Working diagrams to identify the operating range of a bubbling fluidized bed reactor for the CO$_2$ methanation

Jennifer Martin-del-Campo, Jan Kopyscinski*

Department of Chemical Engineering, McGill University, 3610 University Street, Montreal, Quebec H3A 0C5, Canada

* To whom all correspondence should be addressed:

Tel.: +1 514 398 4276

jan.kopyscinski@mcgill.ca
Abstract

Fluidized bed reactors for the catalytic CO₂ methanation is a promising concept within the Power-to-Gas (methane) process. Due to the intermittency of renewable electricity generation and thus hydrogen production, the subsequent methanation reactor should also be able to operate at lower feed flow rates, while maintaining fluidized bed conditions. Bubbling fluidized bed reactors offer the required flexibility as shown with the new type of working diagrams. These working diagrams visualize a decision window for (1) determining the reactor diameter and (2) operating the fluidized bed reactor with a turndown ratio of 0.5 to 1.1. Reducing the turndown ratio (i.e., inlet flow rate) could lead to defluidization, thus increasing temperature or reducing the pressure are alternatives to maintain fluidization conditions. The former method is not desired, as a temperature increase would significantly reduce the CH₄ yield due to thermodynamic constraints and therefore reduce the overall efficiency. An industrial CO₂ methanation reactor, for example, that is designed for 10 bara and 340 °C with a total inlet flow rate of 5000 m³N h⁻¹ (H₂/CO₂ = 4) can be operated at a turndown ratio of 0.5 (2500 m³N h⁻¹) at the same temperature and the same $\dot{u}_0/\dot{u}_{mf}$ ratio by reducing the pressure to 5 bara with only a slight decrease in the CO₂ equilibrium conversion from 96.7% to 94.6%.

Keywords: CO₂ methanation • bubbling fluidized bed • pressure and temperature effects • working diagrams
1 Introduction

Fluidized bed reactors operating in the bubbling regime are ideal for heterogeneous catalyzed reactions, as they allow high heat and mass transfer rates\textsuperscript{1}. In bubbling fluidized bed reactors (BFBR), the mixing of the solid catalyst leads to isothermal conditions along the reactor axis and provides excellent temperature control\textsuperscript{1}. These features make fluidized bed reactors suitable for fast and highly exothermic and endothermic reactions\textsuperscript{2–5}. Moreover, in the case of catalyst deactivation due to coking, the catalyst can easily be replaced or regenerated in the same reactor\textsuperscript{6,7}. For instance, for the Fischer-Tropsch (FT) process, BFBR have been developed at the Cartage Hydrocol FT plant in the USA for High-Temperature FT (HTFT), operating at 305-345 °C and 21-45 bara. SASOL I plant integrated HTFT (340 °C, 20 bara in a Circulating Fluidized Bed) with Low-Temperature FT (LTFT) operating at 230 °C, 27 bara in a BFBR \textsuperscript{8}. On the other hand, BFBR have also proven to be reliable for CO methanation\textsuperscript{9,10}, whereas BFBR for the direct methanation of biogas were studied in a pilot plant in Zurich with stable operation over 1100 h and an average of methane yield of 96%\textsuperscript{11}.

Various quantitative and qualitative working diagrams have been published to classify fluidized bed reactors \textsuperscript{1,12–17}. Kunii and Levenspie\textsuperscript{11} presented a general flow regime diagram, which has been adapted from Grace\textsuperscript{17} and is valid for the whole range of gas-solid contacts. Most reported working diagrams are made for fast fluidization and circulating fluidized beds. Rabinovich and Kalman published a flow regime diagram for pneumatic conveying and fast fluidized bed systems\textsuperscript{16}. Takeuchi et al. proposed a qualitative flow regime diagram for a catalytic cracking catalyst for fast fluidization\textsuperscript{18}. The diagrams are based on experimental studies and define the limits of the fast-fluidization regime in terms of solid mass flux as a function of the superficial gas velocity. In the case of circulating fluidized beds, operating diagrams for the riser operation have been proposed based on
the different solid circulation flux and superficial air velocity through the riser\textsuperscript{[12,15]}. However, the proposed diagrams do not provide specific information for design parameters.

Working diagrams for the bubbling fluidized bed reactors (BFBR) are scarce. The influence of the bed height to diameter ratio for different particle sizes on the minimum bubbling and slugging velocities has been analyzed and plotted in a generalized flow diagram of Reynolds number as a function of Archimedes number\textsuperscript{[13]}. Besides geometric factors, the operation of a bubbling fluidized bed reactor depends on the properties of the gas-solid system and the chemical reaction itself\textsuperscript{[19]}. The most important hydrodynamic parameters are the minimum fluidization velocity ($u_{mf}$), the terminal velocity ($u_t$), and the bubble velocity ($u_b$), which are functions of particle properties (i.e., size, density, sphericity) and fluid properties (i.e., viscosity, density). Ideally, BFBR should operate between the minimum fluidization velocity ($u_{mf}$) and the terminal velocity ($u_t$) to assure that the catalyst particles are fluidized but not entrained\textsuperscript{[20,21]}. Usually, the superficial gas velocity ($u_0$) is 3-10 times the minimum fluidization velocity\textsuperscript{[11]}. Temperature and pressure have different effects on the fluid properties and on the reaction kinetics (e.g., volume contraction vs. expansion), which must be considered in the reactor design. The change in gas volume due to the chemical reaction can significantly affect the hydrodynamics\textsuperscript{[22]}.

For the reactor and process design, two main questions should be answered: (1) \textit{What catalyst particle size should be used?} (2) \textit{What temperature and pressure should be used?} However, additional questions dealing with the operating range of the reactor are important. For example, for a given reactor size: \textit{What range of pressure, temperature, catalyst diameter, and total flow rate can the reactor be operated in?} The latter is essential for processes in which the actual flow rate can vary between 50-120\% of the designed flow rate (i.e., capacity utilization ratio or turndown ratio). The highly exothermic CO$_2$ methanation used within the Power-to-Gas process is such a case\textsuperscript{[11,23,24]}.  


Power-to-Gas is a three-step process in which excess of renewable electricity is used to produce hydrogen via water electrolysis. The hydrogen is subsequently converted with captured carbon dioxide through the Sabatier reaction (CO₂ methanation, see eq. 1) to produce methane (CH₄), which can be stored in the existing natural gas distribution network [25,26]. By doing so, electricity storage and carbon capture can be combined. Besides the CO₂ methanation (eq. 1), the competing reverse water gas shift reaction (eq. 2) and the CO methanation (eq. 3) occur.

\[
\begin{align*}
CO_2 + 4H_2 & \leftrightarrow CH_4 + 2H_2O \quad \Delta H^0_r = -165 \text{ kJ mol}^{-1} \\
CO_2 + H_2 & \leftrightarrow CO + H_2O \quad \Delta H^0_r = 41 \text{ kJ mol}^{-1} \\
CO + 3H_2 & \leftrightarrow CH_4 + H_2O \quad \Delta H^0_r = -206 \text{ kJ mol}^{-1}
\end{align*}
\]

Both the CO₂ and CO methanation are reactions with a considerable volume contraction (max. 40% and 50%, respectively), which might influence the fluidization behavior [19]. From the thermodynamic standpoint, the CO₂ methanation is favored at low temperatures (300 - 350 °C) and high pressures (up to 20 bar). However, high operating pressures are not economical, whereas low operation temperatures require a highly efficient catalyst. Thus, a techno-economical deal must be found [24,25].

Due to the inherent intermittency of renewable electricity, the hydrogen production fluctuates. Even with intermediate H₂ storage, the subsequent methanation reactor should be flexible and have the ability to operate at a lower gas feed (i.e., lower turndown ratio) [27]. Conventionally, bubbling fluidized bed reactors are not designed with the highest flexibility in mind. Therefore, this work presents a new type of operating diagram for BFBR that allows (1) to determine a suitable reactor diameter for a given operating condition and (2) to determine the operating range for a given reactor diameter for the CO₂ methanation. The presented methodology can be applied for other reactions, such as Fischer-Tropsch synthesis or reforming reactions.
2 Methodology

The minimum fluidizing velocity \((u_{mf})\) is the velocity at which the solids will be suspended, i.e. when the pressure drop exceeds the weight of solids (eq. 4) \([1]\).

\[
u_{mf} = \frac{\mu}{2 \cdot d_p \cdot \rho_g} \left( \frac{K_2}{K_1} + \sqrt{\frac{K_2}{K_1}} \right)^2 + \frac{1}{K_1} \frac{4 \cdot d_p^2 \cdot \rho_g \cdot (\rho_s - \rho_g) \cdot g}{\mu^2}
\]  \hspace{1cm} (4)

with \(K_1 = \frac{1.75}{\varepsilon_{mf} \cdot \varphi_s}\) and \(K_2 = \frac{150 \cdot (1-\varepsilon_{mf})}{\varepsilon_{mf} \cdot \varphi_s^2}\). Eq. (4) takes into account all particles ranges, where \(u_{mf}\) is the minimum fluidization velocity \((m \cdot s^{-1})\), \(\rho_s\) is the solid density \((kg \cdot m^{-3})\), \(\rho_g\) is the gas density \((kg \cdot m^{-3})\), \(g\) is the gravitational acceleration \((kg \cdot m \cdot s^{-2})\), \(d_p\) is the particle diameter \((m)\), \(\mu\) is the dynamic viscosity \((Pa \cdot s)\), \(\varphi_s\) is the sphericity of the particle and \(\varepsilon_{mf}\) is the bed voidage \([1]\). On the other hand, the terminal velocity \((u_t)\) refers to the velocity at which the particles are entrained from the bed (eq. 5) \([1]\).

\[
u_t = \left[\frac{4 \cdot d_p \cdot (\rho_s - \rho_g) \cdot g}{3 \cdot \rho_g \cdot C_D}\right]^{1/2}
\]  \hspace{1cm} (5)

Terminal velocity depends on gas density, solid density, particle size, and drag coefficient, \(C_D\). The latter is described by eq. (6) \([28]\).

\[
C_D = \frac{24}{Re_t} \left[ 1 + \left( 8.1716e^{-4.0655 \varphi_s} \right) Re_t^{0.0964 + 0.5565 \varphi_s} \right] + \frac{73.69 \left( e^{-5.0748 \varphi_s} \right) Re_t}{Re_t + 5.378e^{6.2122 \varphi_s}}
\]  \hspace{1cm} (6)

Where \(Re\) is the Reynolds number evaluated at \(u_t\). The Reynolds number depends strongly on the temperature and pressure, as they predominately influence the fluid viscosity and density, respectively.

Considering the assumptions stated above and based on eqs. (4) and (5), working diagrams can be designed to determine the bed diameter and the operating range for different catalyst particle diameters. By fixing one variable, the effect on temperature and pressure changes can be analyzed. The diagrams include a set of curves using constant velocity values, denotes as isotachs. The bed
diameter, $d_{FB}$ (m), can be determined by considering the superficial gas velocity, $u_0 = \dot{V} / A$ and the cross-section of the reactor \( A = 0.25 \cdot \pi \cdot d_{FB}^2 \) as:

$$d_{FB} = \sqrt{\frac{4 \cdot \dot{V}}{\pi \cdot u_0}}$$

(7)

where $\dot{V}$ is the actual volumetric flow rate at reaction conditions $(T, p)$. Using ideal gas relation $\frac{\dot{V} \cdot p}{T} = \frac{\dot{V}_0 \cdot p_0}{T_0}$, the reactor diameter can be expressed with the volumetric flow rate $(\dot{V}_0)$ at standard conditions (i.e., STP, temperature and pressure of $T_0 = 273.15$ K and $p_0 = 1$ bara):

$$d_{FB} = \sqrt{\frac{4 \cdot \dot{V}_0 \cdot p_0 \cdot T}{\pi \cdot u_0 \cdot T_0 \cdot p}}$$

(8)

By plotting eq. (8) as a function of temperature or pressure, the required bed diameter can be determined for various particle sizes. Working diagrams were developed considering two cases, a laboratory and an industrial-scale fluidized bed reactor for the CO$_2$ methanation with the assumptions stated in Table 1.

Carbon dioxide captured from biogas plants is a good source for the CO$_2$ methanation reaction. Assuming that a typical biogas plant produces $\sim$1000 m$_N^3$ h$^{-1}$ of CO$_2$ \cite{29} and a stoichiometric H$_2$ to CO$_2$ ratio, a total volumetric flow rate of 5000 m$_N^3$ h$^{-1}$ (i.e., 100% capacity) was used. In the current study, we considered that the reactor should be able to operate between 50 to 110% of their design capacity (i.e., 2500 to 5500 m$_N^3$ h$^{-1}$) due to the H$_2$ fluctuations, which represents a turndown ratio of 0.5-1.1. The turndown ratio for the fluidized bed reactor is defined as the actual feed flow rate divided by the designed feed flow rate (both in STP). A superficial gas velocity of $u_0 = 6 \cdot u_{mf}$ was chosen to ensure that the reactor operates in the bubbling regime\cite{1,23}. Besides, we have assumed three different
catalyst particle sizes (150, 250, and 500 µm) and not a particle size distribution. The values for
catalyst sphericity and bed voidage at minimum fluidization velocity were taken from the literature\cite{[1]}.

Table 1 Parameters and assumptions used for the operating diagrams

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Assumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed composition</td>
<td>H$_2$/CO$_2$ = 4/1 (stoichiometric)</td>
</tr>
<tr>
<td>Designed capacity (total inlet flow rate)</td>
<td>0.5 mN$^3$ h$^{-1}$ (laboratory/pilot scale), 5000 mN$^3$ h$^{-1}$ (industrial scale)</td>
</tr>
<tr>
<td>Capacity range</td>
<td>50% - 110%</td>
</tr>
<tr>
<td>Temperature, $T$</td>
<td>300 - 500 °C</td>
</tr>
<tr>
<td>Pressure, $p$</td>
<td>1 – 20 bara</td>
</tr>
<tr>
<td>Velocity ratio $u_o/u_{mf}$</td>
<td>6 - 12</td>
</tr>
<tr>
<td>Particle sizes, $d_P$</td>
<td>150, 250 and 500 µm (Geldart B)</td>
</tr>
<tr>
<td>Sphericity $\phi_s$</td>
<td>0.58 $^\text{[1]}$</td>
</tr>
<tr>
<td>Bed voidage $\varepsilon_{mf}$</td>
<td>0.57, 0.55 and 0.54 $^\text{[1]}$</td>
</tr>
<tr>
<td>Catalyst density $\rho_c$</td>
<td>1500 kg m$^{-3}$</td>
</tr>
</tbody>
</table>

As the operating conditions and turndown ratio will affect the amount of methane formed, the
associated chemical energy ($E_{CH_4}$ in MW) is calculated assuming that all unconverted CO$_2$ and H$_2$, as
well as the produced H$_2$O, are separated from CH$_4$. Thus, the chemical energy is directly proportional
to the lower heating value (i.e., heat of combustion) from CH$_4$. 
3 Results and Discussion

3.1 Equilibrium composition

Temperature and pressure have different and opposite effects on the equilibrium composition as illustrated in Figure 1A and B. The main products of the CO₂ methanation, i.e., H₂O and CH₄, are thermodynamically favored at low temperatures and high pressures\[^{30}\]. On the other hand, the formation of CO, a product of the competitive reverse water-gas-shift reaction, is favored at higher temperatures (>450 °C) but not at higher pressures \[^{21,25,30}\]. The equilibrium composition was calculated using the HSC Chemistry v9 software that uses the minimization of the Gibbs energy approach.

The total outlet molar flow rate increased with increasing temperature and slightly decreased with increasing pressure (pink line in Figure 1A and B). In other words, the volume contraction (blue shaded area) decreased when the temperature increased. At 300 °C, a 36% volume reduction is observed; however, as the temperature increases to 500 °C, the gas expands, and hence the volume contraction reduces to 27%.

During the reaction, the influence of temperature and pressure on the actual volumetric flow rates (inlet and outlet) are more pronounced, as visualized in Figure 1C and D, respectively. These effects are very important as the actual volumetric flow rate dictates the gas velocity in the reactor, and hence, the fluidization behavior. For example, the outlet volume flow rate increased from 6,500 m³ h⁻¹ at 300 °C to 10,500 m³ h⁻¹ at 500 °C for 1 bara (Figure 1C). Whereas, the outlet volume flow rate decreased significantly from 7,000 m³ h⁻¹ at 1 bara to less than 500 m³ h⁻¹ at 20 bara at 350 °C (Figure 1D). Therefore, the design and operating conditions of the fluidized bed reactor will be different in each case.
The subsequent calculations have been done with the standard inlet flow rates considering the volume contraction instead of the outlet flow rates as the volume contraction is assumed to occur along the height of the reactor as the reaction progresses.

Figure 1. Equilibrium composition of CO₂ methanation based on (A, B) the molar flow rate and (C, D) the volumetric flow rate as a function of (A, C) temperature at 1 bara and (B, D) pressure at 350 °C. Total inlet flow rate: 5000 m³ h⁻¹ (220 kmol h⁻¹) with H₂/CO₂ = 4/1. Blue shaded parts represent volume contraction.

Normal inlet refers to the inlet at standard conditions (273 K and 1 bara), whereas inlet refers to the volumetric flow rate at operating conditions.

3.2 Bed diameter

The calculations shown in the following diagrams rely on the fact that at the same gas flow rate, different gas velocities can be set by changing the cross-sectional area of the reactor where the bed diameter is directly proportional to the square root of this parameter.
3.2.1 Temperature effect

Figure 2 depicts the calculated bed diameter (eq. 8) (empty tube diameter) as a function of temperature at a constant pressure of 3 bara for a laboratory-scale reactor. The total inlet flow rate was set to 0.5 m³ h⁻¹ with an H₂/CO₂ ratio of 4/1 (Table 1). The grey lines denote the isotachs (constant gas velocity), the black solid and dashed lines refer to the superficial gas velocity ($u_0 = 6 \cdot u_{mf}$) and the terminal velocity ($u_t$), respectively, for catalyst particles with a size of 150, 250 and 500 µm. Since bubbling fluidized beds should operate far from the terminal velocity, the maximum $u_0/u_{mf}$ ratio of 12 was assumed (blue line), resulting in a decision window indicated by the blue shaded area. To fluidize particles with a size of 250 µm, the bed diameter of the BFBR should be within that blue area to ensure proper fluidization.

![Figure 2. Bed diameter as a function of temperature (300-500 °C) at 3 bara for a laboratory-scale reactor. Total inlet flow rate 0.5 m³ h⁻¹, H₂/CO₂ = 4/1. Blue shaded area represents the zone between $6 \cdot u_{mf}$ (bold black line) and $12 \cdot u_{mf}$ (blue line) for a particle size of 250 µm (decision window). Dashed lines ($u_t$).](image)
The analysis showed that a larger bed diameter is required to achieve the necessary gas velocity to fluidize smaller particle sizes with the same flow rate and temperature at 3 bara (Figure 2). A larger bed diameter is also required to fluidize the same particle size (e.g., 250 µm) but at higher temperatures. The plot allows determining a suitable bed diameter as a function of particle size and temperature for a given total volumetric flow rate (STP) and operating pressure. For example, if the laboratory-scale reactor operates at 340°C and 3 bara with 250 µm particles at $6 \cdot u_{mf}$ a bed diameter of 19.5 mm is required. Additionally, the superficial gas velocity of $u_o = 0.22 \text{ m s}^{-1}$ for these conditions can be determined by following the isotachs and their correspondent scale (star 1). If the reactor is operated at a temperature of 460 °C instead of 340 °C, the gas expands, and hence, the cross-sectional area of the reactor increases 1.6 times ($d_{FB} = 24.7 \text{ mm}$) (star 2). For both operating points, the nominal volumetric flow rate and velocity ratio were the same (i.e., 0.5 m$^3$ h$^{-1}$ and $6 \cdot u_{mf}$). Equally, to fluidize smaller catalyst particles of 150 µm an increase of 1.6 times of the reactor diameter is required at 340 °C and 3 bara, whereas a decrease of approx. 50% in the bed diameter is observed when the particle size of the catalyst is increased to 500 µm (stars 3 and 4).

The particle size of the catalyst influences not only the design of the bed diameter but also the bed height to diameter ratio ($H/D$). For instance, considering that the reactor is operated with the same ratio of gas velocity to catalyst amount ($L_N \text{ h}^{-1} \text{ kgCat}^{-1}$) for all particle sizes, $H/D$ ratio changes significantly (i.e., by a factor 3), which could further affect the hydrodynamics (i.e., bubble size), mass transfer as well the final conversion. Assuming the equilibrium conversion is achieved, an increase in temperature would decrease the CO$_2$ conversion from 94.7% at 340 °C to 90.3% at 400 °C (star 5) and 84.3% at 460 °C.

For an industrial reactor, the CO$_2$ methanation reaction would be carried out at higher pressures, thus affecting the bed diameter. The reactor diameters are illustrated as a function of temperature at 3 and
10 bara in Figure 3A and B, respectively, with a nominal inlet flow rate of 5000 m³N h⁻¹ and a ratio $\text{H}_2/\text{CO}_2 = 4$. Increasing the pressure reduces the reactor diameter to keep the same fluidization velocity. For instance, considering the previous example of a reactor operating at 340 °C and 3 bara, with catalyst particles of 250 µm and $u_0/u_{mf} = 6$, a diameter of ~1.9 m is required (star 1) for the industrial-scale reactor. However, if the operating temperature increases to 460 °C, the diameter doubles to 3.9 m, to fluidize 250 µm catalyst particles at $6 \cdot u_{mf}$ (star 2). On the other hand, if the temperature is fixed at 340 °C due to thermodynamics, kinetics or any other constraints, a larger reactor diameter is needed to fluidize smaller particles and vice-versa (i.e., ~3.1 m diameter for 150 µm and ~1 m diameter for 500 µm (stars 3 and 4)). Equally, for a more realistic industrial process in which a higher pressure of 10 bara will favor the CO₂ methanation reaction, the same analysis can be conducted. In this case, the cross-sectional area of the reactor is approx. 3.3 times smaller to keep the gas velocity constant and hence suitable catalyst fluidization. In detail, a diameter of approx. 1.06 m is needed to fluidize 250 µm catalyst particles at $6 \cdot u_{mf}$ at 340 °C (star 5). Hence, it is paramount to decide the total operating pressure prior to determining the reactor size.

As mentioned in section 3.1, the CO₂ conversion is favored at low temperatures and higher pressures due to the exothermicity and volume contraction nature of the reaction. At 340 °C and 10 bara, an equilibrium CO₂ conversion of 96.7% is achieved, which translates to a total energy output of 9.6 MW_{CH₄} (based on the lower heating value of methane). If the temperature is kept constant at 340 °C, and the pressure is reduced to 3 bara, the equilibrium conversion of CO₂ is 94.7%, which corresponds to an energy output of 9.4 MW_{CH₄}. It can be noticed that the energy output between the industrial reactor operating at 3 bara and the 10 bara differs only by 2%. However, the operating cost of the compression increase when increasing the operating pressure. Hence, the advantage of operating at a lower pressure.
Figure 3. Bed diameter as a function of temperature at (A) 3 bara and (B) 10 bara for different particle diameters (150, 250, and 500 µm) for an industrial-scale reactor. Total flow rate of 5000 m³ h⁻¹ with H₂/CO₂ = 4/1 (6·uₘf (bold lines), 12·uᵣ (blue lines), u₄ (dashed lines)).
3.2.2 Pressure effect

Figure 4 presents the effect of pressure on the bed diameter at 340 °C shown for different particle sizes for an industrial-scale reactor. The pressure has an important effect on the bed diameter. At higher pressures, the reactor becomes narrower but higher to keep the volume and mass of the catalyst constant\textsuperscript{[31]}. For fluidizing bigger particles, the reactor could operate at lower pressures, which reduces the operating costs associated with the compression, whereas at higher values of pressure, smaller particles are required. In this case, the particle size needs to be chosen carefully so the catalyst can be fluidized.

![Figure 4. Bed diameter as a function of pressure at 340 °C for different particle diameters (150, 250, and 500 µm) for an industrial-scale reactor. Total flow rate of 5000 m\textsuperscript{3} h\textsuperscript{-1} with H\textsubscript{2}/CO\textsubscript{2} = 4/1 (6·u\textsubscript{mf} (solid lines), 12·u\textsubscript{mf} (blue line), u\textsubscript{t} (dashed lines)).](image-url)
The blue shaded zone represents a decision window to operate the reactor between 1 and 20 bara for a particle size of 250 µm. Working at 20 bara would lead to a slimmer reactor with diameters of 0.52 to 0.74 m. In contrast to the temperature diagrams, it is possible to have one empty tube diameter for the fluidization of particles from 150 to 500 µm with superficial gas velocities between 0.08 and 0.8 m s⁻¹. For example, a fluidized bed with a 1.2 m empty tube diameter can operate with 150, 250, and 500 µm particles at 2.2, 8, and 19 bara (stars 1, 2, and 3), respectively.

Figure 5 shows the energy output (in MWCH₄) of an industrial-scale reactor at a temperature range of 300 to 500 °C for different operating pressures. A CH₄ yield of 100% means that all carbon from CO₂ is being converted to CH₄, which corresponds to a maximum energy output of 9.94 MWCH₄. However, due to thermodynamic constraints, a maximum of 9.6 MWCH₄ is possible at 340 °C and 10 bara. Even though increasing the operating pressure leads to higher CO₂ conversions, the CH₄ energy output depends strongly on the operating temperature. For instance, the energy output only differs by 3% when increasing the pressure from 3 to 20 bar at 340 °C; however, this difference increases to 13% when the temperature increases up to 500 °C. Equally, when the CO₂ methanation reaction is carried out at higher pressures, a change in temperature has a reduced influence on the energy output as a result of the high density of the gas.
Figure 5. Energy output in MW\textsubscript{CH\textsubscript{4}} as a function of temperature for different operating pressures (1, 3, 10, and 20 bar). Total inlet flow rate of 5000 m\textsuperscript{3}h\textsuperscript{-1} and H\textsubscript{2}/CO\textsubscript{2} = 4/1.

### 3.3 Turndown ratio

3.3.1 Temperature effect

Once the bed diameter for the reactor has been chosen, a working diagram can be designed to visualize the capacity or turndown ratio. An example is shown in Figure 6 for an industrial-scale reactor operating at 10 bara and an empty tube diameter of 1.06 m, the reactor diameter was chosen based on Figure 3 with a designed capacity of 100\% (i.e., inlet flow rate of 5000 m\textsuperscript{3}h\textsuperscript{-1}), reaction temperature of 340 °C, and particle size of 250 µm (star 5 in Figure 3 corresponds to star 1 in Figure 6). As the temperature increases, the turndown ratio decreases, as well as the superficial gas velocity represented by the isotachs.
Figure 6. Capacity as a function of temperature assuming volume contraction for different particle diameters (150 and 250 µm), empty tube diameter of 1.06 m, and operating pressure of 10 bara for an industrial-scale reactor. Inlet flow rate H₂/CO₂ = 4/1. (6·$$u_{mf}$$ (solid lines), 12·$$u_{mf}$$ (blue lines), $$u_c$$ (dashed lines)).

The blue shaded area defines a theoretical maximum working range for 250 µm particles with capacity utilization of 50 to 120% (i.e., turndown ratio of 0.5-1.2). If the temperature increases to 400 °C at the same superficial gas velocity (i.e., 0.22 m s⁻¹), the capacity decreases to approx. 80%, which means that the inlet flow rate reduces to 4000 m₃ h⁻¹ (star 2). If less feed gas is available for the CO₂ methanation reactor due to low H₂ production, then the temperature can be increased to maintain the same velocity ratio. However, this would result in a lower CH₄ yield and CO₂ conversion due to equilibrium constraints, as depicted in Figure 1. Hence, the CO₂ conversion and energy output would decrease from 96.7% and 9.6 MW CH₄ (10 bara, 340 °C, 100% capacity) to 92.7% and 7.7
MW\textsubscript{CH4} (10 bara, 420 °C, 80% capacity). This not only represents a decrease of 20% in the CH\textsubscript{4} energy output but also increases the operating temperature by 80 °C, which raises the energy consumption of the system.

On the other hand, keeping pressure and temperature constant at 50% capacity (i.e., inlet flow rate of 2500 m\textsuperscript{3} h\textsuperscript{-1}) would reduce the velocity ratio to \( u_0/umf = 3 \) (\( u_0 = 0.11 \) m s\textsuperscript{-1}) and the total energy produced to 4.8 MW\textsubscript{CH4} (star 3). Considering a volume contraction of 26 – 38 vol\%, it follows that the fluidized bed is likely to destabilize and collapse.

3.3.2 Pressure effect

Increasing the temperature to deal with a lower feed flow rate is not the best solution. Thus, in this section, the effect of pressure on the capacity for the industrial-scale reactor is visualized and discussed (Figure 7). The blue shaded area depicts the operating window to fluidize particles of 250 \( \mu \)m at a temperature of 340 °C in a 1.06 m fluidized bed. Operating pressure of 10 bara corresponds to a design capacity of 100% (i.e., inlet flow rate of 5000 m\textsuperscript{3} h\textsuperscript{-1}) (star 1). Operating the reactor at 50% capacity with the same velocity ratio (6·\( umf \)) would require lowering the total pressure to 5 bara at the same temperature (star 2). At this condition, the CO\textsubscript{2} conversion is slightly lower, with 94.6% compared to 96.7% at 10 bara. The corresponding rated CH\textsubscript{4} output would be 4.8 MW.

In contrast, an increase to 110% capacity (i.e., inlet flow rate of 5500 m\textsuperscript{3} h\textsuperscript{-1}) would require a slight increase in the total pressure to maintain the same velocity ratio. If the pressure is kept constant at 10 bara at 110% capacity, the velocity ratio would slightly increase to \( u_0 = 6.5 \) \( umf \), which is well within the blue shaded area that defines the operating window (star 3). At this condition, a total energy output of 10.6 MW\textsubscript{CH4} could be achieved.
Figure 7. Capacity as a function of pressure assuming volume contraction at 340 °C for different particle diameters (150, 250, and 500 µm) and empty tube reactor diameter of 1.06 m for an industrial-scale reactor.

Total flow rate with H₂/CO₂ = 4/1 ($6 \cdot u_{mf}$ (solid lines), $12 \cdot u_{mf}$ (blue line), $u_t$ (dashed lines)).

This short analysis shows that changing the pressure provides greater flexibility than changing the temperature in terms of turndown ratio/capacity.

Furthermore, the plot shows that the reactor with an empty tube diameter of 1.06 m can be used with a different range of particle sizes (150 to 500 µm). For 500 µm catalyst particles the operating window decreases, while for 150 µm catalyst particles the operating window would be larger compared to the reference case with 250 µm. Larger particles would shift the operation to lower pressure (i.e., 3-5 bara), whereas smaller particles would allow operating the reactor up to 20 bara at 80% capacity at
the same velocity ratio of \( \frac{u_0}{u_{mf}} = 6 \). Operating at 20 bara, would not significantly increase the equilibrium conversion of \( \text{CO}_2 \) and thus the energy output, but will increase the compression operating costs.

4 Conclusions

Power-to-Gas is an industrially relevant process that might be the key to satisfy the increasing global demand for renewable energy. In the Power-to-Gas technology, \( \text{CO}_2 \) methanation is a fundamental step to produce \( \text{CH}_4 \) that can be subsequently injected in the current gas grid distribution or gas storage. In this manuscript, we have developed working diagrams for the \( \text{CO}_2 \) methanation reaction in a bubbling fluidized bed reactor considering different operating temperatures (300 to 500 °C) and pressures (1 to 20 bara). The diagrams shown in this work are a graphical representation of the hydrodynamic equations for BFB reactors and can be used as a base for the reactor design. Moreover, the same methodology to determine design (bed diameter) and operating (turndown ratio) parameters can be applied to other reactions besides \( \text{CO}_2 \) methanation by considering the thermodynamics of the reaction. Adjusting the geometry of the BFB reactor for changing operating conditions such as temperature, pressure, and total flow rate is critical to ensure proper fluidization. These working diagrams consider a given reactor design (bed diameter) and turndown ratio. This means that the reactor can operate in a flexible range of operating conditions depending on the availability of the reactants. Increasing the operating temperature increases slightly the bed diameter due to the gas expansion, whereas increasing the pressure leads to slimmer reactors in order to keep the fluidization velocity. The results showed that the \( \text{CO}_2 \) methanation reaction should be carried out at a lower and more importantly, at a fixed temperature (e.g., 340 °C) to allow a more flexible operation in terms of pressure, particle size of the catalyst and thus turn-down ratio and energy output. Altering the pressure
while maintaining the same velocity ratio might be a good option to adjust for changing turndown ratios of 50 to 110%. can be used as a base for the reactor design.

Acknowledgments

The authors acknowledge funding from the Natural Sciences and Engineering Research Council of Canada (NSERC RGPIN-2014-04685). Jennifer Martin-del-Campo gratefully acknowledges funding from the Consejo Nacional de Ciencia y Tecnologia (CONACyT, Mexico scholarship program) and the Faculty of Engineering through the McGill Engineering Doctoral Award.

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Units</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>( u_{mf} )</td>
<td>([\text{m s}^{-1}])</td>
<td>Minimum fluidization velocity</td>
</tr>
<tr>
<td>( d_p )</td>
<td>([\text{m}])</td>
<td>Particle diameter</td>
</tr>
<tr>
<td>( \rho_s )</td>
<td>([\text{kg m}^{-3}])</td>
<td>Solid density</td>
</tr>
<tr>
<td>( \rho_g )</td>
<td>([\text{kg m}^{-3}])</td>
<td>Gas density</td>
</tr>
<tr>
<td>( g )</td>
<td>([\text{m s}^{-2}])</td>
<td>Gravity</td>
</tr>
<tr>
<td>( \mu )</td>
<td>([\text{Pa s}])</td>
<td>Viscosity</td>
</tr>
<tr>
<td>( \varepsilon_{mf} )</td>
<td>[-]</td>
<td>Bed voidage</td>
</tr>
<tr>
<td>( \varphi_s )</td>
<td>[-]</td>
<td>Sphericity</td>
</tr>
<tr>
<td>( Re )</td>
<td>[-]</td>
<td>Reynolds number</td>
</tr>
</tbody>
</table>
\[ V_o \quad [m^3 \text{ s}] \quad \text{Volumetric flow rate at outlet conditions} \]

\[ T_o \quad [K] \quad \text{Temperature at standard conditions (273.15 K)} \]

\[ P_o \quad [\text{bara}] \quad \text{Pressure at standard conditions (1 bara)} \]

\[ T \quad [\text{°C}] \quad \text{Temperature} \]

\[ p \quad [\text{bara}] \quad \text{Pressure} \]

\[ u_t \quad [m \text{ s}^{-1}] \quad \text{Terminal velocity} \]

\[ M \quad [\text{kg kmol}^{-1}] \quad \text{Molecular weight} \]

\[ x_i \quad [-] \quad \text{Molar fraction of the component in the mixture} \]

\[ C_D \quad \text{Drag coefficient} \]

**Complementary equations**

\[ Re = \frac{u \cdot d_p \cdot \rho_g}{\mu} \]

\[ \mu_m = \sum_{i=1}^{N_{cc}} \frac{x_i \cdot \mu_i}{\sum_{j}^{N_{cc}} x_j \cdot \phi_{ji}} \]

\[ \phi_{ij} = \left[ 1 + \left( \frac{\mu_i}{\mu_j} \right)^{0.5} \cdot \left( \frac{M_i}{M_j} \right)^{0.25} \right]^2 \]

\[ \frac{1}{8 \cdot \left( 1 + \frac{M_i}{M_j} \right)^{0.5}} \]

\[ \mu = \frac{A \cdot T^B}{1 + \frac{C}{T} + \frac{D}{T^2}} \]
References


List of Figures

Figure 1. Equilibrium composition of CO\textsubscript{2} methanation based on (A, B) the molar flow rate and (C, D) the volumetric flow rate as a function of (A, C) temperature at 1 bara and (B, D) pressure at 350 °C. Total inlet flow rate: 5000 m\textsubscript{N}\textsuperscript{3} h\textsuperscript{-1} (220 kmol h\textsuperscript{-1}) with H\textsubscript{2}/CO\textsubscript{2} = 4/1. Blue shaded parts represent volume contraction. Normal inlet refers to the inlet at standard conditions (273 K and 1 bara), whereas inlet refers to the volumetric flow rate at operating conditions.

Figure 2. Bed diameter as a function of temperature (300-500 °C) at 3 bara for a laboratory-scale reactor. Total inlet flow rate 0.5 m\textsubscript{N}\textsuperscript{3} h\textsuperscript{-1}, H\textsubscript{2}/CO\textsubscript{2} = 4/1. Blue shaded area represents the zone between 6·\textit{u}_{mf} (bold black line) and 12·\textit{u}_{mf} (blue line) for a particle size of 250 µm (decision window). Dashed lines (\textit{u}_t).

Figure 3. Bed diameter as a function of temperature at (A) 3 bara and (B) 10 bara for different particle diameters (150, 250, and 500 µm) for an industrial-scale reactor. Total flow rate of 5000 m\textsubscript{N}\textsuperscript{3} h\textsuperscript{-1} with H\textsubscript{2}/CO\textsubscript{2} = 4/1 (6·\textit{u}_{mf} (bold lines), 12·\textit{u}_{mf} (blue lines), \textit{u}_t (dashed lines)).

Figure 4. Bed diameter as a function of pressure at 340 °C for different particle diameters (150, 250, and 500 µm) for an industrial-scale reactor. Total flow rate of 5000 m\textsubscript{N}\textsuperscript{3} h\textsuperscript{-1} with H\textsubscript{2}/CO\textsubscript{2} = 4/1 (6·\textit{u}_{mf} (solid lines), 12·\textit{u}_{mf} (blue line), \textit{u}_t (dashed lines)).

Figure 5. Energy output in MW\textsubscript{CH\textsubscript{4}} as a function of temperature for different operating pressures (1, 3, 10, and 20 bar). Total inlet flow rate of 5000 m\textsubscript{N}\textsuperscript{3} h\textsuperscript{-1} and H\textsubscript{2}/CO\textsubscript{2} = 4/1.

Figure 6. Capacity as a function of temperature assuming volume contraction for different particle diameters (150 and 250 µm), empty tube diameter of 1.06 m, and operating pressure of 10 bara for an industrial-scale reactor. Inlet flow rate H\textsubscript{2}/CO\textsubscript{2} = 4/1. (6·\textit{u}_{mf} (solid lines), 12·\textit{u}_{mf} (blue lines), \textit{u}_t (dashed lines)).
Figure 7. Capacity as a function of pressure assuming volume contraction at 340 °C for different particle diameters (150, 250, and 500 µm) and empty tube reactor diameter of 1.06 m for an industrial-scale reactor. Total flow rate with H₂/CO₂ = 4/1 (6·uₘ_f (solid lines), 12·uₘ_f (blue line), uᵣ (dashed lines)).