Methanol+: Methanol from Carbon Dioxide Utilization and Green Hydrogen

Agreement #: K130117

May 25, 2016

Final Outcomes Report – NON-CONFIDENTIAL Version

Reporting Period: 01 April 2014 to 31 March 2016

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Lead Institution: Quantiam Technologies Inc.
Project Partners: University of Alberta

CCEMC Funds: $500,000
Project Advisor: Mark Summers
Project Completion: 03/31/2016

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1.0 EXECUTIVE SUMMARY

Methanol+ delivers a carbon *negative* solution to high value petrochemical and hydrogen manufacturing in Alberta with global potential. The game changing ***Methanol+*** technology package couples a process technology which utilizes captured carbon dioxide emissions, and hydrogen produced from sunlight and water, to produce methanol, a high value global commodity chemical that is a key building block in polymer production. ***Methanol+*** is a sink for nearly 1.5 tonnes of CO2e per tonne of methanol produced, disrupting the traditional thinking that climate action and commercial success cannot move forward together. ***Methanol+*** delivers global greenhouse gas (GHG) reductions up to 67 MT/Y by 2050 in the fuel additive and olefin production markets alone. In tomorrow's electricity grids comprising large fractions of variable renewable energy sources, chemical fuels like methanol and hydrogen constitute the solution to key challenges in energy storage.

Though best together, these two technologies stand alone in their own right. The CO_2 Utilization technology remains CO_2 negative and cost competitive even when hydrogen is produced via renewable energy powered electrolysis. The Solar Hydrogen technology will disruptively transform the hydrogen production industry. Alberta alone produces over 3.5 MT of hydrogen annually, emitting nearly 40 MT of CO_2. Solar hydrogen will emit less than one tenth of the CO_2.

The economics of ***Methanol+*** are extremely attractive and drive significant commercial opportunity. Several scenarios for revenue streams are envisaged, including catalyst manufacture and sale ($15-150M/Y), licensing our technologies to manufacture methanol, hydrogen or other petrochemicals ($50-250M/Y), as well as the full production and sale of methanol, hydrogen and petrochemicals ($3-35B/Y).

The $1.5 M of total investment to date in ***Methanol+*** includes $0.5 M from the CCEMC grand challenge, and is coupled with our 18 years of experience developing novel catalyst materials have enabled the Consortium, which includes the world class Buriak group at the University of Alberta, to bring the key technologies from concept to fully functioning prototypes in under two years completing the Applied R&D phase. Our project plan culminates in a pilot scale demonstration of our integrated ***Methanol+*** technology in Edmonton.

2.0 PROJECT DESCRIPTION

2.1 Introduction and Background

Since project start in 2013 we have aggressively pursued the development of our Solar Hydrogen and CO_2 Utilization technologies. We adopted a laser focused development strategy that hinged on rapid screening of candidate materials, and maximal automation and streamlining of sample prep, and heavily leveraged best corporate practices for design of experiment. This strategy has paid dividends, allowing us to solve key technological challenges on an extremely accelerated development timeline. We have as a result a library of catalysts for both Solar Hydrogen and methanol production, as well as key reactor and process developments projected to readily advance and enable commercialization.

2.2 Technology Description

The ***Methanol+*** CO_2 Utilization technology relies on catalyst and process technology to convert CO_2 and hydrogen to methanol with increased reactivity and yield at milder process conditions than conventional systems.

The Solar Hydrogen technology absorbs sunlight and converts it to the required energy to convert water into hydrogen and oxygen. This technology package includes the energy capture material, an advanced catalyst as well as a protective coating.

3.0 OUTCOMES AND LEARNINGS

3.1 Milestone M1: ***Methanol+*** Catalyst Test Facility Development

The final design for the catalyst testing facility was that of a conventional, bench-scale, packed bed reactor as this was the most cost-and time-effective solution given the project timeline. As designed, the bench-scale reactor system for screening catalyst candidate materials is capable of a wide range of relevant process variables. The process conditions for CO_2 (and H_2) conversion to methanol are similar to the conventional syngas-to-methanol process which converts a stoichiometric mixture of CO and H_2 to methanol at elevated temperature (ca. 240 °C) and pressure (70-100 bar(a)) over a packed bed of heterogeneous catalyst.

Figure 3.2.1, below, shows the appearance of the Milestone 1 Catalyst Test Facility as-constructed in Quantiam's Research and Development facility, with the principal components labelled.

3.2 Milestone M2: ***Methanol+*** Catalyst Development

Three catalyst families were selected for development after a thorough review of the available literature, two metal-metal oxide based families, and one mixed metal based family.

3.2.1 Summary of Results

A summary of the most promising catalyst candidate materials tested is given below in Table 3.2.1 and Table 3.2.2.

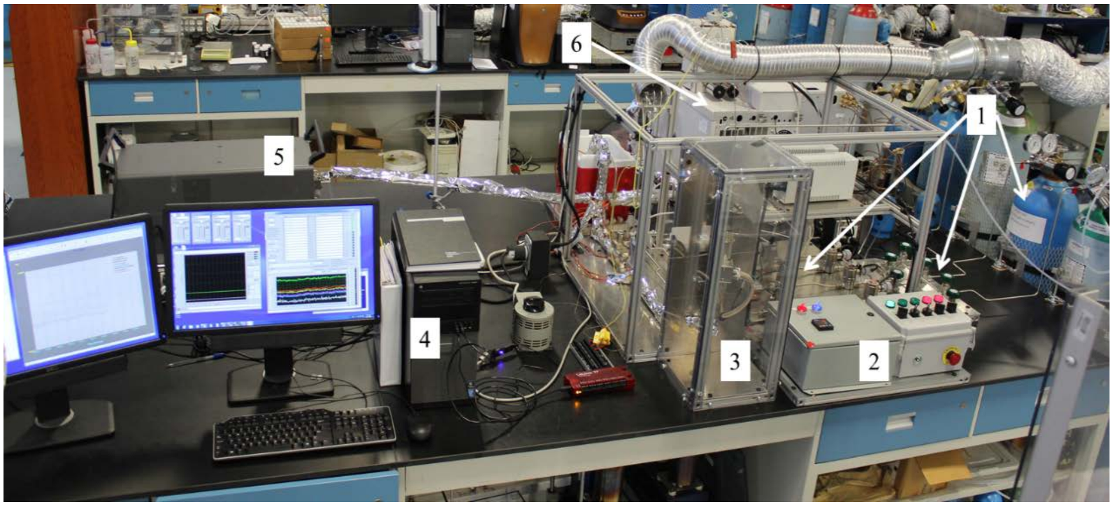

Figure 3.2.1: Photograph of the bench scale CO_2 utilization catalyst testing system showing the principal components: 1) gas delivery system (gas cylinders, purging manifold, solenoid valves, MFCs); 2) reactor solenoid valve and furnace temperature control; 3) reactor vessel and heating jacket in safety enclosure; 4) PC for online process control and monitoring; 5) RGA for on-line tail gas analysis; 6) GC for on-line tail gas analysis.

Table 3.2.1: Summary of catalyst testing results for the most promising catalyst candidates at 1/6th of conventional methanol process severity.

Catalyst	CO_2 Conversion	Selectivity to CH_3OH	CH_3OH Yield
Commercial Catalyst	**1.0**	**1.0**	**1.0**
Catalyst Q1	0.6	3.3	2.2
Catalyst Q2	0.7	2.2	1.6
Catalyst Q3	0.5	2.5	1.4
Catalyst Q4	0.4	3.2	1.1

Table 3.2.2: Summary of catalyst testing results for the most promising catalyst candidates at 1/4 of conventional methanol process severity.

Catalyst	CO_2 Conversion	Selectivity to CH_3OH	CH_3OH Yield
Commercial Catalyst	**1.0**	**1.0**	**1.0**
Catalyst Q1	0.9	8.0	7.0
Catalyst Q5	0.3	7.2	2.5
Catalyst Q2	0.7	2.3	1.6
Catalyst Q3	0.6	1.9	1.5

Testing concentrated on milder process conditions than those used for methanol synthesis from CO_2 using the conventional syngas-to-methanol catalyst. Reducing the process pressure will be critical to maximizing the CO2e reductions possible, since compression is one of the major energy costs in the industrial process[5]. All the candidate materials tested produced only methanol and carbon monoxide as reaction products. In general, the most promising catalyst candidates showed greater selectivity toward methanol production than the candidate catalyst, albeit with reduced carbon dioxide conversion rates. This results in methanol yields which are similar to the commercial catalyst, but with less of the unwanted CO by-product.

In light of these promising results, the Q1-Q5 catalyst families will all be brought forward for further development in Phase 2 of the project, in particular development of new synthesis methods via a nanoparticle route, which shows promise in increasing catalyst activity toward conversion to methanol.

3.3 Milestone M3: Solar Hydrogen Test Facility Development

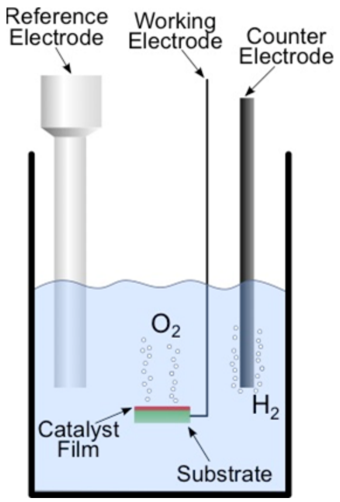

Figure 3.2.2: Schematic of electrochemical test apparatus, in this case indicating a test on an oxygen evolution catalyst.

The University of Alberta research team enabled Quantiam to hit the ground running. Further, we obtained an alpha prototype solar simulator that delivers a best in class match to the solar spectrum. Working in collaboration with a local Alberta company, G2V Optics, we were able to develop a custom, submersible light source. To our knowledge this is a unique piece of technology and positions our testing facility ahead of such institutions as Caltech's Joint Center for Artificial Photosynthesis.

Our rapid screening test system is shown below. The solar simulator, sample holder and counter electrode are all held in place by a 3D printed lid. The sample is exposed to artificial sunlight at a fixed distance of 1 cm from the solar simulator. The 3D printed lid has mounting points for both graphite rod and reference electrode, leading to reproducible electrode positioning for every sample. We have 3 such systems due to the purchase of two additional units from G2V following successful alpha test.

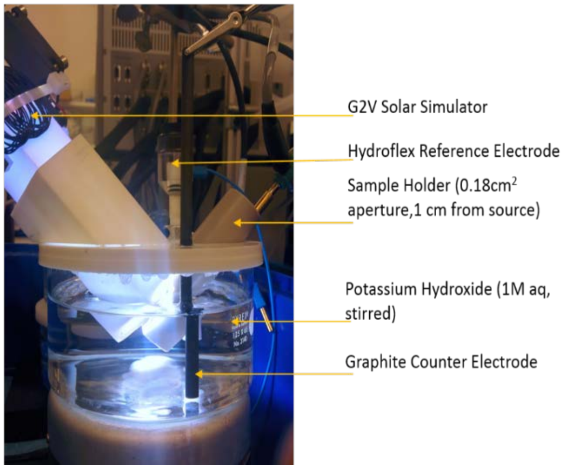

Figure 3.3.1: Solar Hydrogen test facility 1/2 cell test aparatus.

A key metric in developing a prototype reactor system is the measurement and separation of the evolved gases. To this, we developed a custom solar hydrogen prototype reactor. The reactor consists of two chambers, one for the reference electrode and counter electrode, and another for the working electrode separated by a membrane. The reactor was designed for compatibility with the solar simulator and features automated filling and draining of electrolyte, and gas tight fixtures.

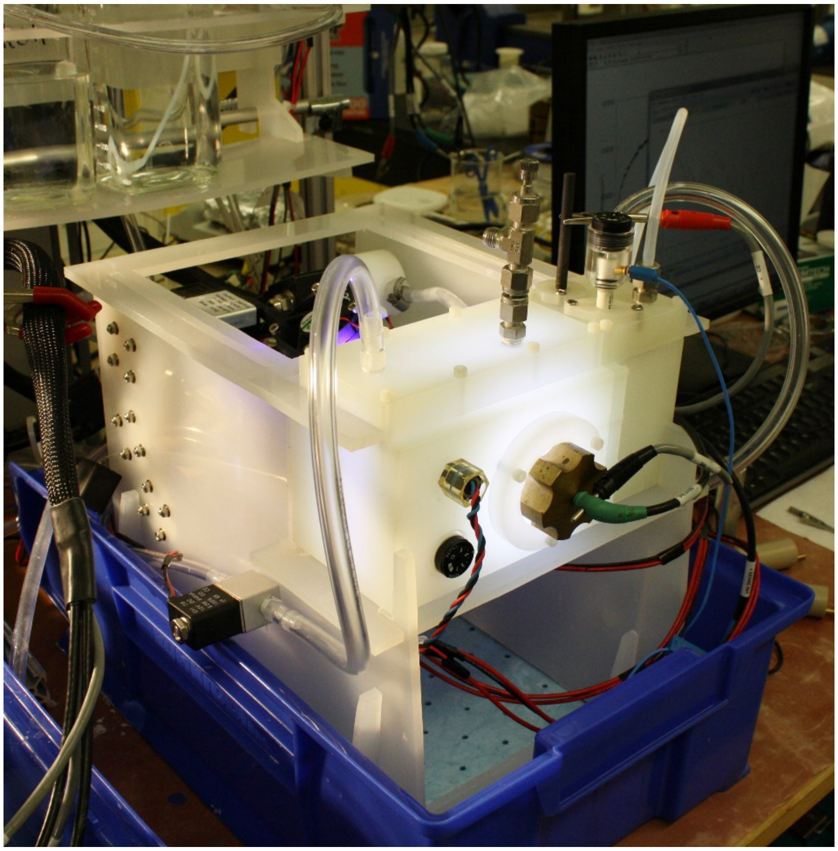

Figure 3.3.2: Lab Prototype Solar Hydrogen Reactor.

3.4 Milestone M4: Solar Hydrogen Catalyst Development

3.4.1 Overall Strategy

Our strategies for catalyst development have evolved considerably over the past two years. We have screened thousands of metal, metal oxide, and alloy compounds. We chose to develop our catalysts on a substrate whose properties were tailored to not impact our measurement of catalyst properties. Electrochemical performance of catalysts is tremendously sensitive to the interface between the substrate and the catalyst under test.

The performance of a photoelectrochemical (PEC) device depends on the properties of both the solar cell and the catalyst. The operating point of a PEC device can be viewed graphically as the intersection of the PV devices JV (current vs. voltage) curve and the catalysts CV (cyclic voltammetry curve). This ultimately determines solar to hydrogen efficiency possible for any given combination of photovoltaic device and half-cell. Additionally we targeted low CO2e solar devices. Potentially these cells have a footprint of 10 g CO2e/kWh, around 25% of a conventional PV device. This choice will improve the carbon footprint of our hydrogen production technology even further.

We demonstrated successful proof-of-concept on previously commercially available cells. At our year 1 project update we demonstrated spontaneous water splitting on a solar cell coated with M1 catalyst with oxygen evolving on the M1 and hydrogen on the back side of the cell.

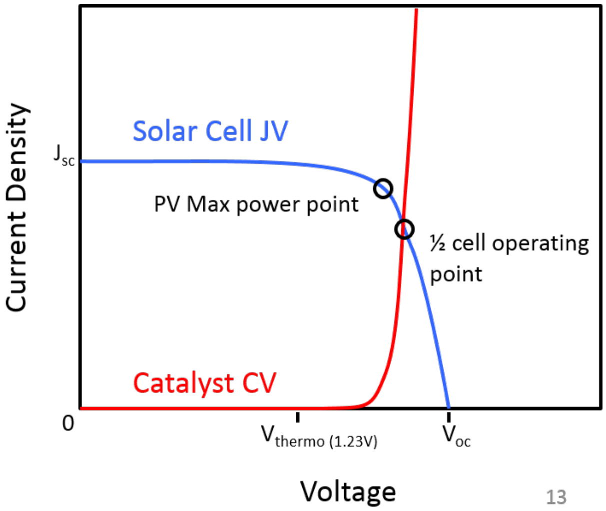

Figure 3.4.1: Relationship between solar cell output and catalyst electrochemistry showing the operating point of a PEC device.

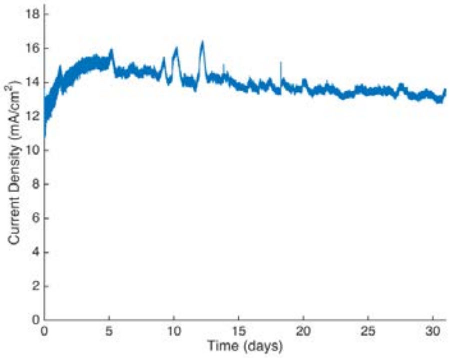

Figure 3.4.2: Stability test data. Film protects solar cell for over 30 days and counting - testing is still underway as of the writing of this report.

We investigated a range of materials to protect the solar cell from the electrolyte. Materials investigated had to satisfy the threefold requirements of high electrical conductivity, high optical transmission and corrosion resistance in highly corrosive electrolyte solution.

We conducted a long term stability testing. As can be seen in the figure, the film is stable over 30 days with no reduction in current observed.

Figure 3.4.3: Large surface area prototype demonstrating spontaneous water splitting.

3.5 Milestone M5: Renewable Hydrogen Strategy Development

Quantiam will simultaneously advance hydrolysis using renewable electricity to underwrite technical risk to the ***Methanol+*** technology as we recognize the higher risks inherent in development of the photocatalytic water splitting technology. As such the ***Methanol+*** technology is compatible with hydrogen sourced from water electrolysis powered by renewable energy sources, which have low CO2e.

The aim of this task is two-fold. We first identify suitable locations in Alberta that have access to renewable energy sources such as wind, solar and hydroelectricity or those that have high renewable energy potential. We then consider the economic and environmental benefits of hydrogen produced via two electrolyzer technologies using a renewable source.

Our results show that Alberta is rich in renewable energy, in particular wind and solar that favours the deployment of our CO_2 Utilization technology using renewable hydrogen as a feedstock. In the near term, the incumbent electrolysis technology, alkaline electrolysis, is the most cost effective solution, though not the least emissive. As such this is the lowest risk technology. As can be seen in Figure 3.5.1 nearly half the province is well suited to the deployment of renewable hydrogen.

At present, SMR hydrogen costs are approximately $1.70 / kg, and we estimate that hydrogen from electrolysis could cost as little as $2.86 / kg. Using current market forecasts for the prices of oil and natural gas, as well as the cost of wind power, we estimate cost parity of the competing technologies by as soon as 2021 under the two-degree scenario price on carbon, though as late as 2033 with no carbon tax at all. This is quite a promising result, as this effectively frees the cost of hydrogen from being tied to the cost of fossil fuels, and shows a clear alternative is on the horizon and could displace the incumbent process of steam methane reforming in less than 20 years.

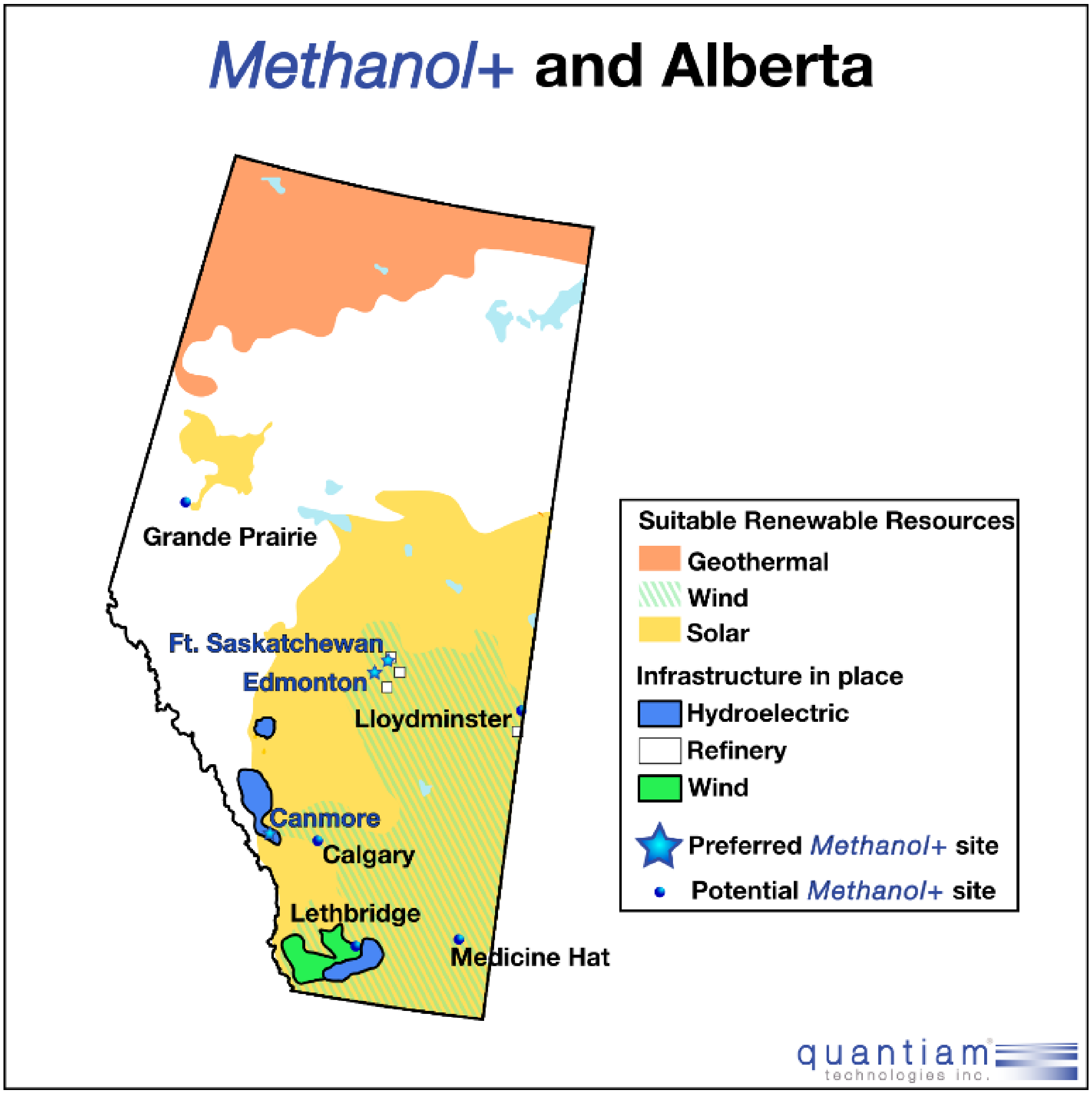

Figure 3.5.1: Map of sites where renewable resource infrastructure or availability enables deployment of CO_2 Utilization technology with renewable hydrogen as feedstock.

4.0 GHG AND NON-GHG IMPACTS

4.1 Qualitative GHG Benefits

The GHG benefits from the ***Methanol+*** technology package are considerable. Hydrogen from steam methane reforming emits over ten times the CO_2 of our Solar Hydrogen technology. Coupled with our CO_2 Utilization technology this delivers a *carbon negative* solution. Not only does the technology deliver a modular solution to the production of valuable chemical feedstocks and fuels locally, it also provides a solution to the challenges we face with global CO_2 levels that are already twice those of pre-industrial times and on course continue to increase. We are at a point where emissions reduction strategies alone cannot be used to reduce these levels, and we must find ways to capture and utilize CO_2 from the atmosphere to affect the desired long-term global outcomes.

Within the province of Alberta alone, assuming commercialization in 2023, the ten year impact of a single 500 kT methanol production facility would be nearly 9 MT of CO_2 *consumed* from the atmosphere and a water savings of 276,000,000 liters of water.

4.2 Quantification of Expected Annual GHG Reductions

The ***Methanol+*** technology directly converts captured carbon dioxide emissions into methanol, resulting in net consumption of 0.82 T CO2e/T of methanol produced, including the projected 0.13 T CO2e/T H_2 produced via Solar Hydrogen. Considering displaced conventional methanol production (0.673 T CO2e/T of methanol), the net GHG reduction of ***Methanol+*** is 1.49 T CO2e/T of methanol produced.

4.3 Non GHG Benefits

The ***Methanol+*** technology package may also yield significant water use reductions over conventional methanol For example the baseline water use for conventional methanol production is approximately 90 T water per T of methanol produced.[5] On the other hand, recent techno-economic analysis of methanol production from CO_2 indicate a water use of only 26.4 T H_2O/T of Methanol[5] Further, the methanol synthesis process produces about 0.5 T of H_2O/T of Methanol and this can be recycled and used for processing (cooling, steam generation) and may be discounted against the total water usage. Taking into account the water usage expected from our hydrogen production, we must also consider that our technology consumes about 8.9 T of water per T of hydrogen; leading to a net water usage of 34.76 T of water per T of methanol, saving 55.2 T of water per T of methanol over the entire process, a savings of 61%.

As a sink for CO_2, ***Methanol+*** is future proof against the ever increasing price on carbon. With taxes already at \$30/T and expected to rise to \$100/T within the next 15 years, incumbent production technologies become decreasingly attractive economically. For example, our most conservative estimates place our Solar Hydrogen production technology to outperform steam methane reforming on a cost basis by 2030. ***Methanol+*** technology is predicted to have greatly improved operating margins vs. incumbent methanol production technologies due to much lower feedstock costs and lowered emissions penalties.

Solar hydrogen production competes favourably with initial investment for SMR, with the added advantage that its modular nature means that small scale facilities are possible with this technology. The cost of initial investment for small scale methane reforms is nearly 10X that of large scale (150MW+ facilities).

5.0 OVERALL CONCLUSIONS

The successful completion of our technical milestones have greenlit continued development of our ***Methanol+*** technology suite. Completion of milestones 1 and 3 have given us world class research facilities for the development and testing of advanced catalyst and reactor designs for both the production of methanol and hydrogen respectively. Using these we have advanced milestones 2 and 4 and developed novel catalysts and reactors that will enable us to bring our ***Methanol+*** technologies to market.

6.0 SCIENTIFIC ACHIEVEMENTS

The Project has generated a number of key scientific results. For example, we have prepared a record of Invention for our water oxidation catalyst technology for Solar Hydrogen Production. Further, we are preparing records of invention for both our reduction catalyst technology for solar hydrogen production as well as for an anti-corrosion coating we have developed for our Solar Hydrogen reactor components.

7.0 NEXT STEPS

Within the next five years, we anticipate that we will be validating our integrated pilot (1000X) systems in a relevant environments. In the case of the Solar Hydrogen technology, this would be an outdoor test facility, at the Quantiam site in Edmonton, AB. In the case of our CO_2 Utilization technology, this would be a pilot demonstration facility in a proposed expansion to the Quantiam site and integrated with our Solar Hydrogen pilot. We anticipate production capacity of these facilities to be approximately 200 kg H_2/Y and 1000 kg methanol/Y.

The next five years of the project constitute successful completion of Phase-2 and substantive progress towards completion of Phase-3 (1000X Pilot Facility). After Project completion we will aggressively pursue remaining Phase-3 deliverables including final technology validation and market assessment. We will advance planning to finance full commercialization with a focus on strategic investors and customers/end-users. Following the next five yea9rs, we will begin Phase-4 (Fully integrated pilot and commercialization) include a greenfield deployment of the ***Methanol+*** technology at 100,000-1,000,000X scale at a site in Alberta in collaboration with a Tier 1 partner, likely a major chemical/petrochemical producer. We will also assess the potential of the Solar Hydrogen technology as a standalone business.

8.0 COMMUNICATIONS PLAN

We are operating in a highly competitive space. As such, all non-disclosed technological innovations will be protected as a trade secret or when disclosed to third parties protected by a non-disclosure agreement. We will communicate non confidential, public, information via our corporate website.

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