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Identifying Commercial Opportunities for the Reverse Water Gas Shift Reaction

*R. Matthew Bown, Miriam Joyce, Qi Zhang, Tomas Ramirez Reina, and Melis S. Duyar**

The reverse water gas shift (RWGS) reaction is a promising technology for introducing carbon dioxide as feedstock to the broader chemical industry through syngas production. While this reaction has attracted significant attention recently for catalyst and process development, there is a need to quantify the net CO_2 consumption of RWGS schemes, while taking into account parameters such as thermodynamics, alongside technoeconomic constraints for feasible process development. Also of particular importance is the consideration of the cost and carbon footprint of hydrogen production. Herein, research needs to enable net carbon-consuming, economically feasible RWGS processes are identified. By considering the scenarios of hydrogen with varying carbon footprints (gray, blue, and green) as well as analyzing the sensitivity to process heating method, it is proposed that the biggest enabling development for RWGS commercial implementation as a CO_2 utilization technology will be the availability of low-cost and low-carbon sources of hydrogen. RWGS catalyst improvements alone will not be sufficient for economic feasibility but are necessary given the prospect of dropping hydrogen prices.

1. Introduction

Climate change is an issue that is central to global prosperity and sustainable development. As a consequence of rising carbon dioxide (CO_2) concentration in the atmosphere (now at 416 ppm), global temperatures have risen by 0.2°C on average per decade.[1] This is leading to negative economic, social, and environmental impacts such as more frequent extreme weather events, harsher climates, rapid melting of sea ice, and ocean acidification, which are on a dangerous pathway to becoming more pronounced.[2] The UK government is the first to commit to becoming carbon neutral by 2050 and to meet this target,[3] methods will need to be implemented to remove CO_2 from the atmosphere or prevent emissions from being released.

Efficient methods to recycle CO_2 can have far reaching benefits such as creation of a lower net emission chemical industry as well as the replacement of traditionally fossil fuel based processes altogether.[4–6] However, CO_2 capture and utilization schemes often face criticism related to their efficiency, economic feasibility and emissions reduction potential.[7] Hence, there is a need in the field to frame CO_2 utilization schemes within context of the broader energy system to identify opportunities for carbon consuming and economically feasible processes.[8–10] The catalytic RWGS reaction, which converts CO_2 into carbon monoxide and water using hydrogen (Equation (1)), is investigated as a process for generating carbon monoxide (CO) or syngas ($CO + H_2$) and significant progress is being made towards scalable RWGS processes.[11]

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \Delta H^o_{298K} = +41\,\text{kJ mol}^{-1} \tag{1}$$

(Standard formation enthalpies (Equations (1) and (2)) calculated from NASA database.[12])

The CO product from RWGS can be used directly as industrial reagent (for carbonylation reactions).[13,14] Alternatively, a mixture of CO and H_2 can be obtained either through post reaction mixing, or by using an initially high H_2/CO_2 ratio in the reactor (excess of stoichiometric) to produce synthesis gas, or "syngas." Commercial processes for converting syngas to methanol and long chain hydrocarbons through Fischer–Tropsch synthesis (FTS) are mature technologies,[15,16] which makes RWGS an attractive platform to feed CO_2 as C1 building block for the chemical industry. Therefore, RWGS catalysts are being explored to develop a commercially viable pathway to recycle carbon.

Normally, an effective catalyst for RWGS reaction should consist of an active metal and metal-oxide support that participate in the reaction steps.[17] Pt, Pd, Rh, Ru, Au, Fe, Mo, Cu, Co, Ni based catalysts typically supported on metal oxides have been shown to catalyze RWGS.[11,18–48] Among these active metals, the first five are noble metals, they are generally popular in CO_2 utilization reaction because of their high hydrogenation activity.[20,24,28–31,33,39,41] However, the high cost hinders the large-scale industry application. In this sense, Cu and Ni are

R. M. Bown, M. Joyce, Q. Zhang, T. R. Reina, M. S. Duyar
Department of Chemical and Process Engineering
University of Surrey
Guildford GU2 7XH, UK
E-mail: m.duyar@surrey.ac.uk

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promising active metals for RWGS due to their comparatively low price and high activity and selectivity.[18,22,24–27,37,38,46] However, both Cu-oxide and Ni-oxide catalysts have tendencies to deactivate in RWGS because of the aggregation of supported copper/nickel particles at high temperatures.[26] Current research on RWGS catalyst development hence is focused on overcoming these problems for Cu or Ni catalysts, as well as pursuing the development of other active metal based catalysts (such as Mo, Co, and Fe) for this reaction.[32,46] The methanation reaction (Equation (2)) competes with RWGS under CO_2 hydrogenation conditions and in developing catalysts for RWGS, it is necessary to identify key areas of improvement while carefully considering thermodynamic constraints

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \qquad \Delta H^{o}_{298K} = -165\,\text{kJ}\,\text{mol}^{-1} \tag{2}$$

As can be seen from Equation (2), CO_2 methanation is an exothermic reaction. Theoretically, the optimal operating window for CO_2 methanation is at low temperatures, where the conversion of CO_2 and CH_4 selectivity can reach close to 100%. Hence, the typical temperature range of CO_2 methanation is 200–500 °C. On the contrary, the RWGS process is thermodynamically favorable at high temperature due to its endothermic nature, and increasing the temperature above 500 °C is favorable for the RWGS reaction.[49] Sometimes, suitable use of catalysts will result in increasing RWGS reaction and suppressing CO_2 methanation. For example, Zhang et al. explored the CO_2 hydrogenation reaction over Ni/Al_2O_3 catalysts with varied Ni loading and they found that lower nickel loading promoted RWGS reaction while methanation of CO_2 dominated at higher nickel loading.[50] Process simulation can offer insight into the optimization of new RWGS catalysts based on end use of the products.

Prior investigations on the feasibility of RWGS have explored the application of this reaction to specific scenarios using techno-economic analysis methods. For example, one such analysis focuses on evaluating RWGS in the context of biogas conversion to methanol, investigating the effects of catalyst choice on the performance of direct and indirect processes for methanol synthesis.[51] Techno-economic analysis has also been used to evaluate the net production cost variation for a RWGS + FTS process.[52] A similar approach has been carried out to compare RWGS with other syngas production schemes such as dry reforming of methane,[53] and to compare RWGS economics for different scenarios using varying sources of flue gas.[54] While such investigations are informative, their insight is tailored to individual scenarios and present only an economic perspective for motivating research and process development needs. An important research gap exists in quantifying the net CO_2 consumption potential of the RWGS process, and evaluating the process design opportunities, by bringing together both thermodynamic and techno-economic considerations. This gap is highlighted in recent articles focusing on the RWGS reaction; for example, a recent perspective on RWGS identifies the need for weighing the thermodynamic benefits of co-feeding excess hydrogen, against process cost changes.[55] It has also been indicated by other researchers that indirect methanol synthesis from CO_2 via a RWGS route can only be feasible using solar energy,[56] and this statement demonstrates the need to conduct sensitivity analyses focusing on the energy source for both hydrogen production and process heating when discussing feasibility of the RWGS reaction. Our present analysis addresses these research gaps by presenting a combined thermodynamic, techno-economic and carbon footprint perspective, to motivate further research needs in RWGS catalyst and process development.

Currently, RWGS is not practiced on an industrial scale, due to both economic and supply chain considerations which need to be identified and overcome to use this reaction as a carbon sink.[57] In this perspective, we investigated the profitability of this reaction for the two likely scenarios of CO and syngas production for downstream chemical synthesis. As the overall aim of the RWGS reaction is to reduce CO_2 emissions we further explore conditions for achieving a net reduction in CO_2 in the RWGS reactor. To determine the net reduction in CO_2 carbon footprint of hydrogen production and reactor heating must be accounted for. Three methods of H_2 production are of interest for the near- and long-term use of RWGS: The so-called grey H_2 is derived from a fossil-fuel source and accounts for 96% of current global hydrogen production.[58] Blue H_2 can be obtained by implementing CO_2 capture in a hydrogen production process from a fossil-fuel source, and green H_2 is obtained from renewable sources.[59] Herein, we focus on representative grey, blue, and green sources of hydrogen to determine the most suitable source based on availability, cost and associated carbon footprint. In reality, it is likely that near-term hydrogen production will not be driven by a single source of energy, but rather a hydrogen mix will be available which can gradually be dominated by green hydrogen as price of electrolysis decreases and grid penetration of renewable electricity increases.[15,58,60] Hence, our analysis is aimed at identifying the point of carbon neutrality for the RWGS reaction, based on the carbon content of hydrogen production and operating conditions for the RWGS reactor. We expand our analysis to process economics for the likely scenarios of CO and syngas production for downstream chemical synthesis. This allows us to identify the carbon footprint and price of hydrogen needed to enable net CO_2 consuming, economically feasible RWGS processes for commercial implementation.

2. The Implications of Thermodynamics on Catalyst Design

The H_2:CO_2 ratio is significant in determining the overall conversion and product selectivity of the reaction. While the stoichiometric H_2:CO_2 ratio is 1:1, using excess H_2 can be a viable way of achieving higher conversions, if the downstream application requires a CO/H_2 mixture and no additional separation is needed. Since probable scenarios of end use of the CO (such as methanol or FT synthesis) will require mixing it with H_2, adjusting H_2:CO_2 ratio provides a means of achieving increased yields. **Figure 1** displays the equilibrium CO_2 conversion and CO selectivity for H_2:CO_2 ratios ranging from 1:1 to 8:1. The positive influence of increasing H_2:CO_2 ratio on conversion can be seen in Figure 1A. The CO_2 conversion increases with the increased H_2:CO_2 inlet gas ratio. For the trend of each single line in this figure, the equilibrium CO_2 conversion drops during low temperature range (400–600 °C) and increases during high temperature range (600–750 °C). This is because CO_2 methanation is the dominant reaction that contributes to the CO_2 conversion

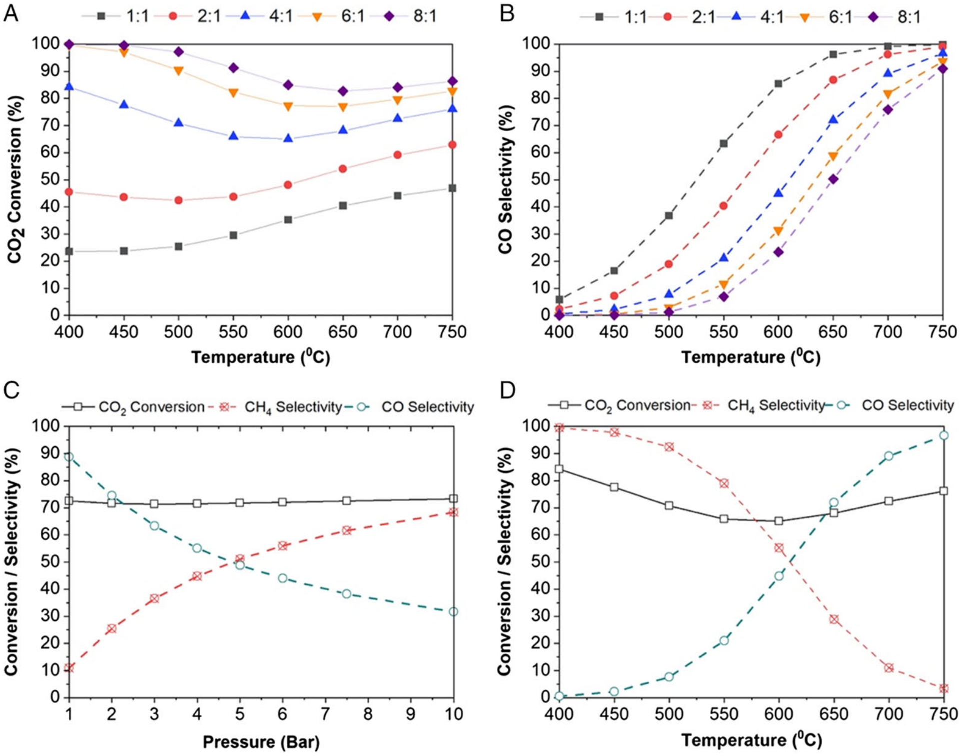

Figure 1. A) Equilibrium CO_2 conversion and B) CO selectivity for the RWGS reaction at 1.013 bar and varying H_2:CO_2 ratios. C) The effect of pressure on equilibrium CO_2 conversion, CH_4 selectivity, and CO selectivity for RWGS using an H_2:CO_2 ratio of 4:1 and temperature of 700°C. D) The effect of temperature on equilibrium CO_2 conversion, CH_4 selectivity, and CO selectivity for RWGS using an H_2:CO_2 ratio of 4:1 and a pressure of 1.01 bar.

during 400–600 °C. As an exothermic reaction, CO_2 methanation is favored at lower temperatures, hence the CO_2 conversion drops as the temperature rises. When the temperature further increases to 600 °C and above, the RWGS reaction is more pronounced so the CO_2 conversion increases as well as the CO selectivity (Figure 1B). This trend can be seen more clearly in high H_2:CO_2 ratios inlet (4:1, 6:1, 8:1) simulation because the competing CO_2 methanation reaction requires a higher H_2:CO_2 ratio than RWGS. For the same reason, equilibrium CO selectivity drops as a result of increasing the H_2:CO_2 ratio (Figure 1B).

From these results it becomes apparent that it is possible to increase the H_2:CO_2 ratio to achieve higher conversions of CO_2, if a catalyst is used that can suppress the methanation reaction (such as 2.5% Ni/Al_2O_3 at low temperatures[50]). Figure 1C,D display variation of conversion and selectivity with pressure and temperature, respectively, for a H_2:CO_2 ratio of 4:1. This ratio was chosen because at high conversions of CO_2 to CO, it will lead to a syngas composition that is typical for industrial methanol synthesis.[16] The selectivity of CO and CH_4 is heavily dependent on pressure (Figure 1C), with higher pressures favoring methanation over RWGS due to the decrease in number of moles of gas upon methanation (Le Chatelier principle). This conclusion has also been confirmed in some experiments. The hydrogenation of CO_2 on Fe/13X catalysts was investigated at ambient and elevated pressures (5–15 bar) by Franken et al. CO is the main reaction product at low pressures of 1 and 5 bar. With increasing pressure, the selectivity toward CH_4 products increases significantly.[61] Hence, operation at atmospheric pressure (1.01 bar) will decrease capital and operating costs while favoring the RWGS reaction. Figure 1D shows that the exothermic methanation reaction is thermodynamically favored at low temperatures while the endothermic RWGS reaction becomes favorable above 600 °C. Hence, we can use thermodynamic analysis to identify optimal conditions for operating at equilibrium for a given downstream application. Suggested conditions of operation for CO production as well as syngas for methanol synthesis and FTS are presented in Table S1, Supporting Information.

This thermodynamic analysis has significant implications on catalyst development research. If a selective catalyst for RWGS that suppresses methanation is used, it is possible to operate at lower temperatures while sacrificing the single pass conversion.[18] Indeed, experimentally, the addition of alkali metals in catalysts has been proved to be an effective way to improve CO selectivity in low temperature range. In our previous work, we demonstrated that Cs-promoted Mo_2C catalyst reaches 100% CO selectivity during 400–500 °C range which makes this catalyst a promising system for the integration of RWGS and syngas gas upgrading unit which typically runs at lower temperatures than the shift reactor.[62] The Na and K have also been shown to be efficient promoters that can improve the CO selectivity of WC for the RWGS reaction at low temperatures (300–350 °C).[63]

However, to develop high conversion CO_2-to-CO/syngas production processes that operate at significantly lower temperatures, it is necessary to explore reactive separation processes that remove products as they are formed,[19] or focus efforts on electrochemical processes for CO_2 reduction,[9,64] which use electricity instead of temperature to drive the reaction. Following this analysis, the development of high RWGS activity and selectivity thermal catalysts for low temperatures would also be applicable for tandem catalysis schemes where a RWGS catalyst operates in synergy with a methanol or FTO (Fischer−Tropsch synthesis to olefin) type catalyst for two-step conversion of CO_2 to liquid fuels in a single reactor.[21] The presence of a second catalyst consuming CO as it is being generated can yield efficient low temperature processes if the end goal is hydrocarbon or methanol production. Recently, Ramirez et al. presented a novel multifunctional catalyst consisting of Fe_2O_3 encapsulated in K_2CO_3 that can transform CO_2 into olefins via the tandem mechanism.[65] Normally, Fe in its different oxidation states is a good RWGS catalyst, iron carbides is responsible for FTS. In this article, the authors demonstrated that with the high loading K, $Fe_2O_3@K_2CO_3$ material can produce olefins from CO_2 with high selectivity and productivity, rivalling existing commercial Fisher–Tropsch catalysts. A CO_2 conversion of 44.2% with a total olefin (C2–C10) selectivity of 62.6%, a CH_4 selectivity of 13.3%, and a CO selectivity of only 12.7% can be achieved at 350 °C, 30 bar, $H_2/CO_2 = 3$, and 10 000 mL g^{-1} h^{-1}. In addition, this catalytic performance is stable for at least 150 h on stream. Given the theoretical possibility and the experimental process, tandem catalysis is gaining importance as a suitable medium term technology that needs to be developed further for a global transition to low carbon energy carriers.[66]

3. Net CO_2 Consumption in RWGS

As RWGS is gaining attention as a CO_2 utilization technique, it is important to determine whether reactor operation will actually result in a net reduction in CO_2 emissions. **Figure 2** displays the variation of net CO_2 consumed during the RWGS process, as a function of CO_2 emissions associated with hydrogen production,[67–69] for the two cases of CO and syngas (for methanol) production. For a process to be net CO_2 consuming, it must lie above the Carbon Neutral line in Figure 2. It can be seen that using blue and green sources of hydrogen and captured CO_2 for the RWGS process, we can achieve a net reduction in CO_2 emissions. It is worth noting that the steam reforming of methane (SRM) also leads to a slight net reduction of emissions in the CO production scenario. This is a result of the high H_2:CO_2 molar ratio (4:1) being produced in SRM, compared to the much lower H_2 requirement (H_2:CO_2 = 1:1) of the RWGS for CO production. When all emissions associated with the process are taken into consideration (process heating, product compression, and transport) it is unlikely that this scenario would lead to reduced CO_2 emissions. Figure 2 highlights the need to consider end product of CO_2 utilization in conjunction with the available hydrogen source, since the carbon footprint of H_2 production is non-zero and CO_2 capture and utilization (CCU) technologies will rely on different sources (or a mixture) in the near term depending on geographical location. While H_2 consumption is a dominant factor in the carbon footprint of the CCU process, it is not the only factor determining net CO_2 consumption, which has prompted us to perform a sensitivity analysis considering other factors as well.

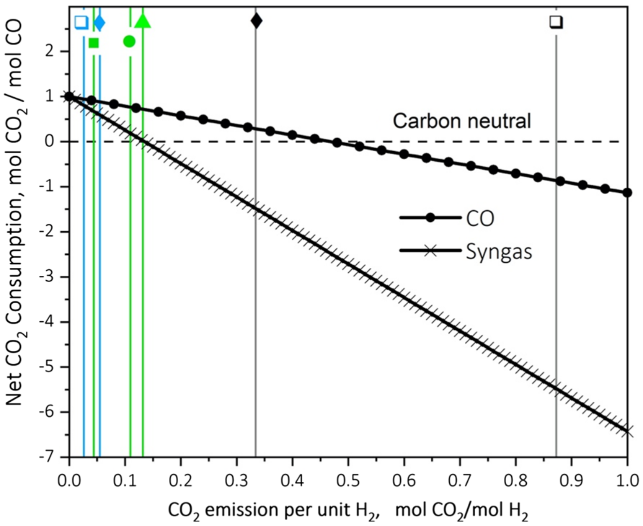

Figure 2. Net CO_2 consumption as a function of CO_2 emission per unit H_2, for RWGS processes optimized for CO production (1:1 H_2:CO_2, 750 °C, 1.013 bar) and syngas production (4:1 H_2:CO_2, 665 °C, 1.013 bar). Vertical lines indicate CO_2 emissions reported for various H_2 generation methods where □ is coal gasification, □ is coal gasification with CCS, ◆ is steam reforming of methane (SRM), ◆ is SRM with CCS, ▲ is biomass gasification, ■ is electrolysis using wind generated electricity, and ■ is electrolysis using solar generated electricity.

For the analysis presented in Figure 2, it has been assumed that contributions to the overall CO_2 emissions from process heating are negligible and H_2 production carbon footprint will be dominant. However, a sensitivity analysis (**Figure 3**) shows the contribution of the RWGS reactor heating source to the overall carbon footprint of the process can become significant in certain cases, in particular when the H_2 carbon footprint is low. In Figure 3, the hydrogen source is assumed to be wind driven electrolysis to illustrate the scenario where emissions from heating would be most pronounced compared to those from the reactants. The consumption of CO_2 from the RWGS reaction is plotted as a negative value on the y-axis. While H_2 carbon footprint dominates the contribution to emissions from RWGS, CO_2 emissions from reactor heating become significant if the end product is CO and the source of heat has a high carbon footprint, such as electrical heating using EU grid electricity.[24] This analysis evaluates RWGS within context of the emerging interest in electrifying industrial thermochemical reactions.[70] In RWGS there is a small margin for any CO_2 emissions, and hence electrification in the absence of a low carbon electrical grid would increase carbon footprint, although the process would still be net CO_2 consuming using some blue and green hydrogen sources.

4. Economic Feasibility

The economic feasibility of operating the RWGS reaction for purposes of producing CO or methanol is dependent on market prices of these products and cost of electricity (details presented in Supporting Information, Process Economics). PV driven electrolysis can provide a sustainable source of H_2 for around

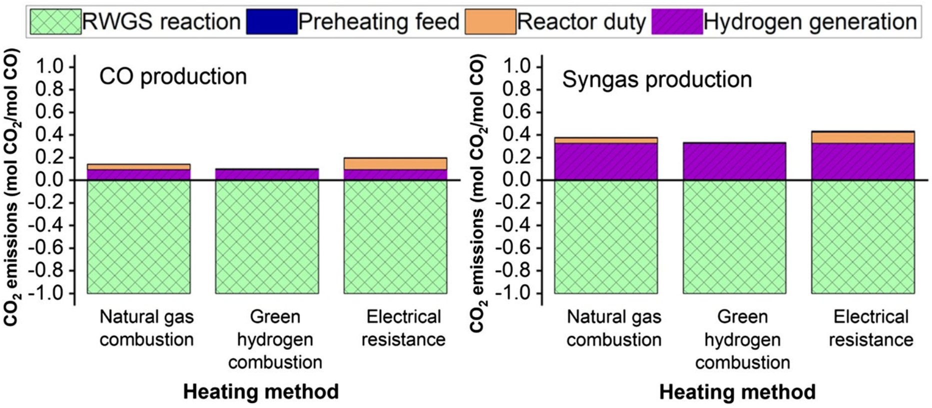

Figure 3. Sensitivity to reactor heating source for a RWGS reactor optimized for CO production and syngas production for methanol, respectively.

$\$12\,\text{kg}^{-1}$[71] when all electricity is provided by the solar panels and none sourced externally from the national grid. The main limiting factor of the technology is the low efficiency of PV cells (17–26%),[72,73] as well as the variable production of electricity. However, it is predicted that by 2030, costs could be more than halved to $\$5.87\,\text{kg}^{-1}$.[71] In comparison, a "grey" H_2 source such as steam reforming methane (SRM) could be used, where natural gas is reacted with steam to produce H_2 and CO. The H_2 price is dictated by the price of natural gas, which currently is $1.88/MMBTU,[74] which means H_2 can be produced for $\$2.08\,\text{kg}^{-1}$.[75] The cost has been reported to be similar for grey hydrogen produced from coal as well.[76] Additionally, "blue" H_2 can be obtained by the same SRM method but with incorporated CCS for a slightly higher cost of $\$2.27\,\text{kg}^{-1}$.[75] While the target application for RWGS is not necessarily CO_2 captured from SRM reacting with H_2 produced by the same method, this is taken as a price indicator for a scenario in which there is access to a hydrogen mix that will contain green, blue, and grey hydrogen.

CO_2 cost varies from the industry it is removed from, but a general cost can be assumed based on the operating cost required for capture. There are two main sources for CO_2: a point source or directly from the atmosphere. A point source would typically cover power plants, refineries or chemical plants. For capture in post-combustion, the most common method is scrubbing of the combustion effluent with a solvent, typically aqueous monoethanolamine (MEA). In this process CO_2 is absorbed from a gas stream, with the CO_2 MEA being subsequently sent to a stripper to isolate a pure product and regenerate the solvent. This method of CO_2 generation results in a CO_2 procurement cost of $70/tonne CO_2 captured.[10] This cost can be further reduced to $44/tonne CO_2 captured when improvements are made to the scrubbing process, such as changing the solvent.[10] Sourcing CO_2 directly from the atmosphere, also known as direct from air capture (DAC) has an associated cost ranging between $30 and $1000/tonne CO_2 captured.[10] This method does pose the benefits of being portable and having a net reduction in CO_2 emissions as CO_2 is removed from the atmosphere rather than created via chemical process.

Based on the aforementioned information, CO_2 as reactant for RWGS is assumed to be captured from a point source of emissions. This gives a cost of $44/tonne CO_2 captured making it considerably cheaper to source than H_2. The cost of CO_2 can however be offset by the savings made by carbon tax exemption. The current carbon tax in the United Kingdom is priced at £18/tonne of CO_2 released,[77] covering part of the cost required for carbon capture. In order for the United Kingdom to meet its emissions targets by 2050, a more aggressive £40/tonne tax will be required.[78] This means the cost of carbon capture will be completely offset by the savings made by tax exemption and subsequently makes the RWGS more economically feasible. However, the cost of H_2 still heavily outweighs the cost of carbon capture and the carbon tax, so this development has a small effect on the overall process economics.

Four scenarios are investigated for each RWGS process (with target products CO and syngas for downstream methanol synthesis) here to compare the current profitability of these processes under various hydrogen pricing scenarios. It has been assumed that the facility performing RWGS is not producing its own hydrogen but purchasing it at market price. 1) CO_2 reactant for RWGS is captured on site (cost[10] included) for an electrified process. 2) CO_2 reactant for RWGS is captured on site (cost[10] included) for a gas heated process. 3) CO_2 reactant for RWGS capture cost is zero for an electrified process. 4) CO_2 reactant for RWGS capture cost is zero for a gas heated process.

These scenarios have been selected to represent the current and projected process economics. For example, currently the cost of CO_2 capture exceeds the tax for emitted CO_2 in the United Kingdom, such that there would be a positive cost associated with a facility capturing its emissions for CO_2 utilization. Hence, the full cost of CO_2 capture has been factored into scenarios 1 and 2 to reflect low level of economic incentive for CO_2 capture. However, with growing investments in large scale CO_2 capture technology, such as the establishment of bioenergy with carbon capture and storage (BECCS) power stations,[79] it is expected that there will be freely available sources of CO_2 even in the short term and suitable incentive schemes will emerge to cover the cost of capture in the long term. This is reflected in scenarios 3 and 4. Gas fired heating is common practice in industry (scenarios 2 and 4) and the least expensive form of industrial heat available. However, a path to electrification of chemical processes can be envisioned with growing renewable electricity production[70] and this is represented by scenarios 1 and 3.

It can be seen from **Figure 4** that H_2 price is a major contributor to economic feasibility of the RWGS reaction. In fact, upon looking closely at the breakdown of operating costs of CO production via scenario 1 (Figure S3, Supporting Information), it can be seen that hydrogen is the biggest contributor to operating costs if it is priced over 1 $\$\ kg^{-1}$. A recent cost perspective from the Hydrogen Council has forecast significant reductions in the cost of renewable hydrogen, predicting that the price will drop to as low as 1–1.50$ kg^{-1} by as early as 2025.[80] Our economic analysis indicates that for CO production this would make the RWGS reaction economically feasible without any added incentivization. The profitability analysis in Figure 4B excludes the operating costs of the downstream methanol synthesis (which are in fact expected to be significant), but investigates whether the high costs of using significantly higher quantities of hydrogen can be offset by the higher revenue generated from making a more valuable product using a typical conversion value for methanol synthesis. Hence, this is meant to give a semi-quantitative picture of the significance of hydrogen cost in such CCU schemes. The already unprofitable nature of the methanol synthesis scenarios under all hydrogen source cases indicates that the RWGS process would supply syngas for a downstream methanol process at a much higher cost than the methane steam reforming process currently used. Thus, hydrogen price drops alone will likely not be sufficient to make this process economically feasible.

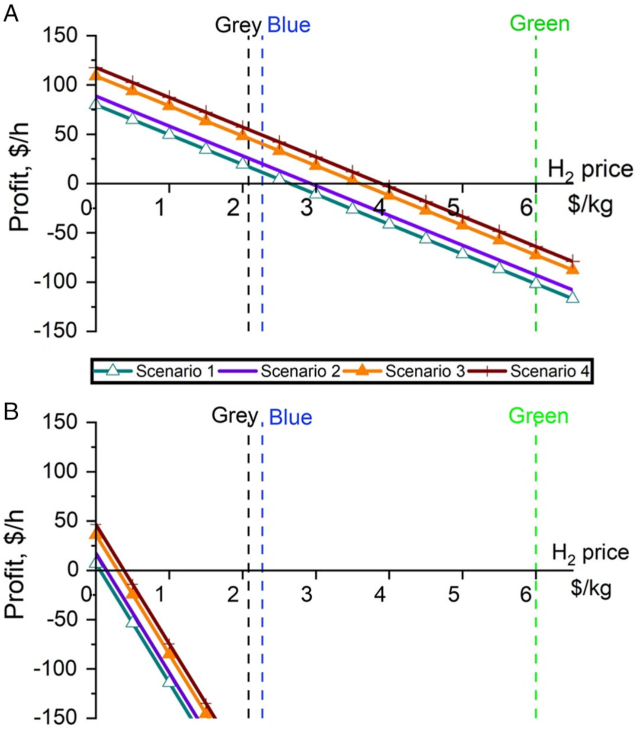

Figure 4. Process profitability for A) CO production, 1:1 H_2:CO_2, 750 °C, 1.013 bar and B) Syngas production (for downstream methanol synthesis) excluding methanol synthesis operating costs, 4:1 H_2:CO_2, 665 °C, 1.013 bar. Vertical lines indicate reported prices for grey, blue, and green hydrogen (see Supporting Information for details).

Considering the carbon footprint and economics of hydrogen production, RWGS for CO production using blue hydrogen is the only technology that can currently be implemented as a net CO_2 consuming and profitable process. However, in the near term, RWGS for CO production is expected to become both profitable and net CO_2 consuming using green hydrogen sources as well, subject to price drops making it competitive with grey hydrogen prices.

To feed captured CO_2 as a building block for the larger chemical industry substantial drops in green H_2 price must be observed, so that more H_2 consuming processes become profitable as well. The implementation of carbon tax or credit systems can accelerate progress in CCU as green H_2 prices drop. Our economic and carbon footprint analyses also highlight the need when developing CCU schemes to target stoichiometrically net CO_2 consuming reactions generating higher market price chemicals (such as diesel range hydrocarbons or higher alcohols). For increased return on investment, FTS can be coupled to RWGS, where the end products targeted have higher market prices compared to methanol. This may open up profitable opportunities to utilize green H_2 at higher prices in the shorter term. As was implied by our thermodynamic study, a promising emerging application of RWGS catalysis is the development of tandem catalytic systems for conversion of CO_2 to liquid fuels with the RWGS serving as first step of the tandem conversion. Given the economic feasibility constraints on syngas production, tandem catalysis again emerges as a worthwhile research subject. It is envisioned that given the availability of low cost, low carbon footprint hydrogen, and synthesis of liquid fuels from CO_2 will be an attractive economic proposition that can displace petroleum as feedstock.

5. Conclusion

The use of blue or green hydrogen as reactant will lead to a net carbon consuming RWGS process. However, there is a significant need for RWGS catalysts to be 100% selective to CO, as any side reaction that consumes hydrogen will result in an increase in CO_2 emissions due to both the carbon footprint of hydrogen used as well as potential carbon footprint of a downstream separation process. Impactful research opportunities exist in catalysis and materials science to focus on selective, low cost catalysts for RWGS, and developing catalysts for decarbonizing and lowering the cost of hydrogen production. If high performance low temperature RWGS catalysts can be developed, tandem catalysis systems can be envisioned for production of liquid fuels. Economic analyses reveal that the biggest factor in enabling commercial opportunities for RWGS will be the decrease in green hydrogen price. Hence, there is a significant research need to develop cost effective green hydrogen production methods. Expected H_2 price decreases will open up opportunities for CO generation, but will not be sufficient to enable cost effective syngas generation for methanol synthesis. Hence, there is also a need to develop more efficient direct or tandem catalytic CO_2 conversion processes utilizing blue or green hydrogen.

6. Experimental Section

Thermodynamic investigations were conducted on CHEMCAD using the Soave–Redlich–Kwong (SRK) fluids package and Gibbs free energy minimization method.[81,82] Effects of varying H_2:CO_2 (reactant ratio), temperature, and pressure were investigated. Detailed information regarding carbon footprint and economic analyses are presented in Supporting Information. For thermodynamic investigations data are presented in terms of metrics relevant to catalyst testing such as conversion and selectivity. These were calculated using Equations (3)–(5) where $\dot{n}_{i_{\text{in}}}$ and $\dot{n}_{i_{\text{out}}}$ are the molar flow rates at the inlet and outlet of the reactor, respectively, for species i (where $i = CO_2$, CO, or CH_4).

$$\text{CO}_2\ \text{Conversion}\ (\%) = \frac{\dot{n}_{\text{CO}_{2\text{in}}} - \dot{n}_{\text{CO}_{2\text{out}}}}{\dot{n}_{\text{CO}_{2\text{in}}}} \times 100 \tag{3}$$

$$\text{CO Selectivity}\ (\%) = \frac{\dot{n}_{\text{CO}_{\text{out}}}}{\dot{n}_{\text{CO}_{2\text{in}}} - \dot{n}_{\text{CO}_{2\text{out}}}} \times 100 \tag{4}$$

$$\text{CH}_4\ \text{Selectivity}\ (\%) = \frac{\dot{n}_{\text{CH}_{4\text{out}}}}{\dot{n}_{\text{CO}_{2\text{in}}} - \dot{n}_{\text{CO}_{2\text{out}}}} \times 100 \tag{5}$$

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

carbon footprint, catalysis, CO_2 recycling, CO_2 utilization, hydrogenation, reverse water gas shift, thermodynamic analysis

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Matthew Bown received his M.Eng. degree in Chemical and Process Engineering from the University of Surrey in 2020, including a research project investigating the use of a molybdenum phosphide catalyst for reverse water gas shift reaction. After graduating, he began working for BOC as a graduate focusing on special gases projects and has recently started a role as a graduate operations engineer in Port Talbot.

Miriam Joyce completed her master's degree in Chemical and Process Engineering at the University of Surrey in 2020. This included a final year research project focusing on the use of a novel nickel phosphide catalyst in the reverse water gas shift reaction. In post-graduation, Miriam is working as a graduate trainee manager for Hanson Cement based at Ribblesdale Cement Works in Lancashire. She is currently involved in projects looking at reducing carbon dioxide production and emissions within the cement industry. These projects focus on a net-zero carbon fuel mix for cement kilns and methods of capturing carbon emissions from kiln exhaust gases.

Qi Zhang is currently a Ph.D. student in the Department of Chemical and Process Engineering at the University of Surrey. She received her B.E. in 2015 and MA.Eng. in 2018, both in Chemistry and Chemical Engineering from Tianjin University of Technology (China). Presently, she works mainly on developing highly efficient transition metal carbides (TMCs) and transition metal phosphides (TMPs) catalysts for gas phase CO_2 conversion reactions.

Tomas R. Reina, Ph.D., AMIChemE, FHEA, FRSC, received his Ph.D. in Chemistry from the University of Seville (Spain) in 2014 and then he moved to the UK, where he has developed his career as catalysis and reaction engineering group leader in the Department of Chemical and Process Engineering at the University of Surrey. His research interests include the development of advanced heterogeneous catalysts for energy and sustainability. In particular, his work is focused on clean hydrogen production, carbon dioxide utilization and biomass valorization.

Melis S. Duyar, Ph.D., AMIChemE, FHEA, MRSC, is a Lecturer of Chemical and Process Engineering at the University of Surrey. She obtained her M.S. (2013) and Ph.D. (2015) from Columbia University and conducted postdoctoral research (2015–2017) at Stanford University. Prior to her academic appointment at the University of Surrey, she worked at the US Department of Energy's SLAC National Accelerator Laboratory as Associate Staff Scientist and was also a Lecturer of Chemical Engineering at Stanford University (2017–2019). Her research interests include CO_2 capture, water purification, and catalytic syntheses of sustainable fuels and chemicals.