

Using H₂ for CO₂ activation on the way towards synthetic fuels

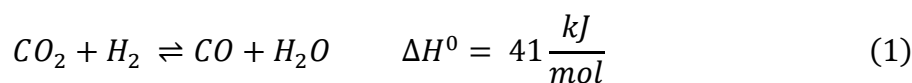
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Introduction

Fighting global warming is probably one of the biggest challenges we must face this century. Therefore, the scientific community is exerting great efforts to reduce anthropogenic CO₂ emissions and decrease its concentration within the atmosphere. In 2022, the combined worldwide operational CO₂ capture plants prevented the emission of almost 50 Mt of CO₂. This capacity is expected to increase 6-fold by 2030, counting only the already planned projects [1]. It shows the companies' desire to limit their CO₂ emissions in the foreseeable future, especially in Europe where it is motivated by the increasing price for the emitted tonne of CO₂. Indeed, the cost of emitting one tonne of CO₂ on the European ETS market has increased from 25 €/tonne in early 2020 to 86 €/tonne in August 2023 [2]. Among the possible CO₂ utilization routes, the production of synthetic fuels by combining CO₂ with H₂ remains the leading option, mainly due to policy incentives. The European Union voted the ReFuelEU Aviation proposal as part of its "Fit for 55" package in April 2023, stating that the market share of synthetic aviation fuels should grow from 0.7% in 2030 to 28% in 2050 [3]. It is particularly interesting for long-freight transportation, namely ships and aircraft, for which hydrogen powering or electrification presents significant limitations. Hence, it would turn the long-haul transport industry into a defossilized, rather than decarbonized industry. Additionally, producing liquid fuels from CO₂ and H₂ offers an energy storage opportunity. Indeed, it is possible to store eight times more energy in traditional liquid fuels than in 700 bar hydrogen and even more when compared to Li-Ion batteries [4]. Those processes are generally referred to as Power-to-fuel processes, as the electricity generated from renewable energies is eventually stored in fuels. Once these fuels are burnt, the stored energy is released, and CO₂ is emitted, but once captured (e.g., by Direct Air Capture), it can be reused as an input of the process, creating a circular usage of carbon.

Practically, CO₂ must be hydrogenated to yield hydrocarbon chains, which can be further upgraded to the desired fuel. Ideally, the CO₂ conversion can be conducted with one reaction on a bifunctional catalyst, i.e. a catalyst capable of activating the highly inert CO₂ molecule and crossing the high C-C coupling barrier required for hydrocarbon chain growth. However, the yields and selectivities obtained from these catalysts are low and demand further improvements to be applicable in large-scale facilities. Therefore, the indirect synthesis is a suitable alternative in which CO₂ is activated in a first reactor, and then the polymerization reaction occurs in a second one. This work investigates principally the first reaction where CO₂ is transformed into CO, which is less stable and thus more adapted to yield complex hydrocarbons, through the reverse water-gas shift (rWGS) reaction:



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Objectives

This work focuses on three main objectives. First and foremost, the goal is to determine the best possible operating conditions for a specific study case and design an optimal rWGS unit accordingly. The discussions conducted in this paper focus on this first objective. The study case corresponds to the experimental installation that will be set up at the University of Liège (ULiège) and that consists in a small pilot-scale Power-to-kerosene process made up of a rWGS reactor followed by a Fischer-Tropsch (FT) reactor. The H_2 necessary for the reactions is produced by three water electrolysis cells, already operating at ULiège and having a combined peak production of $1.5 \text{ Nm}^3/\text{h}$ of H_2 . The reactor numerical model used to size this experimental installation will then be included in a complete process model to study process-related aspects. For instance, it will be possible to determine which recycling option for unreacted gases better suits a Power-to-kerosene process. Indeed, the process consists of a succession of two reaction units (rWGS and FT), bringing various recycling options, as testified by Figure 1. The recycling loop can be isolated around each reaction unit (options A and B), the outlet of the process can be recirculated at its inlet (option C) and additionally between the rWGS and FT units (option D). It is worth mentioning that the literature shows that recycling loops are generally used to intensify Power-to-kerosene processes. In many cases, the loop integrates a combustion unit which burns a fraction of the tail gases to provide heat for the rest of the process, especially for the rWGS reaction [5]–[7].

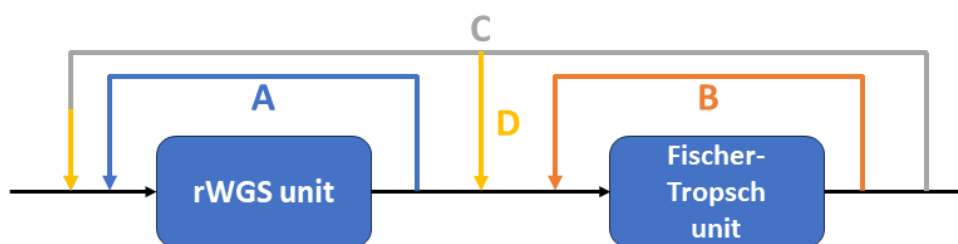


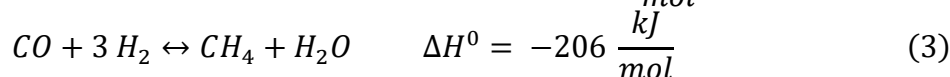
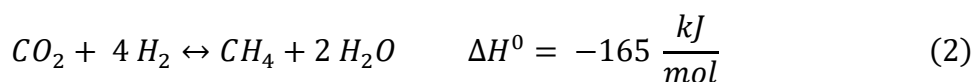
Figure 1 : Recycling loop possibilities between the rWGS and the Fischer-Tropsch units

Concerning the second objective, the scope is not only centred on kerosene production anymore. The aim is to investigate the production of other types of end products and to determine the impact of the end product nature on the rWGS unit design. In other words, the point will be to determine whether the optimal design developed for kerosene synthesis is also suitable for another product synthesis and, thus, whether it is possible to propose a standardized rWGS unit design. Among others, the targetted end products can be gasoline or diesel, which can also be synthesised through the Fischer-Tropsch reaction, methanol, ethanol, dimethyl ether, etc. The last objective of this work is to pass from the steady-state model developed for the first objective to a dynamic model. Indeed, it turns out that modelling of the rWGS reaction, and Power-to-X processes in general, lacks transient considerations. Thus, flexibility analysis is outlined as a crucial perspective in this field to counterbalance this scarcity [8]–[10]. The study of the transient behaviour of these processes is paramount as they rely on the utilisation of renewable energies, which are variable in nature.

Methodology

This thesis combines modelling and experimental work through the installation of the pilot facility at ULiège. The first utilization of the developed model is to design and determine the size of this actual installation. Therefore, the model should be sufficiently precise, which is the reason why the model accounts for the reaction kinetics. Nevertheless, the first developed

model is a simple Gibbs model, i.e. an equilibrium model, which enables the obtention of first insights regarding the influence of operating variables on reaction performance. It also helps to have a first idea of the operating conditions ranges and to compare them with the values found in the literature. The Gibbs model considers the rWGS reaction (see Equation (1)) and also two exothermic parallel methanation reactions, which appear along this one:



In some simulation works, exothermic coking side reactions (Boudouard and Bosch equilibria, methane pyrolysis) are also included in the model. However, these reactions are generally neglected, given the high operating temperature required for the rWGS reaction [5], [6], [11]–[13]. Some results obtained from this equilibrium model are discussed in the following section.

In order to upgrade this equilibrium model, a complete kinetic model was developed in Aspen Custom Modeler (ACM) accounting for material, heat and momentum balances. The utilization of ACM as a simulation software offers some freedom in terms of reactor modelling compared to built-in reactor models from Aspen Plus but still keeps the advantage of the availability of the different Aspen Properties databases. The kinetics implemented in this model were designed for a 2 wt-% Ni/Al₂O₃ catalyst by Vidal Vázquez et al. [14] and were chosen for different reasons. The kinetic model structure of Vidal Vázquez et al. is based on the work of Xu and Froment [15], who developed a model for methane steam reforming, methanation and water-gas shift reactions, which has been used in numerous works in the past. Furthermore, Vidal Vázquez et al.'s kinetics have been presumably used to size a rWGS experimental installation whose size is similar to the one that will be set up at ULiège [16]. Finally, Vidal Vázquez et al. regressed their model with experimental data obtained in a wide range of temperatures (between 550 and 850°C) and pressures (between 1 and 30 bar). This latter point is worth mentioning as most of the rWGS kinetics accessible in the literature are based on experiments conducted at atmospheric pressure and lower temperatures [17]–[20].

Discussion

Table 1 gathers the rWGS reaction operating temperature and pressure referenced in various simulation works. This table comes from a review paper on the rWGS reaction, which is currently in preparation. The operating conditions are discussed in further detail in this future paper [21].

Table 1 - Operating conditions applied for the rWGS reaction in different simulation works

Temperature (°C)	Pressure (bar)	Reference	Temperature (°C)	Pressure (bar)	Reference
900	25	[5]	1000	30	[22]
550 – 950	1 – 25	[6]	950	25 – 30	[23]
900	30	[12]	900	4.2	[24]
665 – 750	1	[25]	1000 – 1200	1 – 30	[20]
350 – 940	1 – 30	[26]	980 – 1000	20	[16]
400 – 700	1	[27]	800	1	[28]

The main message emerging from this table is the high operating temperature required by the rWGS reaction. Although some of the referenced works studied it at a lower temperature, their conclusion regarding the optimal operating temperature is always towards the higher values of their considered range. The general conclusion drawn from these works reveals that the rWGS reaction should be operated above 700°C. There is not a straight conclusion that can be figured out from Table 1 regarding the operating pressure, which is discussed at the end of this section. Those trends are verified using the Gibbs reactor model mentioned previously. Figure 2 shows how the equilibrium composition obtained at the outlet of a Gibbs reactor varies for different operating temperatures. The methane curve justifies the high operating temperature required, as below 700°C, its proportion in the outlet stream starts increasing. Conversely, above this temperature, the amount of CH₄ becomes negligible, and the CO selectivity can be maximized.

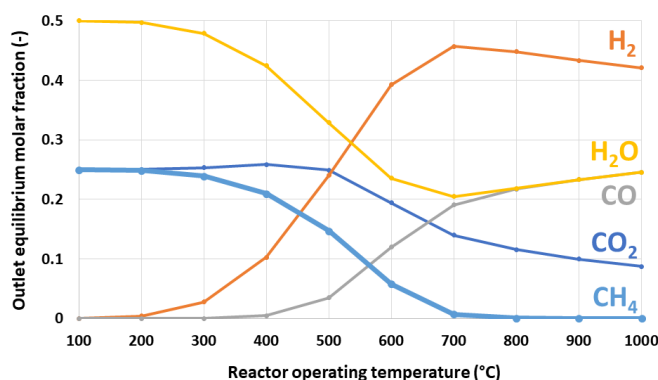


Figure 2 - Equilibrium composition obtained at the outlet of a Gibbs reactor for different operating temperatures at 1 bar and for an inlet H₂/CO₂ = 2

This decrease in the methane curve with temperature is explained by the exothermicity of methanation reactions (see Equations 2 and 3), while the selectivity of CO increases with temperature as the rWGS reaction is endothermic. This competing effect between the rWGS and the methanation reactions also explains the H₂ curve shape. The methanation reactions are favoured at low temperatures, leading to a significant H₂ consumption, induced by its stoichiometric coefficient in Equations 2 and 3. As the temperature rises, those reactions are less and less favoured, and H₂ is less consumed. At 700°C, the conditions start to be optimal for the rWGS reaction, and H₂ consumption is increased by this latter. Yet, the decline rate is slower as its stoichiometric coefficient is now 1 with respect to CO₂.

As mentioned in the previous section, coking side reactions are generally neglected in rWGS reactor models. In order to verify the validity of this assumption, the Gibbs reactor model can be used by comparing a simulation considering those side reactions (dashed line in Figure 3) and a simulation without them (solid line in Figure 3). The CO selectivity is barely impacted by the coking reactions, as depicted in the right-hand side graph, but CO₂ conversion is enhanced at low temperatures, which is explained by the exothermicity of this kind of reaction. However, at high temperatures, the effect of coking reactions is not visible anymore as they become negligible, and these graphs reinforce the assumption of neglecting these reactions in the model, as mentioned in the literature. Concerning the impact of the operating pressure, it turns out that in the range of operating temperatures for the rWGS reaction, the CO₂ conversion and CO selectivity are both favoured at atmospheric pressure. However, Table 1 shows a tendency in some works to operate the reaction at higher pressure. This discrepancy in the optimal pressure for the rWGS reaction comes from process considerations and not only reactor engineering aspects. Indeed, most reactions taking place after the rWGS unit in Power-to-X

processes are generally operated at high pressure. The selection of the optimal rWGS pressure is thus a trade-off between operating at low pressure to hinder side reactions and consequently favour the rWGS reaction or at high pressure to minimize the subsequent compression needs.

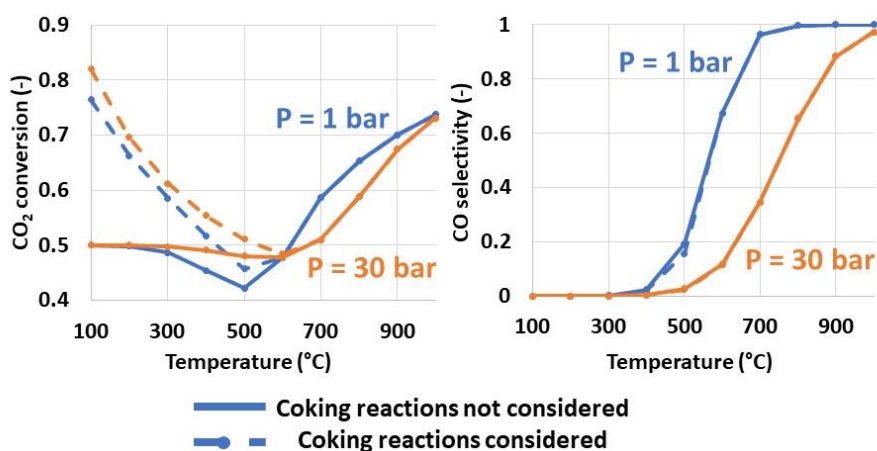


Figure 3 - Influence of temperature and pressure on CO₂ conversion (left) and CO selectivity (right) for a Gibbs reactor model (coking reactions considered or not)

Conclusions

This work investigates the rWGS reaction as an intermediate step in Power-to-X processes, especially to convert CO₂ into CO. This paper focuses on the first objective of this work, namely designing an optimal rWGS unit for integration in a Power-to-kerosene process. The reaction operating conditions referenced in the literature were compiled and validated with a Gibbs reactor model. It turns out that the reaction should be operated above 700°C to maximise CO selectivity, while the optimal pressure must be selected by considering additional process aspects. The kinetic reactor model is already implemented, but the results are discussed in another paper. The upcoming steps will be to use this kinetic model to design the ULiège experimental installation and to include it in a complete Power-to-kerosene process model.

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