanol plant will be supplied with constant grid power under all scenarios and have continuous supply of CO2 from the ethanol plant. When the methanol plant is under turndown due to limited hydrogen supply, then the excess CO2 will be emitted from the ethanol producer as per current practice. This CO2 will not factor into the carbon intensity of methanol as it is considered business as usual for the ethanol producer and is of a biogenic source.

Methanol Market Potential

Global Supply & Demand data shown below, obtained from the Methanol Institute and generated by Methanol Market Services Asia, (MMSA). This data shows the methanol market demand in 2023 was around 107 million MT, with most demand attributed to production of Olefins, Formaldehyde, MTBE, Gasoline blending and acetic acid. To cover this entire demand would require a biogenic CO2 supply of 147 million MT.



MMSA Global Methanol Supply and Demand Balance

Source: https://www.methanol.org/methanol-price-supply-demand/

Biogenic CO2

A potentially significant source of biogenic CO2 emissions is from the US ethanol industry, where the corn fermentation process yields 95-99% purity CO2. The industry is spread across the US, though clustered in the Midwest. Recent studies by Worley identified close to 200 ethanol producers in the US and have a combined capacity of 17,663 MMgal/yr. A gallon of corn ethanol (3.79 litres / ~3kg) also produces 3.08 kg of CO2 and 2.56 kg of distiller grains and soluble (DGS). Hence the total CO2 coproduced from the ethanol industry is expected to be around 54 million tons of CO2.



Geographical distribution of Ethanal Plants in US (Source: EIA)

Many ethanol produces already supply their CO2 as a byproduct to other industries including food & beverage, dry ice applications and most significantly for Enhanced Oil Recovery. The main option of the ethanol industry regarding CO2 management has been in injecting into CO2 pipelines that routes the CO2 for EOR. The ethanol industry supplies over 270 ktpa CO2 via pipelines to Kansas and Texas for EOR. The remaining plants vent their CO2 to atmosphere (approx. 33 million tons) for lack of access to an export route. Recent years has also seen growing opposition to the expanding CO2 pipeline network, which carries safety/environmental concerns as well as opposition from local communities and landowners who wish to retain their property rights.

From the dataset of ethanol plant, the capacities vary significantly from 3 to 400 million gallons per annum, however, the potential for the methanol production is related to the available CO2 emissions. To identify the range of scale of methanol plants (if dedicated to each ethanol plant), the CO2 emissions are converted to an equivalent methanol production rate. The distribution of equivalent dedicated methanol plant capacities are shown in the figure below.



Based on the above, this study has selected a range of standard modular methanol plant capacities of 150, 300, 450,600 and 1000 TPD to assess the impact of scale on the preferred hydrogen technology route. The modular scales of 150, 300, 450, 600 tpd also broadly correspond to licensor small module sizes.

Parameter	Units	Value	-
Temperature	OC	30	
Pressure1	barg	1.8	
CO2	vol%	94.5	
H2O	vol%	4.8	
CH4	vol%	<1	
02	vol%	<0.2	
H2S	mg/Nm3	<5	
Ammonia	mg/Nm3	<5	
Non-methanic VOC	mg/Nm3	<5	
Furan Acetaldehyde etc	mg/Nm3	ppm levels	

The expected specification of CO2 from the ethanol plants is estimated as per the below table:

The above specification allows for low-cost capturing of biogenic CO2 because it can be utilised without pre-treatment with minimal polishing.

Location Context

Under the renewable power scenario for Green & Turquoise Hydrogen, the hydrogen plant and storage facility will be supported via intermittent power supplied via the grid on a PPA tracked hour by hour to a renewable energy supplier. For this high level study the weather data used for wind and solar will be sourced from Renewables Ninja. The proposed location for this study is in the vicinity of the existing Monolith Plant in Nebraska, which is also 21km from an existing 100 million gall/yr ethanol plant owned by E Energy Adams LLC.



Cost/Economic Data

Cost input data is obtained from internal parametric estimation using Worley in-house data based on past vendor quotes, project experience and research. Though some inputs have a greater level of maturity, the overall cost estimation is considered to have a class 5 rating as per the AACE classification system.

This analysis will compare the different technologies using the Levelized Cost of Hydrogen and Methanol (LCOH/LCOM) as well as the Carbon Intensity (CI). Other general public available cost input data is listed in the table below.

Parameter	Value	Unit	Comments
NETL studies - 2023 NG Price for Midwest (IA, IL, MO, WI) US	4.023	\$/MMBTU	The baseline NG cost for this analysis are specified in the 2019 revision of the QGESS report on <u>"Fuel Prices for Selected Feedstocks in National</u> <u>Energy Technology Laboratory [NETL]</u> <u>Studies."</u>
Assumed Base Grid Electricity Price	0.11	\$/kWh	Average Electricity prince in Nebraska is 11.16 cents/kWh, which is ~30% lower than the US national average. Sensitivity analysis (+/- 30%) of electricity price will be carried out on the optimal configurations for each hydrogen technology route.
Methane Value Chain CO2 Intensity	0.07	kgCO2e/kWh	Based on NETL Life Cycle Analysis of Natural Gas Extraction and Power Generation
Electricity CO2 intensity	0.17	kgCO2e/kWh	EIA Data - Nebraska grid CI, Electricity mix:Petroleum-Fired0.1%Natural Gas-Fired7.1%Coal-Fired40.6%Nuclear18.5%Hydroelectric1.7%Wind + (solar)32.1%
Renewable supplier margin	7	%	7% is applied above the LCOE calculated from an optimal mix of wind and solar renewable assets in Nebraska.
Renewable Power Transmission Fee	7	USD/MWh	7 USD/MWh is levied to the LCOE calculated from an optimal mix of wind and solar renewable assets in Nebraska.
Cost of direct CO2 released to atmosphere	20	\$/t CO2eq	Assumed cost of direct CO2 emissions
Cost of CO2 T&S	10	\$/t CO2	Based on NETL study guidelines, the cost of CO2 transport and storage (T&S), on an equivalent dollar per kilogram basis, is added to the LCOH and represents a hypothetical 62 km (100 mile) CO2 pipeline and storage in a deep saline formation in the Midwest. This will be used for the relevant Blue Hydrogen option cases.
WACC	10	%	Weighted average cost of capital assumed as 10% and used for interest rate.
CPI	2	%	2% inflation is applied.
Project Duration	25	year	Years of operation with 3 years of construction starting in 2029
H2 Plant OPEX	3	%of CAPEX	General OPEX taken as 3% of CAPEX of H2 Plant

Note pretreatment of the biogenic CO2 is not required, cost of procuring biogenic CO2 from the ethanol producer is set at a base value of 100 USD/t-CO2 (approx. value of CO2 sold to beverage manufacturers) and will be varied under the sensitivity analysis.