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Integrating the benefits of turquoise hydrogen to decarbonise high-emission industry

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Total indirect greenhouse gas (GHG) emissions from oil and gas operations today are around 5,200 Mt of carbon dioxide equivalent (CO2-eq) yearly, 15% of total energy sector GHG emissions. Most of these emissions occur due to natural gas leaks. Methane, a much more potent GHG than CO2, is the most significant single component of natural gas and, therefore, of these emissions. Part of these emissions results from routine operations such as flaring and venting, representing both an economic and an environmental issue. Many solutions have been developed to recover and use this natural gas instead of venting and flaring it. Three possibilities were simulated with AVEVA PRO/II, and a preliminary economic assessment was carried out with Guthrie’s method. 30 kmol/hr of natural gas fed was assumed, according to average site data, therefore, small-scale plants are suitable. A first solution based on compression, though requiring high OPEX (> 280 k$/y), produces very low emissions yearly (1,140 t CO2-eq/y). Another possibility is to couple flaring to a microturbine for energy generation, but this solution is both uneconomical and has a high environmental impact (> 10,000 t CO2-eq/y). The last technology analysed is thermal methane pyrolysis. This possibility, often disregarded in environmental studies, involves the production of turquoise hydrogen and carbon black. Although characterised by high capital costs (almost 3 M$), it can reduce gaseous emissions since it stores the carbon part of hydrocarbons in the solid matrix that is formed.

* 1. Introduction

The transition to a net zero-carbon economy requires producing renewable fuels and chemicals from hydropower, solar, and wind (Maporti et al., 2022; Mion et al., 2022). Canada is in a position to become a world leader of green and blue hydrogen production with its abundant supply of fresh water and hydropower, which has one of the world's lowest carbon footprints at 0.5 kgCO2-eq/MWh in 2019 (Hydro Québec, 2020).

On the other hand, Canada is among the world’s leading oil and gas producers. Canada’s oil reserves are mainly found in Alberta and Saskatchewan provinces, over an area of 142,000 km2 (Katta et al., 2019). The industry contributes heavily to GHG emissions due to the flaring and venting of the associated solution gas. Flaring and venting increase greenhouse gases (GHG) in the atmosphere, with a consequent increase in the average temperatures (Buzcu-Guven & Harriss, 2012). Even though significant improvements were made recently, in 2020, a total of 620 Mt of CO2-equivalent were released in Canada, and particularly venting emissions contributed to a total of 11 Mt of CO2-equivalent, which represents 1.7 % of the total GHG emissions of Canada in 2020 (Environment and Climate Change Canada, 2022). In Alberta and Saskatchewan, the overall volumes are large: in 2020, 866 Mm3 of gas was flared, and 347 Mm3 was vented in Alberta (Alberta Energy Regulator, 2021), while in Saskatchewan, in 2019, 572 Mm3 of gas was flared, and 465 Mm3 was vented (Emery et al., 2020).

Canadian oil extraction is a key sector for clean technology development. Restrictions and tight regulations have been introduced in the last decades, such as the carbon tax, first introduced in 2018 (Government of Canada, 2022). Many solutions have been developed to either trap or convert natural gas, mainly into hydrogen, instead of venting and flaring it. In the framework of a world that still depends very much on the consumption of fossil fuels, H2 is likely to play a key role in the transition from a fossil fuel economy to a sustainable fuel economy of the future (Abánades et al., 2011).

* 1. Methods

In general, many technologies can be applied to capture or convert associated gas at upstream oil and gas sites. In this paper, three possibilities are discussed. For each, a brief framework of the technology will be provided, along with an economic and environmental assessment. AVEVA PRO/II was used to solve energy and mass balances. The Peng-Robinson equation of state calculated the physical properties of the substances interacting in the process.

The equipment cost was evaluated using Guthrie’s method (Turton et al., 2009). The main assumption introduced is that all these possibilities are intended to be continuous, therefore operative 8760 h/y. The Chemical Engineering Plant Cost Index for 2021, considered a reference, is 699.97. OPEX was evaluated considering one operator for each technology, expenses for energy consumption and a remaining 5 % of the overall CAPEX for additional expenses. The prices of the utilities and the products involved in these technologies are reported in Table 1.

Table 1: Prices of the main consumables and products involved.

|  |  |  |
| --- | --- | --- |
| Consumable/product | Price | Reference |
| Natural gas | 2.6 $/MMBtu | Trading Economics, 2023 |
| Carbon black | 586.74 $/t | YCharts, 2023 |
| Electricity | 0.094 $/kWh | Global Petrol Prices, 2022 |
| Turquoise H2 | 2 $/kg | Bulletin of the Atomic Scientists, 2022 |

The metric considered for environmental impact is carbon intensity, i.e. how much carbon dioxide emissions the specific technology produces. CO2 emissions not only represent an environmental issue, but it has an impact on the economics of the process provided that Canada has raised the federal carbon tax to 50 $/tof CO2 as of April 1st, 2022 (Government of Canada, 2022).

For what concerns natural gas feed inlet, this was set by considering the average volume of gas in m3 either flared or vented daily in Alberta (Alberta Energy Regulator, 2021), corresponding to 30 kmol/h. Its temperature was set equal to 130 °C and its pressure to 1 bar, which, according to field operators, are the average conditions at which the gas exits from the three-phase separator at the extraction site. Last, the composition of natural gas was set according to the Albertian average (Kidnay & Parrish, 2006) (Table 2).

Table 2: Average natural gas composition in the Alberta province (Kidnay & Parrish, 2006).

|  |  |
| --- | --- |
| Compound | Molar fraction [% mol] |
| *Hydrocarbons* |  |
| Methane (CH4) | 80.4 |
| Ethane (C2H6) | 6.6 |
| Propane (C3H8) | 3.1 |
| C4 (n-Butane and iso-Butane) | 2 |
| C5+ | 3 |
| *Non-Hydrocarbons* |  |
| N2 | 3.2 |
| CO2 | 1.7 |

* + 1. Compression

The process of compressing or liquefying natural gas is widely used. It can be achieved using various types of compressors, such as flooded rotary screws, rotary sliding vane, and reciprocating piston compressors (Emery et al., 2020). This possibility helps reduce emissions and generate a saleable product. At the same time, if accessible pipelines to distribute the gas are lacking, finding a use for the compressed gas becomes an actual challenge. Also, the energy costs involved are high. When compressed, natural gas can be employed in a variety of modified engines for different purposes. Also, from a cost point of view, compressed natural gas does not require expensive cryogenic facilities, and the technology is flexible in terms of end users’ locations and natural gas demands (Emery et al., 2020). A standard stainless-steel centrifugal compressor is considered here (Galli et al., 2021), and the pressure is increased from atmospheric conditions to 60 bar. Given the high-pressure ratio, 4 stages were considered (Turton et al., 2009).

* + 1. Gas-to-power technologies: flaring coupled to a microturbine

In gas-to-power technologies, CH4 is combusted and converted to CO2 and H2O in the first step. As such, it will have lower GHG compared to venting. Anyway, this is mostly the same compared to the flaring case. Still, the energy is not wasted in this case but is recovered and transformed into electricity. In addition to reducing emissions, power generation can be more environmentally friendly if it replaces another fossil fuel used to provide power to a site. For example, generating power on-site using associated gas can result in lower emissions than using less-efficient fuel sources like coal in an electrical grid (Emery et al., 2020). Microturbines are increasingly used for small-scale power generation applications because of their compact size and minimal number of moving parts. A microturbine consists of a compressor, a mixing chamber, and an expander. Fuel is compressed and burned in a furnace at 1300°C, modelled as a Gibbs reactor in AVEVA PRO/II. This pressurised gas flow then expands in a turbine, connected to a power generator, that produces shaft work used to drive the compressor (Emery et al., 2020). Typically, a minimum gas pressure of 3-4 bar is required. Here, a compressor discharge pressure of 5 bar was considered.

* + 1. Methane pyrolysis as an alternative to steam methane reforming reaction

The most applied solution to obtain H2 worldwide is steam methane reforming (SMR), which amounts to approximately 48% of the global H2 demand (Sánchez-Bastardo et al., 2020). SMR allows the production of the so-called grey H2. One main issue connected with this H2 production is that CO2 is also produced. In particular, the reaction produces 38.5 grams of CO2 per theoretical MJ of energy from hydrogen combustion, which is then usually vented into the atmosphere (Muradov & Veziroǧlu, 2005).

An alternative solution is outfitting the plant with Carbon Capture and Storage (CCS) technologies to mitigate the emissions. In this way, the so-called blue H2 is produced. A recent study suggests that SMR in the best-case scenario, i.e., using renewable electricity instead of natural gas to power the processes and capturing CO2 afterwards, still causes high GHG emissions, mainly due to the release of fugitive CH4 (Howarth & Jacobson, 2021). Assuming a 3.5 % methane emission rate from natural gas and a 20-years global warming potential, total CO2-equivalent emissions for blue hydrogen are only 9 to 12 times less than for grey hydrogen (Howarth & Jacobson, 2021).

In this context, decarbonising fossil fuels by recovering and sequestering solid carbon instead of gaseous CO2 can be a suitable alternative (Muradov & Veziroǧlu, 2008). This possibility involves the production of turquoise hydrogen, i.e. hydrogen made from the pyrolysis of methane at high temperatures (Diab et al., 2022). The reaction consists of the decomposition of CH4 into its components, H2 and solid carbon. By doing so, gas-phase carbon (CO2) formation is prevented (Sánchez-Bastardo et al., 2021). The CO2 footprint of methane pyrolysis corresponds to the emissions derived from the required electricity and those generated during the extraction and transportation of natural gas. Anyhow, theoretically, there are none during the process itself. In any case, the CO2 emissions corresponding to methane pyrolysis are significantly lower than those derived from well-established fossil fuel-based technologies (Sánchez-Bastardo et al., 2021). However, technical and economic barriers to scaling remain (European Commission, 2020).

Thermal methane pyrolysis was considered to avoid all the issues related to using a catalyst (i.e., coking issues and subsequent decoking operations that cause CO2 formation). First, the feed is split into two parts: one part is burnt in a furnace to energetically sustain the reaction, while the other proceeds into the plant and enters the reactor, where pyrolysis occurs. Flue gases exiting from the furnace preheat the feed to the reactor. An energy transfer efficiency (*η*) of 60 % was considered for the furnace (Pfeifer, 2017). The furnace and the reactor are modelled as Gibbs reactors in AVEVA PRO/II. A temperature of 1000°C in the reactor was set to guarantee an adequate CH4 conversion higher than 90 %. Two phases are expected out of the reactor: a solid one, made of carbon, and a gas one, mainly composed of H2. The solid phase is considered to be carbon black. This allows setting a more conservative hypothesis from an economic point of view since carbon black has the lowest commercial price among the various types of carbon (i.e., graphite, nanotubes, etc.). For the economic analysis, the CH4 furnace was assimilated as a fired heater, while, for the reactor, a preliminary volume was considered by using the volumetric flow rate and a hypothetical residence time of 15 seconds.

* 1. Results and discussion

The main results for each technology are reported in Table 3. The economic potential, which is to be considered a preliminary indicator for economic screening, was calculated by subtracting from the theoretical revenues one-third of the CAPEX, the OPEX and the carbon tax (Turton et al., 2009).

Table 3: Main economic and environmental results for each alternative.

|  |  |  |  |
| --- | --- | --- | --- |
|  | Compression | Flaring + microturbine | Pyrolysis |
| Main product | Compressed natural gas | Electricity | H2 + carbon black |
| Theoretical revenues [$/y] | 541,900 | 436,423 | 3,760,310 |
| CAPEX [$] | 282,136 | 749,990 | 1,168,774 |
| OPEX [$/y] | 280,295 | 131,454 | 319,558 |
| CO2-eq emissions [tCO2-eq/y] | 1,147 | 11,560 | 2,451 |
| Carbon tax [$/y] | 57,350 | 578,000 | 122,550 |
| Economic potential [$/y] | 110,209 | -523,027 | 2,928,610 |

The results in Table 3 show how different the three possibilities are in terms of profitability and environmental impact. As for these numbers, the flaring coupled with the microturbine is the worst alternative. The main issue here is related to the fact that the natural gas feed is burnt completely, causing very high CO2 emissions that also have an impact on the economic potential through the carbon tax. This results in a heavily negative economic potential (Figure 1). This underlines why flaring is usually exploited alone at extraction sites since it is apparently uneconomical once coupled with other strategies.

For what concerns compression, this is one of the best possibilities from both economic and environmental points of view, but only if an appropriate pipeline network is present. Multi-stage compression is needed, but this is simpler to achieve than other solutions. As reported earlier, issues may arise if a pipeline network is not present and able to guarantee an appropriate gas distribution. If this is the case, the overall profitability of the technology is intended to change.

Last, methane pyrolysis presents CAPEX much higher than the other two possibilities. This happens because the installation of a whole process is required rather than just single-unit operations. Still, the process allows to transform natural gas into more valued chemicals, therefore, the economic potential is positive. Pyrolysis looks both profitable and almost carbon-free. In fact, the carbon part of the hydrocarbons is stored within the solid product, which is safe and easy to handle. Anyway, in this case, there is also the need for pipelines to recover and transport produced H2. If this is not the case, the overall profitability of the process can be questioned. The results are summarised in Figure 1.

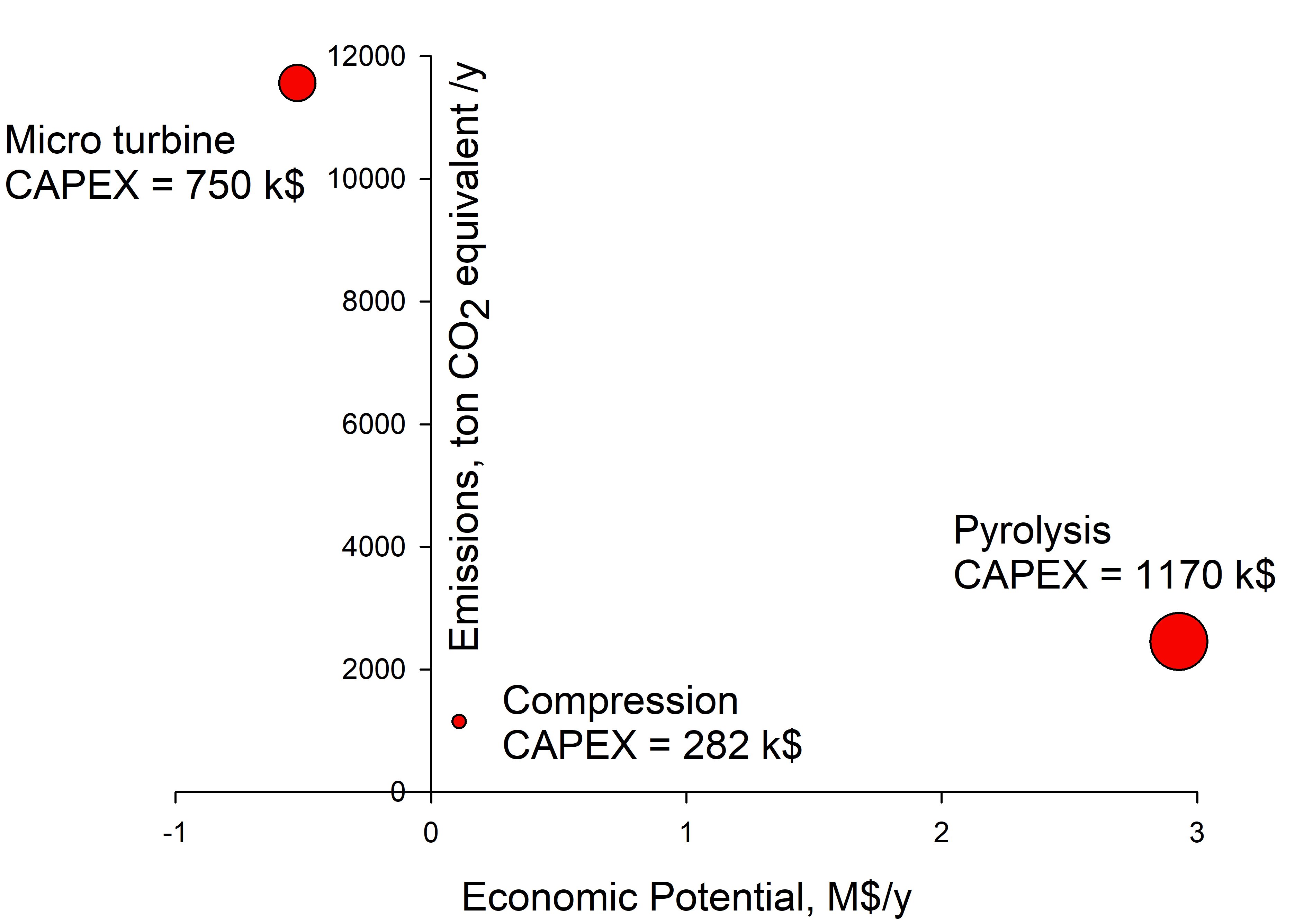


Figure 1: Comparison of the three technologies: Economic potential versus emissions. The size of the symbol is proportional to the CAPEX.

* 1. Conclusions

In the context of a high-emissions industry like oil extraction, it is urgent to find a solution to standard practices such as flaring and venting. In Canada, where these two activities are widely used to dispose of the gas that naturally flows out of the extraction site. This paper discussed three solutions to the problem: compression, flaring coupled to the microturbine, and methane pyrolysis.

The microturbine as developed here is not a feasible solution both from an economic and environmental perspective. In fact, it is characterised by very high CAPEX (750 k$) and GHG emissions (more than 10,000 t/y of CO2 released). One possibility to improve the situation would be to equip the unit with CCS. This would impact the overall costs, but the environmental impact would benefit from that.

Compression has the lowest CAPEX (about 282 k$) and the lowest annual emissions (1,147 t/y). The main possible issue is related to the need for a pipeline network to guarantee the correct supply of this gas to industrial and residential zones.

Methane pyrolysis, the last possibility analysed, is by far the most promising: although it has very high CAPEX (> 1 M$), it presents a very high economic potential (almost 3 M$/y), alongside reduced yearly emissions (2,400 t/y of CO2 emitted). Turquoise H2 is a concrete possibility to help reduce emissions at extraction sites.

It is important to underline that these numbers only represent estimates, which is useful for preliminary considerations. Economic indices would be a better tool for making a proper economic assessment. These numbers are a good starting point for further considerations to avoid flaring and venting. Future work will address methane pyrolysis in more detail through process simulation and techno-economic assessment.

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References

Abánades, A., Ruiz, E., Ferruelo, E. M., Hernández, F., Cabanillas, A., Martínez-Val, J. M., Rubio, J. A., López, C., Gavela, R., Barrera, G., Rubbia, C., Salmieri, D., Rodilla, E., & Gutiérrez, D. (2011). Experimental analysis of direct thermal methane cracking. International Journal of Hydrogen Energy, 36(20), 12877–12886. https://doi.org/10.1016/j.ijhydene.2011.07.081

Alberta Energy Regulator. (2021). Upstream Petroleum Industry Emissions Report - Industry Performance for Year Ending December 31, 2020. www.aer.ca

Bulletin of the Atomic Scientists. (2022). *Price of turquoise H2*. https://thebulletin.org/2022/01/whether-green-blue-or-turquoise-hydrogen-needs-to-be-clean-and-cheap/#:~:text=The%20projected%20price%20of%20turquoise,Blue%20hydrogen.

Buzcu-Guven, B., & Harriss, R. (2012, February). Extent, impacts and remedies of global gas flaring and venting. Carbon Management, 3(1), 95–108. https://doi.org/10.4155/cmt.11.81

Diab, J., Fulcheri, L., Hessel, V., Rohani, V., & Frenklach, M. (2022). Why turquoise hydrogen will be a game changer for the energy transition. International Journal of Hydrogen Energy, 47(61), 25831-25848. https://doi.org/10.1016/j.ijhydene.2022.05.299

Emery, E., Luo, P., & Pattison, D. (2020). Final Report - Potential Technologies to Capture and Utilize Associated Gas at Upstream Oil and Gas Sites in the Duvernay and Viking Petroleum Systems.

Environment and Climate Change Canada. (2022). NATIONAL INVENTORY REPORT 1990-2020: GREENHOUSE GAS SOURCES AND SINKS IN CANADA.

European Commission. (2020). A hydrogen strategy for a climate-neutral Europe.

Galli, F., Lai, J.-J., de Tommaso, J., Pauletto, G., & S.Patience, G. (2021). Gas to Liquids Techno-Economics of Associated Natural Gas, Bio Gas, and Landfill Gas. Processes, 1–15.

Global Petrol Prices. (2022). *Canada Electricity Prices*. https://www.globalpetrolprices.com/Canada/electricity\_prices/#:~:text=Canada%2C%20June%202022%3A%20The%20price,of%20power%2C%20distribution%20and%20taxes.

Government of Canada. (2022). How carbon pricing works. https://www.canada.ca/en/environment-climate-change/services/climate-change/pricing-pollution-how-it-will-work/carbon-pollution-pricing-federal-benchmark-information.html

Howarth, R. W., & Jacobson, M. Z. (2021). How green is blue hydrogen? Energy Science and Engineering, 9(10), 1676–1687. https://doi.org/10.1002/ese3.956

Hydro Québec. (2020). Hydro-Québec’s electricity facts: CO2 emissions and Hydro-Québec Electricity, 1990-2020. www.hydroquebec.com

Katta, A. K., Davis, M., Subramanyam, V., Dar, A. F., Mondal, M. A. H., Ahiduzzaman, M., & Kumar, A. (2019). Assessment of energy demand-based greenhouse gas mitigation options for Canada’s oil sands. Journal of Cleaner Production, 241, 118306. https://doi.org/10.1016/j.jclepro.2019.118306

Kidnay, A. J., & Parrish, W. R. (2006). Fundamentals of Natural Gas Processing. CRC Press, Boca Raton.

Maporti, D., Nardi, R., Guffanti, S., Vianello, C., Mocellin, P., & Pauletto, G. (2022). Techno-economic analysis of electrified biogas reforming. Chemical Engineering Transactions, 96, 163-168. doi:10.3303/CET2296028

Mion, A., Galli, F., Mocellin, P., Guffanti, S. & Pauletto, G. (2022). Electrified methane reforming decarbonises methanol synthesis. Journal of CO2 Utilization, 58, 101911. https://doi.org/10.1016/j.jcou.2022.101911

Muradov, N. Z., & Veziroǧlu, T. N. (2005). From hydrocarbon to hydrogen-carbon to hydrogen economy. International Journal of Hydrogen Energy, 30(3), 225–237. https://doi.org/10.1016/j.ijhydene.2004.03.033

Muradov, N. Z., & Veziroǧlu, T. N. (2008). “Green” path from fossil-based to hydrogen economy: An overview of carbon-neutral technologies. International Journal of Hydrogen Energy, 33(23), 6804–6839. https://doi.org/10.1016/j.ijhydene.2008.08.054

Ozalp, N., Ibrik, K., & Al-Meer, M. (2013). Kinetics and heat transfer analysis of carbon catalyzed solar cracking process. Energy, 55, 74–81. https://doi.org/10.1016/j.energy.2013.02.022

Pfeifer, H. (2017). Industrial Furnaces-Status and Research Challenges. Energy Procedia, 120, 28–40. https://doi.org/10.1016/j.egypro.2017.07.153

Sánchez-Bastardo, N., Schlögl, R., & Ruland, H. (2020). Methane Pyrolysis for CO2-Free H2 Production: A Green Process to Overcome Renewable Energies Unsteadiness. Chemie-Ingenieur-Technik, 92(10), 1596–1609. https://doi.org/10.1002/cite.202000029

Sánchez-Bastardo, N., Schlögl, R., & Ruland, H. (2021). Methane Pyrolysis for Zero-Emission Hydrogen Production: A Potential Bridge Technology from Fossil Fuels to a Renewable and Sustainable Hydrogen Economy. Industrial and Engineering Chemistry Research, 60(32), 11855–11881. https://doi.org/10.1021/acs.iecr.1c01679

Sinnot, R., & Towler, G. “Chapter 10: Transport and Storage of materials”. Chemical Engineering Design, 6th edition, Butterworth-Heinemann (2020), pp. 275-290, 340-347, 372-395, 776-784.

Trading Economics. (2023). *Price of natural gas*. https://tradingeconomics.com/commodity/natural-gas

Turton, R., Bailie, R. C., Whiting, W. B., Shaeiwitz, J. A. “Chapter 7: Estimation of Capital Costs”, “Appendix A: Cost Equations and Curves for the CAPCOST program”. Analysis, Synthesis and Design of Chemical Processes, 3rd edition, Prentice Hall (2009), pp. 177- 209, 923-954, 1283-1309.

YCharts. (2023). *Price of carbon black*. https://ycharts.com/indicators/us\_producer\_price\_index\_chemicals\_and\_allied\_products\_carbon\_black