

Coupling the porous conditional moment closure with the random pore model

Applications to gasification and CO₂ capture

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Abstract Gasification of coal/biomass with in-situ CO₂ capture simultaneously allows production of clean hydrogen at relatively low cost and reduced emission of CO₂ into the atmosphere. Clearly, this technology has a great potential for a future carbon constrained economy. Therefore, the development of a comprehensive, physically-based gasifier model is important. The sub-models that describe reactive transport processes in coal particles as well as in particles of CO₂ sorbent material are among the key sub-models, which provide a necessary input for an overall gasifier model. Both coal and sorbent are materials that have complicated pore structures. The Porous Conditional Moment Closure (PCMC) approach is proven to be adequate for modelling reactive transport through porous media with fixed pore structure. Consumption of coal in the heterogeneous gasification reaction, however, widens the pores and reduces the surface area available for this reaction. At the same time, formation of a carbonate layer narrows the pores in the sorbent material and reduces the reaction rate of CO₂ sorption. In both cases the pore structures are affected. Such changes are not taken into account in the existing PCMC model. In this study, we obtain the parameters of the diffusive tracer distribution based on the pore size distribution given by the widely applied Random Pore Model (RPM), while coupling PCMC with RPM. Such coupling allows taking into account changes in pore structure caused by heterogeneous reactions and thus improves the accuracy of these key sub-models.

Keywords Gasification · CO₂ capture · PCMC · RPM

1 Introduction

The increasing global energy demand that is expected to rise by 40% by 2030 [1] will result in higher CO₂ emission into the atmosphere. This emission is believed to be one the major causes of climate change. The necessity to address the problem of climate change is the impetus behind the evolution of modern energy technologies. Substantial efforts have been devoted worldwide to developing CO₂ mitigation technologies in order to prepare for a carbon constrained economy. In addition to the improvement of energy efficiency and the usage of carbon neutral fuels, such as biomass, CO₂ capture and storage appears to be one of the most prominent options [2].

Various approaches to CO₂ mitigation for coal based power plants, which include pre- and post-combustion capture as well as fuel conversion, are extensively discussed by Wall [3], while the removal of CO₂ from the flue gas was specifically reviewed by Aaron and Tsouris [4]. The post-combustion capture technologies, such as: absorption with liquid solvents and solid adsorbents [5–8], cryogenic distillation [9], membrane separation [10–13] and adsorption on various solid adsorbents [14–18], have been studied worldwide.

Gasification of coal/biomass with in-situ CO₂ capture is an emerging technology aimed at addressing the problem of CO₂ emission mitigation. This technology simultaneously allows production of clean hydrogen at relatively low cost while reducing the release of CO₂ into the atmosphere. The process is schematically presented in Figure 1.

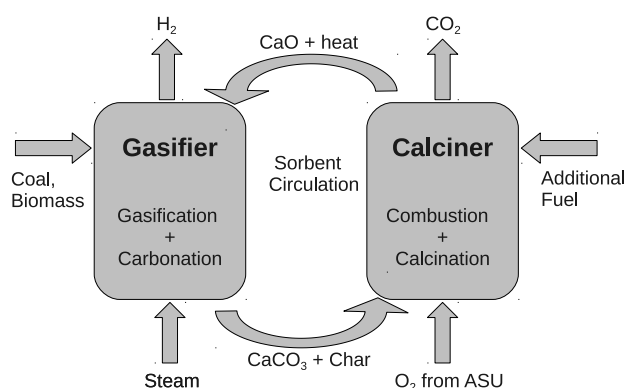


Fig. 1 Schematic representation of the gasification with in-situ CO₂ capture.

In this process, coal reacts with steam in the first reactor that is called a Gasifier to produce H₂, CO₂. The heat required for this reaction is supplied by the exothermic reaction $\text{CaO(s)} + \text{CO}_2\text{(g)} \rightleftharpoons \text{CaCO}_3\text{(s)}$, in which CO₂ is also consumed. In this way, almost pure hydrogen is generated. The reacted carbon adsorption material (CAM) is separated from product gas stream by a cyclone separator and is transferred into the second reactor, known as a Calciner, for regeneration. In the calciner, additional fuel is combusted with O₂ obtained from an air separation unit (ASU) to provide the heat required for the calcination reaction, which generates the sequestration-ready stream of CO₂. The regenerated CAM is transferred back to the gasifier. Although several metal oxides were assessed for this technology, CaO currently appears to be the best option [19].

Physical and chemical processes related to this technology have attracted substantial attention. The reversibility of carbonation/calcination reaction, for example, was studied by Barker [20]. Abandes and Alvarez [21, 22] studied capture efficiency and conversion limits for pure lime and pointed out the decrease in capture capacity with the number of carbonation/calcination cycles. To overcome this problem, Feng *et al.* [23] suggested fabrication of CaO-based sorbents. Significant work has also been done on the computational fluid dynamics (CFD) modelling of fluidised bed gasifiers. Predominantly, such CFD-models are based on the multi-phase Eulerian-Eulerian approach [24–31], which utilises the kinetic theory of granular flow [32].

A comprehensive, physically-based model of the process, which permits optimisation of the operational parameters and can also be used to assist the design of the reactors, is clearly required. Such a model, in its turn, requires an input from two key sub-models, which describe reactive transport in coal and sorbent particles. Both coal and the sorbent are porous materi-

als that have complicated pore structures and coupling the transport through the porous medium with heterogeneous gas-to-solid and homogeneous gas phase reactions is essential for development of such sub-models. Indeed, the flux of CO₂ inside a particle of the sorbent material, for example, is driven by diffusion and pressure gradients, which, in their turn, are caused by the consumption of CO₂ at the pore surfaces inside the particle. Thus, the complexities of transport modelling are coupled with those of modelling the heterogeneous and homogeneous reactions together with the necessity of modelling complex pore structures.

As previously demonstrated [33], models based on the conventional technique of volume averaging [34] neglect inter-pore transport and variations in concentrations of transported gas species within the pores. As a result, such conventional models provide poor predictions for conditions where reactions are fast relative to diffusive transport, which is the case for the problem in question. Recent advances in modelling of the reactive transport through porous media [33, 35] that employ the Conditional Moment Closure (CMC) methodology offer a way to attack the problem in question, provided that the pore structure remains unchanged. Consumption of coal in the heterogeneous gasification reaction, however, widens the pores and reduces the surface area available for this reaction. At the same time, formation of a calcium carbonate layer narrows the pores in sorbent material and reduces the reaction rate of CO₂ sorption. In both cases the pore structures are affected by the reactions and varies with time. Such changes are not taken into account in the existing PCMC model.

The changes in pore structure can be modelled by the Random Pore Model (RPM) suggested by Bhatia and Perlmutter [36, 37] and commonly used in Chemical Engineering [38–43]. RPM predicts the reaction surface area as a function of conversion and an initial pore size distribution, which explains the influence of the initial pore structure observed experimentally in a number of studies [38–44]. In the case of a kinetics controlled regime, RPM is capable of predicting the apparent reaction rate for a porous particle, provided that the reaction rate per unit area is known. In the case of diffusion controlled or intermediate regimes, which are of importance for gasification technologies, the diffusion through a porous structure to the reaction surface plays a key role in determining the apparent reaction rate. This diffusion, however, is not taken into account by RPM. As a result, RPM alone is not sufficient for accurate predictions for the regimes, where diffusion is important. Additional complexity is added by the presence of homogeneous gas phase reactions, which are not treated in RPM either.

In this study, we suggest a model that combines PCMC with RPM, while utilising advantages of both these approaches. The model allows for predicting the apparent reaction rate for particles of porous material in kinetics controlled, intermediate and diffusion controlled regimes and for any given conversion. The model treats homogeneous and heterogeneous reactions as well as diffusion in a unified and consistent way. The software implementing the model is now under development and the results of numerical calculations will be presented elsewhere.

2 Limitations of the conventional treatment of reactive flows in porous media

Conventionally, a porous medium is characterised by two phases: the fluid β -phase and the solid σ -phase. Heterogeneous reactions occur on the surface separating these two phases, which is called β/σ -interface. In the conventional approach [34], *intrinsic* averages are used to characterise the gaseous reactants. For any arbitrary function F , the intrinsic average $\langle F \rangle_\beta$ is given by

$$\langle F \rangle_\beta = \frac{\int_{-\infty}^{\infty} F(y) \beta(y) \Phi(y-x) dy}{\int_{-\infty}^{\infty} \beta(y) \Phi(y-x) dy}. \quad (1)$$

Here, the function $\beta(x)$ is the indicator of the β -phase. That is, $\beta = 1$ in the β -phase and $\beta = 0$ elsewhere. The convolution integral $\int_{-\infty}^{\infty} F(y) \Phi(y-x) dy$ with a bell-shaped weighting function Φ satisfying $\int_{-\infty}^{\infty} \Phi(y) dy = 1$ is called the *superficial* average and denoted as $\langle F \rangle$. The characteristic length scale of Φ is conventionally assumed [33, 34] to be much larger than the characteristic pore size and much smaller than the characteristic length scale of flow parameter variations. In terms of superficial averages, Equation (1) reads

$$\langle F \rangle_\beta = \frac{\langle F\beta \rangle}{\langle \beta \rangle}. \quad (2)$$

Note that in the studies on porous media the word “intrinsic” is used to identify averaging over the β -phase. In the chemical engineering literature, however, the intrinsic reaction rate refers to the reaction rate per unit surface area. We will use both these meanings in the present paper.

Let’s now consider, for example, a heterogeneous reaction $A(g) + B(s) \rightleftharpoons C(g)$ which occurs on β/σ -interface in a porous medium. The regime of this reaction is determined by the balance between the reaction kinetics and the rate of transport of the gaseous reactant to the surface. This balance is described in terms of the Damköhler number Da , which is defined as the

ratio of the chemical reaction rate to the mass transfer rate. Three different regimes: kinetics controlled, intermediate and diffusion controlled are schematically presented in Figure 2. In this figure, the concentration of the gaseous reactant C_A is depicted as a function of the distance to the reactive surface x in each of these three regimes with the same value of the intrinsic average $\langle C_A \rangle_\beta$.

In the case of small Damköhler numbers ($Da \ll 1$), the gaseous reactant is transported to the reactive surface much faster than it is consumed on the β/σ -interface. Changes in its concentration caused by the reaction will be compensated by the diffusive or convective transport almost instantaneously. Then, the concentration $C(x)$ will vary insignificantly around $\langle C_A \rangle_\beta$ with x (see Figure 2(a)). In this kinetics controlled regime, the intrinsic average $\langle C_A \rangle_\beta$ is a good approximation for $C(x)$ and the conventional approach, which is based on intrinsic averages [34], will provide reasonably accurate results.

When the reaction rate is large compared to the transport rate ($Da \gg 1$), all the gaseous reactant arrived at the β/σ -interface will almost instantaneously react with the reactive surface. In this diffusion controlled regime, the rate of the reactant consumption is almost entirely determined by the transport of the gaseous reactant to the reactive surface. In the vicinity of the surface, the reactant concentration is approximately zero (see Figure 2(c)), while its intrinsic average remains large. Clearly, the intrinsic average is an unreasonable approximation for the reactant concentration in this case. As a result, the conventional approach, which does not take into account any dependence on Da , will give unacceptable predictions for diffusion controlled regime.

As demonstrated by Klimenko and Abdel-Jawad [33], the conventional approach also gives poor predictions for the intermediate regime, where the reaction and the transport rates are balanced ($Da \sim 1$). As depicted in Figure 2(b), the concentration of the gaseous reactant varies significantly and the intrinsic average can only be considered as a rough approximation for the actual concentration in this case.

It is not known *a priori*, which of these regimes will be realised. Note, however, that diffusion controlled and intermediate regimes are generally more likely than kinetics controlled regime in high temperature processes. Therefore, the conventional approach is not suitable for modelling gasification and CO_2 -adsorption, which are carried out at high temperatures. To overcome this difficulty, Klimenko and Abdel-Jawad [33] suggested a novel PCMC model. The model involves conditioning on a specially introduced diffusive tracer, which emu-

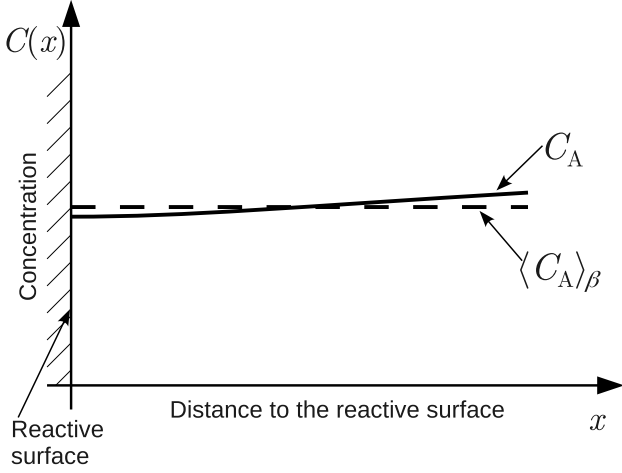
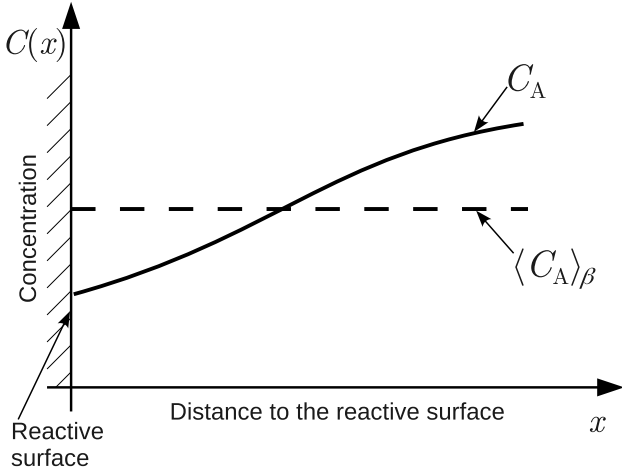
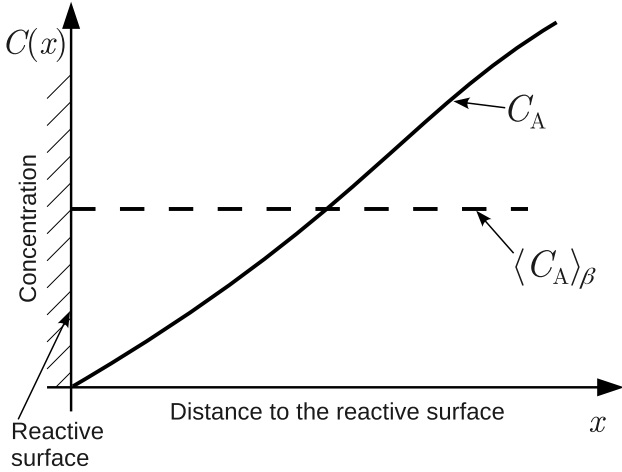
(a) Kinetics controlled regime ($Da \ll 1$)(b) Intermediate regime ($Da \sim 1$)(c) Diffusion controlled regime ($Da \gg 1$)

Fig. 2 Variation in the gaseous reactant concentration in three regimes for the same value of the intrinsic average (schematic view).

lates diffusion in the gaseous phase and allows for taking into account variations in concentrations of reactive species. The PCMC model is outlined below.

3 Porous conditional moment closure

In this section, we present the underlying concepts and major equations of the PCMC model, while referring a reader to the previous works [33, 35, 45] for more details. A comprehensive review of CMC methodology has been done by Klimenko and Bilger [45]. The PCMC model was suggested by Klimenko and Abdel-Jawad [33], while Vladimirov and Klimenko incorporated the treatment of porous media with fractal properties into the model.

The reactive flow within the β -phase is governed by the continuity

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \quad (3)$$

and the species transport

$$\frac{\partial \rho Y_i}{\partial t} + \nabla \cdot (\rho \mathbf{u} Y_i) - \nabla \cdot (\rho D \nabla Y_i) = \rho W_i \quad (4)$$

equations. Here, Y_i are the mass fractions of the gaseous species, ρ and $\mathbf{u}$ are the gas density and velocity, respectively, while W_i are the species production rates in homogeneous gas-phase reactions. For simplicity of formulae, we assume the same diffusion coefficient D for all gaseous species. Note that, in addition to homogeneous reactions, the reactive species concentrations are also affected by heterogeneous reactions. As described below, these reactions are taken into account by specially formulated boundary conditions for PCMC equations.

As discussed in the previous section, the species concentrations and, therefore, their mass fractions can vary significantly near the reactive surface due to heterogeneous reactions. Since conventionally used intrinsic and superficial averages do not allow for taking these variations into consideration, an additional variable has to be introduced to parameterise these variations. This variable should be related to the distance from the reactive surface. At the same time, it is desirable that the variable emulates transport of the gaseous species.

Such a variable Z , which is called a diffusive tracer, is introduced in the PCMC model [33]. In the β -phase, the tracer Z is produced with the constant rate W_Z and is transported in the same way as gaseous species. That is, Z satisfy the conventional species transport equation

$$\frac{\partial \rho Z}{\partial t} + \nabla \cdot (\rho \mathbf{u} Z) - \nabla \cdot (\rho D \nabla Z) = \rho W_Z. \quad (5)$$

Similarity of Equations (4) and (5) ensures that the tracer Z resembles transport of gaseous species. The

same diffusion coefficient D in Equations (4) and (5) provides similarity with diffusion of gaseous species, while the source term ensure uniformity of characteristics of the tracer within the β -phase. Note that the value of W_Z can be set to one without loss of generality.

On the reactive surface, the tracer Z is instantaneously consumed, so that $Z = 0$ at the β/σ -interface. The tracer has positive values in the β -phase, which monotonically decrease towards the reactive surface. Thus, the value of Z characterises the distance from the surface. Furthermore, the infinite (or sufficiently large) rate of consumption of Z on the reactive surface allows for emulating the regimes with large Damköhler numbers (the intermediate and diffusion controlled regimes).

In addition to the intrinsic and superficial averaging, the PCMC model utilises *conditional* Favre (density-weighted) averaging of variables and functions specifying conditions in the reactive flow. For an arbitrary function F , the conditional Favre average $(\overline{F})_z$ is defined as

$$(\overline{F})_z = \frac{\langle F \rho \beta | Z = z \rangle}{\langle \rho \beta | Z = z \rangle} . \quad (6)$$

Here $\langle F | Z = z \rangle$ is the superficial average of F conditioned on the tracer Z being equal to z . The unconditional superficial average $\langle F \rangle$ is then given by

$$\langle F \rangle = \int_0^\infty \langle F | Z = z \rangle P_Z(z) dz , \quad (7)$$

where $P_Z(z)$ is the probability density function (PDF) of Z satisfying

$$\int_0^\infty P_Z(z) dz = 1 . \quad (8)$$

The governing equations can now be expressed in terms of conditional averages. The averaging technique, which utilises the machinery of generalised functions, is described by Klimenko and Bigler [45] in great detail. Using the notation $Q_i \equiv (\overline{Y}_i)_z$ and omitting the terms, which are conventionally neglected in CMC approach [33], we arrive at the following equations of the PCMC model.

$$\frac{\partial Q_i}{\partial t} + (\overline{\mathbf{u}})_z \cdot \nabla Q_i + W_Z \frac{\partial Q_i}{\partial z} = (\overline{W}_i)_z + (\overline{N})_z \frac{\partial^2 Q_i}{\partial z^2} , \quad (9)$$

$$\begin{aligned} \frac{\partial \langle \beta \rho \rangle P_Z}{\partial t} + \nabla \cdot ((\overline{\mathbf{u}})_z \langle \beta \rho \rangle P_Z) + \frac{\partial W_Z \langle \beta \rho \rangle P_Z}{\partial z} \\ + \frac{\partial^2 (\overline{N})_z \langle \beta \rho \rangle P_Z}{\partial z^2} = 0 , \end{aligned} \quad (10)$$

where $N = D(\nabla Z)^2$ is the tracer dissipation.

The boundary conditions for the Z -dimension are obtained with the help of the spatial averaging theorem [34, 46]. Assuming that the β/σ -interface is quasi-stationary and the field of the tracer Z is developed (see Ref. [33] for more details), the boundary conditions for $z = 0$ read

$$-\frac{\varepsilon (\overline{N})_z P_Z}{S} \cdot \frac{\partial Q_i}{\partial z} = \Psi_i(Q_1, Q_2, \dots) , \quad (11)$$

$$(\overline{N})_z P_Z = W_Z . \quad (12)$$

Equation (11) takes into account the heterogeneous reactions at the β/σ -interface. In these equations, S is the surface area per unit volume and $\varepsilon = \langle \beta \rangle$ is the porosity of porous material, while Ψ_i are the mass rates of the heterogeneous gas-to-solid reactions per unit surface area. Note also that left parts in Equation (11) represent mass fluxes of the reactive species to the β/σ -interface.

It is important to note that this treatment of gas-to-solid reactions provides one of the major advances of the PCMC model over the conventional approach. In the PCMC model, the surface reaction rates are functions of the conditional concentrations of reactive species. In contrast to intrinsic and superficial concentrations, which are only available in conventional models, the conditional concentrations are linked to the distance from the reactive surface via conditioning on Z .

4 Distribution and conditional dissipation of the diffusive tracer

In order to close the PCMC equations (9) and (10), consistent modelling of both the distribution P_Z and the conditional dissipation $(\overline{N})_z$ of the tracer Z is required. The distribution of Z depends on the characteristics of the porous medium. Generally, this distribution is not known and needs to be reasonably approximated. In the simplified test case considered by Klimenko and Abdel-Jawad [33], the approximation for P_Z was obtained by matching the results of direct numerical simulations. Such a way of obtaining the P_Z approximation, however, is computationally expensive and requires additional modelling of the pore structure of the material in question, which can be an extremely difficult problem by itself. A more practical method is suggested below.

It is known that the pore structure of coal exhibits fractal properties [47–49]. The geometrical similarity of pore structures at different scales (micro-, meso- and macro-pores) and the large area of fluid/solid interface, which is predominantly located in the smallest

pores, are among those properties. As demonstrated by Vladimirov and Klimenko [35], the distribution of the diffusive tracer asymptotically follows the power law for such media. Using this result, we presume in the present study that P_Z has the following form.

$$P_Z(z) = \begin{cases} \frac{c}{(z+a)^\alpha}; & z \in [0, b] \\ 0; & z > b \end{cases} \quad (13)$$

In this equation, $\alpha \in (0, 1)$, which is linked to the excess fractal dimension, $a > 0$ and $b > 0$ are adjustable parameters of the model, while the normalisation constant c is obtained from the normalisation condition (8). One verifies that

$$c = \frac{1 - \alpha}{(b+a)^{1-\alpha} - a^{1-\alpha}}. \quad (14)$$

The parameters α , a and b are selected by linking PCMC and RPM as discussed in Section 6

The conditional dissipation $(\bar{N})_z$ of the diffusive tracer needs to be selected consistently with the pre-selected P_Z . Rigorously, this involves the numerical integration of Equation (10). Such a procedure, which is described by Devaud *et al* [50] in application to a turbulent combustion, is a very reasonable option, when stochastic characteristics of the Z -field are stationary. In the case of a coal particle gasification or CO_2 -sorption by a CAM particle the pore structures (and, therefore, stochastic characteristics of Z -field) change as the reactions proceed. As a result, the integration of the PDF transport equation is required for each time step. This requirement can be computationally prohibitive for small time steps. Under additional assumptions, however, Equation (10) can be integrated analytically and we opt for using this approach in the present study.

Firstly, we assume a quasi-stationary regime. That is, the Z -field is assumed to be fully developed at each time step. To justify this assumption, we note that a solid matrix is, generally, much denser than a gas phase and the movement of the β/σ -interface is much slower than the gas-phase transport. Then, the partial derivative in time $(\partial(\langle\beta\rho\rangle P_Z)/\partial t)$ can be neglected. Secondly, we note that the reactive surface is predominantly located in the smallest pores, where the convective transport is negligibly small. Since the distribution of Z in proximity to the reactive surface is of particular interest, we can neglect the convective term $(\nabla \cdot ((\bar{\mathbf{u}})_z \langle\beta\rho\rangle P_Z))$ in the PDF transport equation. Integrating once the major balance between the two remaining terms in Equation (10), we obtain

$$W_Z P_Z = - \frac{\partial(\bar{N})_z P_Z}{\partial z}. \quad (15)$$

Integrating Equation(15) from z to ∞ and taking into account that $(\bar{N})_z P_Z \rightarrow 0$ as $z \rightarrow \infty$ gives

$$(\bar{N})_z = \frac{W_Z \int_z^\infty P_Z(\xi) d\xi}{P_Z(z)}. \quad (16)$$

Using Equations (13) and (14), the expression for $(\bar{N})_z$ takes the form

$$(\bar{N})_z = \begin{cases} \frac{W_Z((z+a)^\alpha(b+a)^{1-\alpha} - z - a)}{1 - \alpha}, & z \in [0, b] \\ 0, & z > b. \end{cases} \quad (17)$$

Noting the approximate nature of the above expression for $(\bar{N})_z$, which has been obtained while neglecting the derivative in time and the convection term, special precautions should be taken in a computational procedure to ensure that the conservation integrals are preserved.

5 Linking PCMC with RPM

It is known from the PCMC model (see Refs. [33, 35] for more details) that the ratio of the reactive surface area per unit volume S to the porosity ε is expressed as follows.

$$\frac{S}{\varepsilon} = \left(P_Z \left(\frac{(\bar{N})_z}{D} \right)^{1/2} \right)_{+0}, \quad (18)$$

where the subscript “+0” indicates that the right part is evaluated as the limit for z approaching zero while remaining positive. Using Equations (13) and (17), Equation (18) takes the form

$$\frac{S}{\varepsilon} = \sqrt{\frac{W_Z(1 - \alpha)}{D((b+a)^{1-\alpha}a^\alpha - a)}}. \quad (19)$$

The same ratio S/ε can also be expressed using the equations of RPM. Following Bhatia and Perlmutter [36], we consider a unit volume of porous material. The inner volume of the overlapped cylindrical pores, which is denoted as V in Ref. [36], is equal to the porosity ε . Then, using the Equations (17), (20), (23), (26) from Ref. [36] and rearranging, we obtain

$$\frac{S}{\varepsilon} = \sqrt{\left(\frac{S_o(1 - \varepsilon)}{\varepsilon(1 - \varepsilon_o)} \right)^2 + \frac{4\pi L_o(1 - \varepsilon)^2}{\varepsilon^2(1 - \varepsilon_o)} \ln \left(\frac{1 - \varepsilon_o}{1 - \varepsilon} \right)}. \quad (20)$$

Here the subscript “o” denotes the initial values ($t = 0$), while L is the total length of the overlapped cylindrical pores.

Equation (19) from the PCMC model and Equation (20) from the RPM provide a link between these two models. The porosity $\varepsilon(t)$ as a function of time is calculated by numerically integrating the rate of consumption of the solid matrix over time. That is,

$$\varepsilon(t) = \varepsilon_0 + \int_0^t S(\tau) \sum_i v_i \Psi_i(Q_1(\tau), Q_2(\tau), \dots) d\tau, \quad (21)$$

where v_i is the consumed volume of the solid matrix per unit mass of the reacted gaseous specie “ i ”.

At each time step, Q_i are calculated by integrating Equation (9). The value of ε for the next time step is calculated using Equation (21), while the next value of S is calculated by Equation (20). Then, the parameters of P_Z for the next time step are obtained as described in the next section. After that, the time-cycle continues.

6 Parameters of P_Z

Vladimirov and Klimenko [35] pointed out that the power α in Equation (13) is related to the excess fractal dimension of the β/σ -interface. As the surface reactions proceed, the excess dimension can gradually change over time. Modelling of such changes is an extremely difficult problem by itself. Note also that even the initial value of the excess dimension is not known and needs to be estimated. Given that and the approximate nature of the expression for P_Z (Equation (13)), we opt for a more practical approach and keep α unchanged over time. The value of this adjustable parameter has to be selected by fitting available experimental data.

The parameter b represents the maximum possible value of the tracer Z , which is attained in the centre of the largest pore. For spherical pores, for example, $b = W_Z R_{\max}^2 / 6D$, where $R_{\max}$ is the radius of the largest pore. For an arbitrary pore structure, we assume that b is proportional to the squared size of the largest pore. That is $b \propto R_{\max}^2$. Following Bhatia and Perlmutter [36], we also assume that all pores change uniformly and $\varepsilon \propto R_{\max}^3$. Then, b is given by

$$\frac{b}{b_0} = \left(\frac{\varepsilon}{\varepsilon_0} \right)^{2/3}, \quad (22)$$

where the initial value b_0 is an adjustable parameter of the model selected by fitting experimental data.

Finally, the parameter a is calculated on each time step from Equation (19) with S/ε given by Equation (20). P_Z is now completely defined and is used to obtain the superficial averages by Equation (7).

7 Treatment of a product layer

The presented model is now completely formulated for the case in which the solid matrix is consumed and gaseous species are formed in the course of heterogeneous reactions. There are, however, alternative cases, which are characterised by a formation of a solid layer of the reaction products over the surface of a solid reactant as schematically presented in Figure 3. The adsorption of CO_2 on a CAM particle is an illustrative example of such cases. In this example, a layer of CaCO_3 is formed over the surface of CaO . As pointed out by Bhatia and Perlmutter [37], such a layer imposes additional resistance to the transport of gaseous species towards the reaction surface. Furthermore, as shown in Figure 3, the β/σ -interface ($z = 0$) is separated from the reactive surface by the product layer of the average thickness δ . This requires additional treatment of the boundary conditions for Equation (9).

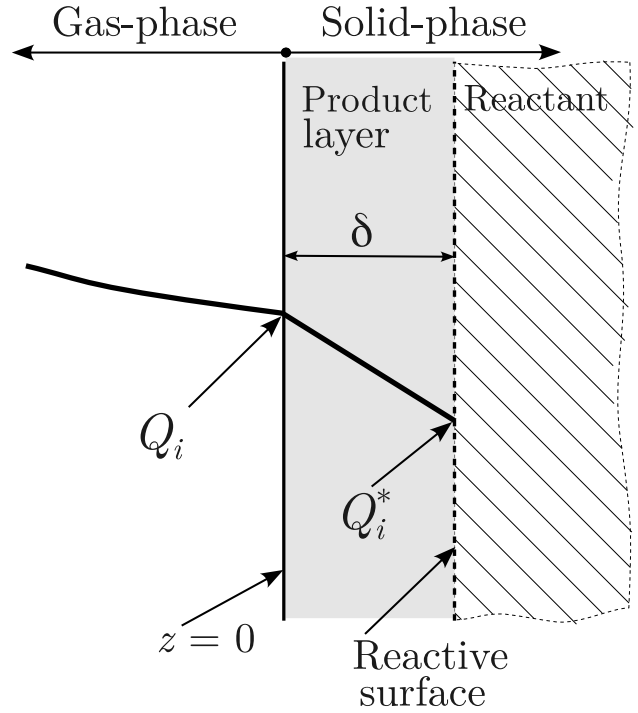


Fig. 3 Schematic representation of the product layer over the reactive surface.

In the presence of the product layer, the boundary conditions for Q_i given by Equation (11) are reformulated for each gaseous specie “ i ” as:

- the equality of mass fluxes to the β/σ -interface within the gas phase and from the interface within the product layer;

- b) the equality of the mass flux to the reactive surface and the mass reaction rate at the surface.

Note that the boundary condition for the tracer dissipation (Equation (12) remains unchanged.

Following Bhatia and Perlmutter [37], we assume that the thickness δ is small compared to the characteristic size of the reactive surface. That is, $\delta \ll \sqrt{S}$. In this case, the mass flux m_i^p of the specie “ i ” in the product layer is approximated as

$$m_i^p = \frac{D^p (Q_i - Q_i^*)}{\delta}, \quad (23)$$

where Q_i^* the average mass fraction of the specie “ i ” at the reactive surface as depicted in Figure 3, while D^p is the diffusion coefficient in the product layer. Then, Equation (11 is replaced by the following two equations:

$$-\frac{\varepsilon(\bar{N})_z P_Z}{S} \cdot \frac{\partial Q_i}{\partial z} = \frac{D^p (Q_i - Q_i^*)}{\delta} \quad (24a)$$

$$\frac{D^p (Q_i - Q_i^*)}{\delta} = \Psi_i(Q_1^*, Q_2^*, \dots). \quad (24b)$$

Note that Q_i^* are not conditioned on z , since the diffusive tracer is not defined in the solid phase. For each specie “ i ”, Q_i^* is an additional variable, which is determined from Equations (24).

The formation of the product layer also alters Equation (21). Recalling that v_i represent the consumed volume of the solid reactant per unit mass of the reacted gaseous specie “ i ”, we let v_i' be the volume of solid products formed per per unit mass of the specie “ i ”. Then, Equation (21) takes the form

$$\varepsilon(t) = \varepsilon_0 + \int_0^t S(\tau) \sum_i (v_i - v_i') \Psi_i(Q_1(\tau), Q_2(\tau), \dots) d\tau, \quad (25)$$

while the average thickness δ of the product layer is given by

$$\delta(t) = \frac{\int_0^t S(\tau) \sum_i v_i' \Psi_i(Q_1(\tau), Q_2(\tau), \dots) d\tau}{S(t)}. \quad (26)$$

If the reaction is of first order (the reaction rate is given by $\Psi_i = kQ_i$, where k is the rate constant), the additional variable Q_i^* can be excluded from Equations (24). In this case, the boundary conditions take the form

$$-\frac{\varepsilon(\bar{N})_z P_Z}{S} \cdot \frac{\partial Q_i}{\partial z} = k_{\text{eff}} Q_i, \quad (27)$$

where the effective rate coefficient k_{eff} is given by

$$k_{\text{eff}} = k \left(1 - \frac{k\delta}{k\delta + D^p} \right). \quad (28)$$

Now consider the case, which is initially (in the absence of the product layer) characterised by a large Damköhler number. As the reaction proceeds and the layer thickness increases, it is seen for Equation (28) that the effective reaction coefficient and, therefore, the Damköhler number decrease. As a result, the reaction switches from the diffusion controlled regime to the intermediate one and further to the kinetics controlled regime. As pointed out by Bhatia and Perlmutter [51], the reaction of carbon dioxide with lime is an example of such cases.

As discussed above, the model suggested in the present study takes into account the variations of the reactive species near the surface and provides advantages over conventional models for intermediate and diffusion controlled regimes. It is important to note that these regimes are of primary concern in modelling of circulating fluidised bed gasifiers with in-situ CO_2 capture, which are characterised by short resident times of bed material particles.

8 Conclusions

A novel approach aimed at modelling reactive flows through porous media is suggested. In contrast to conventional models, which are based on the volume averaging technique and, therefore, neglect inter-pore transport and variations in concentrations of transported gas species in proximity to reactive surface, the suggested approach utilises conditional averaging and takes these variations into account. The new model permits the simultaneous and consistent treatment of both homogeneous and heterogeneous reactions in all regimes, while having substantially better potential than conventional models in intermediate and diffusion controlled regimes, which are characterised by moderate or large Damköhler numbers. Variations in the pore structure caused by gas-to-solid reactions, which have not been considered in the existing conditional models, are handled in the new model by linking it with the widely used random pore model, which allows for predicting the area of the reactive surface as a function of the material porosity. Special attention is paid to the treatment of the product layer formed over the reactive surface in the framework of the model.

This PCMC-RPM model is now being implemented in a numerical code and will initially be used to predict the CO_2 sorption of a single CAM particle. The model

will subsequently be implemented in a gasifier code to model simultaneous coal gasification and CO₂ capture.

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