Hydrogen from Hydrogen Sulphide

Technology Scan and Evaluation

Prepared for COSIA by DeLude Consulting Inc.

June 8, 2017
Executive Summary

DeLude Consulting Inc. was engaged by COSIA to provide a technology scan and evaluation of the potential future options for producing hydrogen from hydrogen sulphide.

The technology scan was conducted via 3 different approaches:

- 3rd party professional search firm
- Use of IHS Engineering Workbench
- DeLude Consulting Inc. independent search

Each independent scan approach yielded acceptable results with significant overlap of identified technologies. The use of the combined approach has some value in providing assurance that the scan is comprehensive.

The combined technology scan results identified a wide variety of potential technologies / approaches for the generation of hydrogen from hydrogen sulphide. However, none of these technologies has yet reached a level of maturity and financial performance that has merited pilot scale demonstration and/or commercial application.

The key technology classes identified in the scan were:

- Thermal Decomposition
  - “Pure thermal”
  - Thermal plasma
  - Catalytically enhanced thermal
  - Thermal with equilibrium shift
  - Oxidative and integrated Claus processes
- Electrolytic processes (both aqueous and non-aqueous)
- Microwave and cold/warm plasma processes
- Photolysis processes (with various catalytic enhancements)
- Complex chemical reaction cycles
  - Bunsen Reaction (HI)
  - Anthraquinone Based Cycles
  - Metal-Sulphide Based Cycles
  - Fe-Cl Cycle (Indirect Electrolysis)
- CH₄/H₂S reforming
Based on an initial pre-screening the following technologies, the following technology categories were dropped from consideration for ranking for the reasons noted:

- Pure thermal processes – prefer to consider catalytic or integrated thermal processes
- Electrolytic processes – no recent progress in the literature, practical fouling and anode performance stability make these options difficult – focus instead on indirect electrolysis option (Fe-Cl)
- Processes generating sulphur oxide or CS₂ side products - due to disposal / market constraints
- Metal sulphide processes with oxidative regeneration - producing sulphur oxide byproducts

The following technologies were selected for more detailed assessment and ranking:

Photocatalytic:
  - Process based on IFP French patent - 2997940 - 2016-03-11 with best suitable patent from literature (potentially nanostructured N-doped TiO₂).

Warm Plasma:

Thermocatalytic:

Oxidative:
  - Superadiabatic process as described in US Patent 9242859

Complex Reaction Network:
  - Process based on Bunsen Reaction (due to link with water cycle R&D – for nuclear applications) – method identified in Wang et al, Fuel Processing Technology 108:55–62 · April 2013
  - Metal sulphide process based on French Patent 2972004 - 2015-03-06

Subsequent to this selection, after discussion with the working group, assessment effort on the photocatalytic and Bunsen reaction options was curtailed due to the lack of good cost data and the complexity of the two processes.

The ranking process included scope differential capital and operating cost estimates to develop a cost of CO₂ avoided based on a cash flow analysis and using a metric of PV (cash flow)/PV (net tons of CO₂ avoided). In all cases, the baseline technologies were Claus/SCOT for H₂S management and SMR/PSA for H₂ production.
The full ranking included an assessment of the following focus areas:

- Technical Viability
- Technical Maturity
- Economic Assessment
- Improvement Potential
- CO₂ Impact (focus area added based on discussions at working team meeting April 28, 2017)
- Risk Assessment (HSE)

The overall ranking suggests that the thermocatalytic, superadiabatic and gliding arc tornado plasma options were most promising followed by the metal sulphide and Fe-Cl indirect electrolysis options. The top 3 technologies noted above all had “improved case” cost of CO₂ avoided under $CDN 50/t CO₂.

Some common challenges for all the technologies include:

- Handling of commercial streams with typical contaminants (CO₂, hydrocarbons, amines, water, ammonia)
- Elemental sulphur extraction and management to avoid plugging/precipitation
- Corrosion and material selection for operating conditions
- Environmental and safety hazards due to dealing with high H₂S gas streams
- H₂ and S recombining into H₂S and/or other competing reaction pathways
- Fouling/poisoning of catalytic and/or electrolytic systems
- Catalyst life cycle costs and regeneration
- Overcoming reliability and performance concerns for commercial applications that must consistently meet stringent sulphur recovery regulations
- Funding for novel technology development and scale-up
- Overall economics and competition with commercial scale CO₂ sequestration

The potential business case for novel H₂ from H₂S technology was considered for in-situ Oil Sands applications, existing Upgrading facility revamps and new greenfield upgrader development.

For both in-situ and upgrading revamps the conclusion is that novel H₂ from H₂S technologies have very limited potential due to the combination of the modest CO₂ reductions that are possible, the difficulty in supplanting existing technologies and the complexity and cost of implementing revamp modifications inside existing facilities. As a result the focus for the economic assessment has been on new upgrading facilities where the best possible case can be developed on a differential cost basis. It must be noted that the cost of pilot/demonstration scale testing has not been included in the assessment of technology costs.

For the Alberta Oil Sands industry, it is suggested that the potential range for future CO₂ avoided for greenfield upgrading applications would be in the order of 0 to 300 kt of CO₂ per year if H₂ from H₂S technology was successfully implemented in three new greenfield upgrader projects with deep hydroprocessing capacity (producing bottomless synthetic crude).
In summary, even if significant technology improvements can be successfully pursued to achieve overall costs below the range of $CDN 50 per t of CO$_2$ avoided, there appears to be relatively modest potential for material CO$_2$ emissions improvement for the Alberta Oil Sands industry. As a result, COSIA’s members would need to consider carefully whether acceleration of hydrogen from H$_2$S technology development should be given future funding priority.
# Table of Contents

Executive Summary........................................................................................................................................... 2  
Introduction ....................................................................................................................................................... 7  
Theoretical Thermodynamics of H₂S Conversion to H₂ and S........................................................................... 8  
Technology Scan Results ................................................................................................................................ 10  
Technology Feasibility / Competitive Considerations and Shortlisting ......................................................... 14  
Baseline Cases for Oil Sands Applications ........................................................................................................ 24  
Current Conventional Technologies for Economic Comparison ..................................................................... 25  
Ranking Metrics – Development of Template for Ranking .............................................................................. 26  
Economic Assessment Template and Key Business Inputs ................................................................................. 29  
Summary of Key Information for Baseline and Shortlisted Technologies ............................................................ 30  
Ranking Results with Comments ....................................................................................................................... 34  
Business Case Assessments – Insitu and Upgrading/Refining Applications ..................................................... 37  
Some Further Observations ............................................................................................................................... 38  
Recommendations for Consideration .................................................................................................................. 39  
References ......................................................................................................................................................... 40  
Datafile Summary .............................................................................................................................................. 46
Introduction

Canada’s Oil Sands Innovation Alliance (COSIA) has identified reduction in Greenhouse Gas (GHG) emissions through novel technology application as one of its key Environmental Priority Areas.

The challenge of earning social license for continued Oil Sands production by reducing production associated GHG emissions down to levels comparable to Middle Eastern conventional crudes requires a drastic change in GHG performance. Hydrogen produced from the conversion of by-product hydrogen sulphide could be used as either a low carbon footprint fuel or to replace hydrogen required for oil sands bitumen upgrading that is currently manufactured by the carbon (and energy) intensive process of steam methane reforming.

COSIA’s GHG EPA chose to explore the potential application of novel technologies for the production of hydrogen and sulphur from hydrogen sulphide with modest CO₂ emission footprint. As part of the work plan, the COSIA GHG EPA engaged DeLude Consulting Inc. to complete a H₂ from H₂S Technology Scan and Evaluation.

The study workplan has included the following key items:
- Global technology scan to identify technologies and key technology attributes
- Development of a qualitative screening template with agreed parameters and weighting
- Qualitative screening of technologies to identify “feasible and promising” ones
- More detailed assessment of a “shortlisted” group of representative technologies
- Identification of benchmark for H₂S management and H₂ production with and without CO₂ sequestration to establish existing competing technologies
- Reporting and documentation of technology scan and screening including an assessment of the best business development case to determine if further effort is warranted

The following sections of the report provide a summary of the theoretical potential of hydrogen from hydrogen sulphide, the results of the technology scan and a first shortlisting of relevant technologies, a ranking of the shortlisted technologies and an assessment of the business case for potential application of the most promising technologies within Oil Sands plants.
Theoretical Thermodynamics of H₂S Conversion to H₂ and S

The key thermodynamic input data required to compare the various options for H₂S management and H₂ production are as follow:

<table>
<thead>
<tr>
<th>Reaction:</th>
<th>ΔH (kJ/g-mole product) (25 deg C, 101.325 kPa)</th>
<th>ΔG (kJ/g-mole product) (25 deg C, 101.325 kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ (g) + 1/8 S₈ (s) → H₂S (g)</td>
<td>-20.4</td>
<td>-33.3</td>
</tr>
<tr>
<td>H₂ (g) + ½ O₂ (g) → H₂O (l)</td>
<td>-285.8</td>
<td>-237.2</td>
</tr>
<tr>
<td>H₂ (g) + ¾ O₂ (g) → H₂O (g)</td>
<td>-241.8</td>
<td>-228.6</td>
</tr>
<tr>
<td>2 H₂ (g) + C (s) → CH₄ (g)</td>
<td>-74.8</td>
<td>-50.8</td>
</tr>
</tbody>
</table>

Assessment of key reactions:

<table>
<thead>
<tr>
<th>Reaction:</th>
<th>ΔH (kJ/g-mole key product) (25 deg C, 101.325 kPa)</th>
<th>ΔG (kJ/g-mole key product) (25 deg C, 101.325 kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂S dissociation:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂S (g) → H₂ (g) + 1/8 S₈ (s)</td>
<td>+ 20.4 (H₂)</td>
<td>+ 33.3 (H₂)</td>
</tr>
<tr>
<td>Steam-methane reforming (SMR):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>¼ CH₄ (g) + ½ H₂O (l) → H₂ (g) + ¾ CO₂ (g)</td>
<td>+ 63.2 (H₂)</td>
<td>+ 32.7 (H₂)</td>
</tr>
<tr>
<td>Claus sulphur recovery (or dissociation followed by hydrogen combustion – net reaction):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂S (g) + ¾ O₂ (g) → H₂O (l) + 1/8 S₈ (s)</td>
<td>- 265.4 (H₂O)</td>
<td>-203.9 (H₂O)</td>
</tr>
<tr>
<td>Hydrogen combustion:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂ (g) + ½ O₂ (g) → H₂O (l)</td>
<td>-285.8 (H₂O)</td>
<td>-237.2 (H₂O)</td>
</tr>
<tr>
<td>Water electrolysis:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O (l) → H₂ (g) + ½ O₂ (g)</td>
<td>+285.8 (H₂)</td>
<td>+237.2 (H₂)</td>
</tr>
</tbody>
</table>

Considering the comparison of H₂S dissociation versus SMR (on its most advantaged theoretical ΔH basis) there appears to be a potential threefold reduction in the energy requirement to produce the same amount of hydrogen and a 15 fold reduction when compared to water electrolysis.

When similarly comparing H₂S dissociation followed by hydrogen utilization as a fuel versus the conversion of H₂S via the Claus process, there is no theoretical advantage for either path (net energy output is identical as the net chemical reaction for the two steps is identical).
However, while the above assessment suggests there is a significant theoretical incentive for dissociation in comparison with SMR and electrolysis for chemical hydrogen production and no theoretical advantage in comparison to Claus in a “fuel hydrogen” situation, we also need to consider the following practical aspects of the conversion reactions in order to understand the deviations from the theoretical minimums and develop an accurate picture of the relative performance of the options:

Potential reasons for deviation from minimum theoretical energy requirement:
- Required reaction conditions for practical levels of conversion (temperature, pressure, catalyst)
- Required product properties for commercial use (liquid sulphur, hydrogen pressure/purity)
- Efficiency of energy delivery to achieve conversion
- Efficiency of excess energy recovery from effluent streams
- Level of conversion achievable and costs for reactant/product separation and reactant recycle or other disposal/management
- Side reactions / byproducts and thermodynamic equilibrium considerations
- Other system heat transfer / work considerations (changes in system pressure/temperature)

While we will cover the key deviations for the various H2S under each technology assessment in their relevant technology sections, we will cover the key aspects of the SMR reaction in the following as an example.

For SMR hydrogen production, high temperature, catalysts and excess steam is used to help drive the reaction to completion. Hydrogen separation uses pressure swing adsorption to achieve the best balance of cost, recovery and product purity. Energy recovery is used to generate the high pressure steam required with excess energy recovered as export steam.

As a first approximation, the overall practical chemical balance for SMR is as follows:

\[1.6 \text{CH}_4 + 2 \text{H}_2\text{O} + 0.6 \text{O}_2 \rightarrow 4 \text{H}_2 + 1.6 \text{CO}_2 + 1.2 \text{H}_2\text{O}\]

\[\Delta H (\text{kJ/g-mole CH}_4) = -175.8\]

The net exothermic reaction is due to the coupling of the exothermic combustion of natural gas and SMR reaction effluent (due to conversion inefficiency) and the net endothermic steam reforming reactions. The overall efficiency of energy transfer from methane to hydrogen on a combustion LHV basis is approximately 73% and the overall system energy efficiency (including exported steam energy credit and power use debit) is in the range of 85%. The net GHG intensity is about 8.9 t CO2 per t of hydrogen product (assuming future Alberta grid average emission intensity of 0.3 t CO2 per MW-h).

It must also be noted that for practical applications in Alberta (taking advantage of available natural gas supply pressure) the SMR hydrogen product pressure is typically in the 2500 kPa (g) range with purity in the range of 99.5%. Any competing technologies will have to provide hydrogen at a similar “baseline commercial conditions” for fair comparison.
Technology Scan Results

In order to ensure a comprehensive search, the technology scan was conducted via 3 different approaches:

1. 3rd party professional search firm, Technology & Patent Research International
2. DeLude Consulting Inc. use of IHS Engineering Workbench search assistant
3. DeLude Consulting Inc. independent search


DeLude Consulting Inc. used COSIA’s corporate license to access to IHS Engineering Workbench and used 6 hours of effort (3 x 2 hour sessions) for both an initial familiarization with the search assistant tool and active searching of the available databases.

DeLude Consulting Inc. used publically available resources in its independent search:
  o Google scholar
  o ScienceOpen
  o Citebase Search
  o DOAJ
  o USPTO databases (PatFT and AppFT)
  o Information Bridge (US DOE and OSTI)

DeLude Consulting Inc. also used library services and database search engines available at the University of Calgary to search and access published peer reviewed articles and dissertations that are not available on publically available open license search resources.

In all three cases the searches identified numerous potential chemical pathways/technologies for the endothermic decomposition of H₂S to H₂ and elemental sulphur, these included the following:
  • Thermal decomposition (including thermal plasma, catalytically enhanced thermal, equilibrium shift and integrated Claus processes)
  • Electrolytic processes (both aqueous and non-aqueous)
  • Microwave and cold/warm plasma processes
  • Photolysis processes (with various catalytic enhancements)
  • Complex chemical reaction cycles (Bunsen reaction, anthraquinone and metal-sulphide systems)
Some specific points on the various search approaches are as follows:

**Technology & Patent Research ( Intellectual Property Search Specialists)**

A “landscape technology scan” was conducted by a full time professional searcher that found:
- 5 main technology classes (71 specific patents identified for follow-up)
- 2 recent English language review articles
- 5 recent foreign language review articles (4 Chinese, 1 Japanese)

In order to keep the cost for the scan quite modest (less than $US 3,500) the scope of the search was constrained to relatively recent patent applications and grants (since 2000) and recent review articles (since 1995). Also there was no request for technical opinions or rankings on the relative benefits or technical viability of the various identified technologies.

The advantage of using a 3rd party is to provide some assurance that no major technology class has been missed in the broad scan of the potentially applicable technologies. The results from the effort can also be used to effectively focus the more detailed technical assessment of the various options which could be attractive.

**IHS Engineering Workbench (toolkit for technology / information searches)**

DeLude Consulting Inc. undertook a search utilizing the toolkit. No specific training in the use of the tool or individual technical assistance from IHS was required (standard application “help” tools were used to understand basic query process, advanced interface and deeper Boolean search capabilities).

The search tool was found to be quite comprehensive and very broad technology scans were easily initiated. The natural language interface was easy to use and robust. The ability to store, track and retrieve search parameters was very useful. The graphical interface did provide some interesting insights on key categories and developers (see figure below for one example of the graphical interface output).
One of the challenges with this tool is that the natural language interface identifies many thousands of related references within the available extensive databases. The large number of references required some significant effort to focus the search on the most relevant items.

DeLude Consulting Inc. used two techniques to attempt to pare down the search results to a more manageable number of the most relevant articles. The first technique was a combination of both restricting the time period and reference databases as well as adding a more explicit Boolean search constraints to the natural language query. The other technique was a more “brute force” method where all the references from a specific search would be dumped to an excel database and then quickly scanned for direct relevance to the current study’s objectives.

It would be helpful if IHS could add features to its tool that would easily allow the following:
- Identification of relevant and “not relevant” references in a search output (with embedded search engine able to improve the focus of the search query and output references through pattern matching techniques)
- Input of specific categories / focus items within the graphical interface to allow different types of search result categorization / customization
DeLude Consulting Inc. Independent Search

Only public domain or publicly available resources (University of Calgary temporary public access) were used. Boolean advanced search parameters were used to restrict the searches to specific domains, time frames and/or key words (i.e. peer reviewed journals).

DeLude Consulting Inc. identified only a few more technologies; however, the searches using the University access identified a number of good recent dissertations and scholarly articles that were very useful in providing business case context and technology overviews in specific technology classes including some explanations of the underlying mechanisms for specific technology options.
Technology Feasibility / Competitive Considerations and Shortlisting

For each key technology class identified in the scan, a brief summary of the main characteristics, challenges, risks and practical application/competitive position considerations are provided.

In all cases some of the key technical hurdles include:

- Handling of commercial streams with typical contaminants (CO₂, hydrocarbons, amines, water, ammonia)
- Elemental sulphur extraction and management to avoid plugging/precipitation
- Corrosion and material selection for operating conditions
- Environmental and safety hazards due to dealing with high H₂S gas streams
- H₂ and S recombining into H₂S and/or other competing reaction pathways
- Fouling/poisoning of catalytic and/or electrolytic systems
- Catalyst life cycle costs and regeneration

Some additional challenges are:

- Overcoming reliability and performance concerns for commercial applications that must consistently meet stringent sulphur recovery regulations
- Funding for novel technology development and scale-up
- Overall economics and competition with commercial scale CO₂ sequestration

The final subsection below provides DeLude Consulting Inc’s. recommended shortlisting to provide a representative selection of scanned technologies for a more detailed assessment and ranking.

Thermal Decomposition Processes

“Pure Thermal”

\[
\text{H}_2\text{S} \xrightarrow{\text{\triangleup}} \text{H}_2 + 0.5 \text{S}_2
\]

In a “pure thermal” process, H₂S is heated by application of an external heat source until the H₂S dissociation reaction begins to occur at about 750° K (477 C). At the high temperature conditions a thermodynamic equilibrium is established between the dissociation reaction and the recombination reaction. The figure below shows the equilibrium concentrations for the various species (H₂S, HS, H₂, S₂, S and H) that can be generated during dissociation reactions at 1 atm pressure and varying temperature levels.
For the temperature range of practical interest of approximately 1000 K (~727 °C) to 1400 K (~1127 °C) pure thermal conversions are in the range of 3 to 30%.

These conversion levels are relatively low and significant capital costs would be incurred to provide suitable materials for the process conditions at the 30% conversion level and to manage the large recycle flow required to deal with a 30% conversion per pass. Also the energy costs for reaching the process conditions would be quite high and the need for rapid quenching of the hot product stream (to avoid rapid recombination reactions) would reduce the effectiveness of any heat recovery equipment.

For these reasons, pure thermal processes using externally supplied process heat are not considered promising candidates for future successful application. These pure thermal technologies are considered as being at a TRL level of 4 (benchscale test on pure components).
Thermal Plasma

\[ \text{H}_2\text{S} \xrightarrow{+\text{hv}} \text{H}_2 + 0.5 \text{S}_2 \]

As a simplified concept, plasma processes create conditions where an electrical discharge is passed through a gas phase causing excitation/ionization/heating of the gas components impacted by the discharge.

In thermal plasma processes, the major contribution of the plasma is to rapidly heat the gas phase to localized reaction temperatures that initiate the desired decomposition reaction but then allow the reacted species to be rapidly quenched by the remainder of the flowing gas phase to inhibit any recombination reaction.

Key challenges with thermal plasma techniques are the difficulties creating a stable arc with high H\textsubscript{2}S content gas at reasonable H\textsubscript{2}S concentrations and operating pressures due the high dielectric constant for H\textsubscript{2}S and also the energy efficiency of the conversion process. These thermal plasma technologies are considered as being at a TRL level of 4 (benchscale test on pure components).

Catalytically enhanced thermal

\[ \text{H}_2\text{S} \xrightarrow{\Delta} \text{H}_2 + 0.5 \text{S}_2 \]

There are catalytic advantages in the operating temperature range below about 1150 deg K (877 deg C). Above that temperature, the thermal reaction kinetics are rapid enough for reasonable reactor volumes without the use of catalysts. However, the temperature region below 1150 deg K provides only very modest conversions (< ~18%) and this makes the cost of recycle and hydrogen / H\textsubscript{2}S separation too high to allow catalytically enhanced thermal to be economically attractive. These catalytically enhanced thermal technologies are considered as being at a TRL level of 4 (benchscale test on pure components).

Thermal with Equilibrium Shift

\[ \text{H}_2\text{S} \xrightarrow{\Delta} \text{H}_2 + 0.5 \text{S}_2 \quad (+ \text{physical separation}) \]

The concept of continuous removal of products to overcome reaction equilibrium constraints has been practiced in various applications to improve overall conversion levels.
The most attractive approach for this reaction system would be a membrane that would operate at high temperature process conditions to remove hydrogen selectively to promote H$_2$S conversion. Unfortunately, the extremely corrosive nature of wet H$_2$S and hydrogen streams at high temperature has not allowed the identification of a suitable membrane that can maintain an acceptable separation performance.

Adsorption, absorption and extraction systems also do not seem to be adaptable to the operating temperature conditions required to achieve conversions in excess of 40%. These thermal with equilibrium shift technologies are considered as being at a TRL level of 4 (benchscale test on pure components).

**Oxidative and Integrated Claus Processes**

$$4\text{H}_2\text{S} + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{H}_2 + 2\text{S}_2$$

Oxidative approaches (such as the “Superadiabatic process”) are theoretically feasible but are challenged by competition with the normal Claus reaction. The Claus side reaction results in a 50 to 75% reduction in hydrogen yield even when pure oxygen is used in place of air. Additionally, the use of pure O$_2$ requires significant power consumption so the net CO$_2$ benefit is further reduced (or may even be eliminated entirely depending on the level of CO$_2$ emissions for power generation). There are some offsetting capital cost advantages that can be realized by using pure oxygen as the downstream H$_2$S recycle/recovery systems are smaller due to the reduced volume of gas being processed. However taking advantage of the capital benefits will reduce future flexibility to manage the full H$_2$S generation if oxygen is not available or if the hydrogen generation system goes off-line.

Integrated Claus processes will require building the full Claus + SCOT train and then integrating the novel technology as “add-on” equipment for the reaction and H$_2$ separation/purification unit operations. The hydrogen recovery step will require further technology advancement due to the high temperature, modest pressure and corrosive components in the gas stream.

These technologies can be relatively modest cost due to the Claus plant similarities and use of H$_2$S combustion as the fuel source for the hydrogen generation reaction. But as noted above the net CO$_2$ benefit from SMR is significantly reduced due to low H$_2$ yields on H$_2$S input. These oxidative and integrated Claus technologies are considered as being at a TRL level of 5 (benchscale test on real feeds with recycle).
**Electrolytic processes (both aqueous and non-aqueous)**

\[ \text{H}_2\text{S} \xrightarrow{+\text{e}^-} \text{H}_2 + 0.5 \text{S}_2 \]

Various electrochemical processes have been noted in the literature. However, at low temperatures sulphur deposition/fouling causes a quick drop-off of cell performance while at higher temperatures (where sulphur deposition is reduced or eliminated) corrosion and cell structural integrity become problematic.

Also for all the direct electrolytic processes examined, energy consumptions far in excess of the minimum theoretical thermodynamic requirement result in high operating costs and a reduction in the net CO\(_2\) benefit due to power generation CO\(_2\) emissions. These electrolytic technologies are considered as being at a TRL level of 4 (benchscale test on pure components).

**Microwave and cold/warm plasma processes**

\[ \text{H}_2\text{S} \xrightarrow{+\text{hv}} \text{H}_2 + 0.5 \text{S}_2 \]

These technologies have some similarity to the thermal plasma except that the key purpose of the plasma/microwave irradiation is to selectively excite the H\(_2\)S molecule in order to initiate the decomposition reaction rather than relying on purely thermal decomposition.

Many different configurations of plasma/microwave reactors have been proposed. It has been observed that the reactor configuration appears to play a large role in the level of input energy required to initiate the decomposition reaction. One theory suggested is that the reaction is actually proceeding by a chain reaction mechanism with [HS\(_x\)]\(^-\) species being formed from an initially excited H\(_2\)S molecule.

Given the good energy efficiency for H\(_2\)S decomposition, some of these technologies show promise. The key technical hurdles include overcoming low operating pressures and/or low H\(_2\)S concentrations due to the high dielectric constant of pure H\(_2\)S gas (resulting in difficulty maintaining a stable plasma arc). Conversion levels also have to be increased in order to reduce H\(_2\)S/H\(_2\) separation and recycle cost. Finally, the ability to scale up the plasma technology while maintaining the very low energy demand will need to be demonstrated. The microwave technologies are considered as being at a TRL level of 6 (Scale-up testing of critical process steps) while the other warm plasma technologies are considered as being at a TRL level of 5 (benchscale test on real feeds with recycle).
Photolysis processes (with various catalytic enhancements)

\[ \text{H}_2\text{S} \xrightarrow{\text{hv}} \text{H}_2 + 0.5 \text{S}_2 \]

Similar to the plasma/microwave processes above, the photo irradiation (with catalytic agent) aims to selectively excite the H\(_2\)S molecule in order to initiate the decomposition reaction.

Numerous researchers are actively investigating potential reaction systems that can harness natural sunlight to fuel the decomposition reaction. However, for upgrading type applications, a reliable and continuous processing of H\(_2\)S is a critical requirement. As a result the practical considerations relating to the collection and/or delivery of light energy and the variation in supply when relying on natural solar collectors make this option unattractive. The alternative of using an artificial light source as a means of delivering energy to the process is too inefficient. These photolytic technologies are considered as being at a TRL level of 3 (modeling assessment – verification of concept).

Complex chemical reaction cycles

Bunsen Reaction (HI)

\[ \text{H}_2\text{S} + \text{H}_2\text{SO}_4 \rightarrow \text{S} + \text{SO}_2 + 2 \text{H}_2\text{O} \]
\[ \text{SO}_2 + 2 \text{H}_2\text{O} + \text{I}_2 \rightarrow \text{H}_2\text{SO}_4 + 2 \text{HI} \]
\[ 2 \text{HI} \rightarrow \text{H}_2 + \text{I}_2 \]

**net:** \[ \text{H}_2\text{S} \rightarrow \text{H}_2 + \text{S} \]

Chemical cycles based on the Bunsen reaction of HI are theoretically feasible; however, the multiple reaction / separation steps and the corrosivity of the reactants under the severe operating conditions required make the conceptual process very difficult to deliver as a practical working solution for hydrogen production from H\(_2\)S. The Bunsen reaction is considered as being at a TRL level of 4 (benchscale test on pure components).
Anthraquinone Based Cycles

While theoretically feasible, the cost of generating the chemical reactants and their stability under practical operating conditions make this option relatively uncompetitive. The anthraquinone based reaction is considered as being at a TRL level of 3 (modeling assessment – verification of concept).

Metal-Sulphide Based Cycles

Metal sulphide cycle processes have some potential. The main challenges for this option are the costs associated with movement and regeneration of solid based adsorbent material.

A configuration based on fluidised bed reaction and regeneration has been suggested with many similarities to commercially applied FCCU technology. This version of the metal sulphide cycle is considered to be at a TRL level of 4 (benchscale test on pure components).

Processes with oxidative regeneration producing SO₂ are considered not suitable due to SO₂ emission limits.
Fe-Cl Cycle (Indirect Electrolysis)

Net reaction:

\[
2\text{FeCl}_3(aq) + \text{H}_2\text{S}(g) \rightarrow 2\text{FeCl}_2(aq) + 2\text{HCl}(aq) + \text{S}
\]

\[
2\text{FeCl}_2(aq) + 2\text{HCl}(aq) \rightarrow \text{H}_2(g) + 2\text{FeCl}_3(aq)
\]

\[
\text{H}_2\text{S} \rightarrow \text{H}_2(g) + \text{S}
\]

The indirect electrolysis process uses aqueous FeCl\textsubscript{3} as the H\textsubscript{2}S absorption and initial reaction agent forming elemental sulfur, FeCl\textsubscript{2} and HCl. After separation of the sulfur, the resulting solution is then passed through the electrolysis cell where hydrogen is evolved and the FeCl\textsubscript{3} solution is regenerated.

Key advantages for this technology option are the potential for offsetting the amine system and separation of sulfur prior to electrolysis (to avoid fouling issues. Key challenges include efficient sulphur separation and solution degradation due to other reactive components in the gas stream. The Fe-Cl cycle is considered to be at a TRL level of 5 (benchscale test on real feeds with recycle) as significant process testing and simulation has been conducted at small scale.
**CH₄/H₂S Reforming Reaction**

\[ \text{CH}_4 + 2\text{H}_2\text{S} \rightarrow 4\text{H}_2 + \text{CS}_2 \]

While the reforming of H₂S using CH₄ is technically feasible, the quantity of CS₂ that would be generated is much larger than the demand in the Canadian market. As a result, this technology was not considered for further ranking evaluation. This technology is considered to be at a TRL level of 6 (scale-up testing of critical process steps).

**Shortlisting Recommendation**

DeLude Consulting Inc. initially recommended the following technologies as the shortlisting for a more detailed ranking process including rough relative economic assessment of the cost of CO₂ avoided. The initial recommendation was endorsed by the COSIA working team on March 30, 2017 as the basis for further work.

- **Photocatalytic:**
  - Process based on IFP French patent - 2997940 - 2016-03-11 with best suitable patent from literature (nanostructured N-doped TiO₂).

- **Warm Plasma:**

- **Thermocatalytic:**

- **Oxidative:**
  - Superadiabatic process as described in US Patent 9242859

- **Complex Reaction Network:**
  - Process based on Bunsen Reaction (due to link with water cycle R&D – for nuclear applications) – method identified in Wang et al, Fuel Processing Technology 108:55–62 · April 2013
  - Metal sulphide process based on French Patent 2972004 - 2015-03-06
The following technology categories were dropped from consideration for ranking at this time for the reasons noted:

- Pure thermal processes – prefer to consider catalytic or integrated thermal processes
- Electrolytic processes – no recent progress in the literature – practical fouling and anode performance stability make these options difficult – focus on indirect electrolysis option (Fe-Cl)
- Processes generating sulphur oxide or CS$_2$ side products due to disposal / market constraints
- Metal sulphide processes with oxidative regeneration (producing sulphur oxide byproducts)

After further engagement with the COSIA working group on April 28, 2017, effort was curtailed on both the photocatalytic and Bunsen reaction options. This was due to the combination of difficulty in finding cost data and the low likelihood of practical and cost effective application for Oil Sands. The key difficulty for the photocatalytic option is the efficiency of providing light energy to initiate the decomposition. Meanwhile, the Bunsen reaction cycle is a complex reaction and separation network that must operate under conditions where extremely high corrosion rates will prevail in order to achieve good conversion levels.
Baseline Cases for Oil Sands Applications

Insitu Oil Sands production:

The assessment has generally used COSIA’s SAGD reference case as documented within: Candor Engineering Ltd.’s Project Report – COSIA SAGD Reference Facilities – March 24, 2017

The only deviation from the reference facility is the consideration of a case with a higher H₂S production than the reference facility based on other public domain reference literature (potential range of 0.05 to 2 t/d of H₂S production – reference facility is at ~ 0.22 t/d H₂S).

Upgrading / Refining:

Upgrading configuration is based on the following:

– 100 kbbl/d bitumen - delayed coking configuration with hydrotreating for production of high value crude product with key parameters being:
  - 500 t/d H₂S production
  - 280 t/d of hydrogen generation
  - production of low sulphur bottomless synthetic crude

Note:
Of the 500 T/d of H₂S, approximately 60 t/d of H₂S (with 30 t of NH₃) is delivered to the sulphur recovery facility in a sour wash water stream that must be stripped to yield a sour water acid gas (SWAG) that must be processed within the sulphur handling units.
Current Conventional Technologies for Economic Comparison

Base Case – Insitu:

Acid Gas re-injection into reservoir

Note that after establishing the base conventional technology for in-situ, a review of the H$_2$S production levels confirmed that a very low quantity of H$_2$S is generated in typical operations. As a result, application of any H$_2$S to H$_2$ technology offers a negligible change in CO$_2$ emissions for in-situ and no detailed assessment of the base conventional technology was undertaken.

Base Case – Upgrading/Refining:

Claus + SCOT for sulphur recovery

SMR with PSA for hydrogen manufacture - both with and without CO$_2$ capture
  - Battery limits H$_2$ conditions are assumed as 99.5% purity and 2500 kPa-g pressure.

Key data for both of these technologies was compiled and is included in the section detailing the key input data.

Of special consideration is that the upgrader sulphur complex will have to accommodate acid gas streams generated by both sour water stripping (sour water acid gas (SWAG) with high ammonia content) and amine regeneration (amine acid gas (AAG) with high H$_2$S content).
Ranking Metrics – Development of Template for Ranking

In order to develop a ranking of the various competing technologies a spreadsheet ranking tool was developed by DeLude Consulting Inc.

The spreadsheet determines an overall relative ranking based on the following focus areas:

- Technical Viability
- Technical Maturity
- Economic Assessment
- Improvement Potential
- CO₂ Impact (focus area added based on discussions at working team meeting April 28, 2017)
- Risk Assessment (HSE)

For technical viability the following items are qualitatively assessed and a score ranging from 0 to 3 is assigned (with 3 being the best score).

- Chemistry established, viable thermodynamics
- Feasible operating conditions (materials, corrosion, erosion)
- Acceptable kinetics established (catalysts if required)
- Level of complexity (number of unit operations)
- Competing pathways (side-reactions, contaminant risks, degradation)

For technical maturity the score is based on the NASA Technical Readiness Level methodology as interpreted for novel process technologies as shown below:

<table>
<thead>
<tr>
<th>Score</th>
<th>TRL Level (Process technology Equivalent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>No evidence of concept development</td>
</tr>
<tr>
<td>1</td>
<td>Chemical concept</td>
</tr>
<tr>
<td>2</td>
<td>Process methodology</td>
</tr>
<tr>
<td>3</td>
<td>Modeling assessment</td>
</tr>
<tr>
<td>4</td>
<td>Benchscale test on pure components</td>
</tr>
<tr>
<td>5</td>
<td>Benchscale tests on real feeds with recycle</td>
</tr>
<tr>
<td>6</td>
<td>Scale-up testing of critical process steps</td>
</tr>
<tr>
<td>7</td>
<td>Integrated pilot scale test</td>
</tr>
<tr>
<td>8</td>
<td>Semi-commercial demonstration plant</td>
</tr>
<tr>
<td>9</td>
<td>First commercial plant operating</td>
</tr>
<tr>
<td>10</td>
<td>Multiple commercial plants operating</td>
</tr>
</tbody>
</table>
For economic assessment, the scoring is based on the cost of CO$_2$ avoided as outlined in the table below. This cost of CO$_2$ avoided is calculated by first determining the net present value of the differential cash flow of the base business case and the base business with implementation of novel technology and then dividing this result by the “net present value” of the CO$_2$ tonnes avoided (using the same discounting factor as was used for the cash flows).

<table>
<thead>
<tr>
<th>scoring</th>
<th>Cost of CO$_2$ avoided</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>CO$_2$ cost &gt; 200 $/t</td>
</tr>
<tr>
<td>1</td>
<td>CO$_2$ cost 160 to 200 $/t</td>
</tr>
<tr>
<td>3</td>
<td>CO$_2$ cost 120 to 160 $/t</td>
</tr>
<tr>
<td>5</td>
<td>CO$_2$ cost 80 to 120 $/t</td>
</tr>
<tr>
<td>7</td>
<td>CO$_2$ cost 40 to 80 $/t</td>
</tr>
<tr>
<td>9</td>
<td>CO$_2$ cost 0 to 40 $/t</td>
</tr>
<tr>
<td>10</td>
<td>CO$_2$ cost &lt; 0 $/t</td>
</tr>
</tbody>
</table>

For determining the scoring for improvement potential, it is a bit more difficult as the ranking for improvement potential needs to consider both the level of baseline performance as well as the magnitude of the potential improvement. The reason for this is that it is much easier to improve a process with a starting point of $CDN 300/t CO$_2$ avoidance cost by $CDN 100/t versus improving a technology already achieving in the range of $CDN 80/t CO$_2$ avoidance cost by $CDN 100/t.

The methodology utilized to provide a balanced assessment is as follows. A first criteria is based on the improved total CO$_2$ avoided cost. A second criteria is the magnitude of the cost improvement. The scores for each of these criteria is determined and then the overall score is based on the multiplication of the two different scores with that result then divided by 6 (with a maximum score of 10). The procedure and scoring is as outlined below:

<table>
<thead>
<tr>
<th>Criteria 1</th>
<th>Improved Total Cost</th>
<th>Criteria 2</th>
<th>Cost Improvement</th>
</tr>
</thead>
<tbody>
<tr>
<td>scoring</td>
<td>Improved CO$_2$ avoided cost</td>
<td>scoring</td>
<td>Level of Cost improvement</td>
</tr>
<tr>
<td>0</td>
<td>CO$_2$ cost &gt; 200 $/t</td>
<td>0</td>
<td>&lt; 5 $/t CO$_2$</td>
</tr>
<tr>
<td>1</td>
<td>CO$_2$ cost 160 to 200 $/t</td>
<td>1</td>
<td>5 to 10 $/t CO$_2$</td>
</tr>
<tr>
<td>3</td>
<td>CO$_2$ cost 120 to 160 $/t</td>
<td>3</td>
<td>10 to 20 $/t CO$_2$</td>
</tr>
<tr>
<td>5</td>
<td>CO$_2$ cost 80 to 120 $/t</td>
<td>5</td>
<td>20 to 40 $/t CO$_2$</td>
</tr>
<tr>
<td>7</td>
<td>CO$_2$ cost 40 to 80 $/t</td>
<td>7</td>
<td>40 to 60 $/t CO$_2$</td>
</tr>
<tr>
<td>9</td>
<td>CO$_2$ cost 0 to 40 $/t</td>
<td>9</td>
<td>60 to 80 $/t CO$_2$</td>
</tr>
<tr>
<td>10</td>
<td>CO$_2$ cost &lt; 0 $/t</td>
<td>10</td>
<td>&gt; 80 $/t CO$_2$</td>
</tr>
</tbody>
</table>

\[
\text{final score: } \frac{\text{criteria 1 score} \times \text{criteria 2 score}}{6}, \text{ capped at maximum } = 10
\]
For CO₂ impact, the scoring is based on the kt/year of CO₂ avoided for the reference Upgrader application as outlined in the table below.

<table>
<thead>
<tr>
<th>Scoring</th>
<th>kt/year CO₂ reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>&lt; 10 kt/year</td>
</tr>
<tr>
<td>1</td>
<td>10 to 25 kt/year</td>
</tr>
<tr>
<td>3</td>
<td>25 to 50 kt/year</td>
</tr>
<tr>
<td>5</td>
<td>50 to 100 kt/year</td>
</tr>
<tr>
<td>7</td>
<td>100 to 250 kt/year</td>
</tr>
<tr>
<td>9</td>
<td>250 to 500 kt/year</td>
</tr>
<tr>
<td>10</td>
<td>&gt;500 kt/year</td>
</tr>
</tbody>
</table>

For risk assessment (HSE), the following items are qualitatively assessed and a score ranging from 0 to 3 is assigned with 3 corresponding to the least added risk (best performance) and 0 corresponding to very high additional risk.

- Operating Conditions risk (high temperature, high pressure, reactivity)
- Corrosion/erosion, system containment risk
- Level of complexity (number of unit operations)
- Human toxicity risk
- Potential environmental impact of spill or release
- Complexity and/or required technical controls
- Regulatory risk - management of required performance by legislation

The overall ranking is based on a weighted combination of the focus area scores with the following weights as agreed with the H₂ from H₂S steering group:

<table>
<thead>
<tr>
<th>Screening Criteria:</th>
<th>Technical viability</th>
<th>Technical Maturation Assessment</th>
<th>Economic Assessment</th>
<th>Improvement potential</th>
<th>CO₂ Impact</th>
<th>Risk Assessment (HSE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weighting: 1 to 5</td>
<td>5</td>
<td>3</td>
<td>5</td>
<td>3</td>
<td>5</td>
<td>4</td>
</tr>
</tbody>
</table>

28
Economic Assessment Template and Key Business Inputs

A simplified economic cash flow tool was developed for assessing the cost of CO₂ avoided. The template economic file as well as the completed assessment files with input for various technology cases are both included in the economic information provided with the reference listing.

The key model inputs are shown below (all $CDN)

<table>
<thead>
<tr>
<th>Description</th>
<th>Symbol</th>
<th>Unit</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ avoided</td>
<td></td>
<td>t/year</td>
<td>(overall net)</td>
</tr>
<tr>
<td>differential capital</td>
<td></td>
<td>M$</td>
<td>(assumed spent over 3 years)</td>
</tr>
<tr>
<td>differential operating cost</td>
<td></td>
<td>M$/year</td>
<td>(2% of initial capital)</td>
</tr>
<tr>
<td>differential maintenance cost</td>
<td></td>
<td>M$/year</td>
<td>(2.5% of initial capital)</td>
</tr>
<tr>
<td>by-product value</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>corporate tax rate</td>
<td></td>
<td>M$/year</td>
<td>(27% used)</td>
</tr>
<tr>
<td>capital depreciation</td>
<td></td>
<td></td>
<td>(10% declining balance)</td>
</tr>
<tr>
<td>discount rate</td>
<td></td>
<td></td>
<td>(10%)</td>
</tr>
</tbody>
</table>

For the purposes of estimating differential operating costs, the following cost assumptions were used:

- **Natural gas price:** $CDN 3 /GJ (HHV)
- **Power price:** $CDN 40 /MW-h

For power usage, the equivalent future Alberta power grid intensity was estimated as 0.3 t CO₂/MW-h.

At the very early level of scope definition it was not possible to accurately determine any difference in operations staffing required for the new technologies as compared to the baseline conventional technologies. However, if in future an assessment of differential staff count could be made between the novel technology and the baseline technology, then the below labour cost would be used.

- **Labour cost:** $CDN 125,000 / differential person-year (12 hour operating shifts)
Summary of Key Information for Baseline and Shortlisted Technologies

The tables included in this section show key information available for each technology on approximate capital costs, key feed/energy input values, by-product quantity estimates, any other material operating expenses (chemicals/catalyst) and net CO₂ emission estimates. For maintenance costs, a straight ratio 2.5% of initial capital is used for yearly costs and for sustaining capital a straight ratio 2.0% of initial capital is used for yearly costs.

For adjusting scope capital costs to a common capacity, a 0.6 power capacity cost scaling has been assumed.

Where some capital cost estimates are available in the literature, the following table of capital cost escalation factors (Nelson-Farrar cost index for refinery) was used to convert costs between different base years to a January 2017 basis. Also for 2017 costs, an exchange rate of $US / $CDN of 0.75 was applied.

<table>
<thead>
<tr>
<th>Year</th>
<th>Cost Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>1982</td>
<td>1010.0</td>
</tr>
<tr>
<td>1995</td>
<td>1392.1</td>
</tr>
<tr>
<td>1996</td>
<td>1418.9</td>
</tr>
<tr>
<td>1997</td>
<td>1449.2</td>
</tr>
<tr>
<td>1998</td>
<td>1477.6</td>
</tr>
<tr>
<td>1999</td>
<td>1497.2</td>
</tr>
<tr>
<td>2000</td>
<td>1542.7</td>
</tr>
<tr>
<td>2001</td>
<td>1579.7</td>
</tr>
<tr>
<td>2002</td>
<td>1642.2</td>
</tr>
<tr>
<td>2003</td>
<td>1710.4</td>
</tr>
<tr>
<td>2004</td>
<td>1833.6</td>
</tr>
<tr>
<td>2005</td>
<td>1918.8</td>
</tr>
<tr>
<td>2006</td>
<td>2008.1</td>
</tr>
<tr>
<td>2007</td>
<td>2106.7</td>
</tr>
<tr>
<td>2008</td>
<td>2251.4</td>
</tr>
<tr>
<td>2009</td>
<td>2217.7</td>
</tr>
<tr>
<td>2010</td>
<td>2337.6</td>
</tr>
<tr>
<td>2011</td>
<td>2389.5</td>
</tr>
<tr>
<td>2012</td>
<td>2465.2</td>
</tr>
<tr>
<td>2013</td>
<td>2489.5</td>
</tr>
<tr>
<td>2014</td>
<td>2555.2</td>
</tr>
<tr>
<td>2015</td>
<td>2553.0</td>
</tr>
<tr>
<td>2016</td>
<td>2480.3</td>
</tr>
<tr>
<td>2017</td>
<td>2455.7</td>
</tr>
</tbody>
</table>

One of the largest challenges in the economic analysis is finding representative and consistent capital and operating cost data that can be reasonably compared across all the technologies. This is especially true for early development novel technologies where micro scale prototype reactors are being used.

Technologies included:
Data was compiled on the following technologies:

Conventional Sulphur Recovery
- Amine $\text{H}_2\text{S}$ treating (Amine)
- 2 stage Claus with Shell Claus Off-Gas Treating (Claus/SCOT)

Conventional Hydrogen Manufacture
- Steam Methane Reforming with PSA for $\text{H}_2$ recovery (SMR/PSA)

Hydrogen compression
- Centrifugal multi-stage compressor systems ($\text{H}_2$ Comp)

Photocatalytic:
- Catalytic method with nanostructured N-doped TiO$_2$ (Ph-Cat)

Warm Plasma:
- Gliding arc plasma process (GAT)

Cool Plasma:
- Coaxial dielectric barrier discharge plasma reactor (DBD)

Thermocatalytic:
- Perovskite oxide catalyst for thermal hydrogen production from $\text{H}_2\text{S}$ (T-Cat)

Oxidative:
- Superadiabatic process using pure oxygen (preferred embodiment) (SADB)

Complex Reaction Networks:
- Bunsen Reaction (HI)
- Metal sulphide (MeS)
- Fe-Cl cycle (indirect electrolysis) (Fe-Cl)
## Capital Cost Data (scoping study accuracy +/- >50%):

<table>
<thead>
<tr>
<th>Technology (short form)</th>
<th>Year</th>
<th>Capacity (H₂S)</th>
<th>Cost (M$ CDN)</th>
<th>Adjusted Capacity</th>
<th>Adjusted Cost (M$ CDN) (2017)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amine</td>
<td>1982</td>
<td>912 (H₂S)</td>
<td>58</td>
<td>500 (H₂S)</td>
<td>98.3</td>
<td>Hart 1983</td>
</tr>
<tr>
<td>SMR/PSA</td>
<td>2016</td>
<td>365 (H₂)</td>
<td>210.</td>
<td>280 (H₂)</td>
<td>177</td>
<td>Air Pdts 2016</td>
</tr>
<tr>
<td>H₂ Comp</td>
<td>2014</td>
<td>50 (H₂)</td>
<td>11.6 (5.9 MW)</td>
<td>29.4 (H₂)</td>
<td>8.5 (3.5 MW)</td>
<td>Almasi 2014</td>
</tr>
<tr>
<td>Ph-Cat</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>No reliable data</td>
</tr>
<tr>
<td>GAT</td>
<td>2010</td>
<td>3.6 (MWe)</td>
<td>28.5</td>
<td>24.6 (MWe)</td>
<td>107.3</td>
<td>Ducharme 2010</td>
</tr>
<tr>
<td>DBD</td>
<td>2010</td>
<td>3.6 (MWe)</td>
<td>28.5</td>
<td>51.1 (MWe)</td>
<td>166.3</td>
<td>Ducharme 2010</td>
</tr>
<tr>
<td>T-Cat</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Claus scaled)</td>
</tr>
<tr>
<td>SADB</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Claus scaled)</td>
</tr>
<tr>
<td>HI</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>No reliable data</td>
</tr>
<tr>
<td>MeS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Netzer 2006</td>
</tr>
<tr>
<td>Fe-Cl</td>
<td>2015</td>
<td>762 (H₂S)</td>
<td>411</td>
<td>500 (H₂S)</td>
<td>409.4</td>
<td>Berrouk 2015</td>
</tr>
</tbody>
</table>

## Key Process Data with Capacity Basis:

<table>
<thead>
<tr>
<th>Technology (short form)</th>
<th>Natural Gas t/d</th>
<th>Power MW</th>
<th>Oxygen Demand t/d</th>
<th>Heat Recovery t/h net steam</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amine</td>
<td>0</td>
<td>2.0</td>
<td>0</td>
<td>-16.0</td>
</tr>
<tr>
<td>(per 500 t/d H₂S feed)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Claus/SCOT</td>
<td>0</td>
<td>8.0</td>
<td>0</td>
<td>+40.3</td>
</tr>
<tr>
<td>SMR/PSA</td>
<td>973.9</td>
<td>3.5</td>
<td>0</td>
<td>+98.2</td>
</tr>
<tr>
<td>(per 100 t/d H₂ product)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂ Comp</td>
<td>0</td>
<td>11.8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(per 100 t/d H₂ product from ~100 kPa-a to 2500 kPa-a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(All H₂S conversion technologies below - basis 500 t/d H₂S feed)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ph-Cat</td>
<td>No reliable data</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GAT</td>
<td>0</td>
<td>24.6</td>
<td>0</td>
<td>26.0</td>
</tr>
<tr>
<td>DBD</td>
<td>0</td>
<td>51.1</td>
<td>0</td>
<td>58.5</td>
</tr>
<tr>
<td>T-Cat</td>
<td>0</td>
<td>8</td>
<td>0</td>
<td>28.2</td>
</tr>
<tr>
<td>SADB</td>
<td>0</td>
<td>4</td>
<td>118</td>
<td>28.2</td>
</tr>
<tr>
<td>HI</td>
<td>No reliable data</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MeS</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Fe-Cl</td>
<td>0</td>
<td>24.9</td>
<td>0</td>
<td>28.5</td>
</tr>
</tbody>
</table>
For all technology economic assessments the following (optimistic) approach was used:

- Baseline is a new grass-roots upgrader complex
- New \( \text{H}_2 \text{S} \) to \( \text{H}_2 \) conversion technology replaces conventional Claus/SCOT for capital and operating cost offset (and for the Fe-CL indirect electrolysis case the amine system is replaced as well)
- \( \text{H}_2 \) yield from new technology allows reduction in size of SMR/PSA unit
- \( \text{H}_2 \) from new technology will be compressed to match SMR outlet pressure (cost addition)
- Net \( \text{CO}_2 \) emissions reduction is after correction for power emissions assuming future grid emissions factor of 0.3 t\( \text{CO}_2 \)/MW-h
- For Sour Water Acid Gas (SWAG) management, it is assumed that a Chevron two stage stripping system is installed that separates and recovers \( \text{NH}_3 \) for sale. The capital and operating cost addition is assumed as overall cost neutral due to the benefit of \( \text{NH}_3 \) sale for fertilizer manufacture.

Data summaries including capital and operating cost information and net hydrogen and \( \text{CO}_2 \) avoided are provided in spreadsheet –

*Summary of costing data for key technologies rev 3.xlsx*

For potential improved cases each technology was considered separately and the following assumptions were applied:

- Ph-Cat - 30% reduction in capital
- GAT - 20% reduction in plasma system capital, 20% reduction in energy demand
- DBD - 33% reduction in energy demand
- T-Cat - 50% reduction in capital for novel technology unit operations
- SADB - pure oxygen generation without \( \text{CO}_2 \) emissions
- HI - 30% reduction in capital
- MeS - 33% reduction in capital
- Fe-CL - 30% reduction in capital, 30% reduction in power

The data summaries for the improved cases are provided in the spreadsheet -

*Summary of costing data for key technologies rev 3 – improved cases.xlsx*
Ranking Results with Comments

The ranking results are summarized in the excel spreadsheet - Screening Criteria for H\textsubscript{2} from H\textsubscript{2}S final summary.xlsx

The overall ranking results are as shown below (maximum possible score of 250):

The thermocatalytic, superadiabatic and gliding arc tornado plasma options show the most promise based on the rankings.

The thermocatalytic and superadiabatic options should be considered lower risk due to being quite comparable and compatible with current Claus/SCOT technology. These two technologies will need improvements in hydrogen separation technology to be fully realized. A drawback to these technologies is the lower potential CO\textsubscript{2} avoided due to the competing Claus reaction being used to provide the required process heat (with loss of net hydrogen production).

The gliding arc tornado plasma (and comparable warm plasma or microwave techniques) are promising but will need a breakthrough on high H\textsubscript{2}S concentration plasma arc initiation and stable operation due to high H\textsubscript{2}S dielectric constant.

Metal sulphide and Fe-Cl cycle technologies are the next most promising of the technologies assessed. The metal sulphide process outlined in the IFP patent includes utilization of about 33% of the hydrogen produced for both heat and power generation to avoid CO\textsubscript{2} emissions associated with either power or process heating.
The net CO₂ avoided for each technology is summarized in the graph below for both the “base” and “improved” cases:

The net CO₂ is calculated after correction for emissions due to imported power demand and/or oxygen supply.

The significant gain in net CO₂ for the “improved” superadiabatic option is mainly due to oxygen supply being assumed at no net CO₂ emissions (either due to O₂ as a byproduct of other separation processes or by utilizing renewable power with no CO₂ emissions for oxygen system electricity demand).

As noted above, the metal sulphide proposed concept shows the best net CO₂ reduction by using 33% of the hydrogen produced to generate the heat and power needed for the H₂S to H₂ conversion.
The cost of CO\(_2\) avoided for each technology is summarized in the graph below for both the “base” and “improved” cases:

**Base and Improved Cost of CO\(_2\) Avoided**

The “top 3” options all show improved case CO\(_2\) avoided costs in the range below $\text{CDN} 50/t.$
**Business Case Assessments – Insitu and Upgrading/Refining Applications**

There is no incentive for investing in hydrogen from H\(_2\)S for in-situ projects due to the low H\(_2\)S generation in the range of 0.05 to 2 t/d for a reasonable scale facility. The potential CO\(_2\) emission improvement in the range of only 3 to 120 kg/d of CO\(_2\) is not material enough to warrant consideration or any marginal investment in a novel technology.

There do not appear to be any suitable prospects for application of hydrogen from H\(_2\)S as an existing refinery or upgrader “bolt-on” opportunity due to the relatively limited potential CO\(_2\) emissions improvement when weighed against the complexity, cost and risk of a implementing a novel technology revamp project within an existing (space constrained) upgrading/refining configuration.

Given the above comments, there only remains the potential for application of hydrogen from H\(_2\)S technology within new upgrading/refining projects as part of integrated oil sands production schemes. However, the prospects for future integrated production/upgrading/refining projects in Alberta is very uncertain. New mine projects that use paraffinic froth treatment (PFT) processing schemes eliminate the need for local upgrading (PFT can be considered a form of partial upgrading that does not generate H\(_2\)S – as it uses physical means to separate and reject low value asphaltenic crude components). Additionally, the costs for Alberta upgrading projects are relatively high due to local labour costs, climate conditions and equipment module delivery constraints. A final consideration is that the regional product demand for upgraded/refined products is already saturated by the existing capacity.

As a result of the above noted points, DeLude Consulting’s opinion is that the potential range of Alberta upgrading/refining projects is 0 to 3 new projects in the next 25 years (after completion of the NorthWest Refining Sturgeon Refinery project) with the more likely outcome being 1 new facility. Also any future upgrading facility may choose to implement new upgrading technologies that are targeted to achieve viscosity and density reductions (with minimum hydrogen use) in order to just meet pipeline transportation requirements rather than pursuing substantial sulphur removal, cracking and hydrogen addition to improve crude quality. So the quantities of H\(_2\)S produced and hydrogen required by upgrading may be significantly lower than the case today.

Taking the above considerations into account, the most likely potential range of Oil Sands industry emissions improvement through application of any new hydrogen from H\(_2\)S technology is in the order of 0 to 100 kt/year with an outside chance of achieving an emissions improvement in the range of 200 kt/year.
Some Further Observations

The cost of utilities (natural gas, power, steam, oxygen, etc) and any related CO₂ emissions can make a major difference in the resulting cost of CO₂ avoided for these technologies and also the relative tanking of these technologies. These changes in cost may also create a greater incentive for the use of a portion of the generated hydrogen for fuel even though this reduces the benefit gained SMR hydrogen replacement.

From a larger Oil Sands industry view, the potential impact of H₂ from H₂S application on CO₂ emissions is quite modest. The maximum anticipated potential improvement of 300 kt/year only represents a 0.4% reduction on current Oil Sands industry emissions which are in the order of 70 Mt/year. Other energy efficiency, production improvement and renewable energy initiatives have significantly larger potential for CO₂ emissions reductions at relatively lower technology development and operating risk.

Technology demonstration costs have not been factored into the economic analysis and may be another significant barrier to technology commercialization.
Conclusions for Working Group Consideration

- There are numerous technologies under development for H\textsubscript{2} production from H\textsubscript{2}S but none have reached demonstration scale.

- Under the optimistic ranking premises used, three technologies were identified as more promising for future development – Thermocatalytic (integrated Claus), Superadiabatic (using pure oxygen) and gliding arc tornado plasma. However, each of these technologies still face significant development hurdles in reaching a commercial scale application.

- The business case for Oil Sands application was assessed for application of H\textsubscript{2} from H\textsubscript{2}S technology in in-situ, upgrader revamp and greenfield upgrader applications with the following findings:
  
  o H\textsubscript{2} from H\textsubscript{2}S technology has very limited value to in-situ Oil Sands production, the maximum potential improvement in CO\textsubscript{2} emissions (based on COSIA SAGD reference case) is approximately 0.001%. (40 kg/day CO\textsubscript{2} reduction on 2519 t/d of CO\textsubscript{2} emissions).

  o Acid gas injection / CO\textsubscript{2} injection should likely be the preferred option for in-situ management of produced acid gases (both CO\textsubscript{2} and H\textsubscript{2}S injection back into a suitable reservoir).

  o While there is some modest potential value to an existing upgrader/refinery complex, there is probably inadequate benefit to challenge the incumbent H\textsubscript{2}S management and H\textsubscript{2} generation technologies due to reliability, cost and revamp project complexity considerations.

  o Future multiple greenfield upgrader applications could yield modest total benefits in the order of 0 to 300 kt/year in CO\textsubscript{2} avoided (compared to the baseline technologies of Claus/SCOT and SMR/PSA) at a cost below $CDN 50/t of CO\textsubscript{2} (if successful development and improvement of one of the more promising technologies is realized).

  o However, the future focus of the industry is likely to be on applying low or no hydrogen use upgrading alternatives to just meet pipeline specifications rather than producing high quality premium synthetic crude products. This would both reduce H\textsubscript{2}S generation and reduce demand for hydrogen – both negatively impacting the future potential CO\textsubscript{2} benefit that could be realized.

- Even if substantial technology improvements can be successfully pursued to achieve overall costs below the range of $CDN 50 per t of CO\textsubscript{2} avoided, there appears to be limited potential for material CO\textsubscript{2} emissions improvement for the overall Alberta Oil Sands industry. Emissions benefits will be dependent on uncertain future development of multiple hydroprocessing based greenfield upgrader projects. As a result, COSIA’s members will need to consider carefully whether acceleration of hydrogen from H\textsubscript{2}S technology development should be given future funding priority.
References

Results of T&PR International’s search and all reviewed reference articles have been compiled into a database with the following file structure:

- Baseline Technologies
- Complex chemical cycles
- Economic Information
- Electrolytic
- General Review Articles
- H2S Reforming with CH4
- Oxidative
- Photochemical
- Plasma and Microwave
- Refining and Upgrading Related References
- SAGD References
- Technology & Patent Research - Report
- Thermal and Thermal-Catalytic

Due to size (280+ MB), the full database is provided separately and is available from COSIA.

A file listing of the contents in each subdirectory is provided below:
Baseline Technologies

Name

- AER - 2017-Feb - ST50A Gas Processing Plants in Alberta.pdf
- Bachu - 2009 - Acid Gas Injection in the Alberta Basin a Commercial-Scale Analogue for CO2 Sequestration.pdf
- CETAC West - 2008 - Efficient Use of Fuel Gas in Sulphur Recovery Units.pdf
- Current Central Hydrogen Production from Natural Gas with CO2 Sequestration version 3.101.xslm
- Current Central Hydrogen Production from Natural Gas without CO2 Sequestration version 3.101.xslm
- DOE - 2003 - How to Calculate the True Cost of Steam.pdf
- DOE - 2012 - Benchmark the Fuel Cost of Steam Generation.pdf
- duPont - 2012 - SRU Solutions - DynaWave-SuperClaus Brochure.pdf
- Goo - 1994 - LARGE PLANT SULFUR RECOVERY PROCESSES STRESS EFFICIENCY.pdf
- Hopper - 2008 - World's First 10000 PSig Sour Gas Injection Compressor.pdf
- Jacobs - 2010 - Comproza Sulfur Solutions - SUPERCLAUS Process.pdf
- Jochua - 2015 - Hydrogen from SMR.pdf
- Kumar - 2014 - Large scale hydrogen production from wind energy.pdf
- Li - 2013 - Economics of Acid Gas Injection with Comparison to Sulfur Recovery in China.pdf
- Mbojdi - 2012 - Steam methane reforming reaction process intensification by using a multi-structured reactor.pdf
- Oladejo - 2016 - A Techno-Economic Assessment of Sustainable Large Scale Hydrogen Production.pdf
- Ramazani - 2001 - PROCLAUS The New Standard for Claus Performance-.pdf
- Roberts - 2011 - Cost Effectiveness of Emissions Abatement Options in European Refineries - CONCAWE.pdf
- Total E&P Canada Ltd - 2007 - Total Upgrader Project - Vol 1 - Section 3 - Project Description.pdf
- Wiechert - 1997 - Acid gas injection eliminates sulfur recovery expense.pdf
- Wenz - 2008 - ECONOMICS OF ACID GAS REINJECTION - AN INNOVATIVE CO2 STORAGE OPPORTUNITY.pdf
- WRI - 2007 - DEVELOPMENT OF A NOVEL OXYGEN SUPPLY PROCESS.pdf
Complex chemical cycles

Name

- Berrouk - 2015 - A process simulation study of hydrogen and sulfur production from hydrogen sulfide using the Fe-CI hybrid process.pdf
- de Silva Nuncio - 2010 - Study on Reaction Between H2S and Sulfuric Acid For H2 Production From a H2S Splitting Cycle.pdf
- French Patent 2972004 - Guilleu - NOUVEAU PROCEDE DE PRODUCTION DE SOUFORE ET D'HYDROGENE A PARTIR DE H2S.pdf
- French Patent 2972004 - H2 from H2S by Chemical Cycle of Metal Disulphide.pdf
- Plummer - 2006 - Chemical mechanisms in hydrogen sulfide decomposition to hydrogen and sulfur.pdf
- Yang - 2010 - THE BUNSEN REACTION IN THE PRESENCE OF ORGANIC SOLVENT IN H2S SPLITTING CYCLE.pdf

Economic Information

Name

- Ulrich - 2006 - cost indices chart.pdf

Electrolytic

Name

- Irondache - 2016 - Recovering_Hydrogen_Sulfide_from_Sulfurous_Waters_with_PEM_fuel_cells.pdf
- Mbah - 2010 - Effect of RuO2-Co3O4 on the performance of H2S electrolytic splitting system.pdf

General Review Articles

Name

- Bartels et al. - 2010 - an economic survey of hydrogen production from conventional and alternative energy sources.pdf
- Chakma - 1995 - Production of hydrogen and sulfur from hydrogen sulfide.pdf
- Dincer - 2012 - Sustainable Hydrogen production.pdf
- Jacobs Consultancy - Assessment of Innovative Applications of Electricity for Oil Sands Development - Phase 1 Report.pdf
- Lemus - 2010 - Updated Hydrogen production costs and parities for conventional and renewable technologies.pdf
- Lulnstra - 1995 - H2 from H2S.pdf
- Reever - 2016 - A review on hydrogen production from hydrogen sulphide by chemical and photochemical methods.pdf
- Technical Readiness Scale - Diagram.pdf
H₂S Reforming with CH₄

Oxidative

Photochemical
Plasma and Microwave

Name

- Argyle - 2007 - Production of hydrogen and sulfur from hydrogen sulfide in a nonthermal-plasma pulsed corona discharge reactor.pdf
- BAGAUTDINOV - 1995 - PLASMA CHEMICAL PRODUCTION OF HYDROGEN FROM H2S-CONTAINING GASES IN MCW DISCHARGE.pdf
- Chen - 2011 - Cost estimate of deNOx - Lesi oxygen generator.pdf
- Goeckner - 2002 - Aspects of Plasma Processing - A brief overview of plasma science in industry.pdf
- Gutzol - 2012 - Plasma assisted dissociation of hydrogen sulfide.pdf
- Huang - 2012 - Removal of H2S from gas stream using combined plasma photolysis technique at atmospheric pressure.pdf
- Nunnally - 2009 - Dissociation of H2S in non-equilibrium arc torch discharge.pdf
- Nunnally - 2014 - Plasma dissociation of H2S with O2 addition.pdf
- Reddy - 2012 - Production of hydrogen and sulfur from hydrogen sulfide assisted by nonthermal plasma.pdf
- Starnate - 2009 - Pilot Test and Optimization of Plasma Based DeNOx.pdf
- Subrahmanyan - 2012 - Catalytic packed bed non-thermal plasma reactor for H2 from H2S.pdf
- Subrahmanyan - 2012 - Production of hydrogen from hydrogen sulfide in a packed-bed DBD reactor.pdf
- Subrahmanyan - 2012 - Production of hydrogen from hydrogen sulfide assisted by dielectric barrier discharge.pdf
- US patent 7455828 - Selinger - PROCESS AND APPARATUS FOR CONVERSION OF H2S TO H2 and S.pdf
- US patent 9090840 - Yoon - HYDROGEN SULFIDE AND CARBONYL SULFIDE REMOVAL APPARATUS USING MICROWAVE PLASMA, AND METHOD THEREOF.pdf
- US patent 9532500 - Mercado - METHOD AND SYSTEM FOR OBTAINING SWEET GAS, SYNTHETIC GAS AND SULFUR FROM NATURAL GAS.pdf
- US patent Application 2015 0375193 - Nunnally - PLASMA DISSOCIATION OF HYDROGEN SULFIDE IN THE PRESENCE OF OXYGEN.pdf
- Westinghouse ANR- Energy - 2010 - Plasma Gasification Brochure.pdf

Refining and Upgrading Related References

Name

- Netzer - 2006 - ALBERTA BITUMEN PROCESSING INTEGRATION.pdf

SAGD References

Name

- Gates - 2012 - New thermal-reactive reservoir engineering model predicts H2S generation in Steam Assisted Gravity Drainage.pdf
- Kapadia - 2014 - On situ hydrogen sulfide evolution and catalytic scavenging in steam-based oil sands recovery processes.pdf

Technology & Patent Research - Report

Name

Thermal and Thermal-Catalytic

Name

2. Al-Shamma - 1989 - KINETIC STUDY FOR THERMAL PRODUCTION OF HYDROGEN FROM H2S BY HETEROGENEOUS CATALYSIS OF VANADIUM SULFIDE.pdf
7. Cox - 1998 - ECONOMICS OF THERMAL DISSOCIATION OF H2S TO PRODUCE H2.pdf
11. Moghimam - 2010 - Numerical study on Thermal dissociation of H2S.pdf
14. US patent 6780396 - Streicher - PROCESS FOR THE PRODUCTION OF A GAS THAT CONTAINS HYDROGEN FROM H2S.pdf
15. US patent 9242859 - Moliner - ZERO EMISSIONS SULPHUR RECOVERY PROCESS WITH CONCURRENT HYDROGEN PRODUCTION.pdf
Datafile Summary

The following powerpoint presentation files and excel worksheet data files, analysis files, ranking files and blank template files were developed as part of the contract work and are available from COSIA.

Presentations:

Name

- Results Summary session - April 27 2017 - updated results.pptx
- Results Summary session - April 27 2017 - preliminary results.pptx
- Progress Update Engagement - March 30 2017.pptx
- H2 from H2S Technology Scan - Update and Screening criteria proposal - Feb 23 2017 rev1.pptx
- H2 from H2S Technology Scan - Search Summary and Update - March 16 2017.pptx
- H2 from H2S Technology Scan - Kick-off Meeting Feb 2 2017.pptx

Technology data:

Name

- Summary of costing data for key technologies rev 2 - improved cases.xlsx
- Summary of costing data for key technologies rev 2.xlsx
- Summary of costing data for key technologies rev 3 - improved cases.xlsx
- Summary of costing data for key technologies rev 3.xlsx
Economic analysis files:

Name

- DBD economics of CO2 avoided improved rev1.xlsx
- DBD economics of CO2 avoided improved rev2 final.xlsx
- FeCL - economics of CO2 avoided improved rev1.xlsx
- FeCL - economics of CO2 avoided improved rev2 final.xlsx
- FeCL - economics of CO2 avoided rev1.xlsx
- FeCL - economics of CO2 avoided rev2 final.xlsx
- FeS2 - economics of CO2 avoided - improved rev1.xlsx
- FeS2 - economics of CO2 avoided - improved rev2 final.xlsx
- FeS2 - economics of CO2 avoided rev1.xlsx
- FeS2 - economics of CO2 avoided rev2 final.xlsx
- Gliding Arc - economics of CO2 avoided improved rev 1.xlsx
- Gliding Arc - economics of CO2 avoided improved rev 2 final.xlsx
- Gliding Arc - economics of CO2 avoided rev 1.xlsx
- Gliding Arc - economics of CO2 avoided rev 2 final.xlsx
- SuperAdiabatic - economics of CO2 avoided improved rev 1.xlsx
- SuperAdiabatic - economics of CO2 avoided improved rev 2 final.xlsx
- SuperAdiabatic - economics of CO2 avoided rev 1.xlsx
- SuperAdiabatic - economics of CO2 avoided rev 2 final.xlsx
- Thermal Catalytic - economics of CO2 avoided improved rev1.xlsx
- Thermal Catalytic - economics of CO2 avoided improved rev2 final.xlsx
- Thermal Catalytic - economics of CO2 avoided rev1.xlsx
- Thermal Catalytic - economics of CO2 avoided rev2 final.xlsx

Technology ranking summary:

Name

- Screening Criteria for H2 from H2S final summary.xlsx
- Screening Criteria for H2 from H2S technology Scan - draft summary - new scoring.xlsx

Blank Template files:

Name

- economics of CO2 avoided - template.xlsx
- Screening Criteria Template - Rev 5.xlsx