Estimate of the Height of Molten Metal Reactors for Methane Cracking

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Methane Cracking represents one of the most promising routes to CO2-free hydrogen production.The methane decomposition reaction is typically carried out in fixed or fluidized catalytic beds, where the metal catalyst is supported on porous ceramic particles. By proper choice of the metal catalyst, the catalytic reaction environment allows to obtain sizeable reaction rates at operating temperatures as low as 700°C. Besides, in solid catalytic beds, the catalyst is swiftly deactivated due to the massive (i.e. stoichiometric) deposition of the solid carbon product. One way to bypass carbon deposition is to use a molten metal bath (which may or may not contain catalytic metal components) as a reaction environment, where methane bubbles are introduced at the bottom of the bath and are progressively converted as they rise through the liquid metal. The key point of this process is that, owing to a large density difference between the solid carbon phase and the molten metal, the solid product of the reaction floats on top of the liquid metal and can be thus mechanically skimmed. In this article, we develop an analytical approach to the estimate of the bath height, which constitutes one of the most critical design parameters of the process. Specifically, based on the observation that in practical applications the reacting bubble is in the kinetics-controlled regime, we obtain the conversion vs time solution for a bubble of given initial size. On the assumption of ideal gaseous mixture behaviour, the knowledge of the conversion curves allows to estimate the bubble diameter as a function of time during the rise of the bubble through the molten metal. This piece of information is then post-processed to obtain the bubble motion as a function of time. The elimination of the time parameter between the two solutions allows to construct a conversion-height map for different diameters of the bubbles.

1. Introduction

Methane (or, more generally, natural gas) Cracking (MC) represents an attractive route to CO2-free hydrogen production, the main other alternative being electrolysis. The MC reaction is typically carried out in fixed or fluidized catalytic beds, where the metal catalyst is supported on porous ceramic particles. This way, appreciable reaction rates can be obtained at temperatures as low as 700°C. The major shortcoming associated with the solid catalyst is its swift deactivation, which is caused by the massive (i.e. stoichiometric) deposition of the solid carbon phase [Parolin et Al, 2021]. Frequent catalysis regeneration is thus required in the process, which impacts adversely on operational costs. Furthermore, in cases where catalyst regeneration is obtained through oxidation of the deposited carbon, the CO2-free character of the overall reaction is altogether lost. For this reason, alternatives that avoid the presence of solid catalyst have been sought. One way to bypass carbon deposition is to use a molten metal bath (which may or may not contain catalytic components) as a reaction environment, where methane bubbles are introduced at the bottom of the bath through a sparger and are progressively converted to hydrogen as they rise through the liquid metal [see, e.g. Pérez et Al, 2013 and therein cited references]. The key point of this process is that, due to a sizeable density difference between the solid carbon phase and the molten metal, the solid carbon produced by the reaction migrates to the top of the liquid metal and can be thus skimmed mechanically.

Notwithstanding its numerous advantages, catalytic cracking of methane in molten liquid baths is still far from industrial maturity, as only laboratory prototypes or small pilot plants have been constructed to date. This is mainly due to the fact that the theoretical modelling of the process, which should serve as guidance for the experimental design, must address a complex intertwined phenomenology, where transport-reaction phenomena occurring in the gas phase within the bubbles are influenced by the external conditions through momentum and heat transfer between the two phases. In this respect, the availability of simple design criteria could provide a useful starting point to select the range of operating conditions of the process. Hinging on some simplifying assumptions, in this contribution we develop an analytical approach for the estimate of the bath height, which constitutes one of the most critical design parameters. To this end, we first derive the conversion vs time solution for a generic gas bubble. On the assumption of ideal gaseous mixture behaviour, the bubble diameter as a function of time during the rise of the bubble can thus be obtained. In turn, the knowledge of the bubble size as a function of time allows to determine the vertical motion of the bubble.

2. Statement of the problem and modelling

The physical setting next described is one where pure methane at assigned flowrate is fed through a sparger at the bottom of a liquid metal bath that is externally heated. Owing to its large thermal conductivity, the liquid metal is assumed at uniform temperature, independently of the heat duty required by the cracking reaction. Depending on the type of sparger used, the characteristic bubble diameter ranges from order few micrometers to few millimeters [Pérez et Al, 2013]. The wide range of bubble diameters characterizing the experimental prototypes discussed in the literature suggests that a preliminary analysis of the transport-reaction regimes governing the overall (effective) rate of methane conversion inside the bubbles may be in place to orient the theoretical/numerical modelling of the process. In this analysis, the most critical aspect is to understand where the elementary reaction steps are taking place, i.e. whether in the bulk of the gas phase or at the gas/liquid metal interface. Many authors consider the non-catalytic methane cracking reaction as occurring in the bulk of the gas [Catalan et Al, 2020] when the temperature exceeds 10^3 °C. Besides, in conditions where metal components possessing catalytic activity towards methane cracking are present in the molten metal bath, the rate of the surface (heterogeneous) reaction at the gas-metal interface largely overcomes that of the bulk (homogeneous) reaction [Upham et Al, 2017]. In what follows, we consider this to be the case. As a consequence, we neglect the effect of the bulk gas reaction on methane conversion. From a thermodynamic standpoint, the methane cracking reaction is an endothermic reaction

$$CH_{4(g)} \rightleftarrows C_{(s)} + 2H_{2(g)}, \qquad \Delta H^0_{298.15} = 74 \, kJ/mol \qquad (1)$$
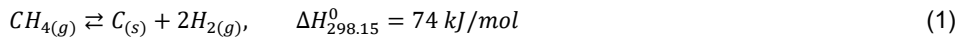
whose advancement increases (doubles) the total number of moles. As such, methane cracking is favoured at high temperatures and low pressures. In what follows, we take $T = 1000$ °C and $P = 1$ atm as representative operating conditions for the temperature and the pressure, respectively.

The reaction kinetics is complex and not yet completely understood. Many authors report that depending on the conditions and on the catalytic environment, different reaction pathways can be observed, some of which are associated with ethane, ethylene, and acetylene intermediates. In what follows, we consider a pseudo-first order expression [Upham et Al, 2017], where a linear first-order reaction kinetics with respect to methane concentration is enforced up to the equilibrium value. At equilibrium, the reaction rate is assumed to drop to zero instantaneously, in order to make the kinetic expression consistent with thermodynamics. Thus, the kinetic expression is given by

$$(-r_{CH_4}) = \begin{cases} k\_s \; C_{CH_4} \; for \; c_{CH_4} < c_{CH_4}^{eq} \\ 0 \qquad \qquad for \; c_{CH_4} \geq c_{CH_4}^{eq} \end{cases} \qquad (2)$$

The conversion of methane in the rising bubble results from a two-step process, namely the diffusion of methane from the center of the bubble to the gas-liquid interface and the surface reaction, the first associated with a characteristic time $\tau_D = R_0^2 / \mathfrak{D}$, the second characterized by a characteristic time $\tau_R = R_0/k_s$. Here, $\mathfrak{D}$ is the diffusion coefficient of methane in the methane/hydrogen gaseous mixture, whereas $k_s[m/s]$ is the kinetic constant of the heterogeneous (surface) reaction. The ratio of these characteristic times can be regarded as a modified Thiele modulus, henceforth denoted as Th, which quantifies the relative importance of transport with respect to kinetics. Depending on the value of this parameter, qualitatively different dynamical behaviors of the reacting system can be observed (see Figure 1).
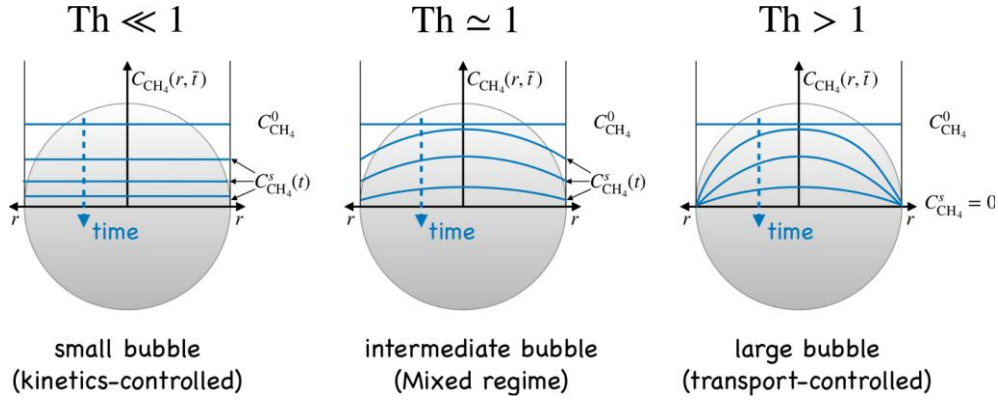
Figure 1: Qualitative evolution of methane concentration profiles for different values of the Thiele modulus.

At low values of Th, the rate-limiting step is the surface reaction: the methane concentration profile is essentially flat and depends only on time. At the other extreme, i.e. for Th>1, the reaction is totally under transport control and methane concentration at the reaction interface vanishes at all times t>0. In this case, the apparent (effective) reaction rate can be predicted by solving a transient pure diffusion problem equipped with zero boundary conditions. When the Thiele modulus is of order unity the profiles and the boundary concentration values depend on both space and time. If one excludes very high temperatures (> 1100 °C), for reasonable values of the bubble size (diameter less than 1 cm) and even in the presence of catalytic components in the molten metal, one finds that the typical reaction regime is controlled by kinetics in that Th < 10^{-3}. This is the case, e.g., of a molten metal bath composed of a mixture of 17% Ni (catalyst) in Bi (non-catalytic component) at T=1000 °C and P= 1 atm [Upham et Al, 2017]. For this case, available experimental data suggest $k_s = 2.3 \cdot 10^{-4}$ [m/s], a value that is two orders of magnitude larger than that of pure Bi (which does not show catalytic activity towards the methane cracking reaction. The value associated with pure Bi can be taken as representative of the combined effect of the homogeneous and the surface reaction in the absence of the catalyst. Because the Ni catalyst has a negligible vapor pressure, it can be assumed that the sizeable increase of the reaction rate is only due to the surface reaction. This implies that in catalytic metal baths, the contribution of the homogeneous reaction can be safely neglected, an assumption that we next enforce. Given the relatively low value of k_s one finds that in typical conditions $k_s < 10^{-3}$ so that the regime is kinetics-controlled and the methane mole balance can be written as

$$\frac{dn_{CH_4}}{dt} = -k_s n_{CH_4} \frac{3}{R(t)} \qquad (3)$$

where R(t) is the instantaneous bubble radius. Besides, the number of moles of hydrogen generated at a given time instant, say $n_{H_2}(t)$ is equal to $n_{H_2}(t) = 2(n_{CH_4}^0 - n_{CH_4}(t))$ which implies that the total number of moles at any time instant is given by $n_{tot}(t) = 2n_{CH_4}^0 + n_{CH_4}(t)$. By assuming ideal behavior for the hydrogen/methane mixture, one can relate the bubble volume (and hence the radius) and the total number of moles, obtaining

$$R(t) = \left(\left(\frac{3\mathcal{R}T}{4\pi P} \right) \left(2n_{CH_4}^0 - n_{CH_4}(t) \right) \right)^{1/3}, \qquad (4)$$

which, substituted in the methane mole balance equation, yields a first-order differential equation that can be solved analytically by separation of variables. In turn, the solution of this equation allows to explicitly derive the bubble size as a function of time and this piece of information can be used to integrate the equation of motion of the bubble. Owing to the large density difference between the gas and the molten metal (four orders of magnitude in the conditions considered), bubble inertia can be neglected, and the instantaneous bubble velocity can be computed by balancing Archimede's lift and viscous drag by the molten metal. Thus, the bubble velocity v(t) is computed as the root of

$$(\rho_m - \rho_g)\frac{4}{3}\pi R^3(t) = \frac{1}{2}f(Re)\,\rho_m v^2(t)\,4\pi R^2(t) \qquad (5)$$

Where f(Re) is the friction factor for viscous fluid motion around a sphere. Note that the bubble velocity is also present implicitly within the friction factor. By solving this equation for any given value of R(t) one obtains the bubble velocity as a function of time, and thus, upon integration of the latter, the bubble motion z(t), where z measures the current height of the center of the bubble with respect to the gas sparger. Eliminating the parameter t between $n_{CH_4}(t)$ and z(t), a direct relationship between the methane conversion and bath height can be made explicit.

3. Results

3.1 Methane conversion and bubble motion

In what follows, the advancement of the cracking reaction is quantified in dimensionless terms by computing the conversion $X(t) = \frac{n^0_{CH_4} - n_{CH_4}(t)}{n^0_{CH_4}}$. Given that both temperature and pressure are kept constant in this analysis, the performance of the reaction is evaluated as a function of the initial bubble size $R(t = 0) = R^0$, which is assumed to range between $50\ \mu m$ and $5\ mm$. Figure 2-A depicts the conversion vs time curves for different values of the initial bubble size (increasing in the direction of the arrow).
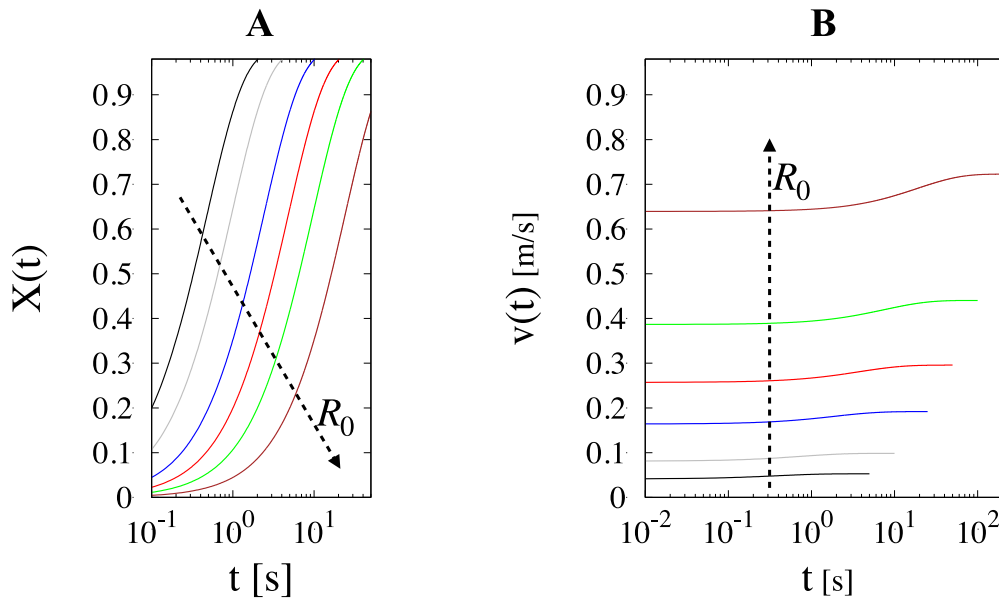

Figure 2: Panel A. Conversion versus time for a bubble of pure methane entering a liquid Ni-Bi metal bath at T=1000 °C and P=1atm. The initial bubble size R^0 increases in the direction of the arrow as $R^0 = 50\ \mu m;\ 100\ \mu m;\ 200\ \mu m;\ 500\ \mu m;\ 1\ mm;\ 2\ mm;\ 5\ mm$. Panel B: bubble velocity vs time for the same bubble dimensions of Panel A.

The data show that the characteristic conversion time is strongly dependent on the initial size of the bubble. For instance, the time to reac 80% conversion ranges from order one second up to 40 seconds when goimng from the smallest to the largest bubble size considered. Panel B of the same figures shows the instantaneous bubble velocity. All of the curves show the same trend where the bubble velocity is weakly increasing with time until it saturates towards a constant value which is about 10% higher than the initial bubble velocity. Here, the bubble acceleration is due to the increasing bubbles size, which, in turn, is a consequence of the fact that the total number of moles in the gas phase increases with time. The analysis of the instantaneous Reynolds number shows that the breakdown of laminar (Stokes) regime occurs when the initial bubble size is equal to $R^0 = 100\ \mu m$ (not shown for brevity).

3.2 Conversion-height map

Upon integrating the time-dependent velocity, the bubble motion $z(t)$ can be obtained, and the elimination of the time parameter between X(t) and $z(t)$ allows to derive a direct relationship between the overall height of the reaction bath and the conversion within the bubble when the latter rises from the molten metal.
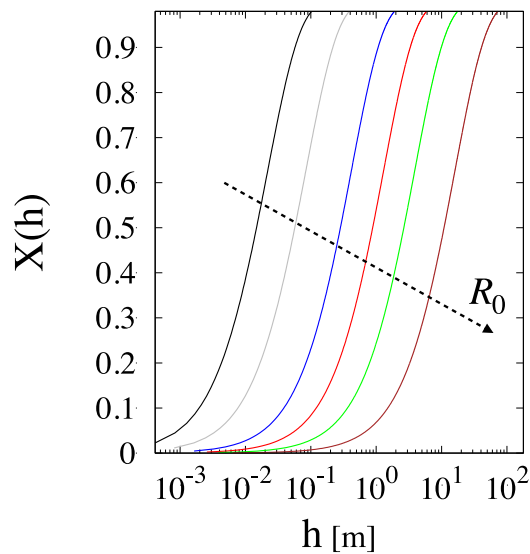
Figure 3: Conversion-height maps for different bubble sizes. The initial bubble radius increases in the direction of the arrow.

Figure 3 shows the results of this approach as a function of the initial bubble radius. As can be gathered by inspection, the height values range in a wider range than the characteristic conversion times (five orders of magnitude are here involved whereas conversion times are distributed in less than three decades, see Figure 2-A). This is ultimately due to a different scaling of Archimedean's lift (proportional to $R^3(t)$) with respect to viscous drag forces, whose dependence on the radius shifts from a proportionality relationship, $F \sim R(t)$, in the Stokes regime, to a square dependence $F \sim R^2(t)$ when the bubble enters the turbulent regime.

By considering a fixed conversion target, say $X_\%$, a different representation of the data depicted in Fig. 3 can be obtained in terms of height, $H(X_\%)$, needed to obtain the conversion target as a function of the initial bubble size (see Figure 4). This representation makes it evident the occurrence of a shift between two regimes when the bubble size increases. For small bubble diameters, $H(X_\%)$ increases approximately as the square root of the bubble size, whereas for large bubbles the increase obeys a 3/2 type power-law. It is worth highlighting that the results depicted in Fig. 4 are quantitatively consistent with the experimental data reported in [Upham et at., 2017] which find a reactor height of the order of one meter to obtain conversion higher than 90% with an initial bubble radius of 1 mm.
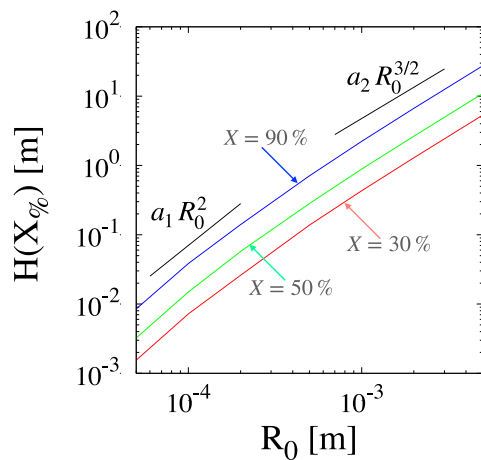

Figure 4: Height to obtain a target conversion value as a function of the initial bubble radius (see main text for details).

4. Conclusions

Molten metal baths represent a promising reaction environment to carry out methane cracking due to the natural separation of the solid carbon phase which prevents catalyst deactivation. We derive an analytical model for predicting methane conversion rate as a function of the residence time of the bubble. The model is based on the assumption that the prevalent contribution to methane conversion is due to the heterogeneous surface reaction at the gas/liquid-metal interface. This assumption is supported by experimental data in the literature that estimate that in favourable conditions (T=1000 °C, P=1atm, presence of metal catalyst) the rate of reaction in the bulk gas phase two orders of magnitude lower than the heterogeneous reaction). Furthermore, an order-of-magnitude analysis shows that in these conditions the reacting system is in the kinetics-controlled regime, which allows to assume that spatial concentration gradients inside the bubble can be neglected. Based on these assumptions and enforcing the validity of ideal gas behavior inside for the hydrogen/methane gas phase, we derive an analytical solution for the molar concentration of the species and the bubble size, wich increases with time due to the increasing number of moles cause by the advancement of the reaction. The influence of the initial bubble size on the conversion time and the bath height is analyzed at fixed temperature and pressure. Two regimes are identified, where the bath height scale with different power laws depending on the initial bubble size. Future work on the subject will address the influence of temperature and pressure on the reactor performance.

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