Numerical evaluation of a pressurized CLC fuel reactor for process intensification

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Abstract – A simulation-based methodology is presented by which a cost optimized CLC reactor can quickly and economically be designed. The methodology is applied to investigate the possibilities of using high temperature and pressure for process intensification of a CLC fuel reactor which reduces an iron oxide oxygen carrier using syngas. For this example, pressure was identified as a much more viable process intensification mechanism than temperature. Reactor cost estimates were then used to find the cost optimized combination of temperature and pressure for this particular reactor.

1 Introduction

Chemical looping combustion is a promising process concept for achieving economically viable power production with integrated CO₂ capture in the near future. The rapid development and commercialization of such a process concept is of great importance considering the long term threat of climate change and the lack of political action needed to make carbon capture economically viable.

This paper combines two ways of addressing this challenge. Firstly, the simulation-based reactor design and optimization methodology herein presented has the potential to significantly accelerate the CLC commercialization process. Due to the complexity of the process, design and optimization is very challenging and requires many small scale-up and demonstration steps. A reliable fundamental modelling approach can significantly accelerate this slow process by evaluating the effects of a wide array of design and operating variables, calculating reactor operating windows and recommending economically optimised reactor designs. Such an approach can increase the size of scale-up increments, speed up the demonstration process and make every demonstration much more economical.

Secondly, the simulation-based reactor design methodology will focus especially on the potentials for process intensification using high temperature and high pressure. Due to the stringent demands on CLC to not only capture CO₂, but also deliver electricity at a cost comparable to standard fossil fuel power stations today, economic matters become very important. Process intensification is a powerful way in which reactor sizes can be reduced and plant efficiency can be increased, ultimately leading to a low cost of electricity.

This paper will demonstrate the methodology of simulation-based design of a cost optimised early demonstration scale (0.5 m ID) fuel reactor. Various reactor setups will be simulated using the well-established two fluid model (TFM) closed by the kinetic theory of granular flows (KTGF) [1-4]. The data from these simulations will subsequently be used to describe reactor performance (the degree of conversion achieved) as a function of fluidization velocity, reactor temperature and pressure. A second order model will then be fitted through all the
combinations of fluidization velocity, reactor temperature and pressure that will attain a pre-
specified degree of fuel conversion. Finally, some roughly estimated cost functions will be
used as an example to find the combination of fluidization velocity, reactor temperature and
pressure that will achieve the pre-specified degree of conversion most economically.

2 List of symbols

2.1 Main Symbol definitions

\( \alpha \) Volume fraction

\( \chi \) Fraction of gas exiting reactor unreacted

\( \phi \) Kinetic energy transfer rate (kg/m.s\(^3\))

\( \gamma \) Dissipation rate (kg/m.s\(^3\))

\( \Theta \) Granular temperature (m\(^2\)/s\(^2\))

\( \rho \) Density (kg/m\(^2\))

\( \varsigma \) Specularity coefficient

\( \tau \) Stress tensor (kg/m.s\(^2\))

\( \tau_s \) Particle shear force at the wall (N)

\( \vec{v} \) Velocity vector (m/s)

\( \nabla \) Del operator / Gradient (1/m)

\( d \) Diameter (m)

\( \bar{g} \) Gravity vector (m/s\(^2\))

\( g_{0,ss} \) Radial distribution function

\( H \) Expanded bed height (m)

\( I \) Identity tensor

\( j \) Diffusive flux ((kg/(m\(^2\).s))

\( K \) Momentum exchange coefficient (kg/(m\(^3\).s))

\( k \) Diffusion coefficient (kg/m.s)

\( k \) Reaction rate constant (mol/(1-n)/(m\(^{2-3n}\).s))

\( M \) Molar weight (kg/kmol)

\( N \) Number of moles (mol)

\( n \) Order of reaction

\( P \) Pressure (Pa)

\( p \) Pressure (Pa)
\( R \) Gas constant (8.314 J/(mol.K))

\( R^H \) Heterogeneous reaction rate (mol/m\(^3\)s)

\( S \) Mass/species source term (kg/(m\(^3\).s))

\( S^o \) Momentum source term (kg/m\(^2\)s\(^2\))

\( S \) Mass/species source term (kg/(m\(^3\).s))

\( s \) Surface area fraction

\( T \) Temperature (K)

\( t \) Time (s)

\( U \) Fluidization velocity (m/s)

\( \bar{U}_{x,||} \) Particle velocity parallel to wall (m/s)

\( V \) Volume (m\(^3\))

\( X \) Reactor performance

\( Y \) Species mass fraction

2.2 Sub- and superscript definitions:

\( \Theta_s \) Granular temperature

\( i \) Species index

\( g \) Gas

\( gs \) Inter-phase

\( \text{max} \) Maximum packing

\( s \) Solids

2.3 Abbreviations

ANOVA Analysis of variance

by Interaction effect

CFD Computational fluid dynamics

KTGF Kinetic theory of granular flows

L Linear effect

Q Quadratic effect

SS Sum of squares

TFM Two fluid model

TGA Thermo-Gravimetric Analysis
3 Simulations

Simulations were carried out both on a 2D planar geometry using the set of KTGF closures most commonly used in the literature.

3.1 Model equations

Conservation equations are solved for each of the two phases present in the simulation. The continuity equations for the gas and solids phases are given below:

$$\frac{\partial}{\partial t}(\alpha_g \rho_g) + \nabla \cdot (\alpha_g \rho_g \vec{v}_g) = \alpha_g S_g$$  \hspace{1cm} \text{Equation 1}

$$\frac{\partial}{\partial t}(\alpha_s \rho_s \vec{v}_s) + \nabla \cdot (\alpha_s \rho_s \vec{v}_s) = \alpha_s S_s$$  \hspace{1cm} \text{Equation 2}

Momentum conservation for the gas phase is written as

$$\frac{\partial}{\partial t}(\alpha_g \rho_g \vec{v}_g) + \nabla \cdot (\alpha_g \rho_g \vec{v}_g \vec{u}_g) = -\nabla p + \nabla \cdot \vec{F}_g + \alpha_g \rho_g \vec{g} + K_{sg} (\vec{u}_g - \vec{u}_s) + S_g^0$$  \hspace{1cm} \text{Equation 3}

And for the solids as

$$\frac{\partial}{\partial t}(\alpha_s \rho_s \vec{v}_s) + \nabla \cdot (\alpha_s \rho_s \vec{v}_s \vec{u}_s) = -\nabla p - \nabla p_s + \nabla \cdot \vec{F}_s + \alpha_s \rho_s \vec{g} + K_{gs} (\vec{u}_g - \vec{u}_s) + S_s^0$$  \hspace{1cm} \text{Equation 4}

The inter-phase momentum exchange coefficient \( K_{gs} = K_{sg} \) was modelled according to the formulation of Syamlal and O’Brien [4].

Solids phase stresses were determined according to the KTGF analogy where the random particle motion is likened to the thermal motion of molecules in a gas using the concept of granular temperature. The conservation equation for granular temperature is given below:

$$\frac{3}{2} \frac{\partial}{\partial t} \left( \alpha_s \rho_s \Theta_s \right) + \nabla \cdot \left( \alpha_s \rho_s \vec{v}_s \Theta_s \right) = \left( -p_s \vec{I} + \vec{F}_s \right) \cdot \nabla \vec{u}_s + \nabla \cdot \left( k_{\Theta s} \nabla \Theta_s \right) - \gamma_{\Theta s} + \phi_{\Theta s}$$  \hspace{1cm} \text{Equation 5}

This partial differential equation was simplified to an algebraic equation by neglecting the convection and diffusion terms – an often used assumption in dense, slow moving fluidized beds where the local generation and dissipation of granular temperature far outweigh the transport by convection and diffusion [5]. The two final terms in Equation 5 are the collisional dissipation of energy [3] and the interphase exchange between the particle fluctuations and the gas phase [1].

Solids stresses are calculated according to shear and bulk [3] viscosities due to particle momentum exchange through translation and collision. The shear viscosity consists of three parts: collisional [1, 4], kinetic [4] and frictional [6].

Granular temperature as well as the radial distribution function (measure of the average distance between particles) is used to determine the solids pressure \( p_s \) in Equation 4. The solids pressure formulation by Lun et al. [3] was complemented by the radial distribution function of Ogawa and Oshima [7].

Finally, Species are also conserved for the gas phase.

$$\frac{\partial}{\partial t}(\alpha_g \rho_{g,j} Y_{g,j}) + \nabla \cdot (\alpha_g \rho_{g,j} \vec{v}_g Y_{g,j}) = \nabla \cdot \vec{J}_{g,j} + \alpha_g S_{g,j}$$  \hspace{1cm} \text{Equation 6}
Further information on the reaction rate (implemented via the source term \( S_{r,i} \)) will be given below. The formulations of the source terms themselves are given in a previous publication by the present authors [8].

Two simplified reactions for the reduction of an iron oxide oxygen carrier with syngas were simulated:

\[
\begin{align*}
H_2 + 3Fe_tO_3 & \rightarrow 2Fe_tO_4 + H_2O \\
CO + 3Fe_2O_3 & \rightarrow 2Fe_tO_4 + CO_2
\end{align*}
\]

Reactions were implemented using the shrinking core methodology [9] with chemical kinetics as the rate limiting step. The formulation of the volumetric reaction rate of CO with Fe_2O_3 is given as an example below:

\[
R_H = -\frac{1}{V} \frac{dN_{CO}}{dt} = \frac{6}{d_z} S_{Fe_2O_3} \alpha_z k \left( \frac{Y_{CO}\rho_d}{M_{CO}} \right)^n
\]

Equation 7

The reaction rate constant was taken from TGA studies performed not only at varying fuel concentrations and temperatures, but also at varying pressures [10]. These reaction rate constants were implemented as follows:

\[
\begin{align*}
\frac{k_{H_2}}{P_0^{1.03}} & = 0.0023 e^{\frac{-24000}{RT_{actual}}} \\
\frac{k_{CO}}{P_0^{0.89}} & = 0.00062 e^{\frac{-29000}{RT_{actual}}}
\end{align*}
\]

Equation 8

The energy conservation equation was not solved under the assumption of isothermal reactor operation. This is usually a good assumption due to the excellent mixing characteristic of fluidized bed reactors.

### 3.2 Boundary conditions

A simple no-slip wall boundary condition was set for the gas phase. The Johnson and Jackson [11] boundary condition was used for the granular phase with a specularity coefficient of 0.5.

\[
\tilde{r}_s = \frac{\pi}{6} \sqrt{3} \frac{\alpha_s}{\alpha_{s,\text{max}}} \rho_s g_{0,\text{st}} \sqrt{\Theta_s} \hat{U}_{s,\parallel}
\]

Equation 9

The inlet condition was specified as a velocity inlet injecting syngas (21.9% H₂, 60.5% CO, 2.7% CO₂, 14.6% N₂ and 0.3% H₂O) at the flowrate required by the specific simulation run in question. The outlet was designated as a pressure outlet at atmospheric pressure.

### 3.3 Flow solver and solver settings

The commercial software package, FLUENT 13.0 was used as the flow solver. The phase coupled SIMPLEx scheme [12] was used for pressure-velocity coupling and the higher order QUICK scheme [13] for the spatial discretization of all remaining equations. First order implicit temporal discretization was used. It has been shown that 2nd order time discretization is necessary for accurate solution of fast-moving riser flows with the TFM [8], but this is not the case for dense bubbling beds where the vast majority of the bed moves relatively slowly.
3.4 Geometry and meshing

The simulated geometry was 0.5 m wide and 2.5 m high and meshed with structured square cells 6.25 mm in size. This cell size is equivalent to about 20 particle diameters and was found to give sufficiently grid independent results. The initial mesh consisted of 50 mm cells which were subsequently refined three times to 6.25 mm. Refinement was done by hanging node adaption only in the lower part of the domain where the bed material resides. This method of grid refinement prevented excessively fine cells in the freeboard region where accurate resolution of the flow field is not important.

3.5 Initial conditions

The solution was initialized with zero velocity and no solids, after which solids were patched in at a volume fraction of 0.6 to the initial static bed height of 0.5 m. The solution was run for the time required for the gas to pass through the reactor five times in order to attain a quasi-steady flow condition. This solution was then used as the initial condition for time-averaging over the time required for the gas to pass through the reactor five more times.

3.6 Simulation summary

A summary of the physical properties and simulation parameters are given in Table 1.

Table 1: Physical properties and simulation parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value or Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas density</td>
<td>Ideal gas law</td>
</tr>
<tr>
<td>Gas viscosity</td>
<td>Sutherland’s formula [14]</td>
</tr>
<tr>
<td>Particle density</td>
<td>3257 kg/m³</td>
</tr>
<tr>
<td>Particle size</td>
<td>300 µm</td>
</tr>
<tr>
<td>Bed dimensions</td>
<td>2.5x0.2 m²</td>
</tr>
<tr>
<td>Particle-particle restitution</td>
<td>0.9</td>
</tr>
<tr>
<td>Specularity coefficient</td>
<td>0.5</td>
</tr>
<tr>
<td>Angle of internal friction</td>
<td>30°</td>
</tr>
<tr>
<td>Friction packing limit</td>
<td>0.55</td>
</tr>
<tr>
<td>Maximum packaging limit</td>
<td>0.63</td>
</tr>
<tr>
<td>Initial static bed height</td>
<td>0.5 m</td>
</tr>
<tr>
<td>Initial solids volume fraction</td>
<td>0.6</td>
</tr>
</tbody>
</table>

4 Data processing

4.1 Variables

The effect of three independent variables on two dependent variables will be investigated the study. The three independent variables are fluidization velocity (U), reactor temperature (T) and reactor pressure (P). For the purpose of the central composite design (more detail in the next section), coded variables will be used to represent these independent variables. The central composite design requires five levels for each independent variable: -1.682, -1, 0, 1, 1.682. These coded variables will be used to represent U, T and P for the remainder of the discussion and are linked to the real fluidization velocity, reactor temperature and pressure as follows:
Here, $U_{\text{actual}}$, $T_{\text{actual}}$ and $P_{\text{actual}}$ are the real fluidization velocity (m/s), reactor temperature (°C) and pressure (atm) and $U$, $T$ and $P$ are the coded variables which will be used in the subsequent analysis. The variables were chosen as indicated in Equation 10 based on prior experience so that a second order model would fit well through the data. If the fluidization velocity is used directly, for example, the reactor performance increases very sharply at low fluidization velocities because the gas residence time is inversely proportional to the fluidization velocity. This very rapid increase produces a lower quality fit to the second order model.

The two dependent variables that will be investigated are the reactor performance and the expanded bed height. The reactor performance was expressed as $\log(CO) - \chi$ where $\chi$ is the fraction of CO that passed through the reactor without reacting. This measure linearizes the reactor performance of a first order reaction, making it possible to accurately interpret data from reactors achieving high conversion. CO conversion was chosen as the performance measure because the CO reaction is the slower of the two reactions simulated.

The expanded bed height was taken as the height where the time averaged solids volume fraction was 0.05 (a position always located at the top of the expanded bed).

### 4.2 The central composite design

The simulation experiments were designed and processed using the experimental design procedure known as a central composite design [15]. Such a design allows for the statistical quantification of the significance of the effect that each independent variable has on each dependent variable and also fits a second order model through the data to describe the response of each dependent variable to changes in the independent variables. It is an ideal tool for optimization studies.

Results from the central composite design will be presented in two ways: An analysis of variance (ANOVA) and some response surfaces created by the second order model. The ANOVA will be used to quantify the significance and relative size of each effect and the response surface will be used to visualize these effects and optimize the reactor design.

The significance of factors in the ANOVA will be defined by the p-value which is an indication of the probability of the observed effect to result purely by random chance. If this value becomes small ($p < 0.05$), the effect is said to be significant because the probability of it arising from pure chance is fairly small. A value of $p < 0.01$ is generally regarded as highly significant. The p-value is calculated from the F-test which weighs the amount of explained variance in the design against the amount of unexplained variance (experimental error, rounding error, averaging error, data not fitting the second order model etc.). This ratio can then be evaluated as a p-value to decide whether the variance is caused by a significant effect or is simply random.

The relative variance explained by each factor will also be given as the percentage of the total sum of squares (SS). The total sum of squares is the sum of all the squared distances
between the various data points and the mean. A larger total sum of squares implies that the data are scattered wide around the mean and there is a lot of variance in the design. This measure will give an indication of the importance of significant effects relative to each other.

Significant factors will then be plotted on a response surface using a second order model in the following form ($C_1$ through $C_9$ are the constants producing the best fit to the data):

$$X = C_1 U + C_2 U^2 + C_3 T + C_4 T^2 + C_5 P + C_6 P^2 + C_7 U T + C_8 U P + C_9 T P$$  \hspace{1cm} \text{Equation 11}

This model will also be further utilized to cost optimise the reactor.

## 5 Results and discussion

The results from the central composite design are reported in Table 2 and will be analysed and discussed further in this section.

*Table 2: Reactor performance and expanded bed height results from the central composite design.*

<table>
<thead>
<tr>
<th>Case</th>
<th>U (m/s)</th>
<th>T (°C)</th>
<th>P (atm)</th>
<th>$X (-\log(\chi_{CO}))$</th>
<th>H (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.250</td>
<td>700.0</td>
<td>2.00</td>
<td>4.99</td>
<td>0.69</td>
</tr>
<tr>
<td>2</td>
<td>0.250</td>
<td>700.0</td>
<td>12.50</td>
<td>2.08</td>
<td>0.72</td>
</tr>
<tr>
<td>3</td>
<td>0.250</td>
<td>1100.0</td>
<td>2.00</td>
<td>6.50</td>
<td>0.76</td>
</tr>
<tr>
<td>4</td>
<td>0.250</td>
<td>1100.0</td>
<td>12.50</td>
<td>2.12</td>
<td>0.75</td>
</tr>
<tr>
<td>5</td>
<td>1.000</td>
<td>700.0</td>
<td>2.00</td>
<td>1.57</td>
<td>1.25</td>
</tr>
<tr>
<td>6</td>
<td>1.000</td>
<td>700.0</td>
<td>12.50</td>
<td>0.62</td>
<td>1.46</td>
</tr>
<tr>
<td>7</td>
<td>1.000</td>
<td>1100.0</td>
<td>2.00</td>
<td>2.25</td>
<td>1.29</td>
</tr>
<tr>
<td>8</td>
<td>1.000</td>
<td>1100.0</td>
<td>12.50</td>
<td>0.98</td>
<td>1.45</td>
</tr>
<tr>
<td>9</td>
<td>0.156</td>
<td>900.0</td>
<td>5.00</td>
<td>6.17</td>
<td>0.62</td>
</tr>
<tr>
<td>10</td>
<td>1.604</td>
<td>900.0</td>
<td>5.00</td>
<td>0.89</td>
<td>1.41</td>
</tr>
<tr>
<td>11</td>
<td>0.500</td>
<td>563.6</td>
<td>5.00</td>
<td>1.48</td>
<td>0.89</td>
</tr>
<tr>
<td>12</td>
<td>0.500</td>
<td>1236.4</td>
<td>5.00</td>
<td>2.74</td>
<td>0.97</td>
</tr>
<tr>
<td>13</td>
<td>0.500</td>
<td>900.0</td>
<td>1.07</td>
<td>4.32</td>
<td>0.95</td>
</tr>
<tr>
<td>14</td>
<td>0.500</td>
<td>900.0</td>
<td>23.35</td>
<td>1.03</td>
<td>1.04</td>
</tr>
<tr>
<td>15 (C)</td>
<td>0.500</td>
<td>900.0</td>
<td>5.00</td>
<td>2.23</td>
<td>0.94</td>
</tr>
<tr>
<td>16 (C)</td>
<td>0.500</td>
<td>900.0</td>
<td>5.00</td>
<td>2.24</td>
<td>0.93</td>
</tr>
</tbody>
</table>
5.1 Analysis of the central composite design

The analysis of variance (ANOVA) of the data in Table 2 is presented in Table 3. In addition, for the purpose of better qualitative understanding, contour plots of the solids volume fraction and CO mole fraction are provided in Figure 1, Figure 2 and Figure 3.

Table 3: ANOVA table summarizing the response of reactor performance and expanded bed height to changes in the three independent variables investigated. Significant effects are shown in bold, while highly significant effects are shown in bold italics. The independent variables are denoted by U (fluidization velocity), T (reactor temperature), and P (reactor pressure). Different effects are indicated by L (linear), Q (quadratic) and by (interaction).

<table>
<thead>
<tr>
<th>Effect</th>
<th>X</th>
<th>H</th>
<th>p-value</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>U(L)</td>
<td></td>
<td></td>
<td>58.05</td>
<td>0.0000</td>
</tr>
<tr>
<td>U(Q)</td>
<td></td>
<td></td>
<td>3.64</td>
<td>0.0001</td>
</tr>
<tr>
<td>T(L)</td>
<td></td>
<td></td>
<td>4.68</td>
<td>0.0001</td>
</tr>
<tr>
<td>T(Q)</td>
<td></td>
<td></td>
<td>0.05</td>
<td>0.3231</td>
</tr>
<tr>
<td>P(L)</td>
<td></td>
<td></td>
<td>28.14</td>
<td>0.0000</td>
</tr>
<tr>
<td>P(Q)</td>
<td></td>
<td></td>
<td>0.38</td>
<td>0.0268</td>
</tr>
<tr>
<td>U(L) by T(L)</td>
<td></td>
<td></td>
<td>0.55</td>
<td>0.0131</td>
</tr>
<tr>
<td>U(L) by P(L)</td>
<td></td>
<td></td>
<td>4.07</td>
<td>0.0001</td>
</tr>
<tr>
<td>T(L) by P(L)</td>
<td></td>
<td></td>
<td>0.15</td>
<td>0.1153</td>
</tr>
<tr>
<td>Error</td>
<td></td>
<td></td>
<td>0.27</td>
<td>2.97</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 1: Qualitative comparison showing the influence of increasing fluidization velocity through instantaneous solids volume fraction (left) and CO mole fraction (right) contours for cases 9 (two images on the left), 15 (two images in the centre) and 10 (two images on the right) in Table 2. The ranges are between 0 and 0.63 for solids volume fraction and between 0 and 0.2 for CO mole fraction.
Figure 2: Qualitative comparison showing the influence of increasing temperature through instantaneous solids volume fraction (left) and CO mole fraction (right) contours for cases 11 (two images on the left), 15 (two images in the centre) and 12 (two images on the right) in Table 2. The ranges are between 0 and 0.63 for solids volume fraction and between 0 and 0.2 for CO mole fraction.

Figure 3: Qualitative comparison showing the influence of increasing pressure through instantaneous solids volume fraction (left) and CO mole fraction (right) contours for cases 13 (two images on the left), 15 (two images in the centre) and 14 (two images on the right) in Table 2. The ranges are between 0 and 0.63 for solids volume fraction and between 0 and 0.2 for CO mole fraction.

The results clearly indicate that the fluidization velocity and the pressure have the largest influence on the reactor performance while the temperature has a much smaller, but still highly significant effect. This is simply because the reaction simulated in this case was not very sensitive to temperature. In fact, a very large increase in temperature from 500°C to 1200°C created only a factor of 4.4 increase in the reaction rate of CO. Had the reaction been run with methane, on the other hand, the same temperature increase would have resulted in a factor 37.4 increase in reaction rate according to the reaction rates determined in [10] and the temperature would have been a much more important factor. In this case, however, it can already be concluded that the temperature will not be an attractive variable for process intensification.

For the bed expansion, it is clear that the changes in gas density and viscosity caused by the large variations in temperature and pressure did not have a significant effect on the macroscopic bed hydrodynamics (although Figure 3 shows some changes to the mesoscale bed structures at the highest pressure investigated). Only the fluidization velocity had the expected highly significant effect on bed expansion.
The responses of the conversion and the bed height to changes in the most significant factors (fluidization velocity and pressure) are given in Figure 4.

![Figure 4: Response of the conversion (X) and the bed height (H) to changes in the fluidization velocity and the reactor pressure.](image)

The variable responses are as expected. As the fluidization velocity is increased (from left to right in Figure 1), the gas residence time and the degree of gas-solid contact decreases, causing a decrease in reactor performance. Similarly, as the pressure is increased (from left to right in Figure 3), the reaction rate constant (Equation 8) decreases in an inversely proportional manner, causing the reactor performance to decrease as well.

When changing from a coded variable of -2 to 2 in Figure 4, the fluidization velocity increases by a factor of 16 and the pressure increases by a factor of 39. This pressure increase will cause a factor 26 decrease in the rate of the CO reaction. In view of these numbers, it is interesting to note that Table 3 shows that the fluidization velocity has a larger impact on the reactor performance than the reactor pressure even though the increase in gas residence time caused by a reduction in the fluidization velocity is smaller than the increase in reaction rate caused by the decrease in reactor pressure. The reason for this is that decreases in the fluidization velocity will not only increase the gas residence time, but also increase the quality of bubble-to-emulsion mass transfer because smaller bubbles will be formed. Decreases in the pressure, however, cause an increase in reaction rate which gradually makes the bubble-to-emulsion mass transfer the rate-limiting step, thereby reducing the impact that further decreases in the reactor pressure can have on the overall reactor performance.

The response of the expanded bed height in Figure 4 shows that the effect of the increase in fluidization velocity is completely dominant. At high fluidization velocities, a possible effect of pressure can be observed, but Table 3 shows that this effect is not statistically significant.

### 5.2 Cost optimization

The first step towards finding the cost optimised combination of reactor pressure and temperature is to decide on the desired degree of reactor performance required. In this example, a value of \( X = -\log(0.01) = 2 \) (99% CO conversion) will be chosen. Once this value is decided, Equation 11 can be used to calculate a number of combinations of \( U \), \( T \) and \( P \) yielding a performance of \( X = 2 \). These data points are shown in Figure 5.
The trade-offs between fluidization velocity, temperature and pressure are clearly visible in Figure 5. It is clear that an increase in pressure has to be balanced by a decrease in fluidization velocity in order to keep the reactor performance constant at 99% CO conversion. Similarly, a decrease in temperature must be balanced by a decrease in fluidization velocity. It is also confirmed once again that the effect of pressure is much larger than the effect of temperature in this case.

Next, the mass flow rate at which gas is fed to the reactor was calculated for each point. Naturally, it is desired that the mass throughput be as large as possible in order to maximise the power production from the CLC unit. The large potential of pressure as a process intensification mechanism stands out in Figure 5. It is shown that, even though the fluidization velocity has to be decreased significantly for higher pressures, the actual mass flow rate increases greatly. This is due to the factor 39 increase in the gas density caused by pressure increases over the range displayed in Figure 5. For the temperature, however, the gas density decreases with increasing temperatures. Figure 5 shows that this completely nullifies the potential of temperature as a process intensification mechanism. Higher temperatures permit the use of larger fluidization velocities, but the reduction in gas density caused by these higher temperatures completely negates this advantage.

In order to find the cost optimised reactor operating point, the reactor cost as a function of temperature and pressure has to be estimated. In this case some simple smooth functions will be used only as an example. It is conceded, however, that these cost functions will be step functions in a real application.

The reactor cost was estimated as indicated below and displayed in Figure 6.

\[
Cost = 10000 + 2000 \left( 4^T + 5^p \right) \quad \text{Equation 12}
\]
The selected cost function results in rapid increases in the reactor cost at larger temperatures and pressures. However, Figure 5 indicates that higher pressures also result in much greater mass flow rates through the reactor. The increases in reactor cost resulting from higher pressure operation can therefore be tolerated up to a point because of this higher gas throughput. Therefore, the ratio of reactor cost over syngas feed rate will be used as optimization parameter and the cost optimized reactor design will be selected where this value is at a minimum. As shown in Figure 6, this results in cost optimized reactor performance at $P = 0.5$ (7.91 atm) and $T = -1$ (700°C) for a reactor achieving 99% syngas conversion.

Naturally, the cost function which is implemented will have a major influence on the location of the cost optimised design point. It is therefore essential that significant effort be invested in determining the cost function (Equation 12) with as much accuracy as at all possible.

6 Conclusions

The potential of using high temperature and high pressure operation to improve reactor economics through process intensification has been evaluated in this study. A simulation-based design and optimisation strategy was used to find the point at which the ratio of the reactor cost over the fuel gas throughput is at a minimum.

For the case studied in this work; the reduction of an iron oxide oxygen carrier with syngas, the reaction rate was not very sensitive to changes in the temperature. For this reason, the influence of temperature as a process intensification variable was limited. The pressure, on the other hand, proved to be an excellent candidate for process intensification, but will still be limited by the increases in reactor cost resulting from higher pressure operation.

The simulation-based design and optimisation strategy proved to be very fast, cost-effective and simple to use. However, the accuracy of the recommendation for cost optimized reactor operation is completely dependent on the calculation of correct cost functions where the reactor cost (or eventually the final cost of electricity) is described as a function of all the
independent variables under investigation. The correct determination of these cost functions is therefore of primary importance in this methodology.

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