Steam-assisted MILD-POX: a flexible process for the production of hydrogen

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Abstract

The aim of the present work is to propose an alternative hydrogen production process using water and sustainable feedstocks to promote the utilisation of cheap and renewable raw materials on a large scale by increasing flexibility, efficiency, and eco-compatibility of existing technologies, without sacrificing their reliability and affordability. The idea to accomplish this aim is to combine non-catalytic Partial Oxidation and MILD combustion technologies by adding water. Thermodynamic equilibrium calculations, accompanied by kinetic modelling, were used to assess and interpret the general behaviour of a potential unit that uses the interaction of these two technologies and to compare the performances over a range of operating conditions of interest. The presented results have shown that thermochemical production of H_2 using the proposed process is theoretically feasible and has the potential to offer many advantages over standard processes.

Introduction

The overall purpose of the present work is to propose and assess an alternative prospective process to produce H_2 based on the combination of conventional noncatalytic partial oxidation (POX) and innovative Moderate or Intense Low-oxygen Dilution (MILD) technologies by adding H_2O .

Although considerable work has been carried out in the separate fields of MILD combustion and POX, the information on the hybrid process is limited. In particular, the establishment of steam-assisted MILD-POX has never been previously investigated. Therefore, the specific objective of the present study is to present a computational investigation of thermodynamic and kinetic features for assessing the influence of the governing parameters, i.e., operating temperature, pressure, carbon/oxygen ratio, H₂O concentration, and residence time on fuel conversion, H₂ yield, and product distribution. The analysis focuses on low/intermediate temperature conditions of practical interest to MILD combustion applications and fuel-rich conditions of interest to POX. Since very little is currently known about this chemical process regarding the impact of the different constituents forming a reactant mixture, the process is characterized using methane (CH₄) as a fuel. Its chemical kinetics is crucial since it constitutes the base of hierarchical chemistry for oxidation processes of bio-derived feedstocks and is sufficiently simple. Methane is among the main components of gaseous biofuels such as biogas, landfill and

pyrolysis gas. Therefore, a good understanding of the behaviour of CH_4 with high concentrations of H_2O is central to optimising the design of the proposed technology for any more complex feedstock. In addition, the use of CH_4 provides a way of comparing the proposed process to conventional steam reforming (SR) and POX, where CH_4 is widely used due to its high hydrogen-to-carbon ratio and, thus, the lowest level of generated by-products.

Thermodynamic and kinetic analysis

The CRECK reaction scheme provides an excellent prediction of the reactions of CH₄ under the conditions of interest [1]. This section aims to use it to theoretically assess and interpret the general behavior of a potential unit that uses the steamassisted MILD-POX route of CH₄ for syngas production and to compare the performances over a range of different operating conditions. The H₂O/CH₄ feeding ratio is selected as the primary variable for the parametric study as dilution variation through internal or external recirculation is the most suitable way to achieve MILD conditions and thus for controlling the process. The H₂O/CH₄ ratio is also essential in industrial SR and POX to prevent carbon deposits. However, while traditional SR and POX generally employ ratios of 3-5 and 0-3, respectively, MILD-POX conditions require this ratio to be from ~ 5 up to 500, which makes the proposed process significantly different from the conventional ones. The H₂O/CH₄ ratio is restricted at its lower end by the MILD combustion definition; namely, the adiabatic temperature increase must be lower than the autoignition temperature. The upper limit of H₂O admixing employed here has been set to have a minimum temperature increase of 10 K, the criterion commonly used for defining the ignition delay time in MILD combustion.

First, a thermodynamic analysis employing Gibbs free energy minimisation has been performed with mixtures of CH₄ and O₂, highly diluted in H₂O, at atmospheric pressure and T_{in} =900 K, to examine the equilibrium conversion limits and product gas yield and composition as a function of process parameters.



Figure 1. Effect of H_2O/CH_4 feeding ratio on the H_2/CH_4^{input} ratio (black lines, left axis) and H_2/CO ratio (red lines, right axis) for $CH_4/O_2/H_2O$ mixtures at equilibrium, T_{in} =900 K, and p=1.0 atm for three CH_4/O_2 feeding ratios. Dotted

lines: CH₄/O₂=1.0. Solid lines: CH₄/O₂=1.5. Dashed lines: CH₄/O₂=2.0. Dashdotted lines: CH₄/O₂=2.0 with H₂O replaced by Ar. Open circles: A-B: τ^{90} <10 s; B-C: 10< τ^{90} <100 s; C-D: 100< τ^{90} <1000 s. Where no circles are reported τ^{90} >1000 s.

Figure 1 shows the effect of the H_2O/CH_4 inlet mole ratio on the reformed gas's equilibrium composition at the adiabatic temperature for three defined CH_4/O_2 inlet mole ratios under MILD-POX conditions, thus T_{in} >autoignition temperature, fuelrich and highly diluted mixtures. The selected CH_4/O_2 ratios (1.0, 1.5, and 2.0) correspond to Φ =2.0, 3.0, and 4.0, where the latter is the one usually employed in conventional POX.

The first interesting result, not displayed in Fig. 1, is that the conversion is always complete for the explored H₂O/CH₄ and CH₄/O₂ ratios. In addition, no free carbon is present, and the expected products are, independent of the operating conditions, only H₂, carbon oxides, and residual H₂O. Therefore, for all the equilibrium results, the product composition is unambiguously presented in terms of H_2/CH_4^{input} and H_2/CO since the main interest is the efficient conversion of CH₄ to H₂. Calculations show that the main trends strongly depend on H₂O addition; in particular, it can be seen that the H_2/CH_4^{input} yield (left axis) first significantly grows with increasing H_2O/CH_4 ratio and then reaches a plateau for values higher than ~50, independent on the CH_4/O_2 ratio. At the same time, the quantitative values of H_2/CH_4^{input} strongly grow with CH₄/O₂ ratio starting from about 1.3-2.0 at CH₄/O₂=1.0 to 2.1-2.95 at CH₄/O₂=2.0. Note that for CH₄/O₂ ratios of 1.5 and 2.0, the H₂/CH₄^{input} ranges from the one typical of POX (~2.0) to the one of SR (~3.0). On the other hand, the H₂/CO ratio (right axis) increases quasi-linearly with the addition of H_2O_1 and the improvement may be considerable. In this case, increasing the CH₄/O₂ ratio does not have a significant influence for a fixed H_2O/CH_4 ratio, but lower CH_4/O_2 ratios can be beneficial because they would allow extending the H₂O/CH₄ range. Surprisingly, the synthesis gas composition in terms of H_2/CO ratio, ranging from 3.0 to 1060, is always significantly higher than that obtainable with conventional processes (1-2 for POX and ~ 3.0 for SR), which is beneficial for H₂ production. Low temperatures favour the H_2 yield and selectivity; thus, from the analysis, it needs to be clarified if the changes in process performances with the addition of H₂O are influenced by a decrease in the adiabatic temperature or by the presence of steam itself. Therefore, an additional case has been investigated at CH₄/O₂=2.0 with argon dilution instead of H₂O (dash-dotted lines). Thermodynamic calculations suggest that the nonlinear increasing trend of H_2/CH_4^{input} is very similar in the case of dilution by an inert gas, which is therefore explained by the fact that the diluent addition to the mixture shifts the adiabatic temperature to lower values. However, the H₂/CH₄^{input} yield drops by a factor of 1.36-1.54, and the conversion is never complete, but ranges from 95 to 97%. On the other hand, increasing the Ar/CH_4 ratio does not influence the H_2/CO ratio, which is ~2.0 in the entire explored range. It confirms that the steam-assisted MILD-POX process extracts H₂ from the hydrocarbon feedstock and H₂O. Indeed, 27-35% of the H₂ produced comes from the steam when CH₄ is used as a feedstock. This

contrasts with some numerical studies [2-4] in which no significant effect of H_2O/CH_4 ratio on H_2 yield was observed. In addition, steam is the only cause for the enhanced H_2/CO ratio. This result justifies using surplus H_2O that increases the syngas yield, the H_2/CO ratio, and the CH₄ conversion.

The description based on thermodynamic analysis is approximate because it can only suggest the potential product composition. However, it does not provide any information on reactor residence times required to achieve proper CH₄ conversion in real systems: thus, calculations must include reaction kinetics. Therefore, zerodimensional, adiabatic simulations have been carried out over the entire range of conditions reported in Fig. 1 employing the PSR code of the ANSYS Chemkin-Pro 2021[®] software, implementing the CRECK reaction mechanism and setting the residence time to 10, 100, and 1000 s. In Fig. 1, the conditions that allow a CH₄ conversion of more than 90% (τ^{90}) at the reactor outlet are shown with open circles. For CH₄/O₂ ratios higher than 1.0, reactions need more than 1000 s to reach equilibrium in the whole H₂O/CH₄ range, which is not practical. A conversion higher than 90% is attained for $\tau < 1000$ s only at CH₄/O₂=1.0 and H₂O/CH₄<16 where the adiabatic temperature ranges from 1300 to 1750 K. These very long residence times are not related to the use of H₂O, because also in the case of dilution with Argon the results are similar. At CH₄/O₂=2.0, τ^{90} <10 s only if H₂O/ or Ar/CH₄=0 (not shown in Fig. 1). As a matter of fact, the non-catalytic POX of hydrocarbons is controlled by reaction kinetics, which, despite being faster than SR, is intrinsically much slower than conventional flame burners, and even an approximation to equilibrium can only be achieved by accepting very high temperatures (1500<T<3000 K), where chemical reactions are sufficiently rapid. Below 1500 K, catalysts are typically added to the POX system to enhance reaction kinetics and approach an acceptable conversion. However, the objective of the present work is to propose a process that can be realised within residence times typical of non-catalytic POX, i.e., $\tau < 50$ s, and adiabatic temperatures typical of MILD combustion, i.e., 1000-1500 K. These factors have given preference to optimal values for the present analysis, namely $T_{in}=1300$ K, p=50 atm, CH₄/O₂=1.5, H₂O/CH₄=21.56, and $\tau=20$ s that allow matching appropriate conditions relevant for a practical application. Before starting the analysis, an array of preliminary computations has been performed using adiabatic and isothermal PSR and PFR to choose the best reactor configuration. An adiabatic PFR approach has been selected to model the system because it maximises the CH₄ conversion. The analysis presented in Fig. 1 shows that H₂O is not only the diluent but may also chemically interact with the oxidation kinetics releasing H₂. Therefore, a fictitious species (H_2O_v) with identical molecular structure and thermodynamic properties to H₂O has been defined in the simulations. This virtual species does, however, not appear in the elementary reactions of the kinetic mechanism. Simulations have been performed diluting the fuel mixtures with H₂O and H_2O_v to understand the chemical contribution of H_2O . In addition, it is known that H₂O may indirectly participate in oxidation chemistry as a third body in termolecular reactions with chaperon efficiencies that are significantly higher than

other collision partners. To isolate this contribution, calculations have been carried out by defining a second fictitious species $(H_2O_v^*)$ with identical molecular structure, thermodynamic properties, and third body efficiencies to H_2O . This virtual species does, however, not appear as a reactant or product in the elementary reactions of the kinetic mechanism. Differences between simulations performed diluting the fuel mixtures with H_2O_v and $H_2O_v^*$ isolate the chemical contribution of H_2O as a collider in termolecular reactions, while differences between simulations with H_2O and $H_2O_v^*$ isolate the direct chemical effect of H_2O in bimolecular reactions. A summary of the results is provided in Table 1, which compares exhaust products for the three simulations under the same conditions. H_2O brings the system to nearly complete conversion and reduces the production of undesirable intermediate compounds, which is essential for the process to be economical. Indeed, for the other two cases, CH_4 conversion is only around 82% at 20 s, and the selectivity to form H_2 and CO_2 is much lower. The fact that dilution by H_2O_v and $H_2O_v^*$ brings the same results means that there is no third-body effect of H_2O .

Table 1. Chemical and third body contributions of H₂O on global outputs in an adiabatic PFR at T_{in} =1300 K, p=50 atm, CH₄/O₂=1.5, H₂O/CH₄=21.56, and τ =20 s.

	H ₂ O dilution	H ₂ O _v dilution	H ₂ O _v * dilution
CH ₄ conversion (%)	98.15	81.65	81.55
H ₂ /CO	11.90	1.71	1.71
H ₂ /CH ₄ ^{input}	2.26	1.14	1.13
Dry composition of	%	%	%
the product gas	H ₂ 70.48	H ₂ 54.32	H ₂ 54.25
	CO 5.92	CO 31.77	CO 31.75
	CO ₂ 23.02	CO ₂ 4.91	CO ₂ 4.94
	CH4 0.58	CH4 8.78	CH4 8.84
		$C_2H_4 0.11$	$C_2H_4 0.11$
	ppm		
	C ₂ H ₄ 1.20	ppm	ppm
	C ₆ H ₆ 11.15	C ₂ H ₆ 36.53	C ₂ H ₆ 37.42
		C ₂ H ₂ 824.44	C ₂ H ₂ 854.58
		C ₃ H ₆ 3.61	C ₃ H ₆ 3.75
		C ₃ H ₄ (Propyne) 8.06	C ₃ H ₄ (Propyne) 8.43
		C ₃ H ₄ (Allene) 2.87	C ₃ H ₄ (Allene) 3.00
		C ₆ H ₆ 210.10	C ₆ H ₆ 234.60

Conclusions

The goal of the present work was to propose the combination of non-catalytic POX and MILD combustion technologies with the addition of H_2O and assess its potential for the efficient generation of H_2 from any sustainable gaseous or liquid feedstock, leaving a minimal environmental footprint. The CRECK chemical kinetic

mechanism was used in the theoretical analysis based on the models' predictive performances. Thermodynamic equilibrium calculations, accompanied by kinetic modeling, were used to interpret and assess the general behavior of a potential unit that uses the steam-assisted MILD-POX route of CH₄ for syngas production and to compare the performances over a range of operating conditions of interest. In particular, the effects of H₂O/CH₄ and CH₄/O₂ ratios, inlet temperature, and pressure on CH₄ conversion, H₂ yield, and product gas composition were computationally investigated. Particular emphasis was devoted to the effect of H₂O on gas-phase chemistry. The presented results demonstrate that thermo-chemical production of H₂ using the proposed process is theoretically feasible and can be accomplished without a catalyst, making the process highly feedstock-flexible and impurity-tolerant. The achieved performances can be even better than those of the existing technologies over a wide range of process parameters, subject to the constraints of characteristic times. In particular, equilibrium favours the formation of H₂ and CO₂ at low adiabatic temperatures and high H_2O/CH_4 and CH_4/O_2 ratios in the input gas. At the same time, reaction kinetics are faster at elevated temperatures and pressures and low H₂O/CH₄ and CH₄/O₂ ratios. Therefore, a compromise must be made among these parameters to maximize performance. The immediate advantage of such an approach is that a very high H₂/CO ratio can be obtained that could eliminate the water gas shift conversion stages, making the reactor more compact and simple than conventional reformers. Moreover, water vapor addition limits the formation of soot precursors due to a "leaning" effect from the release of OH radicals.

Although the present analysis shows that H_2 production via this hybrid system is possible, more experimental and modelling research is required to transform a promising idea into an industrially viable reality. The potential benefits of steamassisted MILD-POX justify spending effort in developing and optimizing this process. In this regard, this study is expected to act as a basis for future investigations.

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