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Abstract:  
Oxidative coupling of methane (OCM) is considered as one of the most promising direct routes to convert methane to ethylene and higher hydrocarbons. However, two key challenges have to be addressed before OCM can be considered as an alternative gas-to-chemical technology, namely the low yields of ethylene and what to do with the substantial heat release of the reaction. Both these challenges can be overcome in the reactor technology that is proposed in this work, i.e. the gas-solid vortex reactor (GSVR) developed at the Laboratory for Chemical Technology. The flow characteristics and bed properties inside the GSVR have already been studied experimentally for a wide range of operating conditions. In this work, non-reactive computational fluid dynamic simulations are combined with 0D/1D reactive simulations to determine the operating conditions and reactor design necessary to achieve C2 yields of 5-15 %.
**Introduction**

Many innovative catalytic technologies have been developed in the past decade as a response to the world’s rapidly growing demand for a more efficient and sustainable exploitation of energy and material resources [1, 2]. The decreasing crude oil reserves, the large amount of natural gas resources (shale gas) and the renewability of methane (biogas) have created a strong economic interest in developing processes that allow methane conversion into more valuable products [3, 4]. Commercial technologies to convert methane to higher hydrocarbons (e.g. Fischer-Tropsch synthesis) are mainly indirect, i.e. they require the production of syngas as a first step, which represents an inherent inefficiency. On the other hand, direct activation of methane and conversion into other useful products still remains one of the most challenging topics that the catalysis community faces nowadays [5].

One of the most promising direct routes to convert methane to ethylene and higher hydrocarbons is the oxidative coupling of methane (OCM). Ever since the pioneering work of Keller and Bhasin [6], OCM continues to attract both industrial as well as academic interest. Although the benefits of OCM have been known for over 30 years, a crucial issue among researchers still remains to find a viable catalyst with the performance needed for commercialization of the process [7]. Furthermore an appropriate reactor technology needs to be developed to address the low yields of ethylene and the strong exothermicity of the reaction [8, 9]. The main challenges to be overcome before OCM can be used as an alternative to steam cracking for the production of ethylene and higher olefins are hence twofold, with catalyst development on the one hand and novel reactor design on the other [10, 11].

Siluria Technologies recently announced the first commercial OCM process, in which a series of nanowire catalysts is used that operate at process temperatures below 600 °C [12]. Although Siluria’s patent application reveals that the single-pass C₂ yield does not meet the target of 25 %, the catalysts are durable over long periods of operation at low process temperatures [13]. Catalytic packed bed reactors are used in Siluria’s demonstration plant, as is the case for the majority of all laboratory-scale OCM reactors [11]. Because of the high exothermicity of the OCM reaction, thermal control of the reactor is an important issue. Most laboratory-scale experimental set-ups use small-diameter tubes and run with very dilute mixtures and low methane conversions [14-16], which is of course not practical for an actual large-scale process. The fluidized bed reactor has been designated as the optimal reactor concept for OCM by different authors [8, 9, 17, 18]. This is mainly because of its beneficial heat transfer characteristics, that cannot be achieved in any type of packed bed reactor.

From the above considerations, it may be clear that some effort is still required before OCM can be considered as an alternative to steam cracking for the production of ethylene and other olefins. Although the door toward successful commercialization has already been opened by Siluria Technologies, further investigation to enhance ethylene yields is still necessary. Catalyst design as well as the development of novel reactor technologies are important to this purpose. In the present work, the focus is on the latter. The gas-solid vortex reactor (GSVR), developed at the Laboratory for Chemical Technology (UGent) is proposed as an excellent reactor choice to demonstrate the OCM process.
Gas-solid vortex reactor technology

Gas-solid fluidized beds (FBs) are known for their enhanced heat and mass transfer characteristics and are therefore widely used for both reactive and non-reactive processes in the chemical industry. The efficiency of heat and mass transfer in these FBs is determined by the relative velocity, the so-called slip velocity, between the gas and the solid phase. As a consequence of the balance between the drag force and the gravitational force, the slip velocity in a conventional gravitational FB is limited by the terminal free-fall velocity of the particles [19]. Higher gas velocities give rise to the formation of bubbles and slugs, which negatively affect the heat and mass transfer efficiency as the extensive gas bypass decreases the gas-solid contact. If the gas flow rate is increased even more, particle entrainment is unavoidable. Higher gas throughput, more uniform fluidization, higher slip velocities, and hence better heat and mass transfer, can be achieved by using a centrifugal force instead of the gravitational force [20-22]. A centrifugally fluidized bed thus emerges as an excellent candidate for process intensification.

Figure 1. Left: Schematic overview of a rotating fluidized bed (RFB) [23]. Right: Schematic representation of a gas-solid vortex unit (GSVU) [24].

Figure 1 shows two possibilities to achieve a centrifugal fluidized bed: using a rotating fluidized bed (RFB), where the particles are set in motion by rotating the operating vessel itself, or using a gas-solid vortex unit (GSVU), where the particles are introduced in a swirling flow field of azimuthally injected gas in a static vessel. In a RFB, the tangential and radial velocity components can be varied independently, as the rotational velocity of the vessel and the injected gas flow rate can be controlled in a separate way. The downside of using RFBs however is the use of mechanically moving parts which imply the risk for mechanical abrasion. In a GSVU the fluidizing gas is injected tangentially through multiple gas inlet slots in the cylindrical wall of the fluidization chamber. The swirling gas transfers tangential momentum to the particles, which in turn start rotating and experience an outward centrifugal force. A fluidized state is reached when the radially inward drag force exerted by the gas overcomes the apparent weight of the solids in the centrifugal field. In contrast to the RFB, it is impossible to control the particle velocity
components in a GSVU independently. Nevertheless, the GSVU is preferred to the RFB as the absence of moving parts makes the unit more appropriate for scale-up [24].

Several industrially relevant processes have been suggested for implementation in a gas-solid vortex reactor (GSVR): fluid catalytic cracking (FCC) [25], coating of cohesive particles [26], gas adsorption [27], drying [28], gasification [29], combustion [30] and pyrolysis [31]. At this moment, the first actually reactive GSVR unit for biomass fast pyrolysis is being tested at the Laboratory for Chemical Technology. Because of its excellent heat transfer characteristics and high gas throughput, this reactor also emerges as an ideal technology for the oxidative coupling of methane (OCM).

**GSVR setup at the Laboratory for Chemical Technology**

A schematic view of the GSVR setup at the Laboratory for Chemical Technology (LCT) is shown in Figure 2 and Figure 3. It basically consists of a cylindrical unit positioned along a vertical axis with eight gas injection slots of 1 mm width, equally distributed over the circumferential wall and tangentially inclined at a 10° angle. A reactor diameter of 80 mm and a length-to-diameter of 0.25, i.e. a reactor length of 15 mm, are defined. The diverging exhaust aims at minimizing the gas backflow and at preserving the swirling flow in the throat. The diverging exhaust wall profile follows an analytical solution for strongly swirling jets. The design of the bottom end wall and exhaust profiles was based on preliminary calculations and CFD simulations as described by Gonzalez-Quiroga et al. [32]. The design of the reactor is such that the inlet slots are easy to replace, so that the number and the angle of the inlet slots can be altered for parametric studies etc. For a given gas flow rate, the thickness of the injection slots determines the magnitude of the gas injection velocity, while the injection angle determines its radial and tangential components. The actual GSVR is operated in semi-batch mode. Solid particles are already present in the inner chamber at the beginning of an experiment. Then the hot fluidizing gas is introduced until a pseudo-steady-state swirling gas-particle flow is established in the reactor.

![Figure 2](image-url)

(a) Experimental setup at the Laboratory for Chemical Technology, and (b) schematic representation of the gas feeding line, jacket and reactor chamber at a horizontal cutting plane.
Figure 3. Flow pattern for gas-only flow in the Gas-Solid Vortex Reactor obtained via computational fluid dynamic simulations. Contours of velocity magnitude are shown in the cutting planes, and the streamlines are colored in grey. (a) Gas inlet, (b) connection of gas inlet to the jacket, (c) gas inlet slots, (d) profiled bottom end wall, (e) diverging exhaust, (f) gas outlet.

**CFD simulations**

Operating conditions (gas flow rates, particle density, temperature) and geometric features (number and angle of inlet slots) are found to have a large effect on the bed stability in the GSVR. Based on CFD simulations we were able to derive a range of operating conditions for which we can obtain a stable bed with the current geometry. The results of one such simulation are shown below. Also experimentally we were able to obtain stable rotating beds over a wide range of operating conditions.

For the presented case nitrogen was used as carrier gas and fed to the GSVR at a flow rate of 10 g/s at 923 K. The properties of the solid particles were chosen in agreement with the OCM catalyst particles that will be used in the GSVR: 1 mm diameter and a density of 2300 kg/m³. Although we were able to obtain a stable bed inside the reactor (see Figure 4a,b), it is clear from Figure 4c that a lot of gas is not retained in the bed but just flows through, hence resulting in a small contact time between the gas and the particles. This is most probably not the ideal scenario if we want to use the reactor for OCM, but by finetuning the operating conditions or using an alternative design, it is possible to obtain the flow conditions required to achieve reasonable conversions and selectivities.
Essential for defining and controlling the GSVR conditions is to determine the residence times and bed properties necessary to obtain reasonable conversions and selectivities for OCM. Therefore, some 0D/1D simulations were performed for different catalysts (La$_2$O$_3$/CaO, Mn/Na$_2$WO$_4$/SiO$_2$, Sn-Li/MgO and Sr/La$_2$O$_3$). As the flow behavior in the GSVR is far from ideal, we can use the “tank-in-series” model to imitate the GSVR in our kinetic study. The idea behind this model is that, given the residence time distribution (RTD) in the actual reactor, it is possible to approximate it by a cascade of CSTR’s. The lower the number of CSTR’s in the series, the better the mixing, and in the limit of $n \to \infty$, ideal plug flow is approximated. The “tank-in-series” model comes down to solving the following equations, for every CSTR $k$ in the series of $n$ reactors:
\[ F^k C_i^k - F^{k-1} C_i^{k-1} = V^k [e_b R_{l,g}^k + R_{l,s}^k (1 - e_b) p_{cat} a_{cat}] \]  
\[ c_{p,g}^{k-1}(T^k - T^{k-1}) = - \sum_{i=1}^{N_g} h_i^k (Y_i^{k-1} - Y_i^k) \]

In these equations \( C_i^k \) is the concentration of species \( i \) in reactor \( k \) [mol m\(^{-3}\)]; \( F^k \) is the volumetric flow rate leaving reactor \( k \) [m\(^3\) s\(^{-1}\)]; \( V^k \) is the volume of reactor \( k \) [m\(^3\)]; \( e_b \) is the bed voidage [m\(^3\) m\(^{-3}\)]; \( R_{l,g}^k \) is the net rate of formation of species \( i \) in reactor \( k \) due to gas phase reactions [mol m\(^3\) m\(^{-3}\) s\(^{-1}\)]; \( R_{l,s}^k \) is the net rate of formation of species \( i \) in reactor \( k \) due to surface reactions [mol m\(^3\) cat \(^{-2}\) s\(^{-1}\)]; \( p_{cat} \) is the catalyst density [kg cat \(^{-1}\) m\(^3\) cat]; \( a_{cat} \) is the specific surface area of the catalyst [m\(^2\) cat kg\(^{-1}\) cat]; \( c_{p,g}^k \) is the specific heat capacity of the gas phase in reactor \( k \) [J kg\(^{-1}\) K\(^{-1}\)]; \( T^k \) is the temperature in reactor \( k \) [K]; \( h_i \) is the specific enthalpy of species \( i \) in reactor \( k \) [J kg\(^{-1}\)]; \( Y_i^k \) is the mass fraction of species \( i \) in reactor \( k \) [-]; and \( N_g \) is the number of species [-]. It is assumed that the surface is in equilibrium with the gas phase. The model equations are solved using an in-house code based on Cantera [33]. A detailed microkinetic model consisting of 39 gas-phase reactions and 26 catalytic reactions [34-37] is used for Sr/La\(_2\)O\(_3\) and Sn-Li/MgO, while a comprehensive model with 10 reactions is used for La\(_2\)O\(_3\)/CaO [38] and Mn/Na\(_2\)WO\(_4\)/SiO\(_2\) [39]. The physical properties of the investigated catalysts are shown in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>Sr/La(_2)O(_3)</th>
<th>Sn-Li/MgO</th>
<th>La(_2)O(_3)/CaO</th>
<th>Mn/Na(_2)WO(_4)/SiO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area</td>
<td>[m(^2) cat/kg cat]</td>
<td>2000</td>
<td>2800</td>
<td>2000</td>
</tr>
<tr>
<td>Density</td>
<td>[kg cat/m(^3) cat]</td>
<td>2300</td>
<td>2300</td>
<td>2300</td>
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For a process like OCM, where gas phase and surface reactions occur simultaneously, there are two important space times, one related to the homogeneous gas phase reactions, the other related to the heterogeneous surface reactions. In the presented study the bed density has been kept constant (hence fixing the second spacetime), and only the gas phase residence time has been varied.

Figure 5 shows the methane conversion and selectivity towards C2 (ethane + ethylene) as a function of mean residence time in a plug flow reactor. The four different catalysts mentioned earlier are compared. The results of Figure 5 are obtained using an isothermal reactor model, so without solving Eq. (2). It follows that the highest C2 yields, i.e. C2 selectivity times CH\(_4\) conversion, are possible using Sr/La\(_2\)O\(_3\), so this type of catalyst has been studied.
Figure 5. (a) Methane conversion, and (b) C2 selectivity as a function of mean residence time in an isothermal plug flow reactor ($n \to \infty$), for different catalysts (CH$_4$/O$_2$=4, T=1023K, p=1.1bara, $\varepsilon_b$=0.6).

Figure 6. (a) Methane conversion as a function of residence time, and (b) C2 selectivities as a function of CH$_4$ conversion in isothermal CSTR’s and PFR’s with Sr/La$_2$O$_3$ catalyst for different operating temperatures and CH$_4$/O$_2$ ratios (p=1.1bara, $\varepsilon_b$=0.6). Lines of constant C2 yield are indicated in grey in the right figure.

Figure 6 shows the methane conversion and C2 selectivity in an isothermal plug flow reactor and perfectly stirred reactor with Sr/La$_2$O$_3$ catalyst for different operating conditions. It follows from the figure that at low conversion, the C2 selectivity in a perfectly stirred reactor is higher than in a plug flow reactor, while the opposite holds for higher conversions. Conversion is always larger in a plug flow reactor. The behavior of the GSVR is in between the plug flow and perfectly stirred regime. The lower the CH$_4$/O$_2$ ratio, the higher the conversion but the lower
the selectivity. For the same CH\textsubscript{4}/O\textsubscript{2} ratio, higher C2 selectivities are found at higher temperatures. From the results in Figure 6 it follows that we should try to design the GSVR such that we can reach residence times of approximately 20-50 ms. In this way, it should be possible to obtain CH\textsubscript{4} conversions of 10-25 % and C2 yields of 5-15 %.

Although Figure 6 seems to speak in favor of the ideal plug flow regime, there are some important practical problems with this type of reactor if it is operated adiabatically instead of isothermally. Figure 7 shows the temperature profile resulting from an adiabatic simulation, i.e. where Eq. (2) is included, with the Sr/La\textsubscript{2}O\textsubscript{3} catalyst. Due to the strong exothermicity of the OCM process, the temperature in the reactor rises quickly. In a packed bed reactor (as idealized by the PFR model in the figures), one should take appropriate measures to prevent reaction runaway. As reported earlier by Pak et al. [40], hot spot formation can be observed in packed bed reactors, even for small-diameter tubes. Here is where the excellent heat transfer characteristics in the GSVR come into play. The more the actual reactor resembles a CSTR, or the higher the degree of mixing (or the lower the number of CSTR’s in the “tank-in-series” model), the more stable the reactor operation. The continuous mixing of the colder feed with the reacting mixture provides a way to control the temperature, so that it becomes possible to operate the GSVR almost isothermally.

![Figure 7](image_url)

**Figure 7.** Temperature [K] as a function of mean residence time on Sr/La\textsubscript{2}O\textsubscript{3} catalyst and with different degrees of mixing, i.e. number of CSTR’s, in the adiabatic “tank-in-series” model. Inlet/operating conditions: CH\textsubscript{4}/O\textsubscript{2}=4(a)/2(b), T=923K, p=1.1bara, \( \varepsilon_b \)=0.6.

**Conclusions**

In this work, a new reactor technology has been studied for the oxidative coupling of methane: the gas-solid vortex reactor (GSVR). Non-reactive computational fluid dynamic simulations were performed to estimate the bed characteristics and flow dynamics for a wide range of operating conditions and reactor designs. Then reactive 0D/1D simulations were performed to evaluate the reactor performance in terms of CH\textsubscript{4} conversions and C2 selectivities. From these reactive simulations it follows that we should design the GSVR in such way that it is possible to reach residence times of approximately 20-50 ms. For Sr/La\textsubscript{2}O\textsubscript{3} catalyst, this would give CH\textsubscript{4} conversions of 10-25 % and C2 yields of 5-15 %.
References


