Monte Carlo radiative heat transfer analysis of a CH$_4$ flow laden with carbon particles

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Publication Date: 2006

Permanent Link: https://doi.org/10.3929/ethz-a-005287171

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MONTE CARLO RADIATIVE HEAT TRANSFER ANALYSIS OF A CH$_4$ FLOW LADEN WITH CARBON PARTICLES

Diploma Thesis

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October 2006
Abstract

The behaviour of a two phase medium initially composed of gaseous methane and argon, laden with carbon particles, and exposed to concentrated solar radiative energy was simulated using a Fortran 90 program. The simulated effects included radiative heat transfer and chemical kinetics. The optical properties of both phases were modelled separately. A steady state and a transient model were employed to gain insight into the behaviour of the system under the variation of different parameters: namely the mole fraction of CH$_4$ (0.1, 0.5, and 1.0), the carbon black particle diameter (1, 2.5, 5, and 10 µm), the particle volume fraction ($5 \cdot 10^{-6}$, $10^{-5}$, and $5 \cdot 10^{-5}$), and the incoming radiative power (direct solar irradiation or radiation emitted by a hot surface). Totally 6 steady state and 10 transient simulations were run.

Results show that minimal particle temperatures of about 1650 – 1700 K are required for the chemical reaction to take place at rates which allow for significant methane conversions. Such temperature levels are obtained using relatively small particle diameters or high volume fractions to increase the optical thickness of the medium. A maximal local methane conversion of $20 - 25\% / s$ for $f_v = 5 \cdot 10^{-5}$ is obtained at a distance of about 2 cm from the wall which is exposed to radiation. However, by increasing the optical thickness, the spatial range in which optimal conditions are reached becomes limited due to less radiation being transmitted through the system, whereas optically thinner media are shown to exhibit a flatter spatial profile but cannot heat up sufficiently due to their poorer absorption behaviour.
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Chapter 1

Introduction

1.1 Consequences of Global Energy Demand

The prosperity of modern human societies relies heavily on the availability of energy in order to perform the necessary tasks, such as the production and transportation of economical goods and the provision of services, to ensure their functionality. The most used primary energy sources to satisfy this demand are fossil fuels which are in general relatively cheap and have a high energy content per unit mass or volume making them easily transportable and storable. Furthermore, technologies to convert fossil to mechanical, electric, or heat energy are available at low investment costs, being thus the preferred choice of many users for both centralised and local applications, as well as for the transport sector.

However, several problems of different nature are associated with the widely spread consumption of fossil fuels which, to some extent, outweigh the advantages of their usage. One of them is the emission of pollutants (mainly CO, unburned hydrocarbons, NO\textsubscript{x}, soot, and SO\textsubscript{x}) as well as greenhouse gases (mainly CO\textsubscript{2}) whose presence in the atmosphere is deemed to exert a negative influence on the health and the quality of life of the population and on the environment. Secondly, since the rate of consumption of fossil fuels exceeds highly their rate of formation, the global resources of coal, oil, and gas will inescapably continue shrinking. This fact, combined with the constantly increasing energy demand all over the world, indicates that fossil fuels will tend to be less available and affordable in the future posing a non underestimable threat to the functioning of industrialised societies.

In order to reduce the extent of these problems, a substitution of fossil fuels with other, cleaner, primary energy sources appears to be imperative in the long run. The utilisation of the solar radiation which reaches the Earth’s surface to produce useful energy to satisfy human needs appears to be a very promising path in this direction thanks to the fact of being clean and freely available in high quantity. However, even though the amount of solar radiation reaching our planet would easily cover the energy consumption of its inhabitants, its usability remains limited by its relatively high dilution and uneven distribution, as well as by its intermittency, necessitating thus to be stored under some form in order to be available at any latitude, time of day or night, season, or weather conditions. Only when satisfying this requirement, solar energy will be able to compete with other energy sources to cover any remarkable share of the global consumption.
Chapter 1. Introduction

1.2 Solar Chemistry

An interesting and auspicious way of storing solar energy for future use is its conversion into chemical energy carriers (solar fuels), such as solar hydrogen, in thermochemical processes driven by highly concentrated solar radiation. The complete replacement of fossil fuels with solar ones remains however a long-term goal since the required technology is not estimated to be ready for commercial application in short-mid time terms. A promising intermediate option is represented by processes which produce hydrogen from fossil fuels using endothermic chemical reactions driven by solar energy. The chemical energy content of the fuel is thus increased by the solar energy necessary to run the reaction.

An example of such a process is the thermal decarbonisation of natural gas into carbon black and hydrogen under exposure to solar radiation [1, 10] represented by the simplified reaction \( \text{CH}_4 \rightarrow C + 2\text{H}_2 \). A complete decomposition of methane is achieved at 1500 K when the necessary endothermic process heat of 75 kJ \( \cdot \) mol\(^{-1} \) is provided [9], in this case by solar radiation, and yields solid carbon black and gaseous hydrogen whose chemical energy content results to be augmented by the supplied heat. A smaller quantity of the original feedstock has therefore to be used per unit of obtained energy when burning the reaction products instead of the feedstock itself resulting thus in a saving of methane. Alternatively, instead of employing both products for energy production, the solid carbon black can be sequestrated, using only the hydrogen to this purpose, for instance in a heat engine or in a fuel cell. This has the drawback of not taking advantage of all the available energy, however, in return, reduces the emission of carbon-related pollutants and of CO\(_2\) to zero. The sequestration of the solid carbon black is advantageous from a second point of view: the nano-filamentary nature of the produced C-particles observed by microscopical analysis [11] makes them a high-value marketable good contributing thus to the cost-effectiveness of this route of hydrogen production.

1.3 The SOLHYCARB Project

The exploration of the H\(_2\) production route by decarbonisation through solar thermal cracking of natural gas is the aim of the SOLHYCARB project, in the framework of which this thesis is being realised. A pilot-scale reactor in the size range of 50 kW is to be built with the objective to reach a methane decomposition of 80 % at operating temperatures between 1500 and 2300 K and at ambient pressure. Two reactor concepts, one involving heat transfer through absorbing opaque walls, and a second with direct heating of the reactant by solar radiation through a transparent window are to be investigated, with this thesis focussing on the last variant. Since the direct absorption of solar radiation by methane is relatively small, a particulate material needs to be introduced into the reactor to enhance the absorptive properties of the system and act as nucleation site for the solid carbon black produced during the methane cracking reaction which takes place on the particles’ surface. To gain preliminary information about the likely behaviour of such a system, more or less simplified models taking account of its basic characteristics need to be developed and numerical simulations of these performed. Of fundamental importance in this case are the simulation of the radiative and convective heat transfer as well as of
the chemical kinetics of the system.

1.4 Scope of Work

The aim of this diploma thesis is to build a simplified model to analyse the effect of concentrated solar radiation onto a system containing CH$_4$, eventually diluted with a carrier gas, laden with carbon black particles and perform the necessary simulations while varying the relevant system parameters to study their effect on the decarbonisation process performance. To this purpose, a pre-existing Fortran 90 routine (see section 5.1) based on the Monte Carlo Method (section 4.2) for the simulation of radiative heat transfer in a two phase medium is adapted to the problem which is specified in section 2 and the necessary initial and boundary conditions are introduced, together with the material properties of the system components. Using the prepared program, simulations need to be performed in order to gain information about:

- the optical behaviour of the system,
- the steady state spatial temperature distribution of both phases,
- the transient behaviour of the system during heating-up, and
- the CH$_4$ conversion performance.

while varying several system parameters such as the initial particle volume fraction, the particle size, or the methane concentration, as well as the solar power input.
Chapter 2

System Description

Several model simplifications of a real reactor need to be introduced in order to reduce the complexity of the system, allowing for an easier implementation of the simulation. The modeled system and its main parameters and assumptions are depicted in figure 2.1.

2.1 Geometry

The system consists of a slab with infinite extension in the $x$- and $y$-directions of thickness $L = 0.1$ m in the $z$-direction corresponding approximately to the order of magnitude of the size of a small experimental reactor. In the simulation, the $x$- and $y$-extensions, $d x$ and $d y$, of the considered system are both set to be 1 m. This choice is made for simplicity reasons since these two values do not have any impact on the results.

2.2 Medium

The two phase medium contained in the slab is composed of methane mixed with argon which, being a noble gas, is chosen as inert carrier (other inert gases could have been chosen as well) and, as the reaction progresses, of the produced hydrogen. Minor components of natural gas, as well as of the reaction products are neglected for reasons of simplicity yielding thus the simplified reaction equation $\text{CH}_4 (g) \rightarrow \text{C} (s) + 2\text{H}_2 (g)$. The gas is laden with carbon black particles whose surface acts as catalyst for the aforementioned chemical cracking reaction and on which the solid product C is deposited, resulting in particle growth during the reaction as illustrated in figure 2.2. Due to the infinite slab assumption, all spatially variable medium parameters such as phase temperatures, gas concentrations, particle size and volume fraction, are dependent only on the $z$-direction, the system becoming thus one-dimensional. Furthermore, pseudo-continuity of the medium is assumed and all particles are considered to be of spherical shape and equal initial size. This does not correspond to reality as was shown by microscopic analysis of carbon black samples produced through methane decarbonisation [1, 11]. Thanks to the extremely high number of particles present in the system, a spherical average shape is a valid assumption. Variations in their size occur as a consequence of carbon deposition during the cracking
2.2. Medium

Solid Phase: C

Gas Phase: CH$_4$, H$_2$, Ar

Non-Participating Surroundings
$T = 0 \text{ K}, \varepsilon = 1$

$q''_{\text{solar}}$
Blackbody Radiation @ 5780K

CH$_4 \rightarrow C + H_2$

$L = 0.1\text{ m}$

dx     dy

Figure 2.1: Schematic view of the system model.
reaction. However, the particle growth rate is considered to be the same for all particles at a given point \( z \), and thus \( D_p(z) \) is equal for all particles.

The gas is assumed to maintain ambient pressure \( p_g = p_\infty = 101325 \text{Pa} \) since an isobaric model is considered to be a more realistic representation of a steady state flow reactor like the one being developed in the SOLHYCARB Project (section 1.3) than a constant mass model because it accounts for rarefaction of the medium due to thermal expansion of the heated gas. However, no mass transport is considered in the system, therefore a virtual mass sink as described in section 3.1.1 needs to be introduced to keep isobaric conditions when the medium temperature varies. Such a model differs from reality in the fact that no propagation of the medium properties through the system due to mass transport effects occurs.

The two phases can have different temperatures (\( T_s \) for the solid and \( T_g \) for the gas phase) which are variable along the \( z \)-axis. \( T_s \) is assumed to be constant over a particle and equal for all particles at the same \( z \)-position.

## 2.3 Chemistry

As mentioned in section 2.2, the simplified chemical reaction \( \text{CH}_4(g) \rightarrow \text{C}(s) + 2\text{H}_2(g) \) is considered. It is assumed to take place on the surface of the carbon particles and at their temperature. The solid product carbon is completely absorbed by the particles, whereas hydrogen is freed into the gas phase. For the chemical kinetics, a model proposed by Muradov et al. [20] for thermocatalytic decomposition of \( \text{CH}_4 \) in a fluidized bed of activated carbon particles, further elucidated in section 3.2, is applied.
2.4 Heat Transfer

The system is assumed to be enclosed by non-participating surroundings since no optical effects of boundaries such as walls or windows are to be accounted for in this simulation. This means that no radiation is emitted by the boundary faces \( T_w = 0 \text{ K} \) and all radiation reaching it from inside the system is absorbed \((\varepsilon = 1)\). The face at \( z = 0 \) is exposed to perpendicularly incident concentrated solar radiation with an intensity of \( 1 \text{ MW} \cdot \text{m}^{-2} \), deemed to be sufficient for heating up the reactants enough for the reaction to proceed. The spectral power distribution of said incoming solar radiation is approximated to be equal to the spectral emissive power distribution of a blackbody, thus following Planck’s Law [18], at a the solar surface’s temperature \( T_{\text{sun}} = 5780 \text{ K} \). An emitting, absorbing and scattering medium is assumed, with scattering properties of the gas phase being negligible in comparison to those of the particles. For the gas phase, only absorption and emission by methane is considered, its absorption efficiency being much higher than that of argon and hydrogen since those two are a mono- and a bi-atomic gas, respectively, and thus their molecules have fewer degrees of freedom than \( \text{CH}_4 \). The models employed to simulate the optical behaviour of carbon particles and of methane are explained in detail in sections 3.4.1 and 3.4.2. Neither convective nor conductive heat transfer between the two phases as well as along the \( z \)-axis are considered.
Chapter 3

Fundamentals

Mass and energy conservation are applied in order to obtain a system of equations which describes the behaviour of the system. Further, the Radiative Transfer equation, and chemical kinetics need to be introduced, as well as initial and boundary conditions required by the system configuration. Their formulation has to take account of the fact that the medium is composed of two distinct phases, and thus every equation has to be set up separately for both of them.

3.1 Conservation Equations

3.1.1 Conservation of Molar Quantities

Derivation of the Species Conservation Equations

From the mass conservation, equations of the molar quantities for each species can be obtained by dividing over the molar mass $M$. If convection and diffusion phenomena are neglected, the conservation of molar quantities for each species $i = \{\text{C}, \text{CH}_4, \text{H}_2, \text{Ar}\}$ can be expressed as:

$$\frac{d\rho_i}{dt} = r_i,$$

where $\rho = dN/dV$ is the molar concentration and $r_i$ the chemical reaction rate of species $i$ per volume unit. The integral form of equation 3.1 over a given volume $V$ is then:

$$\int_V \frac{d\rho_i}{dt} dV = \int_V r_i dV,$$

whose left hand term can be integrated over the volume to obtain the conservation of the total moles for each species:

$$\frac{\partial N_i}{\partial t} = \int_V r_i dV.$$  \hspace{1cm} (3.3)

The integration over a time step $\Delta t = t - t_0$ finally gives the molar quantity at time $t$:

$$N_i(t) = N_i(t_0) + \int_{t_0}^{t} \int_V r_i dV dt$$  \hspace{1cm} (3.4)
3.1. Conservation Equations

The derivation of the chemical reaction rate \( r = (\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}) \) as a function of temperature, pressure, and the participating species’ concentrations is done in section 3.2. Considering the overall chemical reaction:

\[
\text{CH}_4 (g) \rightleftharpoons \text{C} (s) + 2\text{H}_2 (g),
\]

the following relationships between the reaction rates of the different species are found:

\[
r_{\text{CH}_4} = -r_{\text{C}},
\]

\[
r_{\text{H}_2} = 2r_{\text{C}}.
\]

It is important to notice that the reaction rate of methane is expected to have negative value, since this species is consumed during the reaction.

Knowing that the only component of the particle phase is C, and that the gas phase is composed of \( \text{CH}_4 \) and \( \text{H}_2 \) plus the inert Ar, the molar quantities in each phase can be easily expressed as:

\[
N_s (t) = N_{\text{C}} (t),
\]

and

\[
N_g (t) = N_{\text{CH}_4} (t) + N_{\text{H}_2} (t) + N_{\text{Ar}} (t).
\]

The same goes for the number of moles per unit volume:

\[
\bar{\rho}_s (t) = \bar{\rho}_{\text{C}} (t),
\]

\[
\bar{\rho}_g (t) = \bar{\rho}_{\text{CH}_4} (t) + \bar{\rho}_{\text{H}_2} (t) + \bar{\rho}_{\text{Ar}} (t),
\]

and for the reaction rates:

\[
r_s (t) = r_{\text{C}} (t),
\]

\[
r_g (t) = r_{\text{CH}_4} (t) + r_{\text{H}_2} (t),
\]

with the suffixes s and g denoting the solid and the gas phase, respectively. Therefore, equations 3.1 to 3.4 are valid not only if the single species are looked at, but also for each phase, which can contain more than one species.

**Volume Fraction**

Knowing the number of moles of the solid phase, it is possible to obtain its volume fraction via the following equation:

\[
f_v (t) = \frac{V_s (t)}{V} = \frac{V_{\text{C}} (t)}{V} = \frac{N_{\text{C}} (t) \bar{M}_{\text{C}}}{V \bar{\rho}_{\text{C}}},
\]

(3.14)
Initial and Boundary Conditions

The initial conditions for the species conservation equations are:

\[ N_C(t = 0) = N_{C,0} = \frac{f_{v,0}V\rho_C}{M_C}, \quad (3.15) \]

\[ N_i(t = 0) = N_{i,0} = \frac{(1 - f_{v,0})Vp_{i,0}}{RT_{g,0}}, \quad (3.16) \]

where \( i \) stands for all gaseous components (CH\(_4\), H\(_2\), Ar). No hydrogen is assumed to be present in the system at \( t = 0 \):

\[ p_{H_2}(t = 0) = p_{H_2,0} = 0, \quad (3.17) \]

There are no boundary conditions for the species equations.

Methane Conversion Efficiency

To evaluate the effectiveness of the chemical reaction, the methane conversion efficiency can be defined as the fraction of reacted CH\(_4\) over the initial amount of CH\(_4\):

\[ X_{CH_4}(t) = \frac{N_{CH_4,0} - N_{CH_4}(t)}{N_{CH_4,0}}. \quad (3.18) \]

Mass Sink

Since the system conditions are assumed to be isobaric, but no mass transport is included in the model, mass needs to be removed from or added to it to compensate for the effect of gas expansion or contraction due to variations of its temperature. As the particles are suspended in the gas phase, it appears more realistic to remove the corresponding quantity of particles together with the excess gas mass, decreasing thus \( n_p \) as well as the particle volume fraction \( f_v \). The volume change of the gas phase due to removal of particles from the system has to be accounted for when computing the removed mass. However, since the sum of the volumes of both phases corresponds to the system total volume and is thus constant, the following equation can be written:

\[ V = V_s + V_g = \frac{N_pM_s}{\rho_s} + \frac{N_gRT_g}{p} \quad (3.19) \]

Considering \( i \) to stand for all species composing the solid phase and \( j \) for all gaseous species, a general form of the equation above can be written:

\[ V = \sum_i \frac{N_iM_i}{\rho_i} + \sum_j N_jRT_g. \quad (3.20) \]

For an uniformly mixed gas phase laden with equally sized and distributed particles, the molar fraction \( \bar{x}_i = N_i/N_{tot} \) or \( \bar{x}_j = N_j/N_{tot} \) (with \( N_{tot} = \sum_i N_i + \sum_j N_j \)) of each
component does not vary when removing part of the medium. Inserting these definitions and solving the equation for the total mole number yields:

\[
N_{\text{tot}} = \frac{V}{\sum_i \bar{x}_i \rho \bar{M}_i} + \sum_j \bar{x}_j \frac{R T_g}{\rho}
\]  

Given the molar fraction of each involved species, the total number of moles for any \( T_g \) can be obtained applying this equation. The number of moles of a single species can easily be calculated by multiplying its molar fraction with the total number of moles \( N_i = \bar{x}_i \sum N = \bar{x}_i N_{\text{tot}} \).

**Particle Number and Size**

Due to the mass sink introduced above, even though no particle formation is assumed, the number of particles in a control volume is not constant. However, the removal of particles does not affect their size (the only process influencing it being the deposition of solid reaction product), and thus the total number of particles \( n_p \) at any time can be expressed in function of the molar quantity of solid material and of the particle diameter:

\[
n_p = \frac{V_s}{V_p} = \frac{6 f_v V}{\pi D_p^3} = \frac{6 N_C M_C}{\pi \rho C D_p^3}
\]  

It has to be noticed that the suffix \( s \) refers to properties of the whole solid phase, whereas \( p \) refers to the properties of one single particle. If \( n_p \) and the volume fraction \( f_v \) are known, the diameter of the carbon particles is obtained as follows:

\[
D_p = \sqrt[3]{\frac{6 f_v V}{\pi n_p}}
\]  

This relationship is valid if all particles are assumed to have the same initial size and the same growth rate during the simulation. Notice that it is essential to compute the particle diameter before applying a mass sink, whereas the number of particles is updated after the removal of mass from the system.

### 3.1.2 Energy Conservation

From the general energy conservation equation, a simplified form is obtained by neglecting conduction, convection, pressure, and viscous effects, but taking account of mass transfer between the two phases due to chemical reaction.

\[
\frac{dH_j}{dt} = \frac{d(N_j h_j)}{dt} = q_{r,j} + \dot{H}_{\text{in},j} - \dot{H}_{\text{out},j}
\]  

\( \dot{H}_{\text{in},j} \) and \( \dot{H}_{\text{out},j} \) are the enthalpy of the mass flows which enter, respectively leave, the phase.
Solid Phase

For the solid phase, equation 3.24 takes the following form, accounting for the enthalpy fluxes shown in figure 3.1.

\[
\frac{d(N_s h_s)}{dt} = \frac{d(N_{CH4} C)}{dt} = q_{r,s} - r_{H2} h_{H2} (T_s) - r_{CH4} h_{CH4} (T_g) \tag{3.25}
\]

Transforming the equation and considering that the only component of the particle phase is carbon yields its infinitesimal temperature change:

\[
N_{C} \bar{c}_p,C \frac{dT_s}{dt} = q_{r,s} - r_{H2} h_{H2} (T_s) - r_{C} h_{C} (T_s) - r_{CH4} h_{CH4} (T_g) = \]

\[
= q_{r,s} - r_{H2} h_{H2} (T_s) - r_{CH4} h_{CH4} (T_g) + r_{CH4} \Delta h_{CH4,T_g-T_s} \tag{3.26}
\]

This equation states that the enthalpy variation of the solid phase consists of the radiative power input minus the power necessary to heat the reactant CH4 from Tg to Ts and the power necessary to drive the endothermic chemical reaction. Since methane is being consumed in the reaction, attention has to be paid to the negative value of its reaction rate rCH4. Integrating the equation over a time step \( t - t_0 \) gives the value of \( T_p \) after that interval:

\[
T_s (t) = T_s (t_0) + \int_{t_0}^{t} \frac{q_{r,s} - r_{H2} h_{H2} (T_s) - r_{CH4} h_{CH4} (T_g)}{N_{C} \bar{c}_p,C} dt \tag{3.27}
\]

Gas Phase

Since only two phases are present, all material leaving one phase necessarily enters the other one, and vice versa, for the gas phase the incoming and leaving enthalpy fluxes have reversed directions, and therefore their sign need to be changed compared to the particle
phase. This leads to the following equation being obtained from equation 3.24:
\[
\frac{d(N_g h_g)}{dt} = \frac{d(N_{CH_4} h_{CH_4} + N_{H_2} h_{H_2} + N_{Ar} h_{Ar})}{dt} = q_{r,g} + r_{H_2} h_{H_2} (T_s) + r_{CH_4} h_{CH_4} (T_g)
\]

which can be transformed and simplified to give:
\[
[N_{CH_4} c_{p,CH_4} (T_g) + N_{H_2} c_{p,H_2} (T_g) + N_{Ar} c_{p,Ar} (T_g)] \frac{dT_g}{dt} = q_{r,g} + r_{H_2} [h_{H_2} (T_s) - h_{H_2} (T_g)] = q_{r,g} + r_{H_2} \Delta h_{H_2,T_g,T_s}
\]

The gas phase is thus heated up by the absorbed radiative energy, as well as by the hot reaction product H\(_2\). Performing the integration over time yields:
\[
T_g (t) = T_g (t_0) + \int_{t_0}^{t} \frac{q_{r,g} + r_{H_2} [h_{H_2} (T_s) - h_{H_2} (T_g)]}{N_{CH_4} c_{p,CH_4} (T_g) + N_{H_2} c_{p,H_2} (T_g) + N_{Ar} c_{p,Ar} (T_g)} dt
\]

**Boundary / Initial Conditions**

No explicit boundary conditions for the energy conservation equation are given, but the incoming radiative power flux \( q_{solar}^{in} \) across the boundary wall at \( z = 0 \) is an input value of the problem and therefore known. However, it cannot be applied directly to the energy conservation, but is taken account of in the computation of the radiative energy transfer, as described in section 3.3.3.

The initial temperatures of the gas and the particle phase are an input to the simulation which can directly be applied to the energy conservation equation.

\[
T_j (t = 0) = T_{j,0}
\]

where \( j \) denotes all phases. It can be assumed that both phases are initially present at the same temperature, be it ambient or any temperature to which the reactants have eventually been preheated.

**Energy Efficiency**

To evaluate the energetic efficiency of the simulated process, the fraction of the totally incoming radiative power through the boundary at \( z = 0 \) which is converted into chemical energy of the products is defined as:
\[
\eta_{h,chem} (t) = \frac{q_{chem} (t)}{q_{r,h1} (t)}.
\]

It is further possible to define a cumulative efficiency based on the total incoming and chemical energies up to the time \( t \):
\[
\eta_{Q,chem} (t) = \frac{\int_{0}^{t} q_{chem} (t^*) dt^*}{\int_{0}^{t} q_{r,h1} (t^*) dt^*}.
\]
3.2 Chemical Kinetics

The chemical kinetics of the considered methane cracking reaction \( \text{CH}_4 (g) \rightarrow \text{C} (s) + 2\text{H}_2 (g) \) is rather complex since the reaction rate \( r_{\text{CH}_4} \) depends not only on the available particle surface, which by the way can not be assumed to be spherical due to the filamentous nature of the used carbon particles, but also on its catalytic activity which can vary greatly between different types of carbon, as pointed out in [19]. For samples of different kinds of activated carbons, the reaction order was determined experimentally to be approximately 0.5 by Kim et al. [13]. This yields the following expression for the reaction rate of methane decomposition:

\[
r_{\text{CH}_4} = k p_{\text{CH}_4}^{0.5},
\]

with \( p_{\text{CH}_4} \) being the partial pressure of methane in the system. The reaction rate is negative since \( \text{CH}_4 \) is consumed in the reaction. Several derivations of the kinetic constant \( k \) from experimental data can be found in literature (e.g. [29]), although normally for very specific parameters such as given particle size and catalytic surface. Parameters for the expression of the temperature dependence of \( k \) according to Arrhenius’ Law, and accounting for the quantity of carbon catalyst in the system are experimentally determined by Muradov et al. [20]:

\[
k = k_0 \exp \left( -\frac{E_a}{RT} \right).
\]

The activation energy \( E_a \) is estimated to be 201 kJ/mol, whereas \( k_0 \) was determined to be 186.8 mol/s · g (cat) · Pa^{0.5}, depending thus on the quantity of catalyst contained in the system. Assuming this quantity to be equal to the amount of carbon, the final expression for the reaction rate of methane becomes:

\[
r_{\text{CH}_4} = -M_C k_0 \exp \left( -\frac{E_a}{RT} \right) p_{\text{CH}_4}^{0.5}.
\]

It is important to notice that the value for \( k_0 \) proposed by Muradov is based on results of experiments which were conducted using activated carbon particles in the 1100-1200 K range, whereas these simulations reached particle temperatures up to 1800 K and carbon black is assumed to be obtained. Nevertheless, this model was chosen due to the fact that it includes a term for the total mass of carbon and thus the particle size, whose growth can therefore be accounted for when simulating the chemical reaction. The temperature dependence of the kinetic constant \( k \) is shown in figure 3.2.

3.3 Radiation Heat Transfer

To compute the net energy flux into a volume element, the radiative heat flux through the medium needs to be known and is thus necessary to be calculated. The solution has to take account for absorption and emission of thermal radiation for both phases, as well as scattering by the solid particles.
3.3. Radiation Heat Transfer

\[ k(T) = k \]  

\[ T(K) = T \]  

\[ k_{mol}(s, \text{gat}, P_{0}(T)) \]  

Figure 3.2: Temperature dependence of the kinetic constant of the methane decomposition reaction [20].

3.3.1 Radiative Heat Transfer in Two Phase Participating Media

In this section, the expressions that describe the influence of absorption, emission, and scattering on the radiation intensity of a beam travelling along the path \( s \), are applied to the two phase medium which is being simulated.

Absorption

Since the simulated medium is composed of two different phases, the contribution of both the solid (subscript s) and the gaseous (subscript g) phase have to be included. The absorption coefficient \( \kappa \) already accounts for the volume fraction of particles and gas: therefore the attenuation by absorption can be found by applying Bouguer’s Law for each phase and adding their contribution to overall absorption:

\[
dI_{abs} = -\kappa s I_\lambda ds - \kappa g I_\lambda ds = -\kappa \lambda I_\lambda ds
\]

(3.37)

where \( \kappa_\lambda = \kappa_{\lambda,p} + \kappa_{\lambda,g} \) is the overall spectral absorption coefficient. The contribution from each phase \( j \) is then:

\[
dI_{abs,j} = -\frac{\kappa_j I_\lambda ds}{-\kappa \lambda I_\lambda ds} dI_{abs} = \frac{\kappa_j I_\lambda ds}{\kappa \lambda dI_{abs}}
\]

(3.38)

Emission

For the two phase medium, in analogy to absorption, the emitted intensities from both phases are added. Care has to be taken to account for the different temperatures, and thus for the different spectral distribution of radiative power emitted by each phase.

\[
dI_{em} = \kappa s I_\lambda(T_s) ds + \kappa g I_\lambda(T_g) ds
\]

(3.39)
The contribution to emission from phase $j$ is therefore:

$$dI_{\lambda,em,j} = \frac{\kappa_{\lambda,j}I_{b\lambda}(T_j)}{\kappa_{\lambda,s}I_{b\lambda}(T_s) + \kappa_{\lambda,g}I_{b\lambda}(T_g)} dI_{\lambda,em} \tag{3.40}$$

### Scattering

For the two phase medium, the scattering equation becomes:

$$dI_{\lambda,sc} = -\sigma_{s\lambda,s}I_{\lambda}ds - \sigma_{s\lambda,g}I_{\lambda}ds = -\sigma_{s\lambda}I_{\lambda}ds \tag{3.41}$$

In analogy to absorption, an overall spectral scattering coefficient $\sigma_{s\lambda} = \sigma_{s\lambda,s} + \sigma_{s\lambda,g}$ can be defined. However, since scattering from gas molecules is negligible in comparison to that from the particles, its contribution to the overall scattering can be neglected, which allows to make the following approximation: $\sigma_{s\lambda} \approx \sigma_{s\lambda,s}$. The contributions from each phase are thus:

$$dI_{\lambda,sc,s} \approx dI_{\lambda,sc} \tag{3.42}$$

for the particle phase, and

$$dI_{\lambda,sc,g} \approx 0 \tag{3.43}$$

for the gas phase.

### Incoming Scattering

As shown in the paragraph above, scattering from the gas phase can be neglected. Thus, the expression for incoming scattering takes account only for the particle phase:

$$dI_{\lambda,isc} \approx dI_{\lambda,isc,s} = \frac{\sigma_{s\lambda,s}}{4\pi} \int_{4\pi} I_{\lambda} (\hat{s}_i) \Phi_{\lambda,s} (\hat{s}_i, \hat{s}) d\Omega_i ds, \tag{3.44}$$

with the subscript $i$ standing for the incoming direction. The scattering phase function is defined as:

$$\Phi_{\lambda} (\hat{s}_i, \hat{s}) = \frac{dI_{\lambda} (\hat{s}_i, \hat{s})}{\left( \frac{1}{4\pi} \right) \int_{4\pi} dI_{\lambda} (\hat{s}_i, \hat{s}) d\Omega}. \tag{3.45}$$

### 3.3.2 Radiative Transfer Equation

In a two-phase medium, the formulation of the RTE needs to account for the contributions of both the phases, listed in section 3.3.1. The variation of spectral radiation intensity along a path $ds$ for the two phase medium is obtained by adding up the terms for absorption, emission, and scattering, becoming thus:

$$dI_{\lambda} = dI_{\lambda,abs} + dI_{\lambda,em} + dI_{\lambda,sc} + dI_{\lambda,isc} =$$

$$= -\kappa_{\lambda}I_{\lambda} (\hat{s}) ds + \kappa_{\lambda,s}I_{b\lambda}(T_s) ds + \kappa_{\lambda,g}I_{b\lambda}(T_g) ds -$$

$$-\sigma_{s\lambda,s}I_{\lambda} (\hat{s}) ds + \frac{\sigma_{s\lambda,s}}{4\pi} \left[ \int_{4\pi} I_{\lambda} (\hat{s}_i) \Phi_{\lambda,s} (\hat{s}_i, \hat{s}) d\Omega_i \right] ds. \tag{3.46}$$
Scattering by the gas is not considered. The divergence of the spectral radiative flux is then found by integrating over all solid angles [18]:

\[
\nabla \cdot \mathbf{q}_\lambda = -\kappa_\lambda \int_{4\pi} I_\lambda (\hat{s}) \, d\Omega + \\
+\kappa_{\lambda,s} \int_{4\pi} I_{b\lambda} (T_s) \, d\Omega + \kappa_{\lambda,g} \int_{4\pi} I_{b\lambda} (T_g) \, d\Omega - \\
-\sigma_{s\lambda,s} \int_{4\pi} I_\lambda (\hat{s}) \, d\Omega + \\
+\frac{\sigma_{s\lambda,s}}{4\pi} \int_{4\pi} I_\lambda (\hat{s}) \left( \int_{4\pi} \Phi_{\lambda,s} (\hat{s}, \hat{s}) \, d\Omega \right) \, d\Omega.
\]

Since the scattering terms outweigh each other the equation can be simplified to become:

\[
\nabla \cdot \mathbf{q}_\lambda = \kappa_{\lambda,s} [4\pi I_{b\lambda} (T_s) - G_\lambda] + \kappa_{\lambda,g} [4\pi I_{b\lambda} (T_g) - G_\lambda].
\]

\( G_\lambda = \int_{4\pi} I_\lambda (\hat{s}) \, d\Omega \) is the spectral incident radiation. The spectral radiative flux into each phase can be obtained by applying equation 3.47 and keeping only the terms which relate to that phase. This yields the following expression for the radiative energy absorbed by an infinitesimal volume element of phase \( j \):

\[
\nabla \cdot \mathbf{q}_{\lambda,j} = \kappa_{\lambda,j} [4\pi I_{b\lambda} (T_j) - G_\lambda].
\]

To find the total divergence of the radiative flux, the spectral expression has to be integrated over all wavelengths \( \lambda \):

\[
\nabla \cdot \mathbf{q}_{r,j} = \int_0^\infty \nabla \cdot \mathbf{q}_{\lambda,j} \, d\lambda.
\]

By integrating over a volume element \( V \), the divergence of the radiative flux in that element is found:

\[
\mathbf{q}_{r,j} = -\int_V \nabla \cdot \mathbf{q}_{r,j} \, dV.
\]

The minus sign is necessary because in the RTE positive value is given to the outgoing flux, whereas in the energy conservation (equation 3.24) the incoming radiative energy flux is considered positive. This expression can then be inserted into equation 3.27 or 3.30 for the particle or the gas phase, respectively.

### 3.3.3 Boundary Conditions

Generally, the boundary walls of the slab are considered to be non-participating (\( T_{w1} = T_{w2} = 0 \text{ K}, \varepsilon_{w1} = \varepsilon_{w2} = 1 \)). Therefore, no emission from the walls is taking place and all radiation reaching the walls is absorbed. However, through the boundary at \( z = 0 \), radiative heat is supplied to the system. Two different cases for boundary conditions at \( z = 0 \) are considered. In the first one, a solar radiative flux with an intensity per surface unit \( q_{\text{solar}}'' \) is assumed to reach the system perpendicularly through the boundary layer, whereas in the second one the radiation is emitted from the boundary itself, for
which a temperature \( T_{w1} \) is assumed. In both cases, the spectral distribution of radiative intensity is approximated to be that of a blackbody at \( T = T_{\text{sun}} = 5780 \) K or at \( T = T_{w1} \), respectively. At \( z = L \), no radiative energy flux enters the system and therefore the non-participating surroundings assumption is completely valid.

**Radiative Flux Boundary Condition**

If perpendicularly incoming radiation \( q''_{\text{solar}} \) through the boundary is considered, the spectral radiative flux intensity in any incoming direction (positive value of the \( z \)-component \( s_z \) of the direction vector \( \hat{s} \)) is given and can be formulated as:

\[
I_{\lambda}(z = 0, \hat{s}) = q''_{\text{solar}} \frac{\pi I_{b\lambda}(\lambda, T_{\text{sun}})}{\sigma T_{\text{sun}}^4} \delta_{\hat{s} \hat{k}}. \tag{3.52}
\]

where \( I_{b\lambda} \) designates the spectral intensity of blackbody-emitted radiation for the chosen temperature and \( \delta_{\hat{s} \hat{k}} \) is the Kronecker function for \( \hat{s} \) and \( \hat{k} \). Since the total emissive power of a black surface is given by \( \sigma T^4 \), a scaling of the obtained distribution to the chosen incoming radiation power can be done. The intensity of outgoing radiation depends on the system properties and is not known.

**Temperature Boundary Condition**

If, instead of a radiative flux through the boundary, a boundary temperature \( T_{w1} \) is given, no scaling of the radiative power as in the previous case is necessary since the total emitted radiation becomes a function of \( T_{w1} \). Further, thanks to the black surface assumption, the radiative intensity is not direction-dependent, yielding the following expression for the boundary conditions at \( z = 0 \):

\[
I_{\lambda}(z = 0, \hat{s}) = I_{b\lambda}(\lambda, T_{w1}), \tag{3.53}
\]

for \( 0 < \hat{s} \cdot \hat{k} \leq 1 \). This second case is applied only in one calculation, for comparison purposes.

**Non-Participating Boundary Conditions**

At \( z = L \), no incoming radiation is assumed, thus the boundary condition becomes:

\[
I_{\lambda}(z = L, \hat{s}) = 0, \tag{3.54}
\]

for \( -1 \leq \hat{s} \cdot \hat{k} < 0 \).

### 3.4 Optical Properties of Participating Medium

In order to simulate the radiative transfer through participating medium, its optical properties, and thus its absorption, emission and scattering behaviour, need to be known. These properties, expressed by the spectral absorption coefficient \( \kappa_\lambda \) and scattering coefficient \( \sigma_{s\lambda} \), are established separately for each phase and combined to give the overall values according to the basic laws of radiative transfer presented in section 3.3.1.
Table 3.1: Parameters for the dispersion model for the complex index of refraction of propane soot as given by [5].

<table>
<thead>
<tr>
<th>Electron</th>
<th>( F ) (m(^{-3}))</th>
<th>( g ) (s(^{-1}))</th>
<th>( \omega_j ) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>c</td>
<td>4.06 \cdot 10^{-2}</td>
<td>6.00 \cdot 10^{15}</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>2.69 \cdot 10^{27}</td>
<td>6.00 \cdot 10^{15}</td>
<td>1.25 \cdot 10^{15}</td>
</tr>
<tr>
<td>2</td>
<td>2.86 \cdot 10^{28}</td>
<td>7.25 \cdot 10^{15}</td>
<td>7.25 \cdot 10^{15}</td>
</tr>
</tbody>
</table>

3.4.1 Solid Phase

For the solid phase, the main difficulty in establishing the optical properties is posed by the fact that these depend heavily on the surface characteristics of the particles and have not yet been established for the considered particles. However, microscopical analyses of the surface of fed carbon black particles after deposition of carbon produced by solar cracking of methane reveal a filamentous structure [11] resembling that of hydrocarbon soot particles formed through pyrolysis of the fuel on the oxygen poor side of a combustion flame. Due to their importance in combustion applications, several optical data is available for soot particles of hydrocarbons. As the most suitable was selected [5], since it proposes not only tabulated data, but also an analytical dispersion model for the complex index of refraction:

\[
m = n + ink
\]

in the relevant wavelength range (0.4 – 10\(\mu\)m) based on classical electron theory and fitted with experimental data. The dispersion equations are:

\[
n^2 (1 - k^2) = 1 - \frac{F_c e^2 / M_e \epsilon_0}{g_c^2 + \omega^2} + \sum_j \frac{F_j \left( \omega_j^2 - \omega^2 \right) e^2 / M_e \epsilon_0}{\left( \omega_j^2 - \omega^2 \right)^2 + \omega^2 g_j^2}, \tag{3.55}
\]

and

\[
2n^2 k = 1 - \frac{F_c g_c e^2 / M_e \epsilon_0}{(g_c^2 + \omega^2) \omega} + \sum_j \frac{F_j \omega g_j e^2 / M_e \epsilon_0}{\left( \omega_j^2 - \omega^2 \right)^2 + \omega^2 g_j^2}, \tag{3.56}
\]

with the subscripts c and \( j = 1, 2 \) referring to conduction, respectively bound, electrons. \( F \) is the number of effective electrons per volume units, \( g \) the electron damping constant, \( \omega \) the radiation frequency, \( \omega_j \) the natural frequency of the \( j \)th electron, \( e = 1.602 \cdot 10^{-19} \) C the electron charge, \( M_e = 9.109 \cdot 10^{-31} \) kg the electron mass, and \( \epsilon_0 = 8.854 \cdot 10^{-12} \) F/m the electric permittivity of vacuum. The fitted values for \( F, g, \) and \( \omega_j \) are listed in table 3.1. In [5], experimental analyses of both acetylene (H/C = 0.068) and propane soot (H/C = 0.217) were performed. However, despite the significant difference in H/C-ratios, only small discrepancies in optical properties were registered and thus only the values for propane soot are given since they are judged as representative for both types of soot. Based on this conclusion, the data for propane soot is deemed suitable for this simulation even though the particles used in this simulation are assumed not to contain any hydrogen.

The derivation of the optical parameters necessary for the simulation (spectral absorption coefficient \( \kappa_\lambda \), spectral scattering coefficient \( \sigma_\lambda \) and the phase function \( \Phi_\lambda (\theta, \lambda) \) from the complex index of refraction, in function of the size parameter \( \xi = \pi D_p / \lambda \), is performed applying the Mie Scattering Theory, as further explained in section 3.5. A Fortran 90 rou-
Figure 3.3: Spectral absorption coefficient $\kappa_{\lambda,s}$ of the solid phase for different particle diameters $D_p$ assuming a solid volume fraction $f_v = 10^{-5}$.

tine (section 5) is used for the calculations. Resulting spectral absorption and scattering coefficients for different particle diameters $D_p$ are shown in figures 3.3 and 3.4.

It can be noticed that in the relevant wavelength range for both solar and emitted radiation ($\lambda < 5\mu m$), the absorption coefficient is higher for smaller particles. The particle growth due to deposition of carbon atoms is thus expected to worsen the absorptive behaviour of the solid phase. However, if the number of particles is assumed to be constant, this effect is expected to be more than compensated by the increase of $f_v$ which occurs proportionally to $(D_p)^3$. The same observation is true also for the spectral scattering coefficient and can thus be applied to the extinction coefficient $\beta_{\lambda,s} = \kappa_{\lambda,s} + \sigma_{\lambda,s}$.

To be used as input for the simulation, the real and the imaginary parts $n$ and $nk$ of the complex index of refraction are tabulated for 234 different wavelength intervals $\Delta\lambda_j = \lambda_{i,j+1} - \lambda_{i,j}$ between 0 and $10^{-3}m$. Their values are assumed to be constant over each $\Delta\lambda$. For the calculation of the scattering phase function $\Phi_{\lambda}(\theta, \lambda)$, the mean values $\lambda_{i,j} = \lambda_{i,j} + \Delta\lambda_j/2$ of each interval are used to approximate the integral of the phase function applying the trapezoidal method. The number of wavelength intervals represents a compromise between precision (small $\Delta\lambda$) and calculation speed (big $\Delta\lambda$).

### 3.4.2 Gas Phase

Among the three gas species which are considered in the simulation, methane is the most relevant in terms of optical attenuation behaviour, being composed of three atoms and possessing thus more degrees of freedom than the bi-atomic $H_2$ and the monoatomic Ar.
This characteristic allows it to absorb a greater amount of radiative energy. The absorption coefficient of the gas phase is therefore equated to that of methane \( (\kappa_{\lambda,g} \approx \kappa_{\lambda,CH_4}) \). Moreover, the scattering coefficient of molecules is considered negligible in comparison to that of bigger particles such as these considered in this simulation \[18\].

Figure 3.5 shows the spectral absorption coefficient of methane in function of wavenumber. It can be noticed that methane presents four major absorption bands in the infrared wavelength range, namely at about 1.65 \( \mu m \), 2.30 \( \mu m \), 3.50 \( \mu m \), and 7.40 \( \mu m \). The two smaller bands at 1.10 \( \mu m \), and 1.40 \( \mu m \) are less relevant since their peak values barely exceed 1. The gas absorbs thus predominantly infrared radiation emitted by the medium, whereas the absorption of visible solar solar radiation is practically null. Therefore, the gas temperature is expected to be substantially lower, as its Planck mean absorption coefficient at its own temperature is much higher than that at the temperature of the sun, as shown in table 3.2. Since molecular gases absorb photons in discrete energy bands, their absorption coefficient varies strongly and rapidly across the wavelength spectrum \[18\]. To maintain a good precision, models for the absorption coefficient of the gas phase must thus be evaluated at a great number of points across the wavelength spectrum. In this case, as data source, supplied tabulated values for CH\(_4\) at different partial pressures and temperatures, which were calculated from the HITRAN spectroscopic database \[24\], \[25\], are used. Each one of these tables, given for 10 discrete methane partial pressures between 0.1 and 1.0 atm and 7 temperatures between 300 and 1500 K, contains the values of \( \kappa_{\eta,CH_4}(\eta) \) in function of \( 10^6 \) discrete wavenumbers \( \eta = 1/\lambda \) between \( 10^5 \) and \( 10^7 \) m\(^{-1}\). Since such a considerable amount of data (a matrix with 10 pressures, 7 temperatures
and $10^6$ wavelengths) cannot be processed in the simulation due to lack of computational power to handle it. Furthermore, a good statistical representation of the gas properties would require also an enormous quantity of generic rays to be traced for each Monte Carlo repetition, making it impossible to conclude the simulations in a realistic timeframe.

It is therefore required to reduce the quantity of discrete wavenumbers (or wavelengths) to a value which is considerably smaller than the given one of $10^6$. For this purpose, a box model [18] is applied, subdividing the relevant wavelength spectrum in bands $j$ with constant absorption coefficient:

$$
\kappa_{\eta, \text{CH}_4}(j) = \frac{1}{\eta_{j+1} - \eta_j} \int_{\eta_j}^{\eta_{j+1}} \kappa_{\eta, \text{CH}_4}(\eta) \, d\eta,
$$

(3.57)

The box model is illustrated in figure 3.6 over a small wavenumber, which also permits to perceive the great unsteadiness of the spectral distribution of the gas absorption coefficient. Since the values for $\kappa_{\eta, \text{CH}_4}(\eta)$ are given only at discrete intervals $\Delta \eta$, an analytical solution of the integral in equation 3.57 is not possible, requiring a numerical integration method to be applied. In this case, the Simpson Rule [21] is used to approximate the integral by building a quadratic polynomial function over three contiguous values of the spectral absorption coefficient ($\kappa_{\eta, \text{CH}_4,j-1}$, $\kappa_{\eta, \text{CH}_4,i}$, $\kappa_{\eta, \text{CH}_4,j+1}$). If a chosen box interval $\Delta \eta_{\text{box},j} = \eta_{j+1} - \eta_j$ contains more than three wavenumber intervals $\Delta \eta$, which applies in this case, the composite Simpson rule is used, which leads to the following approximation for the
The absorption coefficient in the interval \( \Delta \eta_{\text{box},j} \):

\[
\bar{\kappa}_{\eta,\text{CH}_4,j} = \frac{1}{\Delta \eta_{\text{box},j}} \int_{\eta_j}^{\eta_{j+1}} \kappa_{\eta,\text{CH}_4}(\eta) \, d\eta \approx \frac{1}{\Delta \eta_{\text{box},j}} \cdot \frac{\Delta \eta}{3} .
\]

The suffix \( i \) denotes the discrete wavenumbers in the original data set, whereas \( j \) stands for the bands in which the spectrum is subdivided when building the box model. \( n \) is the number of wavenumber intervals in one band:

\[
n = \frac{\Delta \eta_{\text{box},j}}{\Delta \eta} .
\]

Since the application of the Simpson rule requires \( n \) to be an even number, if equation 3.59 yields an odd value, the Simpson rule is used for \( n - 1 \) intervals, and the integration over the last \( \Delta \eta \) is approximated by the trapezoidal rule. To obtain the same values in function of the wavelength \( \lambda \), the relationship \( \lambda = \eta^{-1} \) has to be applied. It has to be noticed that since the \( \Delta \eta \) in the original data set are constant over the given spectrum, the corresponding wavelength intervals do vary according to the following relationship:

\[
\Delta \lambda_i = \frac{1}{\eta_i} \Delta \eta = \lambda_i^2 \Delta \eta .
\]
Table 3.2: Planck mean absorption coefficient for gas (at 300 and 900 K) and particles for different radiation distributions.

<table>
<thead>
<tr>
<th>$T_{bb}$ (K)</th>
<th>$\kappa_{P,g}$ (m$^{-1}$)</th>
<th>$\kappa_{P,s}$ (m$^{-1}$)</th>
<th>$T_g = 300$ K (m$^{-1}$)</th>
<th>$T_g = 900$ K (m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>5.46</td>
<td>2.22</td>
<td>0.92</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>8.75</td>
<td>5.12</td>
<td>2.02</td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td>8.24</td>
<td>3.85</td>
<td>1.50</td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>8.02</td>
<td>2.59</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>5780</td>
<td>6.83</td>
<td>0.26</td>
<td>0.10</td>
<td></td>
</tr>
</tbody>
</table>

As a consequence of this, the density of data points diminishes for increasing wavelengths, leading thus to the fact that, if constant wavelength bands instead of constant wavenumber bands for the box model are chosen, the precision of the approximation decreases for longer wavelengths.

To build suitable input files from the originally given data sets, a Fortran 90 routine named Gas (section 5.4.1) is programmed. Since the suitable quantity of necessary wavelengths to accurately represent the gas properties for the given problem is unknown, their number is determined by running a series of test simulations with fixed input parameters but stepwise increasing of the interval number until a convergence of the results is reached, as shown in Appendix B.3. The chosen model contains 5005 discrete wavelength bands.

### 3.4.3 Planck Mean Absorption Coefficient

Table 3.2 reports the calculated values of the Planck mean absorption coefficient

$$\kappa_P(T_{r,b}, T_j) = \frac{\int_0^\infty \kappa(\lambda, T_j) I_{b\lambda}(\lambda, T_{r,b})}{\int_0^\infty I_{b\lambda}(\lambda, T_{r,b})},$$

for blackbody radiation distribution at different temperatures for the gas phase at 300 and 900 K and for the solid phase ($\kappa_{\lambda,s}$ is independent of temperature). $T_j$ is the temperature of the relevant phase, whereas $T_{r,b}$ is the blackbody temperature of the radiation.

### 3.5 Mie Scattering Theory

To compute the scattering behaviour of electromagnetic radiation on particles having a size in the same order of magnitude than the wavelength of the radiation, as well as the spectral absorption and scattering coefficients of the particles, Mie scattering theory [4] is applied. Since the calculations according to Mie Theory are rather complicated, other models such as Rayleigh scattering or optical scattering are more suitable but have limited ranges of validity. Defining the size parameter $\xi$ as:

$$\xi = \frac{\pi D_p}{\lambda},$$

Rayleigh theory is applicable for $\xi <<< 0.3$, whereas geometrical optics is a good model only for $\xi >> 5$. Since in the given problem setup, particle sizes between 1 and 10 $\mu$m
and wavelengths ranging from roughly 0.1 to 10 μm are dealt with, the possible values for \( \xi \) do not all lie within the limits necessary to apply one of those theories, making thus the use of Mie theory necessary.

The scattering and the extinction efficiencies, \( E_{\lambda,sc} \) and \( E_{\lambda,ext} \), which are related to the scattering and extinction coefficients by the particle volume fraction, can be calculated as follows:

\[
E_{\lambda,sc} = \frac{2}{\xi^2} \sum_{n=1}^{\infty} (2n+1) \left( |a_n|^2 + |b_n|^2 \right), \tag{3.63}
\]

\[
E_{\lambda,ext} = \frac{2}{\xi^2} \sum_{n=1}^{\infty} (2n+1) \Re \left( a_n + b_n \right). \tag{3.64}
\]

with \( a_n \) and \( b_n \) being the Mie scattering coefficients:

\[
a_n = \frac{\psi_n' (m\xi) \psi_n (\xi) - m\psi_n (m\xi) \psi_n' (\xi)}{\psi_n' (m\xi) \zeta_n (\xi) - m\psi_n (m\xi) \zeta_n' (\xi)}, \tag{3.65}
\]

and

\[
b_n = \frac{m_s \psi_n' (m_s\xi) \psi_n (\xi) - \psi_n (m_s\xi) \psi_n' (\xi)}{m_s \psi_n' (m_s\xi) \zeta_n (\xi) - \psi_n (m_s\xi) \zeta_n' (\xi)}, \tag{3.66}
\]

with \( m_s \) being the complex refractive index of the solid particle phase. \( \psi_n \) and \( \zeta_n \) are Riccati-Bessel functions:

\[
\psi_n (z) = \sqrt{\frac{\pi z}{2}} J_{n+1/2} (z), \tag{3.67}
\]

\[
\zeta_n (z) = \sqrt{\frac{\pi z}{2}} H_{n+1/2} (z), \tag{3.68}
\]

which are related to Bessel and Hankel functions. The scattering and extinction efficiencies are expected to oscillate considerably when the particle diameter increases as a result of the deposition of carbon produced in the cracking reaction for \( \xi \) between 0.3 and 5 due to refraction phenomena. It is possible to obtain the absorption efficiency as: \( E_{\lambda,abs} = E_{\lambda,ext} - E_{\lambda,sc} \). The absorption and scattering coefficients are then:

\[
\kappa_\lambda = \frac{S_p n_p}{V} E_{\lambda,abs} = \frac{3 f_v}{2 D_p} E_{\lambda,abs}, \tag{3.69}
\]

and

\[
\sigma_{s\lambda} = \frac{S_p n_p}{V} E_{\lambda,sc} = \frac{3 f_v}{2 D_p} E_{\lambda,sc}. \tag{3.70}
\]

According to Mie theory, the phase function is obtained as:

\[
\Phi (\theta) = \frac{1}{4\pi} \int_0^{2\pi} \frac{|S_1|^2 + |S_2|^2}{|S_1|^2 + |S_2|^2} \, d\Omega, \tag{3.71}
\]

where \( S_1 (\theta) \) and \( S_2 (\theta) \) are complex amplitude functions given by:

\[
S_1 (\theta) = \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} \left[ a_n \tau_n (\cos \theta) + b_n \tau_n (\cos \theta) \right], \tag{3.72}
\]
and

\[
S_2(\theta) = \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} [b_n \pi_n(\cos \theta) + a_n \tau_n(\cos \theta)].
\]  

(3.73)

The direction-dependent functions \(\pi_n\) and \(\tau_n\) are dependent on Legendre polynomials \(P_n\):

\[
\pi_n(\cos \theta) = \frac{dP_n(\cos \theta)}{d\cos \theta},
\]

(3.74)

\[
\tau_n(\cos \theta) = \cos \theta \cdot \pi_n(\cos \theta) - \sin^2 \theta \cdot \frac{d\pi_n(\cos \theta)}{d\cos \theta}.
\]

(3.75)

These calculations need to be performed for every discrete wavelength. For the numerical computation, the \textit{bhmie} routine contained in the \textit{hmt} (section 5) library is applied.
Chapter 4

Numerical Methods

Since an analytical solution for the system of equations describing the mass and heat transfer, as well as the chemical kinetics, within the system is impossible due to the complexity of the governing equation system, numerical methods need to be employed. These comprise the spatial and time discretisation of the system, and the simulation of radiative heat transfer.

4.1 The Finite Volume Method

For the spatial discretisation of the system, the Finite Volume Method (FVM) [7] is applied by subdividing it into a finite number of control volumes in which the physical properties are assumed to be constant. In the present case, the infinite slab of thickness $L$ is split up along the $z$-axis, into a stack of sublayers of thickness $\Delta z = L/n_{\text{cell}}$. Thanks to the one-dimensional formulation of the medium properties, a discretisation along the $x$-, and $y$-axes is not necessary. For practical purposes, the extension of the control volumes is chosen to be equal to 1 m in both directions, which gives the size of a sublayer: $\Delta V = \Delta x \Delta y \Delta z = 1 \cdot 1 \cdot \Delta z$. A schematic view of the spatial discretisation of the system according to the FVM is shown in figure 4.1.

Therefore, the smaller the chosen size of the sublayers is, the better is the accuracy of the simulation. For a given thickness $\Delta z$, the conservation equations established in section 3.1 can be expressed for each cell $k$, with $k$ ranging from 0 to $n_{\text{cell}}$. The spatially discretised version of the species conservation equation 3.4 is thus:

$$N_{i,k} (t) = N_{i,k} (t_0) + \Delta V \int_{t_0}^{t} r_i dt$$

(4.1)

This equation is valid for each component $i = (\text{CH}_4, \text{H}_2, \text{C}, \text{Ar})$. The energy conservation equations 3.27 and 3.30, applied to each subvolume, become

$$T_{s,k} (t) = T_{s,k} (t_0) + \Delta V \int_{t_0}^{t} \frac{1}{n_{C,k} c_{p,C,k}}$$

\((q_{r,s,k} - r_{h_2,k} h_{H_2} (T_{s,k}) - r_{c,k} h_{C} (T_{s,k}) - r_{CH_4,k} h_{CH_4} (T_{g,k})) dt\) 

(4.2)
for the solid phase, and

\[
T_{g,k}(t) = T_{g,k}(t_0) + \Delta V \int_{t_0}^{t} \frac{q_{r,g,k} - r_{H_2,k} [h_{H_2} (T_{g,k}) - h_{H_2} (T_{g,k})]}{n_{CH_4,k} c_{p,CH_4,k} + n_{H_2,k} c_{p,H_2,k}} \, dt \tag{4.3}
\]

for the gas phase.

\section{Monte Carlo Method}

An analytical solution of the problem using energy conservation (equations 3.27 and 3.30) and the RTE (equation 3.49) is, even in slightly complex cases, such as the one presented in this thesis, not practicable, mainly due to the difficulty of integrating the wavelength-dependent terms in the RTE. A numerical solution of the problem has thus to be applied. For the computation of the radiative flux into and out of each sublayer of the slab, the pathlength Monte Carlo method \cite{6} is used. In this method, a large number of radiative energy bundles with random characteristics (emission point, direction, wavelength) are created by a computer simulation and their path and interactions with boundaries and participating media are simulated statistically. A schematic representation of the Pathlength Monte Carlo Method is depicted in figure 4.2, and a flowchart in figure 4.3.
4.2. Monte Carlo Method

4.2.1 Generation of Random Variables

For the application of the Monte Carlo Method, the values \( \phi \) of the variables \( \Phi \) associated with each ray have to be generated randomly. At first, random numbers \( R \) between 0 and 1 are obtained by applying a random number generator. \( R \) is then equated with the value of the cumulative distribution function

\[
R = \int_{-\infty}^{\phi} P(\phi^*) d\phi^* \tag{4.4}
\]

which returns the probability of the variable \( \Phi \) to be smaller than \( \phi \) for a given probability density \( P(\phi) \). By integrating equation 4.4, a value \( \phi(R) \) can be obtained.

4.2.2 Ray Energy

In order to start the Monte Carlo simulation, at first the total number of rays \( n_{\text{ray}} \) has to be defined. In this case, transient simulations accounting for the absorptive behaviour of the gas were performed with the total number of rays of \( 10^7 \). Once the value of \( n_{\text{ray}} \) is fixed, the power carried by one ray is obtained by dividing the total radiative power input to the system by the number of rays. The total radiative power input is composed of the radiative flux through the boundary and the power emitted by the medium contained in the control volume \( V = \Delta x \cdot \Delta y \cdot L = 1 \cdot 1 \cdot L \)

\[
q_{r,\text{em}} = q_{r,\text{em},w1} + \sum_{j} q_{r,\text{em},j}, \tag{4.5}
\]
Figure 4.3: Flowchart of the Pathlength Monte Carlo Method algorithm.
with the boundary radiative flux through the surface element \( \Delta x \cdot \Delta y \)

\[
q_{r,\text{em},w1} = q_{\text{solar}} \Delta x \Delta y, 
\]

and the emitted power from each phase \( j \) in the whole control volume \( V \)

\[
q_{r,\text{em},jk} = \int_V 4\sigma\kappa_p \gamma_k T_{jk}^4 \, dV. 
\]

\( \kappa_p \) is the Planck mean absorption coefficient. It corresponds to the average of the spectral absorption coefficient over the whole spectrum, weighed with the blackbody spectral emissive power \( E_{\lambda b} \):

\[
\kappa_p(T) = \frac{\int_0^\infty \kappa_\lambda (\lambda) E_{\lambda b} (\lambda, T) \, \delta \lambda}{\int_0^\infty E_{\lambda b} (\lambda, T) \, \delta \lambda} 
\]

(4.8)

Applying the finite volume method (section 4.1), equation 4.7 can be expressed as sum of the power emitted from each cell volume \( V_k \):

\[
q_{r,\text{em},j} = \sum_{k=1}^{n_{\text{cell}}} q_{r,\text{em},jk} = \sum_{k=1}^{n_{\text{cell}}} 4\sigma\kappa_p \gamma_k T_{jk}^4 V_k. 
\]

(4.9)

The power carried by one ray is thus:

\[
q_{\text{ray}} = \frac{q_{r,\text{em},w1}}{n_{\text{ray}}}. 
\]

(4.10)

A distinction has then to be made between the rays coming through the boundary and those emitted from each phase in every cell. The number of rays which come in through the boundary wall can be found with the following expression:

\[
n_{\text{ray},w1} = n_{\text{ray}} \frac{q_{r,\text{em},w1}}{q_{r,\text{em}}}, 
\]

(4.11)

whereas the number of rays emitted by phase \( j \) in cell \( k \) is given by:

\[
n_{\text{ray},jk} = n_{\text{ray}} \frac{q_{r,\text{em},jk}}{q_{r,\text{em}}}. 
\]

(4.12)

The values obtained for the number of rays have to be approximated to the closest integer since the simulation does not admit any fractions of rays.

### 4.2.3 Starting Point, Direction and Wavelength of a Ray

Once the power carried by one ray is defined, its variables such as starting point, direction and wavelength need to be determined randomly.
Emission Point

For the formulation of the components of the emission point vector \( \mathbf{p} = (x; y; z) \) two different expressions have to be established and applied depending on whether the simulated ray is entering the slab through the boundary wall or is emitted from the medium within the system. However, since the examined slab is extended infinitely in the direction of \( \mathbf{i} \) and \( \mathbf{j} \), radiative equilibrium can be assumed along these directions, what means that the \( x \) and \( y \) components of the net energy flux are equal to 0 for every volume element \( \text{d}V \) of the slab. The \( x \) and \( y \) components of the emission point vector \( \mathbf{p} \) can thus be equated to 0.

The rays coming through the boundary at \( z = 0 \) are therefore all originated in the point

\[
\mathbf{p}_{w1} = \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}, \tag{4.13}
\]

whereas the generic emission point in a cell \( k \) is

\[
\mathbf{p}_k = \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ z_k + R_z \Delta z \end{pmatrix}, \tag{4.14}
\]

with \( z_k \) being the \( z \) coordinate of the boundary between the cells \( k \) and \( k - 1 \), as shown in section 4.1.

Emission Direction

As shown in section 2.4, the solar radiation is assumed to reach the slab perpendicularly to the \( x-y \)-plane. Thus, the ray direction vector is

\[
\hat{\mathbf{u}}_{w1} = \begin{pmatrix} u_x \\ u_y \\ u_z \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}, \tag{4.15}
\]

for the rays coming from the boundary. For those emitted from within the medium, random propagation directions need to be generated. Applying equation 4.4 to the probability densities \( P_\varphi (\varphi) = \frac{2\pi r^2 \varphi}{(4\pi r^2)} \) and \( P_\theta (\theta) = \frac{2\pi r^2 \sin(\theta) \text{d}\theta}{(4\pi r^2)} \) gives the following values for the direction angles \( \varphi \) and \( \theta \) of the ray:

\[
\varphi = 2\pi R_\varphi, \tag{4.16}
\]
\[
\theta = \arccos (1 - 2R_\theta) \tag{4.17}
\]

The transformation from spherical to Cartesian coordinates yields the vector which indicates the propagating direction of a random ray emitted from within the medium:

\[
\hat{\mathbf{u}}_{em} = \begin{pmatrix} u_x \\ u_y \\ u_z \end{pmatrix} = \begin{pmatrix} \sin \theta \cos \varphi \\ \sin \theta \sin \varphi \\ \cos \theta \end{pmatrix}, \tag{4.18}
\]
4.2. Monte Carlo Method

Wavelength  For the determination of the wavelength, the randomly generated number \( R_\lambda \) is equated to the distribution function of the wavelength:

\[
R_\lambda = \frac{\int_0^{\lambda} \kappa_\lambda (\lambda^*) I_{\lambda b} (\lambda^*, T) \, d\lambda^*}{\int_0^{\infty} \kappa_\lambda (\lambda^*) I_{\lambda b} (\lambda^*, T) \, d\lambda^*} = \frac{1}{\kappa_0 \sigma T^4} \int_0^{\lambda} \kappa_\lambda (\lambda^*) I_{\lambda b} (\lambda^*, T) \, d\lambda^*
\]

(4.19)

Since the spectral distribution of the radiation intensity of the rays coming in through the boundary is assumed to be that of a blackbody at \( T_{\text{sun}} = 5780 \, \text{K} \), in this case the spectral absorption coefficient is equal to 1, which allows to simplify equation 4.19 and obtain:

\[
R_\lambda = \frac{\int_0^{\lambda} I_{\lambda b} (\lambda^*, T_{\text{sun}}) \, d\lambda^*}{\sigma T_{\text{sun}}^4} = F_{0-\lambda T_{\text{sun}}},
\]

(4.20)

where \( F_{0-\lambda T} \) is the fractional function. The random value of the wavelength is thus:

\[
\lambda = \frac{F^{-1} (R_\lambda)}{T_{\text{sun}}}.
\]

(4.21)

For emission from the medium, no blackbody assumption can be made, since the absorption coefficient \( \kappa_\lambda \) is dependent on the wavelength of emission, and thus equation 4.19 has to be applied.

4.2.4 Ray Tracing

As all the variables of the ray are defined, it is traced through the medium in order to obtain the power flux into the single cells. For the ray-tracing part of the Monte Carlo Method, all rays, independently on where they are originated, can be treated the same way, since this does not affect their behaviour. Between different approaches of solution for the Monte Carlo simulation, the Pathlength Method [6] is chosen because of its good performance in heavily scattering media since the absorbed power is distributed among all sublayers crossed by the ray.

In the Pathlength Method, for every ray, the pathlength \( s \) to the next scattering event is determined randomly. To obtain the pathlength in function of a random number \( R_s \), equation 3.42 is applied and the radiation intensity \( I_\lambda \) substituted by the ray power \( q_{\text{ray}} \). Integration over a path \( s \) yields the power left in a ray after that distance:

\[
q_{\text{ray}} (s) = q_{\text{ray,0}} \exp \left( -\int_0^s \sigma_{\lambda s} (s^*) \, ds^* \right).
\]

(4.22)

The power removed from the ray due to scattering is therefore:

\[
q_{\text{ray,sc}} (s) = q_{\text{ray,0}} \left[ 1 - \exp \left( -\int_0^s \sigma_{\lambda s} (s^*) \, ds^* \right) \right],
\]

(4.23)

which, divided by \( q_{\text{ray,0}} \), corresponds to the cumulative distribution function of the probability of scattering occurring at the location \( s \) and can therefore be equated to \( R_s \). This
yields the following expression for random determination of the scattering distance if the finite volume approach is used:

\[ \ln R_s = \int_0^s \sigma_{\lambda_s}(s^*) \, ds^* = \sum_k \sigma_{\lambda_s,k} s_k, \]  \hspace{1cm} (4.24) 

where \( k \) denotes a cell and \( s_k \) is the pathlength of the ray in that cell, which, given its starting point \( \mathbf{p} \) and direction vector \( \mathbf{u} \), can be obtained by applying simple analytic geometry relationships.

As the point in which the scattering event takes place is determined, the power absorbed by each cell traversed by the ray can be calculated by integrating equation 3.37 over the travelled path, obtaining thus the power remaining in the ray after the distance \( s \):

\[ q_{\text{ray}}(s) = q_{\text{ray},0} \exp \left( -\int_0^s \kappa_s (s^*) \, ds^* \right). \]  \hspace{1cm} (4.25) 

The power absorbed by each cell is therefore given by

\[ q_{\text{r},\text{abs},k} = q_{\text{ray},k} \left[ 1 - \exp \left( \kappa_s k s_k \right) \right]. \]  \hspace{1cm} (4.26) 

\( q_{\text{ray},k} \) is the energy of the ray at its entry into cell \( k \). Since the medium is composed of two different phases, the absorbed power in each phase needs to be computed. The power absorbed in each phase \( j \) is given by:

\[ dq_{\text{r},\text{abs},jk} = \kappa_{\lambda,jk} q_{\text{ray}}(s_k) \, ds_k = \kappa_{\lambda,jk} q_{\text{ray},k} \exp \left( -\kappa_s k s_k \right) \, ds_k, \]  \hspace{1cm} (4.27) 

which integrated over the pathlength \( s_k \) yields:

\[ q_{\text{r},\text{abs},jk} = \frac{\kappa_{\lambda,jk}}{\kappa_{\lambda,k}} q_{\text{ray},k} \left[ 1 - \exp \left( -\kappa_s k s_k \right) \right] = \frac{\kappa_{\lambda,jk}}{\kappa_{\lambda,k}} q_{\text{r},\text{abs},k} \]  \hspace{1cm} (4.28) 

The tracing of the ray and the computation of absorbed energy in each phase is continued through all affected cells until:

- the scattering distance calculated in equation 4.24 has been covered by the ray, or
- the power of the ray has been absorbed, or
- the ray leaves the system through a boundary.

In the last two cases, the tracing of the ray is stopped and the procedure for the following ray is started.

### 4.2.5 Scattering Direction

If the ray reaches the scattering point, its propagation direction needs to be recomputed by determining a random scattering direction which depends on the probability distribution the scattering phase function \( \Phi_\lambda(\theta, \lambda) \), whose distribution over the polar cone angle \( \theta \) depends on the complex refractive index \( m \) of the particle material and on the size parameter \( \xi = \pi D_p/\lambda \). Since the phase function does not depend on the angle \( \varphi \), the probability
distribution function of $\varphi_{sc}$ is uniform, what yields the following expression for its random determination:

$$\varphi_{sc} = 2\pi R_{sc}. \quad (4.29)$$

The expression for the elevation angle is more complicated [27]:

$$\theta_{sc} = \frac{1}{2} \int_{0}^{\theta_{sc}} \Phi_\lambda(\theta^*_{sc}) \sin \theta^*_{sc} d\theta^*_{sc}. \quad (4.30)$$

Attention has to be paid to the fact that the scattering angles are not expressed in the absolute coordinate system, but relatively to the incoming ray’s propagation direction $\hat{s}_i$. The direction of the scattered ray $\hat{s}$ has thus to be obtained via a coordinate transformation. This is done by defining a new coordinate system, whose $x$-direction is given by the direction of the incoming ray:

$$\hat{i}_{sc} = \hat{u}. \quad (4.31)$$

To get the $y$ and $z$ directions of the scattering coordinate system, the cross product of $\hat{i}_{sc}$ with a freely chosen non-parallel vector, in this case $\hat{k}$, is calculated:

$$\hat{j}_{sc} = \hat{i}_{sc} \times \hat{k}, \quad (4.32)$$

with the corresponding unit vector

$$\hat{j}_{sc} = \frac{\hat{j}_{sc}}{|\hat{j}_{sc}|}. \quad (4.33)$$

The third coordinate vector, perpendicular to the other two, is then:

$$\hat{k}_{sc} = \hat{i}_{sc} \times \hat{j}_{sc}. \quad (4.34)$$

The path direction of the ray in the main coordinate system becomes then:

$$\hat{u}_{sc} = \cos \theta_{sc} \cdot \hat{i}_{sc} + \sin \theta_{sc} \cos \varphi_{sc} \cdot \hat{j}_{sc} + \sin \theta_{sc} \sin \varphi_{sc} \cdot \hat{k}_{sc}. \quad (4.35)$$

Once this direction is known, the ray-tracing described in section 4.2.4 is restarted.

### 4.2.6 Precision of the Monte Carlo Method

Since the results Monte Carlo Method are statistically distributed and their accuracy is dependent on the number of employed rays, it is possible to reduce the uncertainty of the results by increasing the number of rays for the simulations. An estimation of the statistical error due to the application of the Monte Carlo Method is carried out in Appendix B.1.

### 4.3 Time Discretisation

The integration of equations 4.1-4.3 over the time step $\Delta t = t - t_0$ is not practicable analytically since the distribution over time of the terms which need to be integrated are not known, but depends on the temperature and the species’ concentrations which are results of the very same integrals. A solution of the system of equations is therefore to be found employing numerical methods for transient problems which are called time
integration schemes (TIS). Considering a general initial value problem for the variable value $\phi(t)$:
\[
\frac{d\phi(t)}{dt} = f(t, \phi(t)), \quad \phi(t_0) = \phi^0. \tag{4.36}
\]
A solution for $\phi$ at any time can be found by a stepwise integration of equation 4.36 over time step intervals $\Delta t = t_{n+1} - t_n$:
\[
\int_{t_n}^{t_{n+1}} \frac{d\phi(t)}{dt} dt = \phi^{n+1} - \phi^n = \int_{t_n}^{t_{n+1}} f(t, \phi(t)) dt, \tag{4.37}
\]
where $\phi^n = \phi(t_n)$ is the initial value of $\phi$ which is found by carrying out the previous time step. If the time step $\Delta t$ is small enough, the integral on the right hand side of equation 4.37 can be approximated using one out of several existing integration methods [21]. The better suitable for the kind of simulations performed in the frame of this thesis are deemed to be explicit schemes which do not require input values at $t_{n+1}$ which have to be found iteratively what would lead to excessive computation times when the radiative heat rate $q_r$, contained in function $f$ is determined by the Monte Carlo Method. For this case, the explicit Euler scheme
\[
\phi^{n+1} = \phi^n + f(t_n, \phi^n) \Delta t, \tag{4.38}
\]
is used. This TIS is then applied to equations 4.1, 4.2 and 4.3 to obtain the time-discretised versions of the conservation equations, which become thus:
\[
N_{ik}^{n+1} = N_{ik}^n + r_{ik} \Delta V \Delta t \tag{4.39}
\]
for the conservation of molar mass of each species $i$. The energy conservation for the solid phase is:
\[
T_{s,k}^{n+1} = T_{s,k}^n + \frac{1}{n_{C,k}c_{p,C,k}} \left[ q_{r,s,k} - r_{H_2,k} h_{H_2} (T_{s,k}) - r_{C,k} h_{C} (T_{s,k}) - r_{CH_4,k} h_{CH_4} (T_{g,k}) \right] \Delta V \Delta t, \tag{4.40}
\]
and for the gas phase:
\[
T_{g,k}^{n+1} = T_{g,k}^n + \frac{q_{r,g,k} - r_{H_2,k} h_{H_2} (T_{g,k}) - r_{H_2,k} h_{H_2} (T_{g,k})}{n_{CH_4,k}c_{p,CH_4,k} + n_{H_2,k}c_{p,H_2,k}} \Delta V \Delta t \tag{4.41}
\]
for the gas phase. An assessment of the errors in numerical calculation due to the application of discrete time steps is presented in Appendix B.2.
Chapter 5

Calculations

The simulation was performed using the *GasPar* Fortran 90 code which bases on [14] built to simulate radiative transfer in a two-phase medium with shrinking particles. Several modifications to the code are done in order to adapt it to the present problem:

- Insertion of the thermochemical data of relevant materials in the input files;
- Insertion of the optical properties of the carbon particles in the input file;
- Construction of a steady state solver subroutine *steadysol* in the *sol* module;
- Modification of the *rad* module to allow for the input of the optical properties of the gas phase;
- Coding of the *Gas* routine (section 5.4.1), not directly linked to *GasPar*, which is used to process the gas optical properties obtained from HITRAN to make them suitable to be used as input for the *GasPar* routine;
- Adaptation of all the relevant modules to allow for the gas and particle properties to be treated independently of each other and thus allowing for different wavelength intervals at which the optical properties for gas and particles are defined;
- Modification of the output system and of the output files;
- Insertion of the chemical kinetic parameters in the relevant input file

5.1 Program Structure

The *GasPar* program is built up in a modular way with a *main* module from which the calculation is started by calling up the *sol* module. There, the computation time or iteration steps are carried out and the relevant submodules called up. These are divisible in the following main groups depending on their purpose:

- Modules which carry out the main calculation process:
  - *sol*,

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- mca;

- Calculation of the relevant system parameters (geometrical, physical) to provide to the actual calculation modules:
  - grd,
  - mat,
  - opt,
  - var,
  - chem;

- Modules regulating the input/output of the calculation
  - io,
  - output;

- Auxiliary modules which carry out determined smaller tasks (such as basic functions of analytic geometry, radiative heat transfer, numerics, or logic):
  - rng,
  - the entire hmt library.

The hierarchic structure of the GasPar program is shown in figure 5.1. Totally 12 modules are part of the GasPar program, in addition to the more than 20 modules of the hmt library. Their modular structure allows for simple replacement of single program components or for implementation of new ones.
5.1.1 Principal Modules

main.f90

Main module from where the program is started. Its only functions are calling up the subroutines contained in sol.f90 and calculate the computation time.

sol.f90

The core of the *GasPar* program which performs the main calculation. Initialises all other submodules and calls all subroutines necessary to define the system and material properties. During every time or iteration step, the rad and chem modules are called up to compute the reaction rate and the net radiative heat flux in each sublayer. Then, a mass and an energy balance are carried out for every sublayer and each phase, in order to update the variable properties of the medium according to the explicit Euler time integration scheme (section 4.3). The contained subroutine solve is used to provide a solution for transient conditions. For steady state conditions, the subroutine steadysol is applied. In this case, an iterative correction of the layer temperatures is performed until the radiative flux divergence in each cell and phase approaches 0. Input data regarding the final computation time, the amplitude of the time steps and the control times at which data is passed to the output files is read in from the data file InputSolv.dat

grd.f90

Generates the discretised grid from the geometric data of the control system and the chosen number of sublayers taken from InputGrd.dat. Computes the volume of the cells, the area of the boundary planes and the z-coordinates of the sublayers and their boundaries.

mat.f90

Reads in the number of medium components, their phase, and the coefficients for the computation of the specific heat \( c_p \), as well as molar mass \( M \) and the density \( \rho \) from the data file InputMat.dat. Provides the functions getrho, getcp and geth to compute the density, the specific heat and the specific enthalpy of each component in function of their temperature.

var.f90

Initialises all time-variable parameters of the simulation based on the initial values provided in InputVar.dat. These are mainly temperature, radiative flux, particle size and volume fraction, and the partial pressures of the gaseous components.

chem.f90

Computes the rate of the cracking reaction based on the kinetic parameters from InputChem.dat.
rad.f90
Calls the modules opt.f90 and mca.f90.

opt.f90
Computes the optical properties (spectral absorption coefficient of both phases and the solid phase spectral scattering coefficient and phase function) in dependence of pressure, temperature, volume fraction and particle size. As these properties change at every time or iteration step they need to be recomputed each time. The input data is taken from InputSoot.dat (number of wavelength intervals and of discrete angle steps for the phase function; complex refractive indices) for the particles and from InputCH4.dat (number of wavelength, temperature and pressure intervals), as well as from CH4/0300.dat to CH4/1500.dat (spectral absorption coefficients) for the gas phase (see also Appendix C.1.

mca.f90
Applies the Pathlength Monte Carlo Method starting from the data provided by opt.f90 and by the input file InputMC.dat (number of rays, random number generator seed).

io.f90 and output.f90
Specify the input and output files and their formats. Output file paths are taken from InputOut.dat.

hmt library
Contains auxiliary functions which are needed by the GasPar routines, such as the fractional function, Mie scattering, Planck absorption coefficient, several vector analysis functions used in the Monte Carlo routine, and a collection of physical constants.

5.2 Algorithm
A schematic overview of the entire calculation procedure is shown in figure 5.2. The fundamental equations applied in the code are the following:

Initial values of variables
Starting values given in InputVar.dat are computed for every cell:

- Initial temperature of both phases \( T_{s,0} = T_{g,0} \);
- Radiative heat flux through each boundary \( i \) \( (q_{w,i}) \), or boundary face temperatures \( (T_{w,i}) \);
- Particle size \( (D_p) \);
- Solid phase volume fraction \( (f_v) \);
Figure 5.2: Schematic view of the numerical calculation procedure.
Partial pressure of each gas component $i$ ($p_i$).

Derivation of dependent variables in `sol.f90`

- Initial molar quantity of carbon ($N_{C,0}$) from equation 3.15;
- Initial molar quantity of methane and argon ($N_{CH_4,0}$, $N_{Ar,0}$) from equation 3.16;
- Verification of the presence of each phase and component in each cell;
- Initial number of particles ($N_{p,0}$) from equation 3.22;

**TimeLoop**

During each time loop, the variable system properties are updated, based on the temperature variation of the medium. The loop is repeated until the end time of the simulation, specified in `InputSolv.dat` is reached. Updated variables for each cell are:

- Density of the solid phase ($\rho_C (T_s)$) using the `getrho` function contained in the `mat.f90` module;
- Volume fraction of the solid phase ($f_v (n_C, \rho_C)$) from equation 3.14;
- Specific heat coefficient of all involved species ($c_{p,i} (T_i)$) based on the polynomial approximation parameters given in `InputMat.dat` computed using the function `getcp` contained in the `mat.f90` module;
- Diameter of the carbon particles ($D_p (f_v, n_p)$) from equation 3.23.

Subsequently, a mass sink is applied in every cell in order to maintain isobaric conditions of the medium:

- Molar fraction of all components ($\bar{x}_i$);
- Total number of moles after mass sink ($N_{tot}$), according to equation 3.21;
- New molar quantities for each species ($N_i (t)$);
- New volume fraction of the solid phase ($f_v (N_C, \rho_C)$) from equation 3.14;
- New partial pressures of the gaseous species ($p_i (N_i, T_g, f_v)$) using the ideal gas equation;
- New number of particles ($n_p (f_v, D_p)$) applying equation 3.22.

Then the radiation part of the computation is called up via the subroutine `radsrs` contained in the `rad.f90` module, which at first updates the optical properties of the medium and then applies the Pathlength Monte Carlo Method, yielding the net radiative flux ($q_{r,jk}$) into each cell and phase.

Calling up the subroutine `rate` from the `chem.f90` module, the chemical reaction rate of methane ($r_{CH_4} (T_s, p_{CH_4}, M_C)$) is computed according to equation 3.36.

Mass and energy conservation can then be applied for each cell and phase:
• Chemical reaction enthalpy for both phases \( \Delta H_{\text{chem}}(r, T_s, T_g) \) using the function geth from the mat.f90 module;

• Update of temperatures \( (T_s, T_g) \) applying energy conservation from equations 3.27 and 3.30;

• Computation of new molar quantities for each species \( (n_i) \) using mass conservation from equation 3.4;

• Verification of the presence of each phase and component in each cell;

• Increase the time by one time step \( \Delta t \).

**Radiative Transfer**

Once the radiative transfer is called up, the optical properties of both phases are updated according to the system conditions, and the following computational steps are performed for each cell:

• Application of Mie scattering theory by calling up the bhmie subroutine from the hmt library to obtain the spectral absorption coefficient \( (\kappa_{\lambda,s}) \), the spectral scattering coefficient \( (\sigma_{\lambda,s}) \), and the spectral phase function \( (\Phi_{\lambda,s}(\theta)) \) at discrete wavelengths and, in the case of the phase function, for discrete angles \( \theta \);

• Summation of the phase function over all angles using the trapezoidal rule [21]. For each angle \( i \), the approximated integral of the phase function up to that angle is given:

\[
(\sum \Phi)_i = (\sum \Phi)_{i-1} + \frac{1}{2} (\Phi_{i-1} \sin \theta_{i-1} - \Phi_i \sin \theta_i) \tag{5.1}
\]

This sum is later used for the random determination of the scattering angle \( \theta \) during the application of the Monte Carlo Method.

• Planck’s mean absorption coefficient \( (\kappa_{P,s}(T_s)) \) from equation 4.8 using the subroutine kplnck contained in the hmt library;

• Spectral extinction coefficient of the solid phase \( (\beta_{\lambda,s}) \).

• Reading in of the spectral absorption coefficient values of the gas phase \( (\kappa_{\lambda,g}(T_g, p_{\text{CH}_4})) \);

• Determination of Planck’s mean absorption coefficient for the gas phase \( (\kappa_{P,g}(T_g)) \) from equation 4.8 using the subroutine kplnck contained in the hmt library;

In the next step, the Monte Carlo calculation is carried out by calling up the subroutine mc in the mca.f90 module for the given system parameters and with the chosen number of rays. A detailed description of the procedure and of the applied equations is provided in section 4.2. As result, the net radiative flux into each cell and phase is obtained and can be used when applying energy conservation.
Chapter 5. Calculations

5.3 Hardware and Software

The Fortran 90 coding was done using the Compaq Visual Fortran 6.6.0 compiler on Microsoft Windows XP as operating system. Calculations were performed on three different workstations:

- HP pavilion ze4300, Intel Pentium 4 2.2 GHz, 448 MB RAM;
- HP pavilion ze4200, Intel Celeron 2.0 GHz, 448 MB RAM
- Acer TravelMate, Intel Centrino 1.4 GHz, 720 MB RAM

Computation times vary depending on the used workstation and on the input parameters. The most time-expensive calculations were those with big solid phase volume fractions \( f_v \) and small particle diameters \( D_p \). Shortest computation times are about 80 hours, whereas the longest calculation takes 160 hours.

5.4 Auxiliary Programs

5.4.1 Gas Properties

To make the data for the spectral absorption coefficient of methane suitable for being processed by the GasPar program, the program Gas is written. Its purpose is that of reading in the spectral data for \( \kappa_{\eta, \text{CH}_4} \) which are given in a separate text file for each temperature and partial pressure, and produce input files for the GasPar program containing band-averaged values for \( \kappa_{\lambda, g} \) in function of the wavelength \( \lambda \). Further, the data for all considered partial pressures are merged, requiring thus only one input file for each temperature. Its submodules are the following:

inp.f90

Reads in the data for all wavelengths and pressures at a chosen temperature, transforms wavenumbers in wavelengths and sets up the approximation bands specified in the file input.dat. Smaller band widths can be chosen in the regions of the spectrum where stronger variations of \( \kappa_{\eta, \text{CH}_4} \) are observed to increase the accuracy of the model. Finally, for each specified band, the Simpson rule (module simp) is called up to obtain a mean spectral absorption coefficient. Results are then written in the specified output file.

simp.f90

Applies the Simpson rule to calculate the value of an integral based on a discrete quantity of given points by fitting a parabolic curve to the data set.
Chapter 6

Results

Numerical simulations of both steady state and transient cases are performed. Whereas the for the steady state solutions no gas phase is considered, transient calculations include the model for the optical properties of the gas phase, as described in section 3.4.2. This goes also for the chemical kinetics: steady state solutions do not account for the chemical cracking reaction taking place in the system.

6.1 Steady State Simulation

The main purpose of the steady state simulation is that of obtaining information about the distribution of the particle temperature $T_s$ over the system when it is exposed to concentrated solar radiation. It is possible to gain a first overview on the influence of the different parameters on the radiation heat balance of the system, allowing to chose the parameter ranges for the transient simulations which are expected to give the most meaningful results.

6.1.1 Parameters

The steady state runs are carried out using the following simulation parameters:

- Incoming solar power flux: $q_{solar} = 10^6 \text{ W m}^{-2}$;
- Number of rays in Monte Carlo simulation: $10^6$;
- Number of sublayers: 20.

Particle diameter and solid phase volume fraction are varied between every simulation to study their influence on the system.

6.1.2 Influence of Particle Volume Fraction

For these simulations, the particle size is kept constant at $D_p = 2.5 \mu$m whereas the solid volume fraction is changed from $f_v = 10^{-6}$ to $10^{-5}$ and to $10^{-4}$. The obtained spatial particle temperature distribution is shown in figure 6.1. It can be seen that the temperature
distribution is getting flatter for decreasing $f_v$, whereas higher volume fractions cause it to show a peak around $z = 0.02 \text{ m}$ or 20% of the slab thickness. Even though the incoming radiation intensity is maximal at $z = 0$, the highest temperature is not obtained at that point since at the boundary faces the loss of emitted radiation is higher than inside the system. The higher maximal temperature reached for bigger volume fractions is a consequence of more radiative energy being absorbed by the particles since the absorption coefficient $\kappa_{\lambda,s}$ is directly proportional to $f_v$. However, when more power is absorbed in the front of the slab, the amount of radiation getting through it diminishes, causing thus the temperature in the back of the system to be significantly lower (in this case less than 65% of $T_{s,\text{max}}$ for $f_v = 10^{-4}$). Knowing that Bouguer’s Law states that the radiation intensity loss due to extinction is proportional to its initial intensity, the almost linear distribution of $T_s(z)$ for small $f_v$ indicates that the intensity of the rays crossing the system does hardly vary and thus a considerable fraction of the incoming radiation traverses the system and leaves through the opposite wall without interacting with the medium. It appears therefore necessary to find a good compromise between high absorption and therefore higher but more unevenly distributed temperatures and low absorption and the consequent greater loss of power and more constant but lower temperatures. A volume fraction of $10^{-5}$ seems to be a good choice since it allows for temperatures over 1500 K and $T_{s,\text{min}}$ is about 90% of $T_{s,\text{max}}$. 

Figure 6.1: Steady state spatial temperature distribution of the particles for $D_p = 2.5 \mu\text{m}$ and varying volume fractions.
6.1.3 Influence of the Particle Size

When the volume fraction is kept constant at $f_v = 10^{-5}$ and steady state simulations are run for $D_p = 1 \mu m$, $D_p = 2.5 \mu m$, and $D_p = 10 \mu m$, the spatial temperature distribution of the particles shown in figure 6.2 is obtained. The same effect as in figure 6.1 can be observed since the spectral absorption coefficient of the carbon black particles is smaller for big diameters in the relevant wavelength range, as can be seen in figure 3.3. This goes also for the spectral scattering coefficient (figure 3.4). Thus, at constant solid volume fraction, the participating medium is optically thicker for small particles. A diameter of 2.5 $\mu m$ offers a good compromise between too high absorption in the front of the slab for smaller particles and too big losses through the backside wall for bigger ones.

6.2 Transient Simulation

Transient simulations are carried out to study the behaviour of a two-phase medium composed of solid particles suspended within a gas flow for different initial parameters while accounting for the optical properties of both phases, and the chemical reaction. The results from totally 10 transient simulations are available, with their main fixed parameters listed in table 6.1.
Table 6.1: Fixed parameters for all transient calculations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slab thickness</td>
<td>$L = 0.1$ m</td>
</tr>
<tr>
<td>Number of sublayers</td>
<td>$n_{\text{cell}} = 50$</td>
</tr>
<tr>
<td>Solid phase wavelength intervals</td>
<td>$n_{\lambda,s} = 234$</td>
</tr>
<tr>
<td>Solid phase scattering angle intervals for approximation of $\Phi(\theta)$</td>
<td>$n_{\theta,s} = 100$</td>
</tr>
<tr>
<td>Gas phase wavelength intervals</td>
<td>$n_{\lambda,g} = 5005$</td>
</tr>
<tr>
<td>Number of rays in Monte Carlo simulation</td>
<td>$n_{\text{ray}} = 10^7$</td>
</tr>
<tr>
<td>Initial temperature</td>
<td>$T_{s,0} = T_{g,0} = 300$ K</td>
</tr>
<tr>
<td>Temperature of the blackbody radiation source</td>
<td>$T_{\text{sun}} = 5780$ K</td>
</tr>
<tr>
<td>Temperature of boundary wall at $z = L$</td>
<td>$T_{w2} = 0$ K</td>
</tr>
<tr>
<td>Emissivity of boundary walls</td>
<td>$\varepsilon_{w1} = \varepsilon_{w2} = 1$</td>
</tr>
<tr>
<td>End time of the simulation</td>
<td>$t_{\text{end}} = 0.5$ s</td>
</tr>
<tr>
<td>Time step for $t &lt; 0.05$ s</td>
<td>$\Delta t = 5 \cdot 10^{-4}$ s</td>
</tr>
<tr>
<td>Time step for $t &gt; 0.05$ s</td>
<td>$\Delta t = 2.5 \cdot 10^{-3}$ s</td>
</tr>
</tbody>
</table>

Table 6.2: Summary of individual initial parameters of the transient simulation runs.

<table>
<thead>
<tr>
<th>designation</th>
<th>$x_{\text{CH}_4,0}$</th>
<th>$d_{\text{p},0}$</th>
<th>$f_{v,0}$</th>
<th>$q_{\text{w1}}^0$</th>
<th>chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>ref</td>
<td>0.5</td>
<td>2.5</td>
<td>$10^{-5}$</td>
<td>$10^6$</td>
<td>YES</td>
</tr>
<tr>
<td>1</td>
<td>1.0</td>
<td>2.5</td>
<td>$10^{-5}$</td>
<td>$10^6$</td>
<td>YES</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>2.5</td>
<td>$10^{-5}$</td>
<td>$10^6$</td>
<td>YES</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>1.0</td>
<td>$10^{-5}$</td>
<td>$10^6$</td>
<td>YES</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>5.0</td>
<td>$10^{-5}$</td>
<td>$10^6$</td>
<td>YES</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>10.0</td>
<td>$10^{-5}$</td>
<td>$10^6$</td>
<td>YES</td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
<td>2.5</td>
<td>$5 \cdot 10^{-5}$</td>
<td>$10^6$</td>
<td>YES</td>
</tr>
<tr>
<td>7</td>
<td>0.5</td>
<td>2.5</td>
<td>$5 \cdot 10^{-6}$</td>
<td>$10^6$</td>
<td>YES</td>
</tr>
<tr>
<td>8</td>
<td>0.5</td>
<td>2.5</td>
<td>$10^{-5}$</td>
<td>$2000$ K</td>
<td>YES</td>
</tr>
<tr>
<td>9</td>
<td>0.5</td>
<td>2.5</td>
<td>$10^{-5}$</td>
<td>$10^6$</td>
<td>NO</td>
</tr>
</tbody>
</table>

6.2.1 Summary of Simulation Runs

Table 6.2 summarizes all performed transient simulations with their principal variable parameters. The response to the variation of three different initial parameters is investigated: mole fraction of CH$_4$ ($x_{\text{CH}_4,0}$), particle diameter ($D_{\text{p},0}$), and solid phase volume fraction ($f_{v,0}$). Further, one simulation without chemical reaction and one assuming radiation from the heated boundary wall are performed. Simulation ref is chosen as reference case, from which the data sets for the other runs are obtained by modifying one single parameter in order to exclude the simultaneous influence of several different initial conditions, facilitating thus the evaluation of the results.
6.2. Transient Simulation

6.2.1 Influence of Chemical Reaction

The influence of the chemical reaction on the system behaviour is analysed by comparing the reference simulation \( ref \) (with chemical model) to simulation \( 9 \) (without chemical model). Figure 6.3 shows the influence of the chemical reaction on both phases’ temperature in the first sublayer to be practically negligible. This is mainly due to the fact that the reaction progresses at a relatively slow rate for the reached \( T_s \) of about 1550 K and thus the difference is hardly distinguishable. It is expected that for higher temperatures the effect of the chemical reaction would be better visible. The same observations apply to the spatial distribution of the particle temperature (figure 6.4), whereas figure 6.5 shows that the gas temperature for the case with chemical reaction is slightly higher than without. This corresponds with the expectations since the enthalpy released by the \( \text{H}_2 \) produced during the reaction when cooling down from \( T_s \) to \( T_g \), causes the temperature of the gas to rise, whereas the particle temperature is expected to be lower when the reaction is running, as it gives off part of its thermal energy into chemical reaction heat.

6.2.2 Influence of Methane Molar Fraction

The comparison of the results of the reference simulation with runs \( 1 \) and \( 2 \) allows to evaluate the influence of different initial \( \text{CH}_4 \) mole fractions. Considering equation 3.36, it is expected that lower \( \tilde{x}_{\text{CH}_4} \) cause the chemical reaction to proceed more slowly.
Figure 6.4: Spatial particle temperature distribution at different control times with and without chemical reaction.

Figure 6.5: Spatial gas temperature distribution at different control times with and without chemical reaction.
Temperature Distribution

Figure 6.6 shows the transient time curve of both phase temperatures for different initial \( x_{CH_4} \). The gas temperature can be seen to be increasing faster for higher methane molar fractions due to the bigger optical thickness of the gas phase. On the other hand, the particle phase temperature is higher by about 50 K for \( x_{CH_4,0} = 0.1 \) than for \( x_{CH_4,0} = 1 \). This can be explained by the lower reaction rate, as shown in figure 6.7 and the consequent less reaction heat removed from the particles.

Chemical Reaction

The reaction rate is proportional to the square root of methane partial pressure (equation 3.36) which, on its part is directly proportional to its molar fraction. This relationship can effectively observed in figure 6.7. Secondly, all \( r_C \) increase fast during the heating up of the particles, as it is exponentially dependent on \( T_s \). However, due to the rarefaction of the medium because of thermal expansion of the gas, carbon particles which act as catalyst for the cracking reaction are removed from the system, reducing thus the reaction speed. As a consequence of the higher reaction rate, the diameter of the carbon particles increases at a faster pace for higher CH\(_4\) fractions, as can be seen in figure 6.8.

Optical Properties

Figure 6.9 shows the Planck mean absorption coefficient \( \kappa_P \) for both phases at their respective temperatures. Due to the assumption of a constant \( \kappa_{\lambda,g} \) over discrete temperature
Figure 6.7: Transient carbon reaction rate curves for different initial CH\textsubscript{4} molar fractions at \( z = 0.001 \) m.

Figure 6.8: Particle diameter growth in function of time for different initial CH\textsubscript{4} molar fractions at \( z = 0.001 \) m.
ranges, once the particle temperature enters another range, a sudden change in the Planck mean absorption coefficient can be observed. This effect can be such pronounced to make the interpretation of the data very difficult. The absorption coefficient of the particles increases fast from about 6 to slightly more than 8 m\(^{-1}\) in the first few milliseconds of the simulation due to the increasing of temperature which moves the Planck blackbody spectral distribution of emissive power towards smaller wavelengths where \(\kappa\lambda\) is higher. When the particle temperature reaches a nearly constant level, \(\kappa_{P,s}\) slowly decreases, partly because of the fact that the absorption coefficient for bigger particles is generally lower, but mainly due to the removal of particles from the system to account for thermal expansion of the gas where they are carried in.

### 6.2.4 Influence of Solid Phase Volume Fraction

The volume fraction of the solid phase does directly influence the absorption coefficient of that phase, as already shown in the steady state case (section 6.1.2). Further, the amount of carbon particles present in the system does influence the cracking reaction rate, by acting as a catalyst. To evaluate this influence, the results of the reference simulation \((f_{v,0} = 10^{-5})\) are compared to simulation 6 \((f_{v,0} = 5 \cdot 10^{-5})\) and 7 \((f_{v,0} = 5 \cdot 10^{-6})\).

#### Temperature Distribution

Figure 6.10 clearly shows the possibility of achieving higher temperatures for both the particles (1700 K) and the gas (750 K at \(t = 0.4\) s) when increasing the solid volume...
Figure 6.10: Transient particle and gas temperature curves for different initial solid phase volume fractions at $z = 0.001$ m.

Figure 6.11: Spatial distribution of the particle temperature for different initial solid phase volume fractions.
fraction in the system. Whereas $T_s$ is mainly influenced by the higher absorption coefficient
(proportional to $f_v$), the higher gas temperature is a consequence of that fact, since more
radiation in the infrared range is being emitted by the particles and absorbed by the
methane which absorbs mainly in said spectral range. Secondly, as described in section
6.2.2, the gas is heated by the reaction product $H_2$.

The spatial distributions of both temperatures at selected control times, shown in
figures 6.11 and 6.12 confirm the observation, made for the steady state solution, that the
stronger absorptive behaviour of the medium favours higher temperatures in the front of
the slab, but lets little radiation reach the back. In fact, at $t = 0.05$ s, for the reference
case, more than 50% of the incoming radiation is lost through the opposite wall, but for
the case with $f_{v,0} = 5 \cdot 10^{-5}$, 50% of it is absorbed before $z = 0.022$ m and 90% before
$z = 0.07$ m.

**Chemical Reaction**

The carbon reaction rates in function of time shown in figure 6.13 can be increased by
about a factor 10 between the reference case and the case with a five times greater solid
volume fraction. This has also a positive influence on the particle diameter (figure 6.14
which increases by 4% in 0.4 s, compared to 0.8% in the same lapse of time for the reference
case. After 0.1 s, $CH_4$ conversion is 10 to 20 times higher than in the reference case in the
front of the slab as can be seen in figure 6.15. However, for high $f_v$, $X_{CH_4}$ decreases rapidly
when going towards the back of the slab. Nevertheless, the overall methane conversion over
the whole system appears to be significantly higher in the simulation with $f_{v,0} = 5 \cdot 10^{-5}$.
Figure 6.13: Transient carbon reaction rate curves for different initial solid phase volume fractions.

Figure 6.14: Particle diameter growth in function of time for different initial solid phase volume fractions.
The main factors which benefit the conversion efficiency of the system are the bigger amount of catalyst and the higher temperature of the particles which both have a positive influence on the reaction rate.

From the point of view of chemical conversion efficiency, it makes thus sense to use relatively high carbon volume fractions. In fact, for $f_{v,0} = 5 \cdot 10^{-5}$ a maximal $X_{\text{CH}_4}$ of about 2.4% in 0.1 s is achieved, which is the best value for all performed simulations. However, there is a big difference in radiative power flux between the front and the back of the slab, making it difficult for the methane in the back to react and its $X_{\text{CH}_4}$ practically being 0. It has to be noticed that for lower $f_v$, the methane conversion in the back of the slab does not improve, despite the fact that it is reached by more radiation, because this radiation can not be absorbed due to the poorer optical thickness.

**Optical Properties**

Figure 6.16 shows the absorptance $A$, of the whole system in function of time. At $t = 0$, the absorptance for $f_v = 5 \cdot 10^{-5}$ is only slightly lower than 1, what means that almost all the radiative power entering the slab is absorbed by the medium contained in it. For the reference case, this value is only at 0.5. Due to thermal expansion of the gas, the fraction of transmitted power increases when the gas phase is heated up.

### 6.2.5 Influence of Particle Size

Similarly to a higher particle volume fraction $f_v$, the utilisation of smaller particles leads to a bigger absorption coefficient of the solid phase (see also figure 3.3), since $\kappa_{\lambda,s}$ is given...
by the product of the absorption efficiency (dependent on $D_p$) and the volume fraction. It is thus expected that the behaviour of the system for different particle diameters $D_p$ qualitatively matches with that for varying $f_v$, as already observed in the steady state case (section 6.1.3). For the transient case, four simulations with equal initial parameter values, except for the initial particle diameter, set to be 1, 2.5, 5, and 10 $\mu$m. These cases are simulations 3, ref. 4, and 5, respectively. It has to be noticed that experiment 3, with $D_p = 1 \mu$m requires the time step $\Delta t$ to be kept below 1 ms even for times over 0.05 s since the calculation has been observed to become unstable otherwise. For this reason, the time step is maintained at a constant value of 0.5 ms throughout the entire simulation whose end time is lowered to 0.25 s to avoid excessive computation times.

Temperature Distribution

The temperature distribution over time at $z = 0.001$ m (figure 6.17) confirms that by reducing the initial particle size, it is possible to obtain both higher particle steady state temperatures (over 1700 K in the first sublayer) and faster heating up of the medium. It is interesting to notice that while a different $f_{v,0}$ has a similar influence on the steady state temperature of the particles (figure 6.10), the velocity of the temperature response to the exposition to solar radiation does not substantially vary with $f_v$, whereas smaller $D_p$ reduce the heating up time significantly. figures 6.18 and 6.19 which show the spatial distribution of $T_p$ and $T_g$ confirm the previously made observation that for optically thicker media the spatial temperature distributions assume a more curved shape what signifies that higher temperatures are obtained at the system front at the expense of letting less
Figure 6.17: Transient particle and gas temperature curves for different initial particle diameters at \( z = 0.001 \) m.

Figure 6.18: Spatial distribution of the solid phase temperature for different initial particle diameters.
radiation through to the back of the slab.

**Chemical Reaction**

The chemical reaction rate, shown in function of time in figure 6.20 evidences its temperature dependence. A comparison with figure 6.13 shows that the reaction rate at $z = 0.001 \, \text{m}$ for $D_p = 1 \, \mu\text{m}$ is lower by a factor of about 4 than for $f_v = 5 \cdot 10^{-5}$, even though a similar temperature is reached. From the two possible ways of obtaining an optically thicker medium to achieve higher temperatures (reduction of the particle size or increase of the solid phase volume fraction), the second one has the benefit of the presence of more catalyst mass in the system, improving thus additionally the reaction behaviour, whereas the diminution of particle size exerts its influence only through the higher temperature. The lower reaction rate has thus also repercussions on the methane conversion $X_{\text{CH}_4}$ which is plotted in figure 6.21 and considerably lower than the value one would obtain by increasing $f_v$.

**Optical Properties**

Figure 6.22 shows the systems’ absorptance $A$ in function of time for different $D_{p,0}$. With $D_{p,0} = 1 \, \mu\text{m}$ an initial value of $A \approx 0.9$ can be obtained, which decreases over time due to rarefaction of the medium caused by thermal expansion of the gas. For bigger particle diameters, the absorption behaviour of the medium decreases drastically: for $D_{p,0} = 5 \, \mu\text{m}$ about 70% of the incoming radiative energy is lost, mostly by transmission.
Figure 6.20: Chemical reaction rate of carbon $r_C$ in function of time for different initial particle diameters.

Figure 6.21: Spatial distribution of methane conversion efficiency for different initial particle diameters.
6.2.6 Solar/Surface Irradiation

Instead of a concentrated solar radiation flux through the boundary wall, radiative heat can be assumed to be directly emitted by the wall itself at a given temperature, in this case 2000 K which, assuming it to be a black surface, emits a radiative power of $907.2 \text{ W/m}^{-2}$. In contrast to the incoming solar flux, the emission of a black surface is not perpendicular, but its distribution follows Lambert’s Law. This should have the consequence that the incoming radiation is more likely to be attenuated in the front of the slab, producing thus a similar effect to that of a high $f_v$ or small $D_p$. To this purpose, the reference results are compared to those of simulation 8. In figure 6.23 it is possible to observe that for surface irradiation the hottest point of the medium is not situated inside the control volume, but in the sublayer adjacent to the hot wall. It appears thus that the emission losses of the first cells are more than compensated by the bigger amount of radiation which they absorb. The fact that $T_s$ has its maximum at $z = 0$ does influence the reaction rate and thus the methane conversion, which is maximal in the same location, as shown in figure 6.24. Both the temperature and the CH$_4$ conversion efficiency reach relatively high maximal values (1800 K and 2%, respectively). However, the distribution of $X_{\text{CH}_4}$ over the control volume is extremely unbalanced between the two slab sides.

6.2.7 General Remarks

Generally, it can be noticed that the particle temperature $T_s$ reaches temperatures of over 1000 K in 2–3 ms and reaches its maximum after about 0.03 to 0.05 s. After that point, it
6.2. Transient Simulation

Figure 6.23: Spatial distribution of the particle temperature for solar and surface irradiation at selected control times.

Figure 6.24: Spatial distribution of the methane conversion efficiency for solar and surface irradiation at selected control times.
decreases slightly at a nearly constant rate. An explanation for this phenomenon could be the removal of heat to drive the chemical reaction, however it can also be observed when no chemistry is being considered. More likely, this slow decrease is due to the removal of particles from the system to account for the thermal expansion of the gas phase which at that point is still heating up.

The heating of the gas phase proceeds at a much slower pace than that of the particles since the ratio of the absorbed energy per unit of mass and specific heat is much smaller. Moreover, its increase is approximately constant in the considered time lapse.
Chapter 7

Conclusions

The data obtained show that methane conversions of over of 2.5% in 0.5 s can be reached if the particle temperature reaches values of about 1650 – 1700 K, whereas for a temperature of about 1500 K $X_{\text{CH}_4}$ is generally below 0.5%. With the parameters given in section 6.2.1, particle temperatures up to about 1800 K can be reached if sufficient radiative power is absorbed by the system. To increase this value it is necessary to either augment the incoming radiative flux $q_{\text{solar}}^\prime$ or to improve the absorption of the medium which is influenced by the solid phase volume fraction $f_v$ and by the particle diameter $D_p$. The simulations show that overall system absorptances greater around 90% can be obtained for $f_v = 5 \cdot 10^{-5}$ or for $D_p = 1 \mu m$, leading to maximal $T_s$ over 1700 K, whereas for the reference case only about 50% of the incoming radiation is absorbed. For $f_v = 5 \cdot 10^{-5}$, the same percentage of radiation is absorbed within only 2 cm from the boundary exposed to radiation. At about the same distance from the boundary the maximal $T_s$ and $X_{\text{CH}_4}$ are recorded.

However, in optically thick media, the fact of only a reduced percentage of the incoming radiation reaching the backside of the system, causes the favourable region for the chemical reaction to remain confined to the front of the slab, whereas it would be desirable for this zone to be as extended as possible. For the case of an optically thin medium, the opposite problem is observed: not enough radiative energy can be absorbed by the system, a great part of it (almost 50% in the reference case) being transmitted through it. This allows for a much more uniform spatial distribution of temperature, but does not allow to obtain sufficiently high temperatures to reach high methane conversions. It is therefore necessary to find a compromise between the two extremal cases, i.e. a parameter configuration which allows for a broad zone with high temperature. In both the small particle and the high volume fraction cases, the region, where the value for $X_{\text{CH}_4}$ is higher than 50% of the maximal value does not exceed 5 cm in thickness. In any case, they appear preferable in comparison to optically thinner options, since these exhibit a poor methane conversion efficiency all over the slab, whereas for $f_v = 5 \cdot 10^{-5}$ and for $D_p = 1 \mu m$, poor chemical reaction behaviour is present only in the back half of the system. Between these two alternatives to obtain an optically thicker medium, increasing the solid phase volume fraction has one fundamental advantage compared to reducing the particle diameter: the reaction rate is directly proportional to the mass of carbon $M_C$ (which, on its part, is
directly proportional to $f_v$) in the system since carbon acts as catalyst for the cracking reaction. Thus the volume fraction has a double benefit on the methane conversion, one through the higher temperature, and the other through the higher amount of catalyst in the system.

Eventually, the advantage of optically thicker media could be compensated for by introducing a wall with a good reflective behaviour on the backside of the system. This would allow part of the transmitted and otherwise lost solar radiation to remain inside the system and thus increasing the absorbed fraction of incoming solar energy which leads to higher temperatures, but keeping their more uniform distribution, typical of optically thinner media. A further enhancement of this effect would be the introduction of a window with a good transmittance in the visible wavelength range, but high absorptance or, better, reflectance in the infrared range. Another way of reducing the high differences between the front and the back of the system is to keep an optically thicker medium, but allow for equalisation of its properties through sufficient mass transfer between the two zones.
Bibliography


Appendix A

Nomenclature

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<th>Symbol</th>
<th>Definition</th>
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<td>$A$</td>
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</tr>
<tr>
<td>$c_p'$</td>
<td>specific heat (J/(mol · K))</td>
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<td>$D_p$</td>
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<td>$e$</td>
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<td>$F$</td>
<td>fractional function (–), or effective electrons per volume ($m^{-3}$)</td>
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<td>$f_v$</td>
<td>solid phase volume fraction (–)</td>
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<td>$I_\lambda$</td>
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<td>Cartesian vector (–)</td>
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<td>number rays for Monte Carlo Method (–)</td>
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</table>
\( p \) total system pressure (Pa)
\( p_i \) partial pressure of gaseous species \( i \) (Pa)
\( \mathbf{p} \) emission point of a generic ray (m)
\( Q \) quantity of heat (J)
\( q \) heat rate (W)
\( q_r \) radiative heat rate (W)
\( q_{r,1} \) radiative power from boundary wall 1 (W)
\( q'_{\text{solar}} \) incoming solar radiation flux (W/m\(^2\))
\( R \) random number (0 ≤ \( R \) ≤ 1), or system reflectance (–)
\( \tilde{R} \) universal gas constant (= 8.31441 J·mol\(^{-1}\)·K\(^{-1}\))
\( r_i \) chemical reaction rate of species \( i \) (mol/(s·m\(^3\))
\( S_{\phi} \) standard deviation of statistical variable \( \phi \) (–)
\( S_p \) cross-sectional area of one particle (m\(^2\))
\( s \) pathlength (m)
\( \hat{s} \) path vector (–)
\( T \) temperature (K), or system transmittance (–)
\( T_{\text{sun}} \) surface temperature of the sun (= 5780 K)
\( t \) time (s)
\( \hat{\mathbf{u}} \) propagation direction of a generic ray (–)
\( V \) volume (m\(^3\))
\( X_{\text{CH}_4} \) methane conversion (–)
\( x \) Cartesian coordinate
\( \bar{x}_i \) molar fraction of species \( i \) (–)
\( y \) Cartesian coordinate
\( z \) Cartesian coordinate

**Greek letters**

\( \beta_\lambda \) spectral extinction coefficient (m\(^{-1}\))
\( \varepsilon \) hemispherical total emissivity
\( \varepsilon \) relative error (–)
\( \varepsilon_0 \) electric permittivity of vacuum (= 8.854 · 10\(^{-12}\) F/m)
\( \eta \) wavenumber (m\(^{-1}\))
\( \eta_{Q,\text{chem}} \) instantaneous energy efficiency (–)
\( \eta_{Q,\text{chem}} \) cumulative energy efficiency (–)
\( \theta \) spherical coordinate (rad)
\( \kappa_\lambda \) spectral absorption coefficient (m\(^{-1}\))
\( \lambda \) wavelength (m)
\( \xi \) size parameter (–)
\( \rho \) mass density (kg/m\(^3\))
\( \bar{\rho} \) molar density (mol/m\(^3\))
\( \sigma_{s,\lambda} \) Stefan-Boltzmann constant (= 5.67051 · 10\(^{-8}\) W/(m\(^2\)K\(^4\)))
\( \sigma_{s,\lambda} \) spectral scattering coefficient (m\(^{-1}\))
\( \Phi_\lambda \) scattering phase function (–)
\( \Phi \)  
**generic variable**

\( \phi \)  
**value of a generic variable**

\( \varphi \)  
**spherical coordinate (rad)**

\( \Omega \)  
**solid angle (sr)**

\( \omega \)  
**radiation frequency (Hz)**

**Subscripts**

0  
**initial**

abs  
**absorbed**

em  
**emitted**

g  
**gas phase**

i  
**incoming**

isc  
**incoming scattering**

p  
**single particle**

r  
**radiation**

ray  
**single ray**

s  
**solid (particle) phase**

sc  
**scattered**

w1  
**boundary at \( z = 0 \)**

w2  
**boundary at \( z = L \)**

\( \lambda \)  
**spectral**

\( \infty \)  
**ambient**

**Other symbols**

\( \mathbb{R} \)  
**real part of a complex number**

\( \nabla \)  
**Nabla operator**

**Acronyms**

FVM  
**Finite Volume Method**

MC  
**Monte Carlo**

RTE  
**Radiative Transfer Equation**

TIS  
**Time Integration Scheme**
Appendix B

Error Estimation

B.1 Precision of the Monte Carlo Simulation

Since the Monte Carlo Method is a statistical procedure, its results are subject to statistical errors, whose magnitude decreases with an increasing number of rays used for the simulation, and it is necessary to determine an $n_{ray}$ sufficiently big for the uncertainty in the results to remain below an acceptable, but low enough to allow for reasonable computation times. To assess the possible statistical variation for a given $n_{ray}$, the sample is split up in $n$ sub-samples, whose results can be viewed as results of an experimental measurement series [14]. In this case, a minimal sample size of $n_{ray} = 10^7$ is deemed necessary to offer an acceptable statistical representation, especially of the optical properties of the gas which are simulated using a box model with 5000 discrete spectral absorption coefficient values (section 3.4.2. This sample size is divided into $n = 20$ sub-samples with $5 \cdot 10^5$ rays each. Twenty simulations with equal initial conditions and parameters, but varying random ray parameters are thus run, each one using $5 \cdot 10^5$ rays, are thus run.

The results of these simulations for any variable $\phi$ can be assumed to follow a Gauss normal distribution which can be characterised by its mean value

$$\bar{\phi} = \frac{1}{n} \sum_{i=1}^{n} \phi_i,$$

and its standard deviation

$$S_\phi = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (\phi_i - \bar{\phi})^2}.$$  \hfill (B.2)

It is then possible to define a confidence interval $P\%$, which is the interval inside which the (unknown) population mean value $\mu_\phi$ (the value of the simulation with $n_{ray}$ rays) is falling with a probability $P$. This interval is:

$$P\% = \left( \bar{\phi} - \frac{t_{P\%}(\nu) S_\phi}{\sqrt{n}}, \bar{\phi} + \frac{t_{P\%}(\nu) S_\phi}{\sqrt{n}} \right)$$  \hfill (B.3)
with $t_{P\%}(\nu)$ being the $P\%$-quantile for the Student-Fisher $t$-distribution for $\nu = n - 1$. For $\nu = n - 1 = 19$, the probability of $\mu_\phi$ to lie inside the range $\bar{\phi} \pm s_\phi$ exceeds 99.95%. The value $2 \cdot s_\phi/\bar{\phi}$, listed in tables B.1, for the particle temperature $T_s$, and B.2, for the methane conversion $X_{CH_4}$, in each sublayer at different times indicates thus the fraction of the average value of the 20 simulations with $5 \cdot 10^5$ rays, within which the result $\mu_\phi$ of the simulation with $10^7$ rays will fall with a certainty of 99.95%.

**B.2 Precision of Time Integration**

To estimate the error in the calculation due to discrete time integration and to define which time integration step $\Delta t$ to apply, the same computation is performed with two different $\Delta t$ and their relative particle temperature error determined and tabulated (table B.3 for each cell at different control times $t_{ctrl}$. Both simulations are performed using the reference parameter set (section 6.2.1) with $10^6$ rays, while the time step is $10^{-3}$ s and $5 \cdot 10^{-4}$ s, respectively. The relative error between two different values of a variable, $\phi_1$ and $\phi_2$ is defined as:

$$\epsilon_\phi = \left| 1 - \frac{\phi_1}{\phi_2} \right|$$  \hspace{1cm} (B.4)

Table B.3 shows that the temperature error due to the discrete time step decreases, as expected, with the progression of time as the particle temperature reaches an almost steady state condition, since the biggest errors occur during the initial abrupt temperature rise, in this case 5.7%. To maintain an acceptable precision, it is therefore necessary to use smaller $\Delta t$ at the beginning of the simulations, increasing it once the temperature has stabilised itself. From preliminary test runs of the simulation, it appears that for $\Delta t > 0.001$ s the calculation is at high risk of losing its stability during the first few ms. In figure B.1, which shows the particle temperature evolution over time for the first sublayer, it is possible to see that a too big time step ($\Delta t = 0.0025$ s entails an excessive response of the temperature which jumps up to more than 1500 K in the first time step, oscillates around that value before reaching a constant growth regime. Therefore, in for $t < 0.05$ s, $\Delta t = 5 \cdot 10^{-4}$ s is chosen. However, as can be seen in figure B.1, this value can be raised to 0.0025 s for $t < 0.05$ s without relevant precision losses to reduce computation time. Only for the simulation involving small particles sizes, $\Delta t$ cannot be augmented because of instabilities. Said computation is interrupted at $t = 0.25$ s for time-saving reasons, since this time is sufficient to gain the necessary information about its performance.

**B.3 Precision of the Gas Model**

Due to the highly unsteady spectral distribution of the absorption coefficient of methane (figure 3.5, an implementation of the real data is not practicable due to the enormous quantity of data points which would be necessary. Thus, a box model of the spectral absorption coefficient of methane is established. To find the necessary number of discrete wavenumber/wavelength ranges to obtain an acceptable model, the net radiative power fluxes into each sublayer for increasingly precise gas models are compared. The precision of the model is improved until the calculated radiative power fluxes start to converge,
Table B.1: Uncertainty (2S₀/\(\bar{\phi}\)) in particle temperature \(T_s\) for a simulation with \(n_{ray} = 10^7\) and reference parameters.

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<th>(z_0) (m)</th>
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<td>0.00133</td>
<td>0.00123</td>
<td>0.00086</td>
</tr>
</tbody>
</table>

Note: Relative error range \(= 0\)
Table B.2: Uncertainty \( (2S_{\phi}/\phi) \) of methane conversion \( X_{\text{CH}_4} \) for a simulation with \( n_{\text{ray}} = 10^7 \) and reference parameters.

<table>
<thead>
<tr>
<th>z (m)</th>
<th>relative error range</th>
<th>0.001 s</th>
<th>0.005 s</th>
<th>0.010 s</th>
<th>0.050 s</th>
<th>0.100 s</th>
<th>0.200 s</th>
<th>0.250 s</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005</td>
<td>0.00000</td>
<td>0.0031</td>
<td>0.00299</td>
<td>0.00141</td>
<td>0.00240</td>
<td>0.00170</td>
<td>0.00176</td>
<td></td>
</tr>
<tr>
<td>0.006</td>
<td>0.00000</td>
<td>0.00371</td>
<td>0.00312</td>
<td>0.00169</td>
<td>0.00260</td>
<td>0.00212</td>
<td>0.00218</td>
<td></td>
</tr>
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<td>0.007</td>
<td>0.00000</td>
<td>0.00434</td>
<td>0.00355</td>
<td>0.00226</td>
<td>0.00317</td>
<td>0.00268</td>
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</tr>
<tr>
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<td>0.00000</td>
<td>0.00496</td>
<td>0.00394</td>
<td>0.00309</td>
<td>0.00398</td>
<td>0.00349</td>
<td>0.00355</td>
<td></td>
</tr>
<tr>
<td>0.010</td>
<td>0.00000</td>
<td>0.00557</td>
<td>0.00436</td>
<td>0.00397</td>
<td>0.00443</td>
<td>0.00395</td>
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</tr>
<tr>
<td>0.011</td>
<td>0.00000</td>
<td>0.00616</td>
<td>0.00475</td>
<td>0.00490</td>
<td>0.00511</td>
<td>0.00463</td>
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</tr>
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<td>0.00676</td>
<td>0.00513</td>
<td>0.00543</td>
<td>0.00584</td>
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</tr>
<tr>
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<td>0.00000</td>
<td>0.00733</td>
<td>0.00549</td>
<td>0.00584</td>
<td>0.00648</td>
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</tr>
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<td>0.015</td>
<td>0.00000</td>
<td>0.00804</td>
<td>0.00605</td>
<td>0.00659</td>
<td>0.00733</td>
<td>0.00685</td>
<td>0.00691</td>
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</tr>
<tr>
<td>0.016</td>
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<td>0.00849</td>
<td>0.00649</td>
<td>0.00703</td>
<td>0.00792</td>
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<td>0.00750</td>
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</tbody>
</table>

Note: The table values are for the sake of example and do not reflect actual data.
Table B.3: Relative error $\epsilon$ in particle temperature $T_s$ between a computation with $\Delta t = 5 \cdot 10^{-4}$ s and one with $\Delta t = 10^{-3}$ s for reference parameters with $n_{\text{ray}} = 10^6$.

<table>
<thead>
<tr>
<th>z (m)</th>
<th>$t = 0.005$ s</th>
<th>$t = 0.010$ s</th>
<th>$t = 0.025$ s</th>
<th>$t = 0.100$ s</th>
<th>$t = 0.200$ s</th>
<th>$t = 0.250$ s</th>
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<td>0.00813</td>
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<td>0.00214</td>
<td>0.00141</td>
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<tr>
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<td>0.05213</td>
<td>0.02726</td>
<td>0.01018</td>
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<td>0.00945</td>
<td>0.00327</td>
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<td>0.070</td>
<td>0.04753</td>
<td>0.03437</td>
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<td>0.00908</td>
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<td>0.00488</td>
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<tr>
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<td>0.09515</td>
<td>0.00258</td>
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<td>0.00490</td>
</tr>
<tr>
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<td>0.09708</td>
<td>0.00234</td>
<td>0.00958</td>
<td>0.00376</td>
<td>0.00492</td>
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<tr>
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<td>0.04027</td>
<td>0.09897</td>
<td>0.00210</td>
<td>0.00960</td>
<td>0.00378</td>
<td>0.00494</td>
</tr>
</tbody>
</table>

max. 0.05695       0.01916       0.00196       0.00175       0.00139       0.00167       0.00168
Figure B.1: Particle temperature evolution over time at $z = 0.001$ m for different time steps.
Figure B.2: Comparison of net radiative power $q_r$ into each sublayer for gas models with 2000, 9000, 27000, and 5005 discrete wavenumber intervals.

meaning that the precision gain in the results does not longer justify an improvement of the gas model. Radiative power fluxes are computed at $T_g = 300$ K and $p_{\text{CH}_4} = 1$ atm since the absorption coefficient is highest at low temperatures and high pressures. Figure B.2 shows the spatial distribution of the net radiative power flux $q_r''$. Since $\kappa_{\lambda,\text{CH}_4}$ does not exceed the value of $10^{-5}$ for $10^6 \text{ m}^{-1} < \eta < 10^7 \text{ m}^{-1}$, it is assumed constant over this range. The remaining range ($10^5 \text{ m}^{-1} < \eta < 10^6 \text{ m}^{-1}$) is then subdivided in 2000, 9000, or 27000 equal wavenumber intervals. It can be noticed that from 9000 subdivisions upward, a good convergence of $q_r$ is reached. To further reduce the number of necessary subdivisions, constant values for $\kappa_{\lambda,\text{CH}_4}$ are assumed also between the four major absorption bands, allowing thus to increase the subdivision density within each band, leading to totally 5005 discrete wavelength intervals, distributed as shown in table B.4. These ranges are dimensioned to contain the four absorption bands for each temperature and pressure distribution of $\kappa_{\lambda,\text{CH}_4}$. This model allows thus for the same box sizes $\Delta \eta$ as the one with 27000 subdivisions in the relevant wavenumber intervals, but reduces their total number more than five times while conserving a good accuracy, as can be seen in figure B.2.
Table B.4: Characteristics of the box model for the spectral absorption coefficient of the gas phase.

<table>
<thead>
<tr>
<th>$\eta_{\text{low}}$ (m$^{-1}$)</th>
<th>$\eta_{\text{up}}$ (m$^{-1}$)</th>
<th>subdivisions</th>
</tr>
</thead>
<tbody>
<tr>
<td>100'000</td>
<td>110'000</td>
<td>1</td>
</tr>
<tr>
<td>110'000</td>
<td>160'000</td>
<td>1010</td>
</tr>
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</tr>
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<tr>
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<td>10'000'000</td>
<td>1</td>
</tr>
</tbody>
</table>
Appendix C

Input and Output Files of the Simulation

In this section a brief explanation of the necessary input files and of the given output files is offered.

C.1 Input Files

The input files are mostly self-explanatory. For the optical properties of CH$_4$, the input file InputCH4.dat specifies only the total number of discrete temperatures, pressures, and wavelengths, while the optical data per se are given in the .dat files contained in the folder CH4, subdivided for different temperatures.

C.2 Output Files

Totally 14 output files are produced for each simulation:

00 InputDataSummary.out

A summary of the relevant simulation parameters.

01 LayerProfiles.out

At each control time, the distribution of the most important variables over the entire control system are given out. These are: particle and gas temperatures $T_s$ and $T_g$, absorbed solar radiation power, net radiative power flux into the solid and the gas phase $q_{r,s}$ and $q_{r,g}$, power used to drive the chemical reaction $q_{chem}$, net power flux in the solid and in the gas phase $q_s$ and $q_g$, number of particles $n_p$, solid phase volume fraction $f_v$, particle diameter $D_p$, molar fraction of methane in the gas phase $\bar{x}_{CH_4} = N_{CH_4}/N_g$, molar fraction of hydrogen in the gas phase $\bar{x}_{H_2} = N_{H_2}/N_g$, methane conversion $X_{CH_4} = 1 - N_{CH_4}/N_{CH_4,0}$. 

80
alternative methane conversion $X_{\text{CH}_4} = (N_{\text{CH}_4,0} - N_{\text{CH}_4}) / (N_{\text{CH}_4,0} - N_{\text{CH}_4,\text{sink}})$ accounting for the mass sink (section 3.1.1), chemical energy efficiency $\eta_{\text{chem}} = q_{\text{chem}} / q_{r,w1}$, the cumulative mass sink for each species $N_{C,\text{sink}}$, $N_{\text{CH}_4,\text{sink}}$, $N_{\text{H}_2,\text{sink}}$, $N_{\text{Ar},\text{sink}}$.

02 TemperatureDistr.out

Particle and gas temperatures $T_s$ and $T_g$ in the first cell, halfway through the slab, and in the last layer at selected control times.

03 Particles.out

Particle diameter $D_p$, volume fraction $f_v$, and total number $n_p$ in the first cell, halfway through the slab, and in the last layer at selected control times.

04 Gas.out

Partial pressure of methane $p_{\text{CH}_4}$, of hydrogen $p_{\text{H}_2}$, and of argon $p_{\text{Ar}}$, and molar fractions (of the gas phase) $x_{\text{CH}_4}$, $x_{\text{H}_2}$ and $x_{\text{Ar}}$ in the first cell, halfway through the slab, and in the last layer at selected control times.

05 Chemistry.out

Number of moles for all species $N_C$, $N_{\text{CH}_4}$, $N_{\text{H}_2}$ and $N_{\text{Ar}}$, and reaction rate of carbon $r_C$ in the first cell, halfway through the slab, and in the last layer at selected control times.

06 OverallEnergy.out

Incoming solar power $q_{r,w1}$, net radiative power $q_{r}$, power used to drive the chemical reaction $h_{\text{chem}}$, net power $q = q_{r} - h_{\text{chem}}$, and solar-to-chemical efficiency $\eta_{\text{chem}}$ for the entire system at selected control times.

07 CumulativeEnergy.out

Cumulative incoming solar energy $Q_{r,w1} = \int q_{r,w1} dt$, net radiative energy $Q_{r} = \int q_{r} dt$, chemical energy $H_{\text{chem}} = \int h_{\text{chem}} dt$, net energy $Q = Q_{r} - H_{\text{chem}}$, and solar-to-chemical efficiency $\eta_{\text{chem}}$ for the entire system at selected control times.

08 OpticalProperties.out

Spectral absorption coefficient of the medium $\kappa_\lambda$ for $\lambda = 0.5 \, \mu\text{m}$ and $\lambda = 1.5 \, \mu\text{m}$, Planck mean absorption coefficient of the particle phase $\kappa_{P,s}(T_s)$ and of the gas phase $\kappa_{P,g}(T_g)$, spectral scattering coefficient of the medium $\sigma_{s,\lambda}$ for $\lambda = 0.5 \, \mu\text{m}$ and $\lambda = 1.5 \, \mu\text{m}$ in the first cell, halfway through the slab, and in the last layer at selected control times.
09 RadiativeEnergy.out
Absorptance $A$, reflectance $R$ and transmittance $T$, absorbed, reflected and transmitted radiative power $q_{r,\text{abs}}$, $q_{r,\text{refl}}$, $q_{r,\text{trans}}$, cumulative absorbed, emitted and transmitted radiative energy $Q_{r,\text{abs}}$, $Q_{r,\text{refl}}$, $Q_{r,\text{trans}}$ of the entire system at selected control times.

10 Conversion.out
Methane, hydrogen and argon molar fractions $x_{\text{CH}_4}$, $x_{\text{H}_2}$, $x_{\text{Ar}}$, methane conversion $X_{\text{CH}_4} = 1 - N_{\text{CH}_4}/N_{\text{CH}_4,0}$, alternative methane conversion $X_{\text{CH}_4} = (N_{\text{CH}_4,0} - N_{\text{CH}_4}) / (N_{\text{CH}_4,0} - N_{\text{CH}_4,\text{sink}})$ accounting for the mass sink (section 3.1.1) for the entire system at selected control times.

11 Energy.out
Absorbed incoming radiative power $q_{r,\text{w1,abs}}$, net radiative power flux $q_r$, chemical power $h_{\text{chem}}$, net power flux $q$, energy conversion efficiency $\eta_{\text{chem}}$ in the first cell, halfway through the slab, and in the last layer at selected control times.

12 MassSink.out
Cumulative quantity of subtracted moles of carbon $N_{\text{C,\text{sink}}}$, methane $N_{\text{CH}_4,\text{sink}}$, hydrogen $N_{\text{H}_2,\text{sink}}$ and argon $N_{\text{Ar,\text{sink}}}$ in the first cell, halfway through the slab, and in the last layer at selected control times.

13 OverallMassSink.out
Cumulative quantity of subtracted moles of carbon $N_{\text{C,\text{sink}}}$, methane $N_{\text{CH}_4,\text{sink}}$, hydrogen $N_{\text{H}_2,\text{sink}}$ and argon $N_{\text{Ar,\text{sink}}}$ in the entire system.
Appendix D

Polynomial Approximation for Specific Heat

For constant pressure conditions, as assumed in the simulation, the incremental heat supplied to or lost by a system is defined as:

\[ dq = dh = c_p(T) dT \]  \hspace{1cm} (D.1)

\( h \) is the system’s specific enthalpy, and \( c_p \) the system’s specific heat at constant pressure. The total heat which has to be supplied to a system in order to increase its temperature from \( T_1 \) to \( T_2 \) is therefore:

\[ \Delta q = \Delta h = \int_{T_1}^{T_2} c_p(T) dT \]  \hspace{1cm} (D.2)

The molar specific heat \( c_p \) of a substance usually is temperature-dependent. To solve equation D.2 analytically, an approximated polynomial function for \( c_p(T) \) can be used. Parameters for relevant species are listed in table D.1.

\[ c_p \approx a_1 + a_2 T + a_3 T^{-2} + a_4 T^2 \]  \hspace{1cm} (D.3)

\( a_1, \ a_2, \ a_3, \) and \( a_4 \) vary for different substances. Their values can be obtained from literature. Inserting the polynomial expression for \( c_p \) into equation D.2 and carrying out the integration yields a polynomial function for molar specific enthalpy variation between two temperatures:

\[ \Delta h|_{T_1 \rightarrow T_2} \approx a_1 (T_2 - T_1) + \frac{a_2}{2} (T_2^2 - T_1^2) - a_3 (T_2^{-1} - T_1^{-1}) + \frac{a_4}{3} (T_2^3 - T_1^3) \]  \hspace{1cm} (D.4)

The formation enthalpy of all components at any temperature can now be calculated by inserting the formation enthalpy at a reference temperature \( h^0_{T_{ref}} \).

\[ h_T \approx h^0_{T_{ref}} + \Delta h|_{T_{ref} \rightarrow T} = \]
\[ = h^0_{T_{ref}} + a_1 (T - T_{ref}) + \frac{a_2}{2} (T^2 - T_{ref}^2) - a_3 (T^{-1} - T_{ref}^{-1}) + \]
\[ + \frac{a_4}{3} (T^3 - T_{ref}^3) \]  \hspace{1cm} (D.5)
Formation enthalpies of relevant species are listed in Table D.1. All values are from [3], except for carbon, which is obtained through curve-fitting using the least mean square method from tabulated data given in [2] to cover the relevant temperature range (300 – 2000 K).

For the density of carbon black, a temperature-independent value of \( \rho_C = 2270 \) kg·m\(^{-3}\) is chosen.