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# Methane Cracking for Carbon Production

S. R. ABRAHAMS<sup>1</sup>, P. BIRKEN<sup>2</sup> M. BLYTH<sup>3</sup>, R. D. CHATTERJEE<sup>1</sup>, M. A. ELLIS<sup>1</sup>, S. MURPHY<sup>4</sup>, D.R.Q. PACHECO<sup>5</sup>, M. D. SHIRLEY<sup>1</sup><sup>†</sup>, M. P. SØRENSEN<sup>6</sup>,

<sup>1</sup> University of Oxford, Oxford, UK
 <sup>2</sup> University of Lund, Lund, Sweden
 <sup>3</sup> University of Bristol, Bristol, UK
 <sup>4</sup> University of Limerick, Limerick, Ireland
 <sup>5</sup> Norwegian University of Science and Technology, Trondheim, Norway
 <sup>6</sup> Technical University of Denmark, Kongens Lyngby, Denmark

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**Communicated by:** Dietmar Hömberg, NTNU Trondheim / WIAS Berlin. Marcus Grasmair, NTNU Trondheim. Siebevan Albada, NTNU Trondheim. Poul G. Hjorth, DTU Kongens Lyngby

Industrial Partner: Elkem ASA

Presenter: J. I. Meling, H. Reynolds

Team Members: S. R. Abrahams, Uni. Oxford; S. W. Biber, Uni. Bristol; P. Birken, Uni. Lund,
M. Blyth, Uni. Bristol; R. D. Chatterjee, Uni. Oxford; M. A. Ellis, Uni. Oxford; J. Jackaman, NTNU Trondheim;
S. Murphy, Uni. Limerick; D. R. Q. Pacheco, NTNU Trondheim; V. Raveendran, Uni. Karlstad;
M. D. Shirley, Uni. Oxford; M. P. Sørensen, DTU Lyngby; B. J. Warmington, Uni. Bristol.
Note: Team members are not necessarily the same as authors; the latter are those who materially contributed to the writing of the report.

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† Corresponding Author: shirley@maths.ox.ac.uk

### Summary

A series of models, focusing on various aspects and spatial scales, have been developed for simulation studies of methane pyrolysis, also called cracking, for carbon production in a laboratory scale test crucible. The background for the use of methane cracking is to capture carbon dioxide emmissions in the production of silicon by carbon looping and in this way reduce the impact on the climate. Partial differential equations have been used to model fluid flow, heat transfer and heat consumption in the pyrolysis. In the process carbon powder is produced and the interaction between powder particles and fluid flow is studied by simulations including heat transport. Both microscale as well as macroscale approaches have been used. A macroscale model for heat transport in a packed fluid bed of carbon powder, including chemical reactions, has been derived, and numerical results presented for a crucible with cylindrical symmetry. Homogenization has been applied in the study of the porous fluid bed of carbon, including methane reactions and heat transport to upscale a microscale model to determine the effective macroscale behaviour. A two fluid model consisting of the methane gas phase and a fluidised carbon phase has been derived also. Computational fluid dynamics simulations have been used to investigate various geometries for the design of the methane gas inlets and provided more desirable inflow geometries of the inlet. Simulation results has been presented for a simple lumped model of the methane cracking reaction, including the effect of heating, inlet and outlet flow from the crucible. The lumped model provides an overall picture in a simple and easy fashion.

### 1 Challenge

Elkem ASA are a major producer of silicon (Si). They are developing a new concept to eliminate all direct carbon dioxide (CO<sub>2</sub>) emissions from their Si production process. The new concept has been developed based on carbon looping, where carbon oxides in the process off-gases are captured, converted to solid carbon, and reused in the process. When successful, this will become a game changer for the global silicon industry.

As part of this new concept, they are investigating an alternative carbon source for the Si production, specifically the carbon by-products from turquoise hydrogen production. Turquoise hydrogen production refers to hydrogen production via the pyrolysis of methane (CH4), also called methane cracking. Utilising carbon produced in this manner benefits Si production by reducing the direct carbon emissions, providing greater security of raw materials, and provide a carbon source of greater purity than wood chips and coal currently used. Additionally it provides process synergy with the growing in hydrogen production industry by utilising a by-product that would otherwise go to waste.

Currently Elkem are still at an experimental stage, with laboratory scale experiments being performed in order to maximise the conversion of methane to hydrogen gas and carbon solid, and explore the ability to control the formation and growth of carbon particles. The challenge presented by Elkem is to develop a mathematical model for their experimental setup which will provide insight into the process and help them guide and interpret their experiments, with the longer term goal of exploring the impact of scaling up to the larger production scale.

#### 2 Introduction

### 2.1 Methane cracking

The overall process of methane cracking occurs in several stages, [2, 12], but can be described by a single overall reaction

$$CH_4(g) \longrightarrow 2H_2(g) + C(s),$$
 (2.1)

where CH4(g) is methane gas, H<sub>2</sub>(g) is hydrogen gas, and C(s) is solid carbon. This overall process is an endothermic reaction with a reaction enthalpy of 75.6 kJ mol<sup>-1</sup> of methane [2]. Although methane cracking can occur in free space, it requires temperatures above 1200 °C which typically make the process unviable economically [2]. Elkem are therefore primarily interested in catalysed reactions where the cracking occurs at active sites on the surface of a solid catalyst. In their experiments Elkem are using small carbon seed particles to provide these active sites. As the reaction rate is strongly temperature dependent, it is often modelled as proportional to an Arrhenius term,  $\exp(-E/(RT))$ , where E the activation energy, R the universal gas constant and T the temperature, and we will use a rate of this form for the remainder of this report. Estimates for the activation energy of methane cracking onto carbon particles are given in [12].

#### 2.2 Experimental setup

The experimental laboratory setup used by Elkem is depicted in Figure 1. It consists of a cylindrical crucible with a gas inlet at the bottom and a gas outlet at the top, all within a furnace with heating elements on its side walls. The gas inlet extends into the crucible and gas flows out of small circular openings on its sides. Dimensions of the setup are given in Table 1. In each experimental run the crucible is filled partway up with a bed of carbon seed particles of a specified initial size. Inert argon gas is then injected to ensure the gas inlet remains clear, and the furnace is heated up to 1200 °C. Once the furnace is fully heated the flow of argon is ceased and replaced with methane. The experiment is then allowed to run for several hours, after which the furnace is switched off and the gas flow stopped and the newly formed carbon extracted. During this period, where the methane cracking occurs, the power drawn by the furnace is adjusted to maintain a constant temperature based on the value measured by thermo-couple outside the crucible, depicted in Figure 1. Based on earlier experiments, where the gas inlet clogged due to carbon forming before it reached the crucible, the incoming gas is cooled such that it enters the crucible at room temperature.

If velocity of the gas injected is low enough then the initial carbon seeds will remain as a packed bed for the entire duration of the experiment. However, for higher velocity flows the bed can be fluidised, with the particles being carried throughout the furnace by the fluid.

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Figure 1. Sketch of the laboratory scale reactor for methane cracking.

Table 1. Dimensions of the experimental setup depicted in Figure 1.

| Dimension   | Value  |
|---|--|
| Furnace width<br>Furnace height   | $6.8 \times 10^{-1} \mathrm{m}$<br>$1.06 \times 10^{-1} \mathrm{m}$  |
| Crucible width  | $5.0 \times 10^{-1} \mathrm{m}$  |
| Gas inlet width   | $5.0 \times 10^{-1} \text{ m}$<br>$2.8 \times 10^{-2} \text{ m}$   |
| Gas inlet height  | $3.3 \times 10^{-2} \mathrm{W/m^2 K}$  |
| Gas inlet hole diameter<br>Gas outlet width   | $2 \times 10^{-3} \text{ kg/m}^3$<br>$8 \times 10^{-3} \text{ m}$  |
| Crucible height<br>Gas inlet width<br>Gas inlet height<br>Gas inlet hole diameter<br>Gas outlet width | $ \begin{array}{c} 5.0 \times 10^{-1}  \mathrm{m} \\ 5.0 \times 10^{-1}  \mathrm{m} \\ 2.8 \times 10^{-2}  \mathrm{m} \\ 3.3 \times 10^{-2}  \mathrm{W/m^2 K} \\ 2 \times 10^{-3}  \mathrm{kg/m^3} \\ 8 \times 10^{-3}  \mathrm{m} \end{array} $ |

In the limited experimental runs Elkem has carried out so far, it has been observed that a hard-packed layer can form in the bottom corners of the crucible, separated from more loose material by a thin layer of crust, as depicted in Figure 2. This hard pack material is undesirable for use in the silicon production process, and so Elkem are also interested in exploring modifications to the geometry of the crucible that prevent this material from forming.



Figure 2. Carbon crust and loose packed carbon material in the bottom of the crucible

In this report we will present a hierarchy of models for investigating different elements of the coupled fluid flow, heat transfer and mass transfer occurring within the crucible under a range of possible assumptions. In §3 we develop a micro-scale model to describe how a carbon seed particle grows over time. In §4 a simple macroscale model for the temperature distribution across the whole crucible is developed to understand the interaction of the injected cold gas, hot crucible walls and endothermic reactions. The effect of different reaction rate parameters is explored. In §5 the method of multiple scales is used to derive a macroscale model for the coupled flow and heat transfer, whose parameters depend upon a microscale model of particle growth. In §6, a multiphase fluid model is developed to investigate the fluidisation of the bed of carbon pellets. In §7 we simulate the incompressible Navier-Stokes equations in a realistic crucible geometry. In §8 we outline how to simulate the movement of carbon particles in a background flow using Lagrangian particle dynamics. In §9 we present an alternative lumped parameter model, based on a fully mixed assumption, to investigate the temporal dynamics of the reactions in the furnace. We conclude in §10.

#### 3 Microscale model

### 3.1 Model outline

We consider a one-dimensional gas phase of infinite radius, surrounding a spherical pellet centered at the origin. Before reaction begins, the gas occupies entirely the region  $s_0 < \bar{r} < \infty$ , where  $s_0$  is the initial radius of the carbon pellet. At time  $\bar{t} = 0$ , the methane at the boundary of the pellet begins to crack and deposit carbon on the interface, causing the pellet to grow. The position of the interface  $\bar{s}(\bar{t})$  [m] is changing in time as the pellet radius increases. This system can be described by a one-dimensional one-phase spherical Stefan

problem, similar to that modelled for the problem of drug diffusion in polymer spheres [14]. We will assume the concentration of methane in the system is always sufficient to ensure methane cracking occurs at the interface, and that the gas flow is slow enough for heat transport to be purely diffusive. Then, the governing equation for the temperature of the gas phase,  $\bar{T}(\bar{r}, \bar{t})$ , is given by

$$\frac{\partial \bar{T}}{\partial \bar{t}} = \frac{\rho c}{k} \frac{1}{\bar{r}^2} \frac{\partial}{\partial \bar{r}} \left[ \bar{r}^2 \frac{\partial \bar{T}}{\partial \bar{r}} \right],\tag{3.1}$$

where  $\rho$  is the density of the gas, c is the specific heat capacity and k is the thermal conductivity.

The boundary grows at a rate proportional to rate of reaction which we assume to be of the form of the Arrhenius equation. This yields

$$\frac{\mathrm{d}\bar{s}}{\mathrm{d}\bar{t}} = V_m \mathcal{A} \exp\left(-\frac{E_a}{R\bar{T}}\right)\Big|_{\bar{r}=\bar{s}(\bar{t})},\tag{3.2}$$

where  $V_m$  is the molar volume of gas,  $\mathcal{A}$  is the pre-exponential factor,  $E_a$  is the activation energy for the reaction and R is the universal gas constant.

We assume that the temperature of the gas tend towards a constant as  $\bar{r} \rightarrow \infty$  and so

$$\frac{\partial T}{\partial \bar{r}} \to 0 \quad \text{as} \quad \bar{r} \to \infty.$$
 (3.3)

We assume the temperature on the boundary of the carbon particle is decreasing exponentially. On  $\bar{r} = \bar{s}(\bar{t})$ ,

$$\bar{T} = T_0 \exp(-\bar{b}\bar{t}), \qquad (3.4)$$

With this choice of boundary condition on  $\bar{r} = \bar{s}(\bar{t})$ , we can study the evolving moving boundary without solving for the temperature profile of the entire region.

Our initial conditions are

$$\bar{T}(\bar{r},0) = T_0, \quad \bar{s}(0) = s_0.$$
 (3.5)

### 3.2 Non-dimensionalisation

We non-dimensionalise as follows:

$$T = \frac{\bar{T}}{T_0}, \quad t = \frac{\bar{t}\mathcal{A}V_m}{s_0}, \quad r = \frac{\bar{r}}{s_0}, \quad s = \frac{\bar{s}}{s_0}.$$
 (3.6)

Equations (3.1)-(3.5) are now

$$\beta \frac{\partial T}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r \frac{\partial T}{\partial r} \right], \tag{3.7}$$

$$\frac{\mathrm{d}s}{\mathrm{d}t} = \exp\left(-\frac{\alpha}{T}\right)\Big|_{r=s(t)},\tag{3.8}$$

$$\frac{\partial T}{\partial r} \to 0 \quad \text{as} \quad r \to \infty. \tag{3.9}$$

$$T|_{r=s(t)} = \exp(-bt),$$
 (3.10)



Figure 3. Growth of carbon pellet radius s(t) with time where  $E_a = 147.37$ , R = 0.5182,  $s_0 = 50e - 6$ , k = 0.137,  $\rho = 0.657$ , c = 4.7,  $V_m = 15$  and  $\mathcal{A} = 1$ .

$$T(r,0) = 1, \quad s(0) = 1.$$
 (3.11)

where

$$\beta = \frac{k}{\rho c s_0 V_m \mathcal{A}}, \quad \alpha = \frac{E_a}{RT_0} \quad \text{and} \quad b = \frac{\bar{b}\rho c s_0^2}{k}.$$
(3.12)

### 3.3 Asymptotic and numerical solutions

Realistic values of our parameter  $\beta$  are of order 1e-4. Equation (3.14) therefore suggests that the temperature profile of the gas is approximately steady state. Looking for a leading order asymptotic solution, we find that

$$\frac{\mathrm{d}s}{\mathrm{d}t} \sim \exp\left(-\frac{\alpha}{\exp(-t)}\right) \tag{3.13}$$

at leading order.

To obtain a numerical solution, we transform equations (3.14)-(3.18) to cartesian coordinates via the following transformation u = rT and immobilise the boundary by setting  $\xi = \frac{r}{s}$ , which yields

$$\beta s^2 \frac{\partial u}{\partial t} - \beta s \xi \frac{\mathrm{d}s}{\mathrm{d}t} \frac{\partial u}{\partial \xi} = \frac{\partial^2 u}{\partial \xi^2},\tag{3.14}$$

$$\frac{\mathrm{d}s}{\mathrm{d}t} = \exp\left(-\frac{\alpha s}{u}\right)\Big|_{\xi=1},\tag{3.15}$$

$$\frac{\partial u}{\partial \xi} \to \frac{u}{\xi} \quad \text{as} \quad \xi \to \infty.$$
 (3.16)

$$u|_{\xi=1} = sexp(-bt).$$
 (3.17)

Our initial conditions are

$$u(\xi, 0) = \xi, \quad s(0) = 1.$$
 (3.18)

We obtain the following results for the growth of the moving boundary or the width of the carbon pellet.

In Figure (3), we can see that the growth rate of the carbon pellet is decreasing with time. Given the temperature on the surface of the pellet is decreasing with time and therefore the reaction rate is slowing, this seems sensible.

Given these results, we can predict the time it takes for the volume of the individual carbon particle to double in size. If  $s_0$  is our initial radius of the carbon pellet, then our initial volume is  $4\pi s_0^3/3$ . This volume is doubled when the radius is  $\sqrt[3]{2}s_0 \ \mu m$ , which occurs after approximately 2.2 hours.

### 4 Macroscale model of the heat transfer in a packed bed

### 4.1 Problem formulation

In this section, rather than modelling the growth of a single particle, we consider a simple model for the temperature distribution with the crucible. We model the crucible as a cylindrical domain with radius a and height h, and so adopt a cylindrical coordinate system  $(r, \theta, z)$ , and will seek axi-symmetric solutions. We assume the gas and pellets are in local thermal equilibrium, and so only consider a single temperature T. We neglect the effect of advective transport by the gas phase, and any change in the material properties due to deposition from the reactions, meaning that the conservation of energy in the crucible can be expressed by the reaction-diffusion equation

$$\frac{\partial}{\partial t} \left( \rho c_p T \right) = \nabla \cdot \left( k \nabla T \right) - \mathcal{S}, \tag{4.1}$$

where  $\rho$  is the bulk density of the solid material,  $c_p$  is the specific heat capacity of the solid material, T is the temperature [in Kelvin], t is time, k is bulk conduction coefficient of heat, and S is the heat sink due to the reaction. Here, the heat sink S is taken to be a function of temperature only.

Although we have only included the effect of conduction, at high temperatures radiative transport may also be important. To consider how this can be modelled we consider the optical thickness of the material. In the optically thin limit the effect of radiation can be approximated in (4.1) by including a term proportional to  $T^4$  [13]. In the optically thick limit, also called the Rosseland approximation, radiation can be approximated by an additional nonlinear diffusion term of the form  $\nabla \cdot (k_{\rm rad}T^3\nabla T)$  [5]. Data for CH4 is available in [21]. However, we neglect such effects in the results presented below.

The energy consumed by the reactions will be proportional to the rate of reaction, which we model using an Arrhenius law,

$$S = S \exp\left(-\frac{E}{RT}\right),\tag{4.2}$$

where S is the prefactor, E the activation energy, and R the universal gas constant.

Along the bottom of the furnace we prescribe a temperature profile that can vary with r, in order to model the effect of the small gas inlet

$$T = T_{\rm in}(r)$$
 at  $z = 0$ , (4.3)

taking as its minimum  $T_{\text{gas}}$ , the temperature of the incoming gas in the experiments. Along the walls we prescribe a constant temperature,

$$T = T_{\text{wall}}$$
 at  $r = a$  (4.4)

as the furnace will adjust the power drawn to maintain this situation. At the top of the crucible we impose no diffusive flux of temperature,

$$\nabla T \cdot \mathbf{n} = 0. \tag{4.5}$$

As we are in a cylindrical domain we also require the solution to be bounded as  $r \to 0$ .

#### 4.2 Non-dimensionalisation

We non-dimensionalise the equations scaling

$$t = \frac{\rho c_p \left( T_{\text{wall}} - T_{\text{in}} \right)}{k} \hat{t}, \ (r, z) = h \left( \hat{r}, \hat{z} \right), \ T = T_{\text{gas}} + \left( T_{\text{in}} - T_{\text{gas}} \right) \hat{T}, \ \mathcal{S} = S \hat{\mathcal{S}},$$
(4.6)

where the timescale was chosen to balance advection. Then, using (4.6) and the axisymmetric assumption, the governing equations (4.1) become

$$\frac{\partial \hat{T}}{\partial \hat{t}} = \frac{1}{\hat{r}} \frac{\partial}{\partial \hat{r}} \left( \hat{r} \frac{\partial \hat{T}}{\partial \hat{r}} \right) + \frac{\partial^2 \hat{T}}{\partial \hat{z}^2} - \eta \exp\left( -\frac{\sigma}{\hat{T}} \right)$$
(4.7)

for  $0 < \hat{r} < \hat{a} = a/h$ , and  $0 < \hat{z} < 1$ , where

$$\eta = \frac{S}{k}, \quad \sigma = \frac{E}{R\left(T_{\text{wall}} - T_{\text{in}}\right)} \tag{4.8}$$

are the dimensionless heat of reaction and activation energy respectively. The boundary conditions become

$$\hat{T} = 0 \quad \text{at } \hat{z} = 0, \tag{4.9a}$$

$$\hat{T} = 1$$
 at  $\hat{r} = \hat{a}$ , (4.9b)

$$\frac{\partial \hat{T}}{\partial \hat{z}} = 0$$
 at  $z = 1$ , (4.9c)

$$T$$
 bounded as  $\hat{r} \to 0$ , (4.9d)

### 4.3 Analytical steady solution

It is possible to solve (4.7)–(4.9d) analytically using an eigenfunction expansion when  $\eta = 0$ , implying there are no reactions. Dropping the hat notation, the steady solution is given by

$$T(r,z) = \sum_{n=1}^{\infty} \frac{1}{I_0\left(\frac{2n+1}{2}\pi a\right)} \frac{4}{(2n+1)\pi} I\left(\frac{2n+1}{2}\pi r\right) \sin\left(\frac{2n+1}{2}\pi z\right),$$
(4.10)

where  $I_{\nu}(x)$  is the modified Bessel function of the first kind. This solution is plotted in Figure 4, with a = 1. While this approach cannot be extended to non-zero  $\eta$  due to the nonlinear dependence of S on T, it does provide a useful test case for our implementation of the numerical solution when  $\eta \neq 0$  in §4.4.

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Figure 4. Analytical solution (4.10) for the steady temperature distribution in the crucible when  $\eta = 0$ .

### 4.4 Numerical Solution

To solve the problem (4.7)–(4.9) numerically, we use a finite difference scheme. We use a second-order accurate central difference scheme for the spatial derivatives, and an explicit Euler method for the temporal derivatives. The solution is found on an equispaced mesh on the domain  $[\varepsilon, \varepsilon + a] \times [0, 1] \times [0, t_{\max}]$ , whose points are given by  $(r, z, t)_{\tilde{r}, \tilde{z}, \tilde{t}} = (\tilde{r}\Delta r + \varepsilon, \tilde{z}\Delta z, \tilde{t}\Delta t)$ , where  $\Delta r, \Delta z$ , and  $\Delta t$  are the grid sizes in the radial, axial, and temporal dimensions respectively. Note that  $\Delta t$  must be kept sufficiently small in comparison to  $\Delta r$  and  $\Delta z$ , to ensure numerical stability. The radial domain has been shifted by some small amount  $\varepsilon \ll \Delta r$  to avoid division by zero at the centreline. Letting  $T(\tilde{r}\Delta r + \varepsilon, \tilde{z}\Delta z, \tilde{t}\Delta t) = \tilde{t}_{r}^{\tilde{t}}$ , denote the temperature at the mesh points, the discretised version of (4.7) is given

$$\begin{split} \tilde{t}^{\tilde{t}+1} &= z \tilde{T}_r + \Delta t \left\{ \frac{1}{\tilde{r}\Delta r + \varepsilon} \left[ \frac{z \tilde{T}_{\tilde{r}+1} - z \tilde{T}_{tr}}{\Delta r} \right] \right. \\ &+ \frac{z \tilde{T}_{\tilde{r}+1} - 2 z \tilde{T}_{\tilde{r}} + z \tilde{T}_{\tilde{r}-1}}{\left(\Delta r\right)^2} + \frac{z + 1 \tilde{T}_{\tilde{r}} - 2 z \tilde{T}_{\tilde{r}} + z - 1 \tilde{T}_{\tilde{r}}}{\left(\Delta z\right)^2} \right\} \\ &- \eta \exp\left(-\frac{\sigma}{\tilde{t}}\right) \quad (4.11) \end{split}$$

Boundary conditions are applied by adding fictitious meshpoints  $(1 + \varepsilon + \Delta r, z) = 1$ to give T = 1 on the outer wall;  $(r, 1 + \Delta z) = (r, 1 - \Delta z)$  to give zero heat-flux at the top of the medium; axisymmetry is approximated using zero flux through the centerline. A boundary condition must also be chosen along the bottom of the domain. Including fictitious points of  $(-\Delta r, z) = 0$  enforces T = 0 as the condition along the bottom boundary. This models a cold bottom along the crucible.

While these results are useful for validation, the entire base of the crucible is unlikely to be at the temperature of the inlet gas, due to heating effects from the furnace. An alternative would be to take  $(-\Delta r, z) = 1$  except at the meshpoint closest to the center axis, for which  $(-\Delta r, \varepsilon) = 0$  is chosen. This models a cold point source at the center line where cold gas is assumed to be injected, and a heat source everywhere else, due to furnace heating. Nevertheless, this model is limited in realism, as it neglects diffusion of the cold methane throughout the medium. As a heuristic description of cooling effects from diffusing inlet gas, we investigate a variable-temperature boundary condition along the bottom. We choose  $T(r,0) = 1 - e^{-\alpha r^2}$ , with  $\alpha = 10$ . As shown in Figure 5, this function varies smoothly, starting at T = 0 around the gas inlet at r = 0, and approaches T = 1 for large r. We refer to this as the variable-temperature boundary condition.

### 4.5 Results

We now use the finite difference scheme to solve the problem on a domain with a = 1, and choose  $\varepsilon = 1 \times 10^{-4}$ ,  $\Delta t = 1 \times 10^{-5}$ , and  $\Delta r = \Delta z = 5 \times 10^{-2}$ . In Figure 6 we plot the steady solution to the problem when  $\eta = 0$ , so that there is no heat sink. There is very good agreement between this numerical solution and the analytical solution shown in Figure 4, suggesting the finite difference scheme described in §4.4 has been correctly implemented.

We now consider the behaviour of the model with the variable temperature boundary condition. Figure 7 shows the steady-state temperature distribution without any reaction terms ( $\eta = 0$ ). Away from a region near the inlet the gas tends to the imposed wall temperature. The effect of the heat sink is shown in Figure 8, which shows a sweep over a range of possible values for the dimensionless heat of reaction  $\eta$  and activation energy  $\sigma$ . Compared to Figure 7, we see that the cold region grows towards the walls as  $\eta$  increases





Figure 5. Temperature imposed at the bottom of the crucible in the variable temperature boundary condition.



Figure 6. Numerical solution for the temperature distribution in the furnace when  $\eta = 0$ .

in size. This suggests that the reaction rate, which increases with temperature, will be largest nearest the sides and bottom of the crucible, and so the pellets will grow the most in these regions. These regions correspond closely to the regions of hard packed material observed in Elkem's experiments, providing evidence for a chemical process causing the formation of the hard packed material, rather than a mechanical process.



Figure 7. Numerically derived steady-state temperature distribution for a crucible with a variable-temperature bottom boundary condition.



Figure 8. Two-parameter sweep showing numerically derived (steady-state) temperature distributions for various values of Arrhenius coefficients  $\eta$  and  $\sigma$ . Axis scales and colour bars are removed for clarity. Colour scheme and axis scaling is the same as Figure 4.

### 5 Homogenised model for heat transport and flow

In Section 4, we considered a heat transport model with a volumetric heat sink (due to the methane cracking reaction) across the crucible. In this section, we focus on incorporating the microscale behaviour, specifically the reaction occuring on the surface of the carbon pellets, and use the method of multiple scales to derive an *effective* macroscale model to describe the heat transport within the crucible and predict the pellet size. For an introduction to mathematical homogenisation via the method of multiple scales see [9]. Classic homogenisation requires a strictly periodic microscale. However, this assumption has been relaxed in more recent work [4, 6]. This work follows the framework by Dalwadi *et al.* [7], who consider solute transport through a filter with an evolving microstructure. They derive an effective advection-diffusion-reaction system for solute concentration which is coupled to the time-dependent microstructure.

### 5.1 Model set-up

We consider the transport of heat, via advection and diffusion, through an array of carbon pellets. We denote the temperature in the gas as  $\hat{T}(\hat{x}, \hat{t})$ , where  $\hat{x}$  denotes the macroscale spatial coordinate and  $\hat{t}$  is time. We adopt a Cartesian coordinate system to derive the effective heat transport model and change to (axisymmetric) cylindrical polar coordinates when solving numerically in Section 5.4. We denote the gas region as  $\omega_G$  and the pellet region as  $\omega_P$  with boundary as  $\partial \omega_P(\hat{x}, \hat{t})$ . The carbon pellets are assumed to be solid obstacles, on the surface of which the endothermic reaction of methane cracking occurs. The carbon pellets are modelled as a collection of non-overlapping spheres, which grow in time, and whose centres are arranged on a cubic lattice at a distance  $\delta l$  apart, where  $\delta$  is a small dimensionless parameter and l is the characteristic lengthscale of the crucible. Thus,  $\delta \ll 1$  is the ratio of pellet separation to crucible length. We denote the pellet radius as  $\hat{s} = \hat{s}(\hat{x}, \hat{t})$ , where  $2\hat{s} \leq \delta l$ . A schematic of this set-up is given in Figure 9. The pellet radius at a rate proportional to the methane cracking reaction rate,  $\hat{\mathcal{R}}(\hat{T})$ .

Further, we assume that we have an incompressible Newtonian fluid within the gas region,  $\omega_G$ , which we obeys Stokes flow. We impose no slip at the pellet surface. We assume that the gas has a constant density,  $\rho$ . For simplicity, we neglect the effects of convection, however we note that more complicated fluid flow models could be utilised and be homogenised in a similar manner (so long as local periodicity is retained).

We assume that there is sufficient methane throughout the domain to so that we are in a *temperature-limited* regime for methane cracking, and therefore do not track methane concentrations throughout the crucible. However, we note that we can model the methane transport analogously, by treating methane as a dilute species where we neglect particle-particle interactions.

The equations governing the flow of fluid throughout the gas region  $\omega_G$  are

$$-\hat{\nabla}\hat{p} + \mu\hat{\nabla}^2\hat{\boldsymbol{u}} = \boldsymbol{0} \quad \text{for } \hat{\boldsymbol{x}} \in \omega_G, \tag{5.1a}$$

$$\nabla \cdot \hat{\boldsymbol{u}} = 0 \quad \text{for } \hat{\boldsymbol{x}} \in \omega_G, \tag{5.1b}$$

$$\boldsymbol{n} \cdot \hat{\boldsymbol{u}} = \boldsymbol{n} \cdot \hat{\boldsymbol{u}}_{\partial \omega_P} \quad \text{for } \hat{\boldsymbol{x}} \in \partial \omega_P,$$
 (5.1c)

where  $\hat{u}$  is the fluid velocity,  $\hat{p}$  is the fluid pressure, and n is the outward pointing unit

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Figure 9. (Left) Schematic of the crucible domain considered. The shaded region represents the bed of carbon pellets. (**Right**) Schematic of the microscale pellet bed structure. The orange region represents the gas region, and the grey regions represent the carbon pellet regions.

normal to the fluid (that is, point from the fluid into the pellet), and the pellet boundary velocity  $\hat{u}_{\partial\omega_P}$  is related to the rate of reaction via:

$$\boldsymbol{n} \cdot \hat{\boldsymbol{u}}_{\partial \omega_P} = -\frac{\partial \hat{s}}{\partial \hat{t}}.$$
(5.2)

The governing equation for conservation of heat within the gas region is

$$\frac{\mathrm{D}}{\mathrm{D}\hat{t}}\left(\rho c_p \hat{T}\right) = \hat{\nabla} \cdot \left(k\nabla \hat{T}\right),\tag{5.3}$$

where  $\rho$  is the density of the gas,  $c_p$  is the specific heat capacity of the gas, and k is the thermal conductivity of the gas, and here  $\hat{\nabla}$  refers to the nabla operator with respect to  $\hat{x}$ . We note that the dilution term in  $\hat{\nabla} \cdot (\hat{T}\hat{u}) = \hat{u}\hat{\nabla} \cdot (\hat{T}) + \hat{T}\hat{\nabla} \cdot (\hat{u})$  is zero due to the incompressibility assumption, and we write Equation (5.3) in terms of thermal diffusivity,

 $D = k/(\rho c_p)$  to obtain

$$\frac{\partial T}{\partial \hat{t}} + \hat{\boldsymbol{u}} \cdot \hat{\nabla} \hat{T} = \hat{\nabla} \cdot \left( D \nabla \hat{T} \right) \quad \text{for } \hat{\boldsymbol{x}} \in \omega_G(\hat{\boldsymbol{x}}, \hat{t}).$$
(5.4)

At the pellet-gas boundary,  $\partial \omega_P(\hat{x}, \hat{t})$ , we have a partially absorbing Robin boundary condition due to the endothermic reaction at the pellet surface removing heat from the system,

$$\boldsymbol{n} \cdot \left( (\hat{\boldsymbol{u}} - \hat{\boldsymbol{u}}_{\partial \omega_P}) \hat{T} - D \hat{\nabla} \hat{T} \right) = \hat{\mathcal{R}}(\hat{T}) \quad \text{at } \hat{\boldsymbol{x}} \in \partial \omega_P(\hat{\boldsymbol{x}}, \hat{t}),$$
(5.5)

where  $\hat{\mathcal{R}}$  is the heat sink due to the reaction, which we assume depends on temperature  $(\hat{\mathcal{R}} \geq 0 \text{ represents an endothermic reaction})$ . For the following analysis, we retain this general form, however one could impose, *e.g.* the Arrhenius law, Equation (4.2). The no slip condition at the pellet boundary implies  $\hat{\boldsymbol{u}} = \hat{\boldsymbol{u}}_{\partial\omega_P}$  at  $\partial\omega_P(\hat{\boldsymbol{x}}, \hat{t})$ . This condition reduces to

$$\boldsymbol{n} \cdot (D\hat{\nabla}\hat{T}) = -\hat{\mathcal{R}}(\hat{T}) \quad \text{at } \hat{\boldsymbol{x}} \in \partial \omega_P(\hat{\boldsymbol{x}}, \hat{t}).$$
(5.6)

To close the system, we impose a model to relate the pellet growth to the rate of reaction (as in Section 3),

$$\frac{\partial \hat{s}}{\partial \hat{t}} = \hat{\gamma} \hat{\mathcal{R}}(\hat{t}) = -\hat{\gamma} \boldsymbol{n} \cdot (D \hat{\nabla} \hat{T}), \qquad (5.7)$$

where the constant  $\hat{\gamma}$  is the volume of carbon deposited on the pellet per reaction.

### 5.2 Non-dimensionalisation

We non-dimensionalise using the scalings:

$$\hat{T} = T_{\text{wall}}T, \quad \hat{\boldsymbol{x}} = l\boldsymbol{x}, \quad \hat{t} = \frac{\delta l}{\hat{\gamma}[\hat{\mathcal{R}}]}, \quad \hat{\boldsymbol{u}} = \mathcal{U}\boldsymbol{u}, \quad \hat{p} = \frac{\mu\mathcal{U}}{\delta^2 l}p,$$
(5.8)

where  $[\hat{\mathcal{R}}]$  and  $\mathcal{U}$  are the characteristic reaction rate and fluid velocity, respectively. The time scaling is chosen to balance pellet growth and the pressure scaling is chosen to balance the macroscale pressure gradient with the microscale viscous forces. The flow problem Equation (5.1) becomes

$$-\nabla p + \delta^2 \nabla^2 \boldsymbol{u} = \boldsymbol{0} \quad \text{for } \boldsymbol{x} \in \Omega_G, \tag{5.9a}$$

$$\nabla \cdot \boldsymbol{u} = 0 \quad \text{for } \boldsymbol{x} \in \Omega_G, \tag{5.9b}$$

$$\boldsymbol{u} = -\delta\beta \frac{\partial s}{\partial t} \boldsymbol{n} \quad \text{for } \boldsymbol{x} \in \partial\Omega_P,$$
 (5.9c)

where  $\beta = \hat{\gamma}[\hat{\mathcal{R}}]/\delta l$ . For the heat transport equation, Equations (5.4), (5.6) and (5.7) become

$$\beta \frac{\partial T}{\partial t} + \boldsymbol{u} \cdot \nabla T = \nabla \cdot \left(\frac{1}{\operatorname{Pe}_T} \nabla T\right) \quad \text{for } \boldsymbol{x} \in \Omega_G(\boldsymbol{x}, t), \tag{5.10a}$$

$$\boldsymbol{n} \cdot \left(\frac{1}{\operatorname{Pe}_T} \nabla T\right) = -\delta k \mathcal{R}(T) \quad \text{at } \boldsymbol{x} \in \partial \Omega_P(\boldsymbol{x}, t), \tag{5.10b}$$

$$\frac{\partial s}{\partial t} = \mathcal{R}(T) \quad \text{at } \boldsymbol{x} \in \partial \Omega_P(\boldsymbol{x}, t),$$
 (5.10c)

where  $\text{Pe}_T = \mathcal{U}l/D$  is the Péclet number and  $k = 1/\delta \mathcal{U}$ .

We assume that  $\beta$ , Pe<sub>T</sub>, and k are all  $\mathcal{O}(1)$ . (We note that one could explore other asymptotic limits, and refer the reader to [6, 7] for further explanation of this.) The carbon pellets now form a cubic lattice of spheres, a distance  $\delta$  apart. A carbon pellet with centre  $\boldsymbol{x}$  has radius  $\delta s(\boldsymbol{x}, t)$ , see Figure 10.

#### 5.3 Method of multiple scales analysis

We now begin the homogenisation of the governing equations for fluid flow and heat transport Equations (5.9) and (5.10) via the method of multiple scales.

Following standard homogenisation framework, we introduce a microscale spatial variable,  $\boldsymbol{X}$ , defined by

$$\boldsymbol{X} = \frac{\boldsymbol{x} - \lfloor \boldsymbol{x} \rfloor}{\delta} - \boldsymbol{b}, \tag{5.11}$$

where **b** is a translation vector,  $\mathbf{b} = (1/2, 1/2, 1/2)^T$ , so  $\mathbf{X} \in [-1/2, 1/2]^3$ , defined in unit cell  $\Omega(\mathbf{x}, t)$ , centred around one carbon pellet. We impose periodicity in  $\mathbf{X}$ , to remove the extra degree of freedom introducing this microscale variable brings. This unit cell is dependent on the macroscale spatial variable, as we allow there to be variation in temperature and pellet size over a long macroscale lengthscale, but with negligible variation between neighbouring cells. The spatial derivatives transform as:

$$\nabla \to \nabla_{\boldsymbol{x}} + \frac{1}{\delta} \nabla_{\boldsymbol{X}}, \qquad (5.12)$$

where  $\nabla_{\boldsymbol{x}}$  and  $\nabla_{\boldsymbol{X}}$  denote the nabla operators in the  $\boldsymbol{x}$ - and  $\boldsymbol{X}$ -coordinate systems, respectively. The unit normal to the boundary  $\partial \Omega_P(\boldsymbol{x},t)$  also transforms. To understand how it depends on both spatial variables, we define  $\chi(\boldsymbol{x},\boldsymbol{X}) = \|\boldsymbol{X}\| - s(\boldsymbol{x},t)$ , so  $\chi = 0$ gives  $\partial \Omega_P(\boldsymbol{x},t)$ . Since the normal to the boundary is proportional to the gradient of the surface  $\nabla \chi$ , we use Equation (5.12) and find

$$\boldsymbol{n} = \frac{\nabla \chi}{|\nabla \chi|} \Rightarrow \boldsymbol{n} = \frac{\boldsymbol{n}_{\boldsymbol{X}} + \delta \nabla_{\boldsymbol{x}} s}{\|\boldsymbol{n}_{\boldsymbol{X}} + \delta \nabla_{\boldsymbol{x}} s\|},$$
(5.13)

where we define

$$\boldsymbol{n}_{\boldsymbol{X}} = -\frac{|\boldsymbol{X}|}{\|\boldsymbol{X}\|},\tag{5.14}$$

as the outward unit normal to the pellet boundary,  $\partial \Omega_P(\boldsymbol{x}, t)$ , and the term " $\delta \nabla_{\boldsymbol{x}} s$ " accounts for the macroscale variation in s. Since our aim is to determine the effective macroscale behaviour over the entire macroscale domain, we introduce the macroscale porosity,  $\phi(\boldsymbol{x}, t)$ , defined as

$$\phi(\boldsymbol{x},t) = \frac{\|\Omega_G(\boldsymbol{x},t)\|}{\|\Omega(\boldsymbol{x},t)\|}.$$
(5.15)

We note that the porosity is dependent on the pellet radius s and this relationship is

$$\phi(\mathbf{x},t) = \|\Omega_G(\mathbf{x},t)\| = \frac{4}{3}\pi(s(\mathbf{x},t)^3).$$
(5.16)



Figure 10. Two-dimensional projection of the three-dimensional domain we consider in Section 5.3.

### 5.3.1 Flow problem

Under the transformation Equation (5.12), the flow problem becomes

$$-\left(\frac{1}{\delta}\nabla_{\boldsymbol{X}} + \nabla_{\boldsymbol{x}}\right)p + \left(\nabla_{\boldsymbol{X}} + \delta\nabla_{\boldsymbol{x}}\right)^{2}\boldsymbol{u} = \boldsymbol{0} \quad \text{for } \boldsymbol{X} \in \Omega_{G}(\boldsymbol{x}, t),$$
(5.17a)

$$(\nabla_{\boldsymbol{X}} + \delta \nabla_{\boldsymbol{x}}) \cdot \boldsymbol{u} = 0 \quad \text{for } \boldsymbol{X} \in \Omega_G(\boldsymbol{x}, t),$$
 (5.17b)

$$\boldsymbol{u} = -\delta\beta \frac{\partial s}{\partial t} \boldsymbol{n}_{\boldsymbol{X}} + \mathcal{O}(\delta^2) \quad \text{for } \boldsymbol{X} \in \partial\Omega_P(\boldsymbol{x}, t), \tag{5.17c}$$

 $\boldsymbol{u}, p$  periodic, for  $\boldsymbol{X} \in \partial \Omega$ . (5.17d)

We pose an asymptotic expansion in the limit  $\delta \to 0$ :

$$f \sim f_0 + \delta f_1 + \delta^2 f_2 + \dots, \text{ where } f \in \{u, p\}.$$
 (5.18)

At leading order, we find that the leading-order pressure  $p_0$  is independent of the microscale,

$$p_0 = p_0(\boldsymbol{x}, t). \tag{5.19}$$

Proceeding to the next order, we find

$$-\nabla_{\boldsymbol{X}} p_1 + \nabla_{\boldsymbol{X}}^2 \boldsymbol{u}_0 = \nabla_{\boldsymbol{x}} p_0 \quad \text{for } \boldsymbol{X} \in \Omega_G(\boldsymbol{x}, t),$$
(5.20a)

$$\nabla_{\boldsymbol{X}} \cdot \boldsymbol{u}_0 = 0 \quad \text{for } \boldsymbol{X} \in \Omega_G(\boldsymbol{x}, t). \tag{5.20b}$$

(5.20c)

Since these equations are linear, to reduce the parameter dependence of the problem, we

seek solutions of the form:

$$\boldsymbol{u}_0 = -\mathbf{K}(\boldsymbol{x}, \boldsymbol{X}, t) \nabla_{\boldsymbol{x}} p_0, \qquad (5.21a)$$

$$p_1 = -\boldsymbol{\Pi}(\boldsymbol{x}, \boldsymbol{X}, t) \nabla_{\boldsymbol{x}} p_0 + \bar{p}(\boldsymbol{x}, t), \qquad (5.21b)$$

where  $\bar{p}$  is an arbitrary function (which we do not need to solve for to determine the leading order flow solution), and the matrix function  $\mathbf{K}$  and the vector function  $\boldsymbol{\Pi}$ satisfy the *cell problem*:

$$\mathbf{I} - \nabla_{\boldsymbol{X}} \boldsymbol{\Pi} + \nabla^2 \mathbf{K} = \mathbf{0} \quad \text{for } \boldsymbol{X} \in \Omega_G(\boldsymbol{x}, t), \tag{5.22a}$$

$$\nabla_{\boldsymbol{X}} \cdot \mathbf{K} = \mathbf{0} \quad \text{for } \boldsymbol{X} \in \Omega_G(\boldsymbol{x}, t), \tag{5.22b}$$

$$\mathbf{K} = \mathbf{0} \quad \text{for } \mathbf{X} \in \partial \Omega_P(\mathbf{x}, t), \tag{5.22c}$$

**K**, 
$$\boldsymbol{\Pi}$$
 periodic on  $\partial\Omega$ . (5.22d)

Next, we integrate Equation (5.20a) over  $\Omega_G$  and define the volumetric average fluid velocity,

$$\bar{\boldsymbol{u}}(\boldsymbol{x},t) = \frac{1}{\|\boldsymbol{\Omega}(\boldsymbol{x},t)\|} \int_{\boldsymbol{\Omega}} \boldsymbol{u}(\boldsymbol{x},\boldsymbol{X},t) \, \mathrm{d}\boldsymbol{X} = \int_{\boldsymbol{\Omega}_{G}} \boldsymbol{u}(\boldsymbol{x},\boldsymbol{X},t) \, \mathrm{d}\boldsymbol{X}, \quad (5.23)$$

where we impose  $\boldsymbol{u} = 0$  in  $\Omega_G$ , and use the boundary condition Equation (5.20b) to obtain a homogenised version of Darcy flow,

$$\bar{\boldsymbol{u}}(\boldsymbol{x},t) = -\mathcal{K}(\phi)\nabla_{\boldsymbol{x}}p \tag{5.24}$$

at leading order, where  $\mathcal{K}(\phi)$  is a scalar function containing the relevant information about the microscale pellet structure and is defined by

$$\mathcal{K}(\phi)\mathbf{I} = \int_{\Omega_G} \mathbf{K} \, \mathrm{d}\mathbf{X}.$$
 (5.25)

We note that  $\int_{\Omega_G} \mathbf{K} \, \mathrm{d} \mathbf{X}$  is a multiple of the identity matrix due to the symmetry of the cell problem. One would obtain a non-isotropic effective permeability if the cell problem did not have symmetry in 3 orthogonal planes, (e.g. spheroids or ellipsoids).

To close the homogenised flow model, we consider the  $\mathcal{O}(\delta)$  terms in Equation (5.17),

$$\nabla_{\boldsymbol{X}} \cdot \boldsymbol{u}_1 + \nabla_{\boldsymbol{x}} \cdot \boldsymbol{u}_0 = 0 \quad \text{for } \boldsymbol{X} \in \Omega_G(\boldsymbol{x}, t), \tag{5.26a}$$

$$\boldsymbol{u}_1 = -\beta \frac{\partial s}{\partial t} \boldsymbol{n}_{\boldsymbol{X}} \quad \text{for } \boldsymbol{X} \in \partial \Omega_P(\boldsymbol{x}, t),$$
 (5.26b)

$$\boldsymbol{u}_1 \text{ periodic} \quad \text{for } \boldsymbol{X} \in \partial \Omega.$$
 (5.26c)

We integrate Equation (5.26a) over  $\Omega_G(\boldsymbol{x}, t)$ ,

$$\int_{\Omega_G} \nabla_{\boldsymbol{X}} \cdot \boldsymbol{u}_1 \, \mathrm{d}\boldsymbol{X} + \int_{\Omega_G} \nabla_{\boldsymbol{x}} \cdot \boldsymbol{u}_0 \, \mathrm{d}\boldsymbol{X} = 0, \qquad (5.27a)$$

$$\underbrace{\int_{\partial\Omega_P} \boldsymbol{u}_1 \cdot \boldsymbol{n}_{\boldsymbol{X}} \, \mathrm{d}A}_{\text{minimative dimensions of the second states}} + \underbrace{\nabla_{\boldsymbol{x}} \cdot \left(\int_{\Omega_G} \boldsymbol{u}_0 \, \mathrm{d}\boldsymbol{X}\right) - \int_{\partial\omega_P} -\boldsymbol{n}_{\boldsymbol{X}} \cdot (\nabla_{\boldsymbol{x}}s)\boldsymbol{u}_0 \, \mathrm{d}A}_{\text{minimative dimensions of the second states}} = 0, \quad (5.27\mathrm{b})$$

using divergence theorem

using RTT component-wise

using Equation (5.26b) on the first term and the no slip condition  $u_0 = 0$  on  $\partial \Omega_P$ , we find

$$\int_{\partial \omega_P} -\beta \frac{\partial s}{\partial t} \, \mathrm{d}A + \nabla_{\boldsymbol{x}} \cdot \bar{\boldsymbol{u}} = 0.$$
(5.27c)

Thus, we obtain a continuity equation for the fluid velocity

$$\nabla_{\boldsymbol{x}} \cdot \bar{\boldsymbol{u}} = \beta \|\partial \Omega_P(\boldsymbol{x}, t)\| \frac{\partial s}{\partial t}.$$
(5.28)

The system given by Equations (5.24) and (5.28) determines the flow problem, with its dependence on the microscale structure. Hence, homogenisation of the Stokes flow gives Darcy flow for the macroscopic velocity  $\bar{u}$ , as expected.

### 5.3.2~Heat~transport~problem

Next, we consider the homogenisation of the heat transport problem and we proceed in a similar manner to Section 5.3.1.

Under the transformation Equations (5.12) and (5.13), the governing equations for heat transport Equation (5.10) become:

$$\delta^{2}\beta \frac{\partial T}{\partial t} + \delta \boldsymbol{u} \cdot (\nabla_{\boldsymbol{X}} + \delta \nabla_{\boldsymbol{x}}) T$$
  
=  $(\nabla_{\boldsymbol{X}} + \delta \nabla_{\boldsymbol{x}}) \cdot (\operatorname{Pe}_{T}^{-1} (\nabla_{\boldsymbol{X}} + \delta \nabla_{\boldsymbol{x}}) T)$  for  $\boldsymbol{x} \in \Omega_{G}(\boldsymbol{x}, t)$ , (5.29a)

$$\frac{\boldsymbol{n}_{\boldsymbol{X}} + \delta \nabla_{\boldsymbol{x}} s}{\|\boldsymbol{n}_{\boldsymbol{X}} + \delta \nabla_{\boldsymbol{x}} s\|} \cdot \left( \operatorname{Pe}_{T}^{-1} \left( \nabla_{\boldsymbol{X}} + \delta \nabla_{\boldsymbol{x}} \right) T \right) = -\delta^{2} k \mathcal{R}(T) \quad \text{at } \boldsymbol{x} \in \partial \Omega_{P}(\boldsymbol{x}, t), \quad (5.29b)$$

$$\frac{\partial s}{\partial t} = \mathcal{R}(T) \quad \text{at } \boldsymbol{x} \in \partial \Omega_P(\boldsymbol{x}, t), \quad (5.29c)$$

$$T, \ \boldsymbol{u} \text{ periodic} \quad \text{at } \boldsymbol{x} \in \partial \Omega.$$
 (5.29d)

Again, we pose an asymptotic expansion in the limit  $\delta \to 0$ :

$$\boldsymbol{u} \sim \boldsymbol{u}_0 + \delta \boldsymbol{u}_1 + \delta^2 \boldsymbol{u}_2 + \dots , \qquad (5.30)$$

$$T \sim T_0 + \delta T_1 + \delta^2 T_2 + \dots$$
 (5.31)

At leading order  $(\mathcal{O}(1))$ , we find that the leading order temperature  $T_0$  is independent of the microscale,

$$T_0 = T_0(\boldsymbol{x}, t).$$
 (5.32)

At the next order (the  $\mathcal{O}(\delta)$  terms in Equation (5.29)), the heat transport model is

$$0 = \operatorname{Pe}_T^{-1} \nabla_{\boldsymbol{X}}^2 T_1 \quad \text{for } \boldsymbol{x} \in \Omega_G(\boldsymbol{x}, t),$$
 (5.33a)

$$\boldsymbol{n}_{\boldsymbol{X}} \cdot \left( \operatorname{Pe}_{T}^{-1} \left( \nabla_{\boldsymbol{X}} T_{1} + \nabla_{\boldsymbol{x}} T_{0} \right) \right) = 0 \quad \text{at } \boldsymbol{x} \in \partial \Omega_{P}(\boldsymbol{x}, t),$$
(5.33b)

$$T_1$$
 periodic at  $\boldsymbol{x} \in \partial \Omega$ . (5.33c)

We seek a solution for  $T_1$  of the form

$$T_1(\boldsymbol{x}, \boldsymbol{X}, t) = -\boldsymbol{\Gamma}(\boldsymbol{x}, \boldsymbol{X}, t) \cdot \nabla_{\boldsymbol{X}} T_0 + \tilde{T}(\boldsymbol{x}, t), \qquad (5.34)$$

where  $\tilde{T}$  is an arbitrary function. The components of vector function  $\boldsymbol{\Gamma}$  satisfy the *cell* 

problem, for i = 1, 2, 3:

$$0 = \nabla_{\boldsymbol{X}}^2 \Gamma_i \quad \text{for } \boldsymbol{x} \in \Omega_G(\boldsymbol{x}, t), \tag{5.35a}$$

$$\boldsymbol{n}_{\boldsymbol{X},i} = \boldsymbol{n}_{\boldsymbol{X}} \cdot \nabla_{\boldsymbol{X}} \Gamma_i \quad \text{for } \boldsymbol{x} \in \partial \Omega_P(\boldsymbol{x},t), \tag{5.35b}$$

$$\Gamma_i \text{ periodic} \quad \text{for } \boldsymbol{x} \in \partial \Omega, \tag{5.35c}$$

Proceeding to  $\mathcal{O}(\delta^2)$  of Equation (5.29),

$$\beta \frac{\partial T_0}{\partial t} + \boldsymbol{u}_0 \cdot \nabla_{\boldsymbol{X}} T_1 + \boldsymbol{u}_1 \cdot \nabla_{\boldsymbol{X}} T_0 + \boldsymbol{u}_0 \nabla_{\boldsymbol{x}} \cdot T_0$$
  
=  $\operatorname{Pe}_T^{-1} \left[ \nabla_{\boldsymbol{X}} \cdot (\nabla_{\boldsymbol{X}} T_2 + \nabla_{\boldsymbol{x}} T_1) + \nabla_{\boldsymbol{x}} \cdot (\nabla_{\boldsymbol{X}} T_1 + \nabla_{\boldsymbol{x}} T_0) \right] \text{ for } \boldsymbol{x} \in \Omega_G(\boldsymbol{x}, t),$   
(5.36a)

$$\operatorname{Pe}_{T}^{-1}\left[\boldsymbol{n}_{\boldsymbol{X}}\cdot\left(\nabla_{\boldsymbol{X}}T_{2}+\nabla_{\boldsymbol{x}}T_{1}\right)+\left(\nabla_{\boldsymbol{x}}s\right)\cdot\left(\nabla_{\boldsymbol{X}}T_{1}+\nabla_{\boldsymbol{x}}T_{0}\right)\right]=k\mathcal{R}(T_{0}) \quad \text{at } \boldsymbol{x}\in\partial\Omega_{P}(\boldsymbol{x},t),$$
(5.36b)

 $T_2$ ,  $\boldsymbol{u}_1$  periodic at  $\boldsymbol{x} \in \partial \Omega$ , (5.36c)

where we have taken the leading order term in the expansion of  $\mathcal{R}(T) \sim \mathcal{R}(T_0 + \delta T_1 + ...)$ . We integrate Equation (5.36a) over  $\Omega_G(\boldsymbol{x}, t)$ , and note  $\nabla_{\boldsymbol{X}} T_0 = 0$  in  $\Omega_G$ , to find

$$\underbrace{\int_{\Omega_G(\boldsymbol{x},t)} \beta \frac{\partial T_0}{\partial t} \, \mathrm{d}\boldsymbol{X}}_{(\dagger_1)} + \underbrace{\int_{\Omega_G(\boldsymbol{x},t)} \boldsymbol{u}_0 \cdot \nabla_{\boldsymbol{x}} T_0 \, \mathrm{d}\boldsymbol{X}}_{(\dagger_2)} + \underbrace{\int_{\Omega_G(\boldsymbol{x},t)} \boldsymbol{u}_0 \cdot \nabla_{\boldsymbol{X}} T_1 \, \mathrm{d}\boldsymbol{X}}_{(\dagger_3)}_{(\dagger_3)} = \operatorname{Pe}_T^{-1} \int_{\Omega_G(\boldsymbol{x},t)} \underbrace{\nabla_{\boldsymbol{X}} \cdot (\nabla_{\boldsymbol{X}} T_2 + \nabla_{\boldsymbol{x}} T_1)}_{(\dagger_4)} + \underbrace{\nabla_{\boldsymbol{x}} \cdot (\nabla_{\boldsymbol{X}} T_1 + \nabla_{\boldsymbol{x}} T_0)}_{(\dagger_5)} \, \mathrm{d}\boldsymbol{X}. \quad (5.37)$$

We simplify the  $(\hat{i}_i)$  terms as follows:

$$\begin{aligned} (\widehat{1}_{1}): \quad \int_{\Omega_{G}(\boldsymbol{x},t)} \beta \frac{\partial T_{0}}{\partial t} \, \mathrm{d}\boldsymbol{X} &= \underbrace{\beta \frac{\partial}{\partial t} \left( \int_{\Omega_{G}} T_{0} \, \mathrm{d}\boldsymbol{X} \right) - \beta \int_{\partial\Omega_{P}} \frac{\partial s}{\partial t} T_{0} \, \mathrm{d}\boldsymbol{A};}_{\text{by RTT}} \end{aligned}$$
(5.38)  

$$(\widehat{1}_{2}): \quad \int_{\Omega_{G}(\boldsymbol{x},t)} \boldsymbol{u}_{0} \cdot \nabla_{\boldsymbol{x}} T_{0} \, \mathrm{d}\boldsymbol{X} &= \int_{\Omega_{G}} \nabla_{\boldsymbol{x}} \cdot (\boldsymbol{u}_{0}T_{0}) - T_{0} \left( \nabla_{\boldsymbol{x}} \cdot \boldsymbol{u}_{0} \right) \, \mathrm{d}\boldsymbol{X} \\ &= \int_{\Omega_{G}} \nabla_{\boldsymbol{x}} \cdot (\boldsymbol{u}_{0}T_{0}) \, \mathrm{d}\boldsymbol{X} - \underbrace{\int_{\Omega_{G}} -T_{0} \left( \nabla_{\boldsymbol{X}} \cdot \boldsymbol{u}_{1} \right) \, \mathrm{d}\boldsymbol{X},}_{\text{using Equation (5.26a)}} \\ &= \int_{\Omega_{G}} \nabla_{\boldsymbol{x}} \cdot (\boldsymbol{u}_{0}T_{0}) \, \mathrm{d}\boldsymbol{X} - \underbrace{\int_{\partial\Omega_{P}} -(\boldsymbol{u}_{1} \cdot \boldsymbol{n}_{\boldsymbol{X}}) T_{0} \, \mathrm{d}\boldsymbol{A},}_{\text{using divergence theorem}} \\ &= \int_{\Omega_{G}} \nabla_{\boldsymbol{x}} \cdot (\boldsymbol{u}_{0}T_{0}) \, \mathrm{d}\boldsymbol{X} + \underbrace{\beta \int_{\partial\Omega_{P}} \frac{\partial s}{\partial t} T_{0} \, \mathrm{d}\boldsymbol{A},}_{\text{using Equation (5.26b)}} \\ &= \nabla_{\boldsymbol{x}} \cdot \left( \int_{\Omega_{G}} \boldsymbol{u}_{0}T_{0} \, \mathrm{d}\boldsymbol{X} \right) + \int_{\partial\Omega_{P}} (\nabla_{\boldsymbol{x}}s) \cdot \underbrace{(\boldsymbol{u}_{0}T_{0})}_{\boldsymbol{u}_{0}=0 \text{ on } \partial\Omega_{P}} \, \mathrm{d}\boldsymbol{A} + \beta \int_{\partial\Omega_{P}} \frac{\partial s}{\partial t} T_{0} \, \mathrm{d}\boldsymbol{A}, \end{aligned}$$
(5.39)

$$(f_3): \int_{\Omega_G(\boldsymbol{x},t)} \boldsymbol{u}_0 \cdot \nabla_{\boldsymbol{X}} T_1 \, \mathrm{d}\boldsymbol{X} = \int_{\Omega_G} \nabla_{\boldsymbol{X}} \cdot (\boldsymbol{u}_0 T_1) - T_1 \underbrace{(\nabla_{\boldsymbol{X}} \cdot \boldsymbol{u}_0)}_{\text{Equation (5.20b)}} \, \mathrm{d}\boldsymbol{X}$$

$$= \int_{\Omega_G} -\boldsymbol{n}_{\boldsymbol{X}} \cdot (\boldsymbol{u}_0 T_1) \, \mathrm{d}\boldsymbol{A} = \underbrace{0} \qquad (5.40)$$

$$\underbrace{\int \partial \Omega_P}_{\text{by divergence theorem}} \quad u_0 = 0 \text{ on } \partial \Omega_P$$

$$(\widehat{\uparrow}_{4}): \int_{\Omega_{G}(\boldsymbol{x},t)} \nabla_{\boldsymbol{X}} \cdot (\nabla_{\boldsymbol{X}} T_{2} + \nabla_{\boldsymbol{x}} T_{1}) \, \mathrm{d}\boldsymbol{X} = \underbrace{\int_{\partial\Omega_{P}} -\boldsymbol{n}_{\boldsymbol{X}} \cdot (\nabla_{\boldsymbol{X}} T_{2} + \nabla_{\boldsymbol{x}} T_{1}) \, \mathrm{d}\boldsymbol{A}}_{\text{using divergence theorem}}$$
(5.41)

$$(f_{5}): \int_{\Omega_{G}(\boldsymbol{x},t)} \nabla_{\boldsymbol{x}} \cdot (\nabla_{\boldsymbol{X}} T_{1} + \nabla_{\boldsymbol{x}} T_{0}) \, \mathrm{d}\boldsymbol{X}$$

$$= \underbrace{\nabla_{\boldsymbol{x}} \cdot \left( \int_{\Omega_{G}} \nabla_{\boldsymbol{X}} T_{1} + \nabla_{\boldsymbol{X}} T_{0} \, \mathrm{d}\boldsymbol{X} \right) - \int_{\partial\Omega_{P}} (\nabla_{\boldsymbol{x}} s) \cdot (\nabla_{\boldsymbol{X}} T_{1} + \nabla_{\boldsymbol{x}} T_{0}) \, \mathrm{d}\boldsymbol{A}}_{\text{using RTT component-wise}}. (5.42)$$

Note, we have used Reynolds transport theorem (component-wise) on  $\int_{\Omega_G} \nabla_{\boldsymbol{X}} \cdot (\dots)$  terms (see Appendix A of [3]).

Thus, the governing equation Equation (5.36a) becomes

$$\beta \frac{\partial}{\partial t} \left( \int_{\Omega_G} T_0 \, \mathrm{d} \mathbf{X} \right) - \beta \int_{\partial \Omega_P} \frac{\partial s}{\partial t} T_0 \, \mathrm{d} A + \nabla_{\mathbf{x}} \cdot \left( \int_{\Omega_G} \mathbf{u}_0 T_0 \, \mathrm{d} \mathbf{X} \right) + \beta \int_{\partial \Omega_P} \frac{\partial s}{\partial t} T_0 \, \mathrm{d} A$$
$$= \operatorname{Pe}_T^{-1} \left[ \int_{\partial \Omega_P} -\mathbf{n}_{\mathbf{X}} \cdot (\nabla_{\mathbf{X}} T_2 + \nabla_{\mathbf{x}} T_1) \, \mathrm{d} A - \int_{\partial \Omega_P} (\nabla_{\mathbf{x}} s) \cdot (\nabla_{\mathbf{X}} T_1 + \nabla_{\mathbf{x}} T_0) \, \mathrm{d} A$$
$$+ \nabla_{\mathbf{x}} \cdot \left( \int_{\Omega_G} \nabla_{\mathbf{X}} T_1 + \nabla_{\mathbf{X}} T_0 \, \mathrm{d} \mathbf{X} \right) \right]$$
(5.43)

We use the boundary condition on the pellet surface Equation (5.36b) to replace the surface integrals on the RHS of Equation (5.43),

$$\beta \frac{\partial}{\partial t} \left( \int_{\Omega_G} T_0 \, \mathrm{d} \mathbf{X} \right) = \nabla_{\mathbf{x}} \cdot \left( \int_{\Omega_G} \operatorname{Pe}_T^{-1} \left[ \nabla_{\mathbf{X}} T_1 + \nabla_{\mathbf{X}} T_0 \right] - \mathbf{u}_0 T_0 \, \mathrm{d} \mathbf{X} \right) \\ - \int_{\partial \Omega_P} k \mathcal{R}(T_0) \, \mathrm{d} A.$$
(5.44)

Recalling that  $T_0 = T_0(\boldsymbol{x}, t)$ , *i.e.* independent of the microscale  $\boldsymbol{X}$ , and writing  $\nabla_{\boldsymbol{X}} T_1 = -\nabla_{\boldsymbol{X}} \boldsymbol{\Gamma} \cdot \nabla_{\boldsymbol{x}} T_0$ , we write Equation (5.44) as

$$\beta \frac{\partial}{\partial t} \left( \|\Omega_G\| T_0 \right) = \nabla_{\boldsymbol{x}} \cdot \left( \operatorname{Pe}_T^{-1} \left[ \int_{\Omega_G} (\mathbf{I} - \mathbf{J}_{\boldsymbol{\Gamma}}^{\mathsf{T}}) \, \mathrm{d} \boldsymbol{X} \right] \nabla_{\boldsymbol{x}} T_0 - \left[ \int_{\Omega_G} \boldsymbol{u}_0 \, \mathrm{d} \boldsymbol{X} \right] T_0 \right) - \|\partial \Omega_P\| \, k \mathcal{R}(T_0),$$

$$(5.45)$$

where  $(\mathbf{J}_{\boldsymbol{\Gamma}}^{\mathsf{T}})_{ij} = \partial \Gamma_j / \partial X_i$  is the transpose of the Jacobian matrix of  $\boldsymbol{\Gamma}$ , which we recall is the solution to the cell problem Equation (5.35).

We recall the volumetric average fluid velocity  $\bar{u}$  given in Equation (5.23), and define the volumetric average temperature within the crucible, where we impose the pellet to have uniform temperature (which is the same as the temperature at the pellet boundary

 $\partial \Omega_P$ ),

$$\bar{T} = \frac{1}{\|\Omega\|} \int_{\Omega} T \, \mathrm{d}\boldsymbol{X} = \frac{1}{\|\Omega\|} \left( \int_{\Omega_G} T \, \mathrm{d}\boldsymbol{X} + \int_{\Omega_P} T \, \mathrm{d}\boldsymbol{X} \right), \tag{5.46}$$

$$\sim \frac{1}{\|\Omega\|} \left( T_0 \|\Omega_G\| + T_{\text{pellet}} \|\Omega_P\| \right) \sim T_0, \tag{5.47}$$

since  $T_0 = T_0(\boldsymbol{x}, t)$  and therefore  $T_{\text{pellet}} = T_0$ . Therefore, we can write Equation (5.45) in terms of the volumetric average temperature  $\bar{T}$  and velocity  $\bar{\boldsymbol{u}}$ ,

$$\beta \frac{\partial}{\partial t} \left( \|\Omega_G\| \bar{T} \right) = \nabla_{\boldsymbol{x}} \cdot \left( D_{\text{eff}}(s) \nabla_{\boldsymbol{x}} \bar{T} - \bar{\boldsymbol{u}} \bar{T} \right) - \|\partial \Omega_P\| k \mathcal{R}(T_0), \tag{5.48}$$

where we define the effective diffusivity  $D_{\text{eff}}$  as

$$D_{\text{eff}}\mathbf{I} = \operatorname{Pe}_{T}^{-1} \left( \mathbf{I} - \int_{\Omega_{G}} \mathbf{J}_{\Gamma}^{\mathsf{T}} \, \mathrm{d} \mathbf{X} \right).$$
 (5.49)

### 5.4 Results

The homogenised system of equations for coupled fluid flow (volumetric average flow  $\bar{u}$ ) and heat transport (volumetric average temperature  $\bar{T}$ ) within the crucible are:

$$\beta \frac{\partial}{\partial t} \left( \|\Omega_G\| \bar{T} \right) = \nabla_{\boldsymbol{x}} \cdot \left( D_{\text{eff}}(s) \nabla_{\boldsymbol{x}} \bar{T} - \bar{\boldsymbol{u}} \bar{T} \right) - \|\partial\Omega_P\| \, k \mathcal{R}(T_0), \tag{5.50a}$$

$$\frac{\partial s}{\partial t} = \mathcal{R}(\bar{T}),$$
 (5.50b)

with flow governed by

$$\bar{\boldsymbol{u}} = -\mathcal{K}(\phi)\nabla_{\boldsymbol{x}} p, \qquad (5.50c)$$

$$\nabla_{\boldsymbol{x}} \cdot \bar{\boldsymbol{u}} = \beta \|\partial \Omega_P\| \frac{\partial s}{\partial t}, \qquad (5.50d)$$

and porosity related to pellet radius via

$$\phi(\boldsymbol{x},t) = \frac{4}{3}\pi s^3, \qquad (5.50e)$$

and the volume of the gas region and surface area of carbon pellet given by

$$\|\Omega_G\| = \frac{4}{3}\pi s^3, \qquad \|\partial\Omega_P\| = 4\pi s^2,$$
 (5.50f)

where the effective heat diffusivity  $D_{\text{eff}}(s(\boldsymbol{x},t))$  is given by Equation (5.49) and the effective permeability  $\mathcal{K}(\phi(s))$  is given by Equation (5.25). This system is an effective reaction-advection-diffusion model coupled to an effective Darcy's law governing the gas flow within the crucible. The RHS of the compressibility condition Equation (5.50d) accounts for the incompressible fluid being pushed out of the cell as the pellet increases in size.

We find that the volumetric heat sink term is dependent on the surface area of the carbon pellet. This method of multiple scale analysis shows that the general heat sink coefficient in Equation (4.1) should be time-dependent and increasing proportional to the pellet radius squared,  $S \propto s^2$ , which can vary spatially within the crucible.

We can solve this system within the crucible geometry subject to appropriate boundary and initial conditions to determine the flow profile, the temperature, and the pellet radius across the entire crucible.

We compare the homogenised model to the macroscale model considered in Section 4, by considering the no-flow case. We model the crucible as a cylinder with dimesionless radius 1 and height 2. We assume axisymmetry and convert into a cylindrical polars coordinate system. Our domain is given by  $[r, z] \in [0, 1] \times [0, 2]$ . Thus far, we have worked with an arbitrary reaction term  $\mathcal{R}(\bar{T})$ . To compare the homogenised model results to those obtained in Section 4.5, we choose an Arrhenius heat sink law:

$$\mathcal{R}(\bar{T}) = \exp\left(-\frac{b}{c\bar{T}}\right). \tag{5.51}$$

We consider both the uniform and Gaussian inlet boundary conditions introduced in Section 4.

We impose the following the boundary and initial conditions on temperature T for the system given by Equation (5.50) (with  $\bar{u} = 0$ ):

$$D_{\text{eff}}(s)\frac{\partial T}{\partial z} = 0 \quad \text{at } z = 1,$$
 (5.52a)

$$D_{\text{eff}}(s)\frac{\partial T}{\partial r} = 0 \quad \text{at } r = 0,$$
 (5.52b)

$$T = 1$$
 at  $r = 1$ , (5.52c)

$$T = 1$$
 at  $t = 0$ , (5.52d)

where we impose one of the following boundary conditions at the inlet z = 0,

UNIFORM: 
$$\overline{T} = 0$$
 at  $z = 0$ , (5.52e)

GAUSSIAN: 
$$\bar{T} = 1 - \exp(-10r^2)$$
 at  $z = 0$ , (5.52f)

We solve the model (Equations (5.50) and (5.52)) numerically using the finite element package COMSOL Multiphysics<sup>R</sup>. We note that the cell problems Equations (5.21) and (5.35) can be solved *a priori* to determine how  $\mathcal{K}(s)$  and  $D_{\text{eff}}(s)$  behave as functions of pellet radius, *s*. We refer the reader to [8] for further details of our approach to numerical solution of the homogenised model. 5 An example of a solution for temperature  $\overline{T}(r, z, t)$  and pellet radius s(r, z, t) is shown in Figure 11.



(b) Pellet radius

Figure 11. Results for the model given by Equations (5.50) and (5.52) for (left) uniform (Equation (5.52e)) and (right) Gaussian boundary conditions (Equation (5.52f)).

### 6 Two-Fluid Model: methane gas and non-Newtonian variably fluidised carbon pellets

In this section we explore a multi-phase fluid model. The carbon particles are treated as one fluid phase; this can accommodate both the packed bed and fluidised carbon. The gases can be treated as separate phases (methane and hydrogen) or one overall gas phase (methane + hydrogen). This method of modelling solid particles within a fluid is used in similar physical situations as the one considered here, for example, for modelling particles in a landslide [20]. Figure 12 illustrates the modelling context.

Here we consider the case of two phases (one particle phase and one total gas phase). We denote the carbon particle phase with i = c and the total gas phase as i = g. Each phase i satisfies the same set of equations.

A phase fraction  $\phi_i$  gives the fractional volume of phase i at each location, with the constraint

$$\Sigma_i \phi_i = 1. \tag{6.1}$$

The concentration of each phase is therefore  $\phi_i \rho_i$ , where  $\rho_i$  is the density of phase *i*.

Each phase satisfies a mass conservation equation,

$$\frac{\partial}{\partial t} \left( \phi_i \right) + \nabla \cdot \left( \phi_i \mathbf{u}_i \right) = \frac{f_i}{\rho_i},\tag{6.2}$$

where  $f_i$  is the production or loss rate of phase *i*, and  $u_i$  is the velocity. The production rate  $f_c$  will be related to the reaction rate of the methane, as will the production (or loss) rate  $f_q$ .

Both phases satisfy the conservation of momentum equation,

$$\frac{\partial}{\partial t} \left( \rho_i \phi_i \mathbf{u}_i \right) + \nabla \cdot \left( \rho_i \phi_i \mathbf{u}_i \otimes \mathbf{u}_i \right) = \nabla \cdot \left( 2\phi_i \nu_i \rho_i \mathcal{E}_i \right) - \phi_i \nabla p_i + \phi_i \rho_i \mathbf{g} + \Sigma_j \left[ K_{i,j} \left( \mathbf{u}_i - \mathbf{u}_j \right) \right].$$
(6.3)

The first term on the right hand side of this equation represents viscous forces. In the gas phase, the coefficient of viscosity,  $\nu_g$ , is a known constant but for the particle phase,  $\nu_c$  is an effective viscosity that is modelled in Section 6.1 below. Operator  $\mathcal{E}_i$  is simply the rate-of-deformation tensor, that is, the symmetric gradient of  $\mathbf{u}_i$ . The second term on the right hand side is the pressure gradient: for the gas phase,  $p_c = p$  the total pressure, while for the particle phase  $p_c = p + p_s$  where  $p_s$  is an additional pressure due to inter-particle interaction. The third term on the right corresponds to the gravitational force. The final term represents an effective drag force due to the interaction of phases, where  $K_{i,j}$  is the coefficient of drag on phase *i* due to phase *j*. These details are simply summarised in the word equation (Figure 13) for a reader less familiar with Navier-Stokes.

An additional energy conservation equation is included to find the temperature of each phase. This is necessary if the phases are allowed to be compressible and will be necessary to calculate the temperature-dependent reaction rates.

$$\frac{\partial}{\partial t} \left( \phi_i \rho_i c_{p,i} T_i \right) + \nabla \cdot \left( \phi_i \rho_i c_{p,i} T_i \mathbf{u}_i \right) = \nabla \cdot \left( K_i \nabla T_i \right) + \Sigma_j \mathcal{D}_{i,j} + \Sigma_j Q_{i,j}.$$
(6.4)

where  $T_i$  is the temperature of phase *i*,  $K_i$  is the coefficient of thermal conductivity in



Figure 12. Diagrams of regimes described by granular flow model and summary of the key parameters.



Figure 13. Word equation to summarise competing accelerations in the crucible.

phase i,  $\mathcal{D}_{i,j}$  is the coefficient of thermal diffusion from phase i to phase j, the form of which is discussed in section 6.2, and  $Q_{i,j}$  is the energy source due to reactions from phase i to phase j. The form of  $Q_{i,j}$  is not discussed here but is proportional to the reaction rate at a given location. Physically, the last two terms on the right hand side of this equation are, respectively, the transfer of heat to phase i from all other phases via diffusion and reactions respectively.

### 6.1 Viscosity of particle phase

To model granular flow as a fluid-like motion, we need a non-Newtonian law. The idea is to have an effective or apparent viscosity  $\nu_c$  depending locally on the flow itself. For example, a higher pressure between particles leads to more friction, which can be modelled as an increase in effective viscosity. A state-of-the-art model for that is [17, 20]

$$\nu_c = \nu_{\infty} + \frac{c + \mu p_s}{2\bar{\phi}\rho_c |\mathcal{E}_c|} (1 - \mathrm{e}^{-m|\mathcal{E}_c|}), \qquad (6.5)$$

in which  $p_s$  is the particle pressure,  $\bar{\phi}$  is the reference packing density,  $\nu_{\infty}$  is a limit plastic viscosity, m is a large regularisation parameter (it should ideally be infinity, or as large as the numerical solver can handle), c indicates the strength of cohesive forces, and  $\mu$  is the so-called friction factor, usually given as a function of the inertia number I:

$$\mu(I) = \mu_s + \frac{\mu_d - \mu_s}{1 + I_0/I}, \quad I := \frac{2d|\mathcal{E}_c|}{\sqrt{p_s/\rho_c}}, \tag{6.6}$$

with d being the particle diameter and the remaining coefficients being empirical constants. The theory behind such models is not simple, and we recommend Refs. [18, 17, 20] for details. The particle pressure  $p_s$  also requires some modelling, see for instance Ref. [20].

Since some of these material parameters are not simple to obtain experimentally, we recommend here a parameter sweep (after appropriate non-dimensionalisation of all flow equations) to determine what parameter ranges yield solutions that best reproduce experiments.

#### 6.2 Drag forces between phases

The interaction parameter, *int*, as shown in Fig. 12, describes the relative importance of gas-on-carbon drag to momentum evolution. The relevant timescale,  $\Delta t$ , would at first be determined by how quickly the experiment is ramped up. Later, it would be an eddy timescale relating to how turbulent the flow is. The full equation for the drag is [20]

$$K_{c,g} = \frac{150\phi_c^2 \rho_g \nu_g}{\phi_g^2 d^2} + \frac{1.75\rho_g \phi_c}{\phi_g d} |\mathbf{u}_g - \mathbf{u}_c|$$
(6.7)

where the quadratic term is included for stability purposes; note that the subscript labelling is reversed the reference.

### 6.3 Boundary conditions

An approach to the numerical solution of the equations would be to use the open-source toolkit OpenFOAM( $\hat{\mathbf{R}}$ ) as in [20]. Partial-slip conditions should be implemented at the crucible walls [22]. However, dynamics with no-slip and full-slip conditions can first be explored. The inflow/ outflow conditions will be based off the experimental/industrial set up.

#### 7 Computational fluid dynamics simulation of exact geometry

Since, the model in §6 is computationally expensive to implement, we have also simulated the flow of an incompressible viscous fluid, through a two-dimensional projection of the geometry depicted in Figure 1. These simulations were done using Matlab's CFD-Tool package [19], allowing the input of a geometry and selection of boundary conditions and parameter values, including fluid input velocity, pressure differentials and boundary temperatures which it then converts to a finite volume problem solved through the 'open-FOAM' solver. This means more complex aspects of the crucible such as the multiple horizontal methane inputs and the constricted top could be included in the simulation.





Figure 14. Simulation of the incompressible Navier-Stokes equations in (a) A twodimensional peoject of the current experimental setup, depicted in Figure 1, and (b) a conical geometry proposed to prevent the development of the hard packed layer, depicted in Figure 2.

The results of two simulations are shown in Figure 14. The first was run with a two dimensional representation of the crucible geometry as it currently exists (Figure 14 a). The second was run with a conical insert represented at the base of the crucible (Figure 14 b), which has been suggested as a modification to avoid the buildup of packed material, depicted in Figure 2. These results show that the proposed geometry does avoid regions of almost zero gas flow in the bottom corners of the crucible, but further work would be required to see if this prevents the buildup.

### 8 Lagrangian Particle Dynamics

An alternative approach to the above is to consider the carbon as particles moving in a flow, due to forces acting on them. The equation of motion for one particle with mass m and velocity  $\mathbf{v}_p$  is derived from Newton's law

$$m\dot{\mathbf{v}}_p = F_d + F_g.$$

Assuming a spherical particle with diameter d, subject to a flow from a gas with density  $\rho_q$  and velocity  $\mathbf{v}$ , (found by simulations such as in §7), the drag force is given by

$$|F_d| = \frac{1}{2}\rho_g A \|\mathbf{v} - \mathbf{v}_p\|^2 c_d = \frac{\pi}{16}\rho_g d^2 \|\mathbf{v} - \mathbf{v}_p\|^2.$$

Additionally, the gravitational force on the particle is given by

$$|F_g| = \rho_C V g = \frac{\pi}{6} \rho_C d^3 g,$$

where  $\rho_C$  is the density of carbon and g the gravitational constant.

A 50  $\mu$  particle will float if methane blows it upwards at  $\sqrt{3}$  m/s.

The input to this model is the vector field of the gas velocity, and the density of the gas mixture. It can be obtained by any of the macroscale models discussed in section 9.

Additionally, interactions of the particle with it's environment have to be modelled. A standard assumption would be that the interaction between the particle and the flow is one-way, so that the flow is not affected by the particle. Also, particles can interact with each other. The simplest case is to assume no interaction at all, followed by having perfectly elastic collisions between particles. A more complex model could take cohesion between particles (and the wall) into account. Finally, the interaction with the wall needs to be modelled. Again, the simplest assumption is that the particle bounces off the wall without loss of momentum. In a numerical implementation, one thus needs to track the position of particles compared to the wall and check if they have crossed the wall during a time step, to then correct their position.

With the simple assumptions, simulating 1000 particles requires only a small amount of computing ressources, whereas the model can become quite cumbersome with the more realistic assumptions.

### 9 Simple lumped parameter model

### 9.1 Model formulation

In this section we shall consider a fully stirred model of the methane cracking in a crucible following Paxman et al. [15, 16]. Dependent variables as concentration and temperature are considered spatially homogeneous leading to a simple system of ordinary differential equations, i.e. a lumped model. The model has been derived from a full system of partial differential equations, that is the heat equation including the fluid flow, reactions, diffusion and heat conductivity. Using the divergence theorem on this model provides boundary conditions, from which we easily extract the correct terms for inflow and outflow of reactants in the simple lumped model. Similarly for heating through the crucible walls and advective contributions from the inflow and outflow.

The model by Paxman et al. in [15] considers bobles of methane in a molten media of Sn. The bobles contain methane and the reactants from a cracking process. Heat is transferred from the molten media to the gas in the bobles, which in turn are material insulated so no reactants are flowing in or out of the bubles. However, in our crucible methan is flowing into the reaction chamber and reactants are flowing out. We need to add transport terms into and out of the crucible in our case.

The concentration of methane we denote  $[CH_4]$  measured in units of kg/m<sup>3</sup>.  $[CH_4]$  is a function of time t measured in s (seconds). The temperature of the gas in the crucible we denote  $T_g$  measured in units of Kelvin K. The volume of the crucible is  $\Omega$  and q is the volume flow given by  $q = u_{in}S_{in}$  at the inlet. Here  $u_{in}$  is the inlet flow velocity of methane and  $S_{in}$  is the inlet area. Assuming constant density  $\rho_g$  and using mass conservation the inlet flow equals the outlet flow. With  $u_{out}$  being the outflow velocity and  $S_{out}$  being the outflow area we have from mass conservation that  $q = u_{out}S_{out}$ . The Arrhenius reaction rate  $R_r$  (4.2) in the form given in [15] reads

Methane Cracking for Carbon Production

| Parameter            | Value / Values                     | Parameter description   |
|----------------------|------------------------------------|---|
| $k_0$                | $6 \cdot 10^{11} \ 1/s$            | Factor in the Arrhenius law Eq. (??)                          |
| $E_a$                | 250  kJ/mol                        | Activation energy for methane cracking                        |
| $\hat{M}$            | 16.042  kg/kmol                    | Molar mass of methane   |
| $\hat{C}_p$          | 86  kJ/(kmol K)                    | Molar Specific heat capacity of methane at                    |
|                      | , , , ,                            | T=1200K (rough estimate)                                      |
| $C_p$                | $5.36 \cdot 10^3 \text{ J/(kg K)}$ | Specific heat capacity of methane $C_p = \hat{C}_p / \hat{M}$ |
| $h_f$                | $75 \cdot 10^3 \text{ kJ/kmol}$    | Energy (enthalpy) of formation of methane                     |
| $\hat{R}$            | 8.314 J/(mol K)                    | Universal gas constant  |
| R                    | 518.26  J/(kg K)                   | Gas constant for methane $R = \hat{R}/\hat{M}$                |
| $h = \kappa h_{con}$ | $100 \text{ W/(m^2 K)}$            | Thermal convection coefficient for forced convec-             |
|                      |                                    | tion. Rough order of magnitude guess                          |
| $ ho_g$              | $0.163~\mathrm{kg/m}^3$            | Density of methane at $T=1200$ K. Rough estimate              |
| $T_b$                | $1200 {\rm K}$                     | Temperature of the crucible boundaries                        |
| $[CH_4]_{in}$        | $0.6671 \text{ kg/m}^3$            | Density of methane at the inlet and at $T=293$ K.             |
| $S_w$                | $0.171 \mathrm{\ m^2}$             | Total surface area of the crucible. Estimate based            |
|                      |                                    | on sketches   |
| $S_{in}$             | $2.5 \cdot 10^{-5} \text{ m}^2$    | Total area of influx holes. Estimate based on                 |
|                      | 4 2                                | sketches  |
| $S_{out}$            | $4.5 \cdot 10^{-4} \text{ m}^2$    | Area of outflux hole. Estimate based on sketches              |
| Ω                    | $4.25 \cdot 10^{-3} \text{ m}^{3}$ | Volume of the crucible. Estimate based on                     |
|                      |                                    | sketches  |
|                      |                                    |   |

Table 2. Parameter values used in the lumped model [11, 10, 1]

$$R_r = k_0 \exp(\frac{-E_a}{\hat{R}T_g}) . \tag{9.1}$$

Here  $E_a$  is the activation energy for methane cracking,  $k_0$  is the prefactor in the Arrhenius law and  $\hat{R}$  is the molar gas constant. Note that introducing the pressure P, volume v, mass M and temperature T, the gas constant R in the ideal gas law Pv = MRT is given on mass basis. The units of R is here J/(kg K). On molar basis we have  $Pv = N\hat{R}T$ , where N is the number of molecules in units of mol. Introducing the molar mass  $\hat{M} = M/N$ the relation between the gas constant on molar basis and mass basis is  $\hat{R} = \hat{M}R$  in units of J/(mol K) [11]. We can now write the dynamical equation for the reaction, with flow in and out of the crucible as follows [15]

$$\frac{d[\text{CH}_4]}{dt} = -k_0 \exp(\frac{-E_a}{\hat{R}T_a})[\text{CH}_4] + \frac{q}{\Omega}([\text{CH}_4]_{in}) - [\text{CH}_4])$$
(9.2)

The term  $[CH_4]_{in}$  denotes the input concentration of methane, which is kept fixed. We introduce the parameter  $h_f$  as the heat of formation of methane, and the heat convection parameter  $h_{con}$  from the crucible walls to the gas. The specific heat of the gas at constant pressure we denote  $C_p$  and the heat conductivity we shall denote  $\kappa$ . With  $S_w$  being the surface area of the heated crucible walls and  $T_{in}$  being a fixed inlet temperature of methane, we obtain the heat equation [15]

$$\frac{dT_g}{dt} = -\frac{h_f k_0}{\rho_g \hat{C}_p} \exp(\frac{-E_a}{\hat{R}T_g}) [CH_4] + \frac{\kappa h_{con} S_w}{\rho_g C_p \Omega} (T_b - T_g) + \frac{q}{\Omega} (T_{in} - T_g)$$
(9.3)

Here  $\Omega$  is the volume of the crucible and  $S_w$  is the surface area of the heated walls of the crucible. In the simulations we have used a value of the thermal convection coefficient  $h = \kappa h_{con}$  in the range 10 W/(m<sup>2</sup> K) - 500 W/(m<sup>2</sup> K) corresponding to forced convection by fluid flow [10]. The heat capacity dependents on temperature, but we have used a fixed value of  $C_p$  estimated roughly at  $T_g = 1200$ K. See Table 2 for the actual value chosen. On molar basis and in the range 300K - 850K the temperature dependence of the heat capacitance  $\hat{C}_p$  of methane is [11]

$$\hat{C}_p = (18.93 + 0.0555 \text{ K}^{-1} T_q) \text{ kJ/(kmolK)}$$
 (9.4)

Tables of the heat capacity for methane and other physical and chemical properties can also be found in [1]. As mentioned previously the density of the methane gas depends on temperature and can be calculated from the ideal gas law [11].

### 9.2 Numerical results

In the following section we present numerical results for the lumped model in Eqs. (9.2) and (9.3). The parameter values are taken from Table 2. Even though the heat capacity of methane and the density of methane is temperature dependent, we have fixed the values of  $C_p$  and  $\rho_g$  at values corresponding to the temperature  $T_g = 1200$ K. This means that the transients observed in the numerical results are only indicative and not precise.

In figure 15 we show two simulations of the methane concentration  $[CH_4]$  in kg/m<sup>3</sup> as function of time t in seconds s for two different volume flows q = 0.5 litre/s (blue curve) and q = 0.1 litre/s (red curve). The initial conditions are  $[CH_4] = 0.6671$  kg/m<sup>3</sup> and  $T_g = 293$ K. For the high volume flow all methane is not converted to carbon and hydrogen. For the lower volume flow the methane stays longer in the crucible, and now the figure shows that all methane is converted. For the given parameter values and with q = 0.1 litre/s we obtain stationary state after  $t \approx 8$ s.

Figure 16 shows the temperature  $T_g$  of the methane gas as function of time for the same volume flows as above, that is q = 0.5 litre/s (blue curve) and q = 0.1 litre/s (red curve). For the high volume flow the methane gas is cooled due to the cold methane influx at  $T_g = 293$ K to a temperature around  $T_g = 1100$  K in the stationary state. For the low volume flow this cooling effect becomes smaller and the methane gas stays longer in the crucible and thereby can heat to nearly  $T_g = 1200$ K, which is the temperature of the crucible walls.

In the presentation of the numerical results we have shown the concentration of methane and the the temperature of methane as function of time and simulated to stationary state. Other physical variables of interest can be calculated from the lumped model. Those are energy supplied to the gas from the crucible walls and energy losses from advection of the cold methane gas into the crucible and exit of hot gas from the outlet. We can

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Figure 15. Simulations of the lumped model in Eqs. (9.2) and (9.3) for the volume flows q = 0.5 litre/s (blue curve) and q = 0.1 litre/s (red curve). Other parameter values are given in Table 2. The density of methane [CH<sub>4</sub>] in kg/m<sup>3</sup> is shown as function of time t measured in seconds s. The initial conditions are  $[CH_4](0) = 0.6671$  kg/m<sup>3</sup> and  $T_g(0) = 293$ K.



Figure 16. Simulations of the lumped model in Eqs. (9.2) and (9.3) for the volume flows q = 0.5 litre/s (blue curve) and q = 0.1 litre/s (red curve). Other parameter values are given in Table 2. The temperature of methane  $T_g$  in K is shown as function of time t measured in seconds s. The initial conditions are  $[CH_4](0) = 0.6671$  kg/m<sup>3</sup> and  $T_g(0) = 293$ K.

also extract the yield of carbon and hydrogen from the reaction. Further development of the model is relevant. We have assumed pure methane flowing into the crucible. In the crucible we have a mixture of methane, hydrogen, carbon, and other intermediate products. Hence we have a mixture of gasses, and from a thermo dynamical perspective we need to take this into consideration. Finally, The model can be extended to the case of spatial dependence of methane concentration and temperature. This calls for a model based on partial differential equations, that is fluid dynamics in conjunction with reactions and heat transfer in an advected flow.

### 10 Discussion

We have investigated methane cracking for producing carbon, which subsequently be used in the Si production. This process reduces the CO<sub>2</sub> emissions in the production of Si and provides a purer carbon source. The problem of optimising methane cracking using carbon seeds is currently under investigated by Elkem using laboratory scale experiments, and our work here has focused on modelling the coupled fluid dynamics, thermodynamics and chemical reactions, occurring in these experiments, to aid in this optimisation.

We developed and solved a microscale model for the growth of a carbon particle, under the assumption of an imposed particle temperature distribution. For future work we would like to consider the case where the particles temperature must be found as part of the solution, in order to understand how much the particle will grow before there is insufficient energy in the particle to maintain the reaction.

We also derived a model for the temperature distribution in a cylindrical crucible, assuming only reactions and diffusive heat transfer. This model was solved numerically using a finite difference scheme. We investigated how the size the dimensionless reaction rate and activation energy of the reaction altered the temperature distribution inside the crucible.

We then considered a homogenisation approach (via the method of multiple scales) to systematically upscale the microscale behaviour of the heat transport and gas flow through a bed of carbon pellets. We consider heat to be transported via advection and diffusion, with an endothermic reaction occurring at the surface of the carbon pellets. The pellet grows in size due to carbon deposition at a rate proportional to the reaction. This approach enabled us to derive the appropriate effective macroscale model for coupled heat transport and gas flow. We found that we can model the heat sink due to reaction as a general volumetric sink term - as used in the macroscale model - which should be temporally and spatially dependent and scale with pellet radius squared. We solve this model numerically using COMSOL Multiphysics<sup>(R)</sup>, and found the particle size was largest in the regions that were hottest in the steady solution.

A simple two-fluid model is derived for the methane gas and a fluidised bed of carbon pellets in order to investigate the possibility of fluidisation of the bed.

Using openFOAM we simulated the flow of an incompressible viscous fluid through the current experimental setup, and the new setup Elkem proposed to prevent the buildup of a hard packed layer in the crucible. We found that the proposed geometry lead to a more uniform flow at the bottom of the furnace. This flow could also be used to simulate the movement of the carbon particles using Lagrangian particle dynamics. This would be useful predict the onset of fluidisation.

Finally, we have derived a lumped model for the methane cracking, including inlet and outlet of reactants and considering inlet temperature of methane equal to ordinary room temperature. The lumped model provides information about desirable inflow rates, residence time of methane in the crucible, energy consumption and quantities of produced chemical species.

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