



An Assessment of Dry Reforming of Methane: A Mitigated Approach to Technology Investment

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Abstract

Dry reforming of methane (DRM) is a reaction of methane and carbon dioxide to produce synthesis gas (syngas), a hydrogen and carbon monoxide (H_2/CO) mixture, which can have applications in the petrochemicals sector. While DRM is topical at face value, it does produce a syngas with a low H_2/CO ratio not typically used by the industry. This article highlights a desktop literature survey of practical application of a progressive approach to technology investment decisions. Key technical and business risks associated with funding the development of a high-performance DRM catalyst was identified. The study indicated the cost implications of integrating DRM technology with a Fischer-Tropsch (FT) plant where a deficit of H_2 in the syngas, >1 , requires external supply to increase it to an applicable ratio of 2. The article also compares DRM and its hydrogen-lean syngas with existing syngas production technologies such as steam methane reforming (SMR) and partial oxidation (PO). It also includes an overview of the reactions that influence DRM's catalyst performance and an integrated impact assessment of DRM when applied to a specific use application.

Keywords: Syngas, methane reforming, catalyst deactivation, carbon utilisation, process flow scheme

1. Introduction

Technologies that are in line with sustainable development are currently at the centre of the on-going climate crisis. As such, in a generally depressed economy facing unprecedented global challenges such as climate change, there is increasing focus on maximising the prospect of impact when investing in technology development [1, 2]. While it is often not certain how technologies at conceptual stage can create more than just academic impact, there is much benefit in following a risk-mitigated approach to technology investment in line with the United Nation's Sustainable Development Goals (UN SDGs) [3]. All too often, development work is justified by identifying white space in the prior art which is at times supported by generic market size indicators and associated projected growth rate metrics [4]. There is a real risk of creating technology alternatives that are scientifically interesting but ultimately uncompetitive. By considering the potential for real world impact prior to embarking on detailed scientific study, research and development (R&D) efforts can be focused. Such front-end loading need not be onerous and can be achieved by framing key risks and doing only fit-for-purpose R&D to understand if investment is warranted. This article provides an overview of screening outcomes for (DRM) as a prospective technology that has potential to address challenges associated with climate change.

2. Literature review

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DRM is a reaction of CO_2 and CH_4 to produce syngas [5-7]. DRM could be considered as an interesting choice as it utilises two of the most harmful greenhouse gases (GHGs) and has potential for industrial application [8, 9]. It is important to note that whereas the stoichiometric ratio of the syngas product is 1, it may be less due to side reactions that consume the hydrogen produced [10]. The syngas produced from DRM may be used for multiple downstream processes such as FT synthesis, methanol production, etc. If the ratio is adjusted, according to Afzal et al (2018), by supplementing H_2 from an external plant [11]. Furthermore, DRM processes can be carried out using biogas as a CH_4 -rich stream which makes the technology more attractive as it utilises low-carbon energy sources but it is acknowledged that the availability of biogas at scale is a limitation [9, 11, 12].

While opportunity screening is not unique, it is most effective when it is focused on understanding success factors and built into ways of working R&D. A desktop study was used to screen DRM technology for downstream applications including: Literature review, engineering flowsheets, and key technology indicators. The approach was multi-disciplinary and introduced an engineering solution while catalyst fundamentals were considered. Clear articulation of market relevance, business potential and indication that developing a differentiated solution is possible was key. The following topics were prioritised outcomes:

- DRM context, chemistry and deactivation mechanisms
- Syngas, and its downstream applications
- DRM performance within an integrated process flow scheme
- Risk evaluation of DRM performance in a FT Gas-to-liquids (GTL) plant

3. DRM chemistry and deactivation mechanisms

The DRM reaction is endothermic, Equation (Eqn) 1, and conventionally employs nickel-based, heterogenous catalysts to decrease the activation energy [13, 14]. Albeit other metals can be used as active sites, nickel (Ni) has numerous advantages such as high abundance and performance, and low cost [15]. However, one of the drawbacks of the Ni-based catalysts in DRM is deactivation which results in loss of activity. Furthermore, the syngas ratio at unity limits the downstream application of the DRM processes, however, the quality of the H_2 -lean syngas may be augmented by removal of CO or supplemented by H_2 from an external source i.e. green or low-carbon hydrogen [11]. In addition, bi- or tri-reforming of methane can be utilised where DRM is combined with SMR and PO albeit the water-gas shift reaction may also take place [16].

Whilst bi- and tri-reforming have advantages such as decreased energy consumption, graphitic carbon removal by O_2 and H_2O in feed, etc., the presence of O_2 and H_2O may deactivate the catalyst via reoxidation of the active sites [16, 17]. In comparison to SMR, and PO, Eqns 2-3, DRM utilises two prominent GHGs and can also be used in the valorisation of biogas (CH_4 and CO_2) thereby making the process more sustainable and renewable [18]. Furthermore, the syngas gas ratio in SMR is 3:1, 2:1 in PO, and 1:1 in DRM. This is in favour of SMR and PO due to the excess hydrogen as, compared with DRM, they don't require supplementary H_2 if they are used as feedstocks to well-known syngas processes e.g. FT and methanol synthesis [17]. Nevertheless, although not commonly reported, unadjusted DRM syngas can be used for production of olefins via an FT-mediated process, oxygenates, etc. However, one of the biggest issues is catalyst deactivation via carbon laydown and sintering which warrant innovative catalyst design for good performance [19, 20].





The DRM reaction is performed at 1 bar, temperatures of 650 °C to 850 °C and a CH₄/CO₂ ratio of 1:1 [14]. Due to the endothermicity of DRM, an increase in temperature increases CH₄ and CO₂ conversions whereas deactivation occurs due to coke formation [21]. However, the latter can be suppressed in the presence of steam such as the case in bi-reforming albeit it may result in the reverse Water-Gas Shift (rWGS). Due to side reactions such as the rWGS at higher temperature, the H₂/CO ratio decreases to less than 1 as excess CO is produced. Reactions that may occur during DRM are shown below whereas Eqns 4-8 are responsible for catalyst deactivation via coke formation [9, 10]. An increase in pressure above 1 bar also results in decreased CH₄ and CO₂ conversions. Furthermore, the type of carbon deposited on the catalysts may vary between catalysts and depends on the temperature at which the reaction is carried out [18].

Reverse water-gas shift



Methane decomposition



CO hydrogenation



CO disproportionation



CO₂ hydrogenation



Coke-induced deactivation of DRM catalysts is due to multiple factors such as the methane decomposition and Boudard reactions, Eqns 5-6. Sintering of Ni active sites also results in catalyst deactivation [22]. As highlighted, deactivation by coke formation can be prevented by adding steam or the use of metals in the catalysts that promote gasification of carbon deposits [23]. Whilst there are various type of carbon that may form on the surface of the catalyst, depending on the reaction temperature, whisker or filamentous carbon is the most prevalent in DRM. Whisker carbon laydown takes place due to methane TCD, and disproportionation of CO [20]. According to Rostrup-Nielsen et al (2002), the formation of filamentous carbon is a multi-step process where elemental carbon from the dissociative adsorption of CH₄ and CO migrates to an exposed part of the Ni active sites followed by nucleation to form a whisker [24]. Indeed, carbon laydown contributes to deactivation of the catalyst due to pore blockage, breakage of catalyst particles which causes pressure drop, and surface coverage of active sites [8]. The deactivation of DRM catalysts is also likely to occur due oxidation of active sites, especially in the presence of oxidants such as steam and O₂ in the reactor [25]. Furthermore, strong metal-support interactions (SMSIs) can also decrease the activity of the catalysts due to the attenuation of active sites.

Therefore, to enhance the performance of the catalysts used in DRM and to minimize deactivation due to sintering and coking, the use of novel Ni-based, catalysts with a focus on various physicochemical properties such as oxygen vacancies, and surface basicity for CO₂ adsorption and conversion, and promotion of CH₄ dissociative adsorption must be considered. The selection of the novel catalysts must be based on the mitigation of deactivation due to coking. Furthermore, alternative catalysts should also be pursued to tweak process parameters i.e. low conversions, selectivity, etc. The addition of suitable promoters should also be explored to alleviate any deactivation or poor performance.

4. Syngas applications and DRM in context

A review of industrial syngas applications was completed with specific interest in lean hydrogen applications (H_2/CO ratios ≤ 1). While several potential applications for conventional syngas are reported such as the production of liquid fuels i.e. synthetic diesel, dimethyl ether, and methanol, lean hydrogen applications are uncommon [26]. This highlights the risk in developing DRM without considering the business case impacts of low H_2/CO ratios.

The FT process emerged as the most widely used technology for converting syngas into liquid hydrocarbons, which can be further refined into fuels and chemicals [27, 28]. Mature processes utilise natural gas, steam and oxygen as feedstocks for the production of syngas [29]. The process can use reforming techniques such as the Haldor Topsøe autothermal reforming technology (ATR) for the syngas generating unit. The FT unit typically receives syngas with an H_2/CO of approximately 2 [30]. If the ATR were to be replaced by DRM, supplementary H_2 stream will be required so as to not impact downstream production of hydrocarbon products. Methanol synthesis is also common in industry, however, the required H_2/CO ratio also significantly exceeds the unity gas produced by DRM [31].

It is therefore clear that a screening business case should account for an imported source of H_2 to inform an investment decision [6]. Based on industrial applicability and availability of information, syngas to FT was selected. Using technical information from Sasol's public domain disclosure of its planned 96 000 barrels per day (bbl/day) Canada GTL facility, a high-level mass balance was used as a baseline to determine the impact of DRM replacing an ATR process.

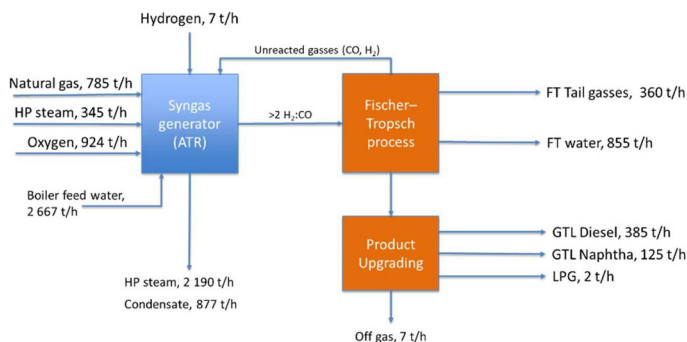


Figure 1. A simplified process flow diagram for a FT process adapted from the Canada GTL Project.

Error! Reference source not found. SASOL's environmental impact assessment document and typical FT operating parameters were used to assess the impact of replacing ATR technology with DRM. The assumptions included gases exiting from the FT unit with an H_2/CO ratio of 1.1, whereas natural gas has a heating value of 50 megajoule/kilogram (MJ/kg) while the recycled off gases were at 12 MJ/kg.

Indicative and best-case DRM performance was determined from literature. The concept of producing liquid fuels from CO₂ using DRM and FT synthesis is not new. William Luyben (2016) previously reported a scenario where a combination of DRM and SRM is used to adjust the H₂/CO ratio for FT synthesis with particular emphasis on incorporating the DRM reaction to convert the CO₂ into a CO-rich syngas. The work discussed a study wherein the required syngas ratio of ~2 was achieved by integrating the DRM process with a SRM process to make up for the required ratio of H₂ [28]. The study was based on producing a syngas feed to the FT process, containing 15,005 kilomole/hour (kmol/h) of H₂ and 7580 kmol/h of CO from a total of 5885 kmol/h CH₄ feed (from DRM and SMR) to produce syngas feed for the FT process. DRM performance inferred from Luyben was used as a baseline for replacing the ATR technology, Figure 1, with DRM technology for the production of syngas instead [28]. By fixing the baseline scheme's syngas flow and H₂/CO to the FT process, the downstream processes are unaffected. Excess H₂ required was then assumed to be supplemented by import as opposed to integrating SMR to make up the H₂ shortfall. Aside from the H₂ shortfall, DRM also requires additional heat input which the ATR would have generated through reforming. The DRM performance assumes 100% conversion of CH₄ and CO₂, which is optimistic, however, for the purposes of this study, this will give a best-case scenario for the application of DRM.

The key performance indicators for heat and mass balance scaling for the adapted scheme are:

- The process has close to 100% conversion, which provides an optimistic view of the business case
- Each reactant (CH₄ and CO₂) is fed equimolar to the process at a rate of 25.4% of total molar flow of product gas
- Assuming 75% efficiency in using fuel gas, the heat required for the reaction is ~24.95 kilowatt/kilomole (kW/kmol) of product gas

5. DRM performance within an integrated process flow scheme

It is worth noting that the integrated heat and mass balances were not performed using a simulation software but were rather rationalised as follows:

1. The amount of CO required for the baseline process was fixed. DRM was assumed to produce sufficient H₂ to achieve a syngas ratio of 0.9 and the balance of H₂ had to be imported. The estimated amount required is around 110 tph. At a green H₂ price of \$5/kg, the cost impact is up to \$13 million (mln) per day on this 96 000 bbl/day scale facility. Even with savings for equipment such as cryogenic oxygen supply, this level of cost is not sustainable.
2. Natural gas savings when using DRM are offset by the endothermic nature of the reaction. On an overall basis (accounting for facility fuel requirements), the natural gas savings were estimated to be \$1.2 mln at this scale.
3. At the most optimistic assumptions, the annual quantity of organic biomass required to produce biogas on the scale required, is around 40 million tons. This is far in excess of the South Africa's availability and is not practical on this scale. The option of running only the DRM furnace with biogas is also not practical due to the volumes of the feed required.

6. Conclusions

A business case for DRM was scrutinised via a desktop study including careful consideration of competing commodity prices. Even though a facility that incorporates DRM will save a large amount of capital expenditure by not having to invest in air separation, the annual losses cannot be sustained. The assessment revealed certain price sensitivities and technical interventions that can be mitigated to some extent. Reducing the price of green hydrogen helps, but even when going below optimistic forecasts, the case is not positive. It was noted that natural gas price is less of a lever than hydrogen cost. Improving H_2/CO ratio to 1.2 has some effect on the business case and water co-feeding can mitigate the shortfalls, but only to an extent. Any incentives for reducing CO_2 or for processing it has not been taken into account, but current values of CO_2 tax do not shift the position significantly. It is difficult to price the benefit of selling products that originate from CO_2 into the market but considering that these will enter commodity markets at this scale, demanding premium to cover the shortfall is optimistic. While the outcome may not seem optimal, it should be noted that this is a high-level study and is restricted to large-scale application based on the current economic landscape. A fundamental catalyst study can still support a strategic impetus if it focuses on intrinsically improving hydrogen production and reconsiders the business impacts with small-scale applications.

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Declaration of interest. The authors are not aware of any conflicts of interest.

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