Doctoral Thesis

Hydrogen production by solar thermal steam gasification of coal

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HYDROGEN PRODUCTION BY
SOLAR THERMAL STEAM GASIFICATION OF COAL

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH

for the degree of
Doctor of Technical Sciences

presented by

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2005
Preface

This work is analyzing the production of hydrogen by the thermal steam gasification of coal in a chemical reactor when highly concentrated thermal radiation is the energy source of the endothermic reaction. This process is an example for the energetic transformation of concentrated solar irradiation to a chemical energy carrier that is easily storable and transportable. Simultaneously, by using coal only as a chemical reactant and solar energy as the source for the high temperature process heat, it represents a decarbonization process, where the carbon is removed from the actual chemical energy carrier before electricity generation, thus providing the potential for a significant reduction of CO₂ emissions. Also, the direct irradiation of the coal provides a very efficient mean of heat transfer directly to the coal's particle surface, where the endothermic reaction is taking place, notably superior to the indirect form of heat transfer in conventional gasifiers.

The major motivation behind this work lays in the fact that today's energy economy is largely based on the use of fossil fuels, i.e. coal and oil. And, since the earth's oil reserves will run out in foreseeable future, there will be a need for an replacement of oil, i.e. for a chemical energy carrier with a high energy density that is favorable, e.g., for individual transport. The solar steam gasification of coal has the potential to make use of the coal reserves, which are estimated to still last a few centuries at the present consumption rate, for the production of such a replacement, and has the further advantage that it represents a combination of novel and conventional processes, and therefore provides a transfer of solar technology to the industry, because it links the new solar technology with a well known and established process. It is therefore important to study the novel aspects of the solar process, which is, in particular, the radiative heat transfer as the primary energy source.

At this place I also want to take the opportunity to thank all the persons that supported me in doing this work and that have contributed to its successful completion.

In particular I want to express my gratitude to Prof. Aldo Steinfeld, who supervised my doctoral studies and supported me in every aspect of my work. His enthusiasm and his appreciation have been essential for the successful accomplishment of my thesis.

I thank Prof. Dimos Poulikakos for taking over the co-examination of my final report.
I am grateful to Reto Müller for his outstanding effort during his diploma thesis, to Dominic Trommer for his contribution to the final kinetic model, to Pascale Buchel for the realization of the first preliminary experiments, and to Dr. Wojciech Lipinski, Jörg Petrasch, and Andreas Z'Graggen for their collaboration in terms of modeling.

I thank Dr. David Hirsch, Philipp Haueter, Peter Häberling, Max Brack, Alwin Frei, and Thomas Osinga for their help during the experimental campaigns and for the maintenance of the solar simulator.

I thank all the not by name mentioned members of the Professorship of Renewable Energy Carriers at ETH and the Laboratory for Solar Technology at PSI for their great commitment to this research field.

I am deeply grateful to my family, to my mother for her continuous and ongoing support during all my life and studying, to my father who awoke my interest in science already in young years by his enthusiastic explanations and by his own life’s example, and to my brothers Max and Clemens, for their help whenever needed.

Very special thanks go to my wife Viktoria, for her understanding and support in all aspects, scientific or not; and for all the time that I couldn’t spend with her being occupied with my work, and to her family, for their encouragement and their scientific suggestions.

Finally, I want to acknowledge the financial support of the Swiss Federal Institute of Technology (ETH), and the Swiss Federal Office of Energy (BFE).

Zurich, July 2005

Peter von Zedtwitz
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Abstract

The steam-gasification of coal (peat, lignite, bituminous, and anthracite) into syngas is investigated using concentrated solar energy as the source of high-temperature process heat. The advantages of the solar driven process over the conventional one are three-fold: (1) the calorific value of the fuel is upgraded, (2) the gaseous products are not contaminated by combustion by-products, and (3) the discharge of pollutants to the environment is avoided. A 2nd-law analysis is carried out for a blackbody solar cavity-receiver/reactor operated at 1350 K and subjected to a mean solar flux concentration ratio of 2000. Two technically viable routes for generating electricity using the gasification products are examined: (1) syngas is used to fuel a 55%-efficient combined Brayton-Rankine cycle; and (2) syngas is further processed to H₂ (by water-shift gas reaction followed by H₂/CO₂ separation) which is used to fuel a 65%-efficient fuel cell. The maximum exergy efficiency, defined as the ratio of electric power output to the thermal power input (solar power plus heating value of reactants), reaches 50% for the combined cycle route and 46% for the fuel cell route. Both of these routes offer a net gain in the electrical output by a factor varying in the range 1.7-1.9, depending on the coal type and the power generation route, vis-à-vis the direct use of coal for fueling a 35%-efficient Rankine cycle. Specific CO₂ emissions amounts to 0.49-0.56 kg CO₂/kWhₑ, about half as much as the specific emissions discharged by conventional coal-fired power plants.

The reaction kinetics of steam gasification of charcoal are investigated for a quartz tubular reactor containing a fluidized bed and directly exposed to an external source of concentrated radiation. Langmuir-Hinshelwood type rate laws are formulated based on elementary reaction mechanisms describing reversible adsorption/desorption processes and irreversible surface chemistry. Assuming plug flow conditions and steady state, the rate constants are computed by matching theoretical and experimental results and their temperature dependence is determined by imposing an Arrhenius-type rate law.

A heat and mass transfer numerical model has been developed to simulate the steam-gasification of coal or charcoal in a fluidized-bed or a packed-bed chemical reactor. The reactor consists of a transparent quartz tube containing a bed of coal particles subjected to a flow of steam and directly exposed to an external source of concentrated
radiation. With this arrangement, the coal particles serve simultaneously as radiant absorbers and chemical reactants, providing efficient heat and mass transport. Specific focus of the model is the fundamental understanding of the radiation heat transfer within the bed, and its coupling to the chemical reaction kinetics. The Monte Carlo (MC) ray tracing method is used to determine the radiative transfer from the source to the reactor, through the reactor quartz layer, and within the bed. Spectral and directional dependent optical properties are employed for both the quartz tube and the particle bed. Refraction and reflection at the quartz/air boundaries as well as absorption and emission within the quartz layer are considered. The bed is treated as an absorbing-emitting-scattering participating medium. Two approaches are examined to describe the radiative transfer within the bed region for large particles of size parameter \( > 10 \). In the first approach, the bed is modeled as a continuous medium, using spectral absorption and scattering coefficients based on measured spectral reflectivity, and scattering phase functions for diffuse reflecting spherical particles. In the second approach, the bed is modeled as a cloud of randomly-positioned spherical particles, with diffuse spectral reflection, absorption, and emission taking place at the particle surface. A one-dimensional grid has been applied to divide the bed region into elemental disks in axial direction. Mass and energy conservation equations that account for radiation, convection, conduction, chemical reaction, particle-mixing, and enthalpy change are applied in each element and solved numerically to calculate temperature profiles throughout the bed for particles, gas phase, and quartz tube. The system is solved iteratively due to the cross-dependence of heat-balances (radiation terms) and MC method (temperature dependent optical properties). Each iteration step requires a complete Monte Carlo ray tracing loop. The kinetic model derived in the kinetic study is used to describe the chemical reaction; the fluid dynamic behavior is modeled using empirical data. The numerical model provides a tool for pre-design and optimization of fluidized and packed bed chemical reactors subjected to high flux irradiation.

Validation is accomplished by comparing the numerically computed flux distribution, temperature profiles, product gas composition, and reaction extent with experimental data that has been obtained from tests in a quartz tubular reactor containing a bed of charcoal particles that is directly exposed to high-flux irradiation. The radiation source consisted of a high-pressure argon arc close-coupled to precision elliptical-trough mirrors to produce continuous radiative power at peak fluxes exceeding 4250 kW/m\(^2\),
mostly at visible wavelengths with additional power in the near IR and UV. For the packed bed, the temperature increases monotonically because the intensive internal radiative exchange approaches a conduction-like heat transfer within the bed. For the fluidized bed, the temperature increases rapidly in the first one-quarter of the bed and then reaches an almost constant value because of the strong fluidization in the upper bed region derived from the 5-fold volumetric growth due to gas formation and thermal expansion. Above 1450 K, the product composition consisted mainly of an equimolar mixture of H₂ and CO, a syngas quality that is notably superior than that typically obtained in autothermal gasification reactors (with internal combustion of coal for process heat), besides the additional benefit of the upgraded calorific value.
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Zusammenfassung


Resultaten; die Temperaturabhängigkeit wurde bestimmt unter Annahme eines Geschwindigkeitsgesetzes nach Arrhenius.


Nomenclature

**Abbreviations**

- CC: combined cycle
- CPC: compound parabolic concentrator
- ETH: Swiss Federal Institute of Technology Zurich
- FRP: Free random placement
- FC: fuel cell
- GC: gas chromatograph
- IR: infrared
- MC: Monte Carlo ray tracing
- PBA: Packed bed algorithm
- PSA: pressure swing adsorption
- RC: Rankine cycle
- TC: Thermocouple
- UV: ultra violet

**Dimensionless numbers**

- $Bi$: Biot number (-)
- $Nu$: Nusselt number (-)
- $Pr$: Prandtl number (-)
- $Ra$: Rayleigh number (-)
- $Re$: Reynolds number (-)
- $Sh$: Sherwood number (-)

**Chemical species**

- $Ar$: argon
- $C$: carbon, charcoal
- $CH_4$: methane
- $CH_3O_y$: coal with defined H/C, and O/C ratio
- CO: carbon monoxide
CO₂  carbon dioxide
H, H₂  hydrogen
H₂O  water, steam
N, N₂  nitrogen
O, O₂  oxygen
S  sulfur

Latin symbols

A  area (m²)
a  mass specific surface area (m²·g⁻¹)
a  absorption coefficient (m⁻¹)
C  mean solar flux concentration ratio (-)
Cᵢ  inactive carbon site (mol)
d  diameter (m)
dV  volume of element (m³)
dₘ  thickness of quartz tube wall (m)
dₓ  height of element in bed region (m)
Eₐ  activation energy (kJ·mol⁻¹)
EGF  electric gain factor (-)
EmCO₂  specific CO₂ emission (kg·J⁻¹)
EO  specific electric output (J·kg⁻¹)
eₐb  spectral hemispherical blackbody emissive power (W·m⁻²·μm⁻¹)
F₀⁻→ₜ  blackbody fractional function (-)
F⁻¹₀⁻→ₜ  inverse fractional function (μm·K)
g  gravity (m·s⁻²)
H  enthalpy flow (W)
h  convective heat transfer coefficient (W·m⁻²·K⁻¹)
hᵢₜ  specific enthalpy of species i at temperature T (kJ·mol⁻¹)
\( \hat{h}_{i,T} \) mass specific enthalpy of species \( i \) at temperature \( T \) (kJ·kg\(^{-1}\))

\( I \) normal beam insolation (kW·m\(^{-2}\))

\( i_{s} \) spectral intensity (W·m\(^{-2}\)·\( \mu \text{m}^{-1}\))

\( \mathcal{I} \) irreversibility (W·K\(^{-1}\))

\( K_{i} \) complex rate constant \( i \) (mol·m\(^{-3}\)·s\(^{-1}\)·Pa\(^{-1}\)) or (Pa\(^{-1}\))

\( K_{i,o} \) frequency factor of complex rate constant \( i \) (mol·m\(^{-3}\)·s\(^{-1}\)·Pa\(^{-1}\)) or (Pa\(^{-1}\))

\( k \) thermal conductivity (W·m\(^{-1}\)·K\(^{-1}\))

\( k_{i} \) rate constant \( i \) (mol·m\(^{-3}\)·s\(^{-1}\)·Pa\(^{-1}\)) or (Pa\(^{-1}\))

\( k_{i,o} \) frequency factor of a rate constant \( i \) (mol·m\(^{-3}\)·s\(^{-1}\)·Pa\(^{-1}\)) or (Pa\(^{-1}\))

\( k_{m} \) mass transfer coefficient (m·s\(^{-1}\))

\( LHV \) low heating value (kJ·kg\(^{-1}\))

\( M \) molar weight (g·mol\(^{-1}\))

\( m \) mass (kg)

\( \dot{m} \) mass flow-rate (kg·s\(^{-1}\))

\( N \) counter for rays (-)

\( n \) refractive index (-)

\( n \) number of bed elements (-)

\( \dot{n} \) molar flow (mol·s\(^{-1}\))

\( \hat{n} \) normal unit vector on surface in hit point (m)

\( N_{p} \) particle number density (m\(^{-3}\))

\( P_{\text{arc}} \) emitted power by Ar arc (W)

\( p_{i} \) partial pressure for component \( i \) (Pa)

\( p_{t} \) total pressure (Pa)

\( \dot{Q} \) thermal power (W)

\( r \) radius (m)

\( \hat{r} \) vector to the ray's origin (m)

\( r_{f} \) rate of surface reaction for species \( i \) (mol·m\(^{-3}\)·s\(^{-1}\))
\( R \) random number chosen from a uniform set \([0,1]\) (-)

\( R_u \) universal gas constant \((8.3144 \text{ J mol}^{-1} \text{ K}^{-1})\)

\( S \) reflecting surface (-), \( S(x,y,z)=0 \)

\( s_{i,T} \) specific entropy of species \( i \) at temperature \( T \) \((\text{J mol}^{-1} \text{ K}^{-1})\)

\( \dot{s}_{i,T} \) mass specific entropy of species \( i \) at temperature \( T \) \((\text{J kg}^{-1} \text{ K}^{-1})\)

\( T \) temperature (K)

\( t \) path length (m)

\( t_e \) path length to extinction (m)

\( t_b \) path length to next boundary (m)

\( \hat{u} \) unit vector of ray's direction (m)

\( u_o \) superficial velocity \((\text{m s}^{-1})\)

\( V \) volume \((\text{m}^3)\)

\( w \) power carried by single ray \((\text{W})\)

\( W \) work output \((\text{W})\)

\( \chi_i \) fractional conversion for species \( i \) (-)

\( \dot{\chi}_i \) fractional conversion rate for species \( i \) \((\text{s}^{-1})\)

\( x \) Cartesian coordinate (m)

\( x \) H/C molar ratio in coal feedstock (-)

\( y \) Cartesian coordinate (m)

\( y \) O/C molar ratio in coal feedstock (-)

\( y \) mole fraction (-)

\( z \) Cartesian coordinate (m)

**Greek symbols**

\( \alpha \) absorptivity (-)

\( \Delta G \) Gibbs free energy change \((\text{kJ g}^{-1})\)

\( \Delta H \) enthalpy change \((\text{kJ g}^{-1})\)

\( \Delta S \) entropy change \((\text{kJ g}^{-1} \text{ K}^{-1})\)

\( \varepsilon_f \) convergence criterion for heat balances \((\text{W})\)
$\varepsilon_m$ solid fraction in mixed region (-)

$\varepsilon_k$ solid fraction in packed bed (-)

$\varepsilon_{res}$ residuum used in kinetic study (-)

$\varepsilon_s$ mean solid fraction (-)

$\varepsilon_v$ mean void fraction (-)

$\eta$ efficiency

$\eta_{rec}$ recovery rate (-)

$\theta$ angle (rad)

$\Theta_i$ fractional surface coverage by species $i$ (-)

$\Theta_v$ fraction of vacant surface sites (-)

$\kappa$ extinction coefficient ($m^2$)

$\lambda$ wavelength (m)

$\mu$ kinematic viscosity ($kg/(m\cdot s)$)

$\xi$ size parameter (-)

$\rho$ density ($kg/m^3$)

$\rho_s$ spectral reflectivity (-)

$\sigma$ Stefan-Boltzmann constant ($5.6705 \times 10^{-8} W/m^2K^4$)

$\sigma$ scattering coefficient ($m^2$)

$\tau$ gas residence time (s)

$\Phi$ phase function (-)

$\varphi$ angle (rad)

$\phi_{\text{half}}$ half volume fraction of moving particles (-)

$\phi_{ij}$ interaction parameter for calculation of gas mixture properties (-)

$\phi_s$ sphericity (-)

$\psi$ angle (rad)

$\Omega$ albedo (-)
Latin Subscripts

\( a \) ambient
\( abs \) absorbed
\( absorption \) absorption
\( am \) arc mirror
\( b \) bed region
\( bb \) bed bottom
\( bt \) bed top
\( Carnot \) Carnot
\( CC \) combined cycle
\( cd \) conduction
\( chm \) chemistry
\( cmb \) combustion
\( coal \) coal
\( dx \) per element dx
\( e \) electrical
\( em \) emitted
\( ex \) exergy
\( ex \) relector exit
\( exp \) experimental
\( FC \) fuel cell
\( g \) gas phase
\( gr \) granular
\( HE \) heat exchanger
\( i \) index
\( j \) index
\( k \) packed bed
\( in \) incoming
\( inp \) input
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>mf</td>
<td>minimum fluidization</td>
</tr>
<tr>
<td>mir</td>
<td>solar simulator reflector</td>
</tr>
<tr>
<td>mix</td>
<td>particle mixing</td>
</tr>
<tr>
<td>net</td>
<td>net power</td>
</tr>
<tr>
<td>out</td>
<td>outgoing</td>
</tr>
<tr>
<td>P</td>
<td>Planck mean</td>
</tr>
<tr>
<td>p</td>
<td>particle</td>
</tr>
<tr>
<td>pg</td>
<td>particle to gas</td>
</tr>
<tr>
<td>PSA</td>
<td>pressure swing adsorption</td>
</tr>
<tr>
<td>q</td>
<td>quartz</td>
</tr>
<tr>
<td>qa</td>
<td>quartz to surrounding air</td>
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<tr>
<td>qg</td>
<td>quartz to gas</td>
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<td>quench</td>
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<td>r</td>
<td>reaction</td>
</tr>
<tr>
<td>r</td>
<td>reflected</td>
</tr>
<tr>
<td>rb</td>
<td>reactor bottom</td>
</tr>
<tr>
<td>reactor</td>
<td>reactor</td>
</tr>
<tr>
<td>reradiation</td>
<td>reradiation</td>
</tr>
<tr>
<td>RC</td>
<td>Rankine cycle</td>
</tr>
<tr>
<td>rt</td>
<td>reactor top</td>
</tr>
<tr>
<td>SCM</td>
<td>solar contribution to mix</td>
</tr>
<tr>
<td>solar</td>
<td>solar</td>
</tr>
<tr>
<td>sim</td>
<td>simulated</td>
</tr>
<tr>
<td>t</td>
<td>total</td>
</tr>
<tr>
<td>t</td>
<td>top</td>
</tr>
<tr>
<td>WGS</td>
<td>water gas shift</td>
</tr>
</tbody>
</table>

**Greek Subscripts**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>λ</td>
<td>spectral (wavelength dependent)</td>
</tr>
</tbody>
</table>
\( \phi \)  
boundary for mixed fraction distribution

**Latin superscripts**

\( i \) for/in element \( i \)

\( (m) \) iteration step
1 Introduction

Coal and Solar Fuels

Coal is the world’s most plentiful fossil fuel resource, with known reserves estimated to last a few centuries at the present consumption rate. Many coal reserves exist in regions with high solar insolation, e.g. in Central America (United States, Mexico), Southern Europe (Greece), Asia (China, India), Africa (South Africa), and Northern Australia [4,5,6]. However, about 1 kg CO₂ kg/kWhₑ, along with other greenhouse gases and pollutants, is emitted by a typical coal-fired power plant [1]. These emissions can be significantly reduced or even completely eliminated by substituting coal by cleaner fuels, e.g. solar fuels. The production of solar fuels, such as solar hydrogen and solar methanol, which can be long-termed stored and long-ranged transported, can overcome the principal drawbacks of solar energy, namely being a diluted, intermittent, and, unequally distributed source. A review of the process technology for producing solar fuels is given by Steinfeld and Palumbo [2].

Intermediate strategy

The substitution of fossil fuels with solar fuels is a long-term goal requiring the development of novel technologies. Strategically, it is desirable to consider mid-term goals aiming at the development of hybrid solar/fossil endothermic processes in which fossil fuels are used exclusively as the chemical source for H₂ production, and solar energy as the source of high-temperature process heat. They offer viable and efficient routes for fossil fuel decarbonization and CO₂ mitigation [2,3]. An important example of such a hybrid process is the endothermic steam-gasification of coal to synthesis gas (syngas). The syngas product, besides being a high-quality fluid fuel for efficient combined-cycles and fuel cells, is cleaner than its solid feedstock because its energy content has been upgraded by solar energy, i.e. their calorific value is increased above the value of the coal due to the solar power needed to drive the endothermic reaction. The mix of coal and solar energy creates a link between today’s coal-based technology and tomorrow’s solar chemical technology. It also builds bridges between present and future energy economies because of the potential of solar energy to become a viable economic path once the cost of energy will account for the environmental externalities from burning fossil fuels. The transition from coal to solar fuels can occur smoothly,
and the lead-time for transferring important solar technology to industry can be reduced. Hybrid solar/coal processes that mix coal with solar energy, such as the solar steam gasification of coal, provide an important transition path to a more sustainable energy-supply system, because it links the new technology with well known and established industrial processes.

**Conventional coal gasification vs. Solar coal gasification**

Several chemical aspects of the gasification of solid carbonaceous materials are summarized in the literature [4,5,7,8,38,40,41]. In conventional gasifiers, the energy required for heating the reactants and for the heat of the reaction is supplied by burning a significant portion of the feedstock, either directly by internal combustion [41], or indirectly by external combustion. Internal combustion, as applied in autothermal reactors, results in the contamination of the gaseous products while external combustion, as applied in allothermal reactors, results in a lower thermal efficiency because of the irreversibilities associated with indirect heat transfer. Alternatively, the advantages of supplying solar energy for process heat are three-fold: (1) the calorific value of the feedstock is upgraded, (2) the gaseous products are not contaminated by the byproducts of combustion; and (3) the discharge of pollutants to the environment is avoided. Furthermore, the direct irradiation of reactants provides a very efficient means of heat transfer directly to the reaction site, the surface of the particles, where the energy is needed for the surface reaction, and so it is bypassing the limitations imposed by heat exchangers.

**Review of earlier work**

The gasification of carbonaceous materials and related reactions have been performed using concentrated solar energy in exploratory early studies with coal, oil shales, biomass, and other carbon-containing feedstock [9,10,11,12,13,29,33]. More recently, the CO₂ - gasification of coal was investigated using a fluidized bed reactor under direct irradiation [32]. Several solar reactor concepts have been proposed and tested with small-scale prototypes [27,28,35]. The heat transfer characteristics of coal gasification using an external radiative source have been investigated by Belghit et al. [24]. The direct irradiation of particle suspensions provided an efficient means of heat transfer directly to the reaction site, as corroborated as well in previous experimental studies [42,43,44,45].
Numerous studies have been performed in the area of numerical modeling of fluidized bed systems. The modeled thermochemical processes included gasification, pyrolysis, and combustion of carbonaceous materials (coal, biomass, emulsions, etc.) [46,47,48,49]. Chejne and Hernandez [46] presented a one-dimensional steady state mathematical model for the simulation of coal gasification processes, and validated the model with experimental data. Werther and Hartge [47] developed a model for industrial fluidized bed reactors with particular focus on solid attrition, recovery, and chemical performance of the fluidized-bed reactor, and illustrated the importance of solid recovery for high reactor performance. Luo at al. [48] presented a model for wood pyrolysis in a fluidized bed reactor and studied the effect of reaction temperature on wood pyrolysis behavior. Yan et al. [50] found the net flow modeling from the emulsion to the gas phase for bubbling and pressurized fluidized bed gasifiers allowed better prediction of experimental results, and presented an extended model capable of simulating pilot-scale, full scale and pressurized fluidized-bed coal gasifiers [51]. Yang and Zhang [49] examined the effect of the combustion product distribution coefficient and deduced suggested values for different reactor types. For processes carried out at above 1300 K, radiative transfer within the fluidized particulate media and among the fluidized bed and reactor walls becomes a predominant mode of heat transfer [52,53,54,55,56]. Mazza et al. [52] evaluated the radiative heat transfer properties in dense particulate media. Szekely and Fisher [53] studied bed to wall radiation heat transfer at low temperature and estimated radiative heat transfer to become significant at about 1000°C. Yamada et al. [54] developed a method for evaluating the radiation heat exchange between a heat transfer surface and fluidized particles. Yang et al. [55] studied the radiative heat transfer between high-temperature fluidized beds and immersed walls, and Luan at al. [56] proposed a model for suspension-to-wall heat transfer including conductive, convective and radiative heat transfer. Both found good agreement with experimental results. Examples of recent applications of the Monte Carlo (MC) ray-tracing method include the modeling of pulverized coal fired furnaces [58], of real gas mixtures [59], of particle clouds having spectral and directional dependent properties [60,61,62], and of directly irradiated solid-gas systems undergoing thermochemical transformations [63,64].
Content outline

Chapter 2 presents a Second-Law analysis for determining the maximum exergy efficiency of the solar thermal gasification process and for identifying the major sources of irreversibility. This information determines the constraints to be imposed on the design and efficient operation of a solar chemical reactor. Further, two technically viable routes for extracting power from the chemical products are examined, and a base for comparing them with electricity generation by conventional coal-fired power plants is established.

Chapter 3 describes setup and data analysis of the experimental steam gasification of charcoal in a laboratory scale tubular quartz reactor, containing a fluidized bed of charcoal particles, directly exposed to an external source of concentrated radiation.

Chapter 4 presents a kinetic analysis of the steam-gasification of charcoal. The kinetic rate laws are formulated based on the analysis of elementary reaction mechanisms, and the rate constants are computed by matching theoretical and experimental data obtained from the gasification experiments.

Chapter 5 represents the most important part of this work. A numerical model was developed to simulate a directly-irradiated tubular quartz reactor in the ETH's high-flux solar simulator. The Monte Carlo (MC) ray-tracing method is applied to solve the 3D radiative exchange within the particulate bed and within the reactor walls. The modeled chemical reactor consists of a quartz tube containing a fluidized-bed or packed-bed of coal particles undergoing steam gasification. The external source of concentrated thermal radiation delivers the required high-temperature process heat. Mass and energy conservation equations are formulated coupling radiation to conduction, convection, particle mixing, chemical reaction, and enthalpy change and are solved numerically to calculate temperatures, gas composition, and reaction extent.

Chapter 6 presents the validation of the numerically computed flux distribution, the temperature profiles, and product gas composition, with experimental data obtained from tests with the quartz tubular reactor containing a fluidized or packed bed of charcoal particles, that is directly exposed to high-flux irradiation.

Finally, Chapter 7 gives a summary of the work that has been conducted and an outlook with suggestions how it might be continued and improved.
2 Thermodynamic Analysis

2.1 Introduction

The thermodynamics of steam-gasification of coal into syngas are examined using concentrated solar energy as the source of high-temperature process heat. Two technically viable routes for generating electricity using the gasification products are considered: (1) syngas is used to fuel a combined Brayton-Rankine cycle; and (2) syngas is further processed to H₂, which is used to fuel a H₂/O₂ fuel cell. A 2nd-law analysis is carried out to identify the major sources of irreversibility, and their effect on the overall energy conversion efficiency is examined. This allows the comparison of the two routes against each other, and also against a conventional cycle, where coal is used to fuel a Rankine cycle.

2.2 Equilibrium Compositions and Enthalpies

The steam-gasification of coal is a complex process. The overall chemical conversion, however, can be represented by the simplified net reaction:

\[ \text{CH}_x\text{O}_y + (1-y)\text{H}_2\text{O} = \left( \frac{x}{2} + 1 - y \right)\text{H}_2 + \text{CO} \]  (2-1)

where \( x \) and \( y \) are the elemental molar ratios of H/C and O/C in coal, respectively. The chemical product is synthesis gas (syngas), whose quality depends on \( x \) and \( y \). Table 2.1 shows the chemical composition, the heating value, and the elemental molar ratios for four different types of coal that cover a wide range of coal qualities: peat, lignite, bituminous, and anthracite. In the analysis that follows, sulfur compounds and other impurities contained in the raw materials are assumed to be cleaned out prior to the gasification process. The moisture content is also not accounted for in Eq. (2-1), but the stoichiometric addition of water can be adjusted accordingly.

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Table 2.1. Main elemental chemical composition in wt%, low heating value (LHV) in kJ/kg, and elemental molar ratios of H/C and O/C, for four types of coal [4].

<table>
<thead>
<tr>
<th>Coal type</th>
<th>Units</th>
<th>Peat</th>
<th>Lignite</th>
<th>Bituminous</th>
<th>Anthracite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>wt%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>wt%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>wt%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>wt%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>wt%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>LHV</td>
<td>kJ/kg</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>x (H/C ratio)</td>
<td>mol/mol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>y (O/C ratio)</td>
<td>mol/mol</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coa type</th>
<th>Units</th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>N</th>
<th>S</th>
<th>LHV</th>
<th>x</th>
<th>y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peat</td>
<td>wt%</td>
<td>58.20</td>
<td>5.63</td>
<td>34.02</td>
<td>1.94</td>
<td>0.21</td>
<td>23'500</td>
<td>1.16</td>
<td>0.44</td>
</tr>
<tr>
<td>Lignite</td>
<td>wt%</td>
<td>71.40</td>
<td>4.79</td>
<td>21.87</td>
<td>1.34</td>
<td>0.60</td>
<td>28'500</td>
<td>0.81</td>
<td>0.23</td>
</tr>
<tr>
<td>Bituminous</td>
<td>wt%</td>
<td>82.60</td>
<td>4.97</td>
<td>9.38</td>
<td>1.55</td>
<td>1.50</td>
<td>34'000'</td>
<td>0.72</td>
<td>0.09</td>
</tr>
<tr>
<td>Anthracite</td>
<td>wt%</td>
<td>92.20</td>
<td>3.30</td>
<td>3.37</td>
<td>0.15</td>
<td>0.98</td>
<td>35'700</td>
<td>0.43</td>
<td>0.03</td>
</tr>
</tbody>
</table>

*average of values reported in the literature [4,5,7]

Equation (2-1) summarizes the overall reaction. A group of competing intermediate reactions, which are essential for the successful gasification, need also be considered. These are:

- **Boudouard equilibrium**
  \[
  C_{(g)} + CO_2 = 2CO
  \]  \hspace{1cm} (2-2)

- **Methane cracking – hydrogasification**
  \[
  C_{(g)} + 2H_2 = CH_4
  \]  \hspace{1cm} (2-3)

- **Reforming – methanation**
  \[
  CH_4 + H_2O = CO + 3H_2
  \]  \hspace{1cm} (2-4)

- **Water-gas shift**
  \[
  CO + H_2O = CO_2 + H_2
  \]  \hspace{1cm} (2-5)

All of these reactions depend strongly on the temperature as well as on the pressure and the carbon/oxygen ratio, and determine the relative amounts of H₂, H₂O, CO, CO₂, CH₄ in the gas phase, and C_{(g)} in the solid phase.

The HSC Outokumpu code [14] was used to compute the equilibrium composition of the system C₃HₓOᵧ+(1-y)H₂O at 1 bar and over the range of temperatures of interest. Fig. 2.1 shows the results for anthracite (C_{1.045}O_{0.09}). Species whose mole fraction is less than 10⁻⁵ have been omitted. Below about 700 K, C_{(g)}, CH₄, CO₂, H₂O are the thermodynamically stable components. In the temperature range 800-1100 K, they are used up by a combination of reactions (2-1) to (2-5). When the gasification goes to completion, at above 1200 K, the system consists of a single gas phase containing H₂.
and CO in a molar ratio equal to \((x/2 + 1 - y)\). The \(H_2/CO\) molar ratio characterizes the quality of the syngas. It varies between 1.14 for peat gasification to 1.27 for bituminous coal gasification. The syngas quality is notably higher than the one typically obtained when heat is supplied by internal combustion of coal, besides the additional benefit of avoiding contamination by undesirable combustion byproducts.

![Equilibrium composition of the system C\(_6\)H\(_5\)O\(_y\)+(\(1-y\))H\(_2\)O as a function of temperature, for dried and desulfurized anthracite coal (C\(_6\)H\(_{43}\)O\(_{29}\)). Omitted is the formation of by-products derived from impurities present in the feedstock.](image)

Figure 2.1. Equilibrium composition of the system C\(_6\)H\(_5\)O\(_y\)+(\(1-y\))H\(_2\)O as a function of temperature, for dried and desulfurized anthracite coal (C\(_6\)H\(_{43}\)O\(_{29}\)). Omitted is the formation of by-products derived from impurities present in the feedstock.

Fig. 2.2 shows the percent yield of \(H_2\) and CO as a function of temperature. At above 1350 K, the yield for both exceeds 99%. The results for the other three types of coal are very similar to the ones shown in Figs. 2.1 and 2.2, and the same conclusions can be drawn regarding temperature requirements.

Reaction (2-1) proceeds endothermically in the 800-1500 K range. Figure 2.3 shows the enthalpy change of reaction (2-1) as a function of temperature \(T\) for the four types of coal, when the reactants are fed at 300 K and the products are obtained at reactor temperature \(T\) having an equilibrium composition given in Fig 2.1.
Figure 2.2. Variation of the percent yield of H₂ and CO with temperature for the gasification of anthracite coal, assuming equilibrium composition.

Figure 2.3. Enthalpy change of reaction (2-1) as a function of temperature $T$ for the four types of coal, when the reactants are fed at 300 K and the products are obtained at reactor temperature $T$ having the equilibrium composition as given in Fig. 2.1.
The reference enthalpy of coal at ambient temperature was calculated by evaluating the combustion reaction

\[ \text{C}_x\text{H}_y\text{O}_z + \left(1+\frac{x}{4}-\frac{y}{2}\right)\text{O}_2 = \frac{x}{2}\text{H}_2\text{O}(g) + \text{CO}_2 \]  

(2-6)

at 300 K. The enthalpy change of reaction (2-6) at 300 K is, by definition, given by the heating value of coal (see Table 2.1). And so the (mass) specific reference enthalpy of coal is calculated as

\[ \frac{n_{\text{H}_2\text{O}}}{n_{\text{coal}}} \cdot h_{\text{H}_2\text{O},\text{T}_a} + \frac{n_{\text{CO}_2}}{n_{\text{coal}}} \cdot h_{\text{CO}_2,\text{T}_a} - \frac{n_{\text{O}}}{n_{\text{coal}}} \cdot h_{\text{O},\text{T}_a} + \text{LHV}_{\text{coal}} \]  

(2-7)

where \( h_{i,T} \) is the (mole) specific enthalpy of species \( i \) at temperature \( T \). \( T_a \) is the ambient temperature. The molar flows are given by

\[ \hat{n}_{\text{H}_2\text{O}} = \frac{\hat{m}_{\text{coal}}}{2} \cdot \frac{1}{\text{M}_c + x\text{M}_H + y\text{M}_O} \]

\[ \hat{n}_{\text{CO}_2} = \frac{\hat{m}_{\text{coal}}}{\text{M}_c + x\text{M}_H + y\text{M}_O} \]

\[ \hat{n}_{\text{O}} = \frac{\hat{m}_{\text{coal}}}{x} \cdot \frac{1}{\text{M}_c + x\text{M}_H + y\text{M}_O} \]

(2-8)

where \( \text{M}_i \) is the molecular weight of element \( i \).

Fig. 2.3 shows that there is a substantial difference in the amount of heat required for gasifying the different types of coal. For example, gasifying anthracite coal requires 7, 40, and 86% more energy than gasifying bituminous, lignite, and peat coal, respectively. Part of the reason for the different gasification enthalpies arises from the fact that more water is needed per unit weight of coal gasified as the molar ratio \( \text{O}/\text{C} \) of coal decreases, see Eq. (2-1), and consequently more energy is needed for producing steam at the required temperature. Contrariness, the enthalpy change decreases with decreasing molar ratio \( \text{H}/\text{C} \), but its effect is secondary.

2.3 2nd-Law Analysis

A 2nd-law (exergy) analysis is carried out for calculating the maximum exergy efficiency, following the derivation described by Steinfeld et al. [15]. The complete process flow sheet is shown in Fig. 2.4, with several optional routes grouped in boxes A to D. Box A depicts the solar coal gasification process and includes the solar concentration system,
the solar reactor, a heat exchanger, and a quencher. Boxes B and C depict two technically feasible routes for generating electricity from the chemical products of the solar coal gasification. These routes are: 1) (Box B) syngas is used to fuel a combined Brayton-Rankine cycle; and 2) (Box C) syngas is processed to \( \text{H}_2 \) by the water-shift gas reaction followed by \( \text{H}_2/\text{CO}_2 \) separation, and \( \text{H}_2 \) is used to fuel a \( \text{H}_2/\text{O}_2 \) fuel cell. Box D depicts a third, conventional route for electricity generation by using coal to fuel a Rankine cycle. The complete process is carried out at a constant pressure of 1 bar. In practice, pressure drops will occur throughout the system and supplemental pumping work will be required. The mass flow rate of coal, \( \dot{m}_{\text{coal}} \), was set to 1 g s\(^{-1}\) in the calculations.
Figure 2.4. Flow sheet diagram used for the 2nd-Law Analysis. Box A depicts the solar coal gasification process. Boxes B and C depict two technically feasible routes for generating electricity from the chemical products of box A, namely: 1) (Box B) syngas is used to fuel a combined Brayton-Rankine cycle; and 2) (Box C) syngas is processed to H\(_2\) and used to fuel a H\(_2\)/O\(_2\) fuel cell. Box D depicts the third (conventional) route of using coal to fuel a Rankine cycle.
Solar Concentration System

The solar concentrating plant is assumed to be a solar tower or a solar tower-reflector system for large-scale collection and concentration of solar energy at power levels of several megawatts. The solar tower system, also referred to as the central-receiver system, uses a field of heliostats (i.e. two-axis tracking parabolic mirrors) to focus the sunrays onto a receiver mounted on top of a centrally located tower [16]. The solar tower-reflector system, also referred to as the beam-down system, is based on the Cassegrain optical configuration that uses a hyperboloidal reflector positioned at the top of the tower to further re-direct the concentrated sunlight down to the reactor located on the ground level [17]. Both of these concentrating systems are capable of achieving power flux intensities equivalent to solar concentration ratios $C$ of 5000 and higher by applying non-imaging secondary concentrators (usually compound parabolic concentrators, also known as CPCs [18]) in tandem with the primary focusing heliostat field. The solar flux concentration ratio $C$ is defined as the ratio of the mean solar flux intensity achieved at the reactor's aperture after concentration to the incident beam normal insolation, thus

$$C = \frac{\int_{A_{ap}} q' dA'}{I \cdot A_{ap}}$$

(2-9)

where $A_{ap}$ is the reactor's aperture, and $I$ is the normal beam insolation. $C$ is a dimensionless number, sometimes reported in units of 'suns'. Such high radiation fluxes correspond to stagnation temperatures exceeding 3000 K and allow the conversion of concentrated solar radiation to thermal reservoirs at 1500 K and above. The stagnation temperature is the highest temperature an ideal blackbody receiver is capable of achieving when energy is being re-radiated as fast as it is absorbed. It is given by

$$T_{stog} = \sqrt[4]{\frac{C \cdot I}{\sigma}}$$

(2-10)

where $\sigma$ is the Stefan-Boltzmann constant. The optical efficiency of the solar concentrating system is defined as the portion of solar beam radiation incident over the heliostat field that is delivered as concentrated solar power to the receiver-reactor. It accounts for reflectivity, shading, alignment, and spillage losses due to geometrical and tracking imperfections. Since the process exergy efficiency, as it will be defined in
Eq. (2-31), is based on the solar power coming from the solar concentrating system, the optical efficiency is not included in the calculations.

**Solar Reactor**

The solar reactor is assumed to be a cavity-receiver operating at $T_3$. Its capability to absorb incoming concentrated solar energy is expressed by the solar energy absorption efficiency, $\eta_{\text{absorption}}$, defined as the net rate at which energy is being absorbed, $\dot{Q}_{\text{reactor,net}}$, divided by the solar power input through the reactor’s aperture coming from the solar concentrating system, $\dot{Q}_{\text{solar}}$. For a perfectly insulated blackbody cavity-receiver (no convection or conduction heat losses; cavity’s effective absorptivity and emissivity equal to 1), it is given by

$$\eta_{\text{absorption}} = \frac{\dot{Q}_{\text{reactor,net}}}{\dot{Q}_{\text{solar}}} = 1 - \left( \frac{\sigma T_3^4}{I C} \right)$$

(2-11)

where $I$ is the normal beam insolation, $C$ is the mean flux concentration ratio over the solar reactor’s aperture, $T_3$ is the nominal reactor temperature, and $\sigma$ is the Stefan-Boltzmann constant.

The reactants coal and steam enter the solar reactor and are further heated to $T_3$. Only steam is assumed to be preheated from $T_1$ to $T_2$ in a heat exchanger, i.e. coal enters the solar reactor at $T_1$ and steam at $T_2$. Chemical equilibrium at $T_3$ is assumed to be achieved inside the reactor, given in Fig. 2.1. The net power absorbed in the solar reactor should match the enthalpy change per unit time of the reaction

$$\dot{Q}_{\text{reactor,net}} = \sum_j \dot{n}_{j,\text{out}} h_{j,i_1} - (\dot{n}_{H_2O,in} h_{H_2O,i_3} + \dot{m}_{\text{coal}} \dot{h}_{\text{coal},i_1})$$

(2-12)

where $\dot{n}_j$ is the equilibrium mole flow, for $j = C, \text{CH}_4, \text{CO}, \text{CO}_2, \text{H}_2, \text{H}_2\text{O}$, and $\dot{n}_{H_2O,in}$ is the molar flow of steam into the reactor

$$\dot{n}_{H_2O,in} = (1 - y) \cdot \frac{\dot{m}_{\text{coal}}}{M_C + xM_H + yM_O}$$

(2-13)

The enthalpy change of reaction (per kg of coal) is plotted in Fig. 2.3 as a function of $T_3$, for $T_2 = 300K$. The irreversibility in the solar reactor arises from the non-reversible
chemical transformation, heat transfer to the reactor, and re-radiation losses to the surroundings

\[ \text{Irr}_{\text{reactor}} = \frac{\dot{Q}_{\text{solar}}}{T_3} + \frac{\dot{Q}_{\text{radiation}}}{T_a} + \left( \sum_j \dot{n}_{j,\text{out}} s_{j,T_1} \right) - \left( \dot{n}_{H_2O,\text{in}} s_{H_2O,T_3} + \dot{m}_{\text{coal}} \tilde{s}_{\text{coal},T_a} \right) \]  \hspace{1cm} (2-14)

where \( \dot{Q}_{\text{radiation}} \) denotes the radiation heat loss by the reactor at \( T_3 \) to the surroundings at \( T_1 \), given by

\[ \dot{Q}_{\text{radiation}} = (1 - \eta_{\text{absorption}}) \dot{Q}_{\text{solar}} \]  \hspace{1cm} (2-15)

The entropy of coal has been calculated assuming the entropies values of \( \{ C + 0.5xH_2 + 0.5yO_2 \} \) for coal \( \{ C,H_xO_y \} \); which introduces an error, but does not affect the identification of the main irreversibly sources. The mass specific entropy of coal is then

\[ \tilde{s}_{\text{coal},T_a} = \frac{s_{C,T_a} + \frac{x}{2} s_{H_2,T_a} + \frac{y}{2} s_{O_2,T_a}}{M_C + xM_H + yM_O} \]  \hspace{1cm} (2-16)

**Heat Exchanger**

The reactants are pre-heated in an adiabatic countercurrent-flow heat exchanger where some portion of the sensible heat of the products is transferred to the reactants. \( H_2O \) enters at ambient temperature \( T_1 \) and exit at \( T_2 \); the products enter at \( T_3 \) and exit at \( T_4 \). It is assumed that the composition of the reactants and products remain unchanged during the heating and cooling processes inside the heat exchanger. If \( \dot{Q}_{\text{HE}} \) is the power transferred from the products to the reactants and \( \eta_{\text{HE}} \) the heat recovery factor, then

\[ \dot{Q}_{\text{HE}} = \dot{n}_{H_2O,\text{in}} (h_{H_2O,T_1} - h_{H_2O,T_3}) = \sum_j \dot{n}_{j,\text{out}} (h_{j,T_1} - h_{j,T_3}) \]  \hspace{1cm} (2-17)

\[ \eta_{\text{HE}} = \frac{\dot{Q}_{\text{HE}}}{\sum_j \dot{n}_{j,\text{out}} (h_{j,T_1} - h_{j,T_3})} \]  \hspace{1cm} (2-18)

The heat transfer across finite temperature differences causes the following irreversibilities that are intrinsic to the heat exchanger.
\[ l_{r_{HE}} = n_{H_2O,in}(s_{H_2O,T_i} - s_{H_2O,T_i}) + \sum_j n_{j,out}(s_{j,T_i} - s_{j,T_i}) \] (2-19)

**Quench**

After leaving the heat exchanger the products are cooled quickly to ambient temperature \( T_i \). The chemical composition of the products remains unchanged upon cooling in the quencher. The power lost during quenching is

\[ Q_{\text{quench}} = -\sum_j n_{j,out}(h_{j,T_i} - h_{j,T_i}) \] (2-20)

The irreversibility associated with quenching is

\[ l_{r_{\text{quench}}} = \frac{Q_{\text{quench}}}{T_a} + \sum_j n_{j,out}(s_{j,T_i} - s_{j,T_i}) \] (2-21)

**Combined Cycle route**

The chemical output of Box A is syngas at ambient temperature, having the equilibrium composition determined in Fig. 2.2 for \( T_s \). Boxes B and C of Fig. 2.4 represent two viable routes for extracting power from the syngas. Box B features a combined Brayton-Rankine cycle fueled by syngas. Its work output \( W_{\text{cc}} \) and rejected heat \( Q_{\text{cc}} \) are given by

\[ \Delta H_{\text{cc}} = (\hat{n}_{CO,\text{cc}}h_{CO,T_i} + \hat{n}_{H_2O,\text{cc}}h_{H_2O,T_i}) - (\hat{n}_{H_2,O,out}h_{H_2,O,T_i} + \hat{n}_{CO,O,out}h_{CO,O,T_i} + \hat{n}_{O_2,cc}h_{O_2,T_i}) \]

\[ W_{\text{cc}} = n_{cc} \Delta H_{\text{cc}} \]

\[ Q_{\text{cc}} = (1-n_{cc}) \Delta H_{\text{cc}} \] (2-22)

where \( n_{cc} \) denotes the cycle efficiency, assumed 55%. The mole flows for incoming \( O_2 \) and outgoing \( H_2O, CO_2 \) are

\[ \hat{n}_{O_2,cc} = \left( \frac{\hat{n}_{H_2,O,out} + \hat{n}_{CO,O,out}}{2} \right) \]

\[ \hat{n}_{H_2O,cc} = \hat{n}_{H_2,O,out} \]

\[ \hat{n}_{CO_2,cc} = \hat{n}_{CO,O,out} \] (2-23)
Fuel Cell route

Box C features a water-gas shift reactor, a heat exchanger, a separator, a quencher, and a H₂/O₂ fuel cell. The water gas shift reaction,

\[ \text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2 \]  \hspace{1cm} (2-24)

is exothermic and proceeds catalytically at 700 K. It can be carried out in an autothermal reactor in which the heat liberated is used to heat the reactants. Alternatively, a heat exchanger can precede the water-gas shift reactor to preheat the reactants by recovering a portion of the sensible heat of the products. In either case, the surplus of heat is assumed to be lost to the surroundings. As can be seen in Eq. (2-24), an additional mole of H₂ is produced for each mole of CO in the syngas, thus the molar flow after the water-gas shift reactor is given by

\[ \dot{n}_{\text{H}_2,\text{WGS}} = \dot{n}_{\text{H}_2,\text{out}} + \dot{n}_{\text{CO},\text{out}} \]
\[ \dot{n}_{\text{CO},\text{WGS}} = \dot{n}_{\text{CO},\text{out}} \]  \hspace{1cm} (2-25)

The H₂/CO₂ separation unit is assumed to be based on the pressure swing adsorption technique (PSA) at a recovery rate \( \eta_{\text{rec,PSA}} \) of 90 % [19], i.e. the molar flow of H₂ after separation, and still mixed gas after separation is

\[ \dot{n}_{\text{H}_2,\text{PSA}} = \eta_{\text{rec,PSA}} \dot{n}_{\text{H}_2,\text{WGS}} \]
\[ \dot{n}_{\text{H}_2,\text{mix}} = (1 - \eta_{\text{rec,PSA}}) \dot{n}_{\text{H}_2,\text{WGS}} \]
\[ \dot{n}_{\text{CO},\text{PSA}} = \dot{n}_{\text{CO},\text{WGS}} \]  \hspace{1cm} (2-26)

The minimum energy expenditure is equal to the \( \Delta G \) of unmixing

\[ \Delta G_{\text{PSA}} = T_d \cdot R_u \left( \frac{\dot{n}_{\text{H}_2,\text{mix}} \ln{\frac{\dot{n}_{\text{H}_2,\text{mix}} + \dot{n}_{\text{CO},\text{PSA}}}{\dot{n}_{\text{H}_2,\text{mix}} + \dot{n}_{\text{CO},\text{PSA}}}} + \dot{n}_{\text{CO},\text{mix}} \ln{\frac{\dot{n}_{\text{CO},\text{PSA}}}{\dot{n}_{\text{CO},\text{mix}} + \dot{n}_{\text{CO},\text{PSA}}}} \right) - \dot{n}_{\text{H}_2,\text{WGS}} \ln{\frac{\dot{n}_{\text{H}_2,\text{WGS}} + \dot{n}_{\text{CO},\text{WGS}}}{\dot{n}_{\text{H}_2,\text{WGS}} + \dot{n}_{\text{CO},\text{WGS}}}} - \dot{n}_{\text{CO},\text{WGS}} \ln{\frac{\dot{n}_{\text{CO},\text{WGS}}}{\dot{n}_{\text{H}_2,\text{WGS}} + \dot{n}_{\text{CO},\text{WGS}}}} \]  \hspace{1cm} (2-27)

which amounts to about 1 % of the electric output of the fuel cell.

Finally, H₂ is used to fuel a H₂/O₂ fuel cell. \( \dot{W}_{\text{FC}} \) and \( \dot{Q}_{\text{FC}} \) are the work output and heat rejected, respectively given by

\[ \dot{W}_{\text{FC}} = -\eta_{\text{FC}} \cdot \dot{n}_{\text{H}_2,\text{PSA}} \left( g_{\text{H}_2\text{O}(\text{t}_a)} - g_{\text{H}_2,\text{t}_a} - \frac{1}{2} g_{\text{O}_2,\text{t}_a} \right) \]  \hspace{1cm} (2-28)
\[ Q_{FC} = -T_a \cdot \dot{h}_{H_2,PSA} \left( s_{H_2,0}(T_a) - s_{H_2,T_a} - \frac{1}{2} s_{O_2,T_a} \right) \]  

(2-29)

where \( \eta_{FC} \) denotes the conversion efficiency of the \( \text{H}_2/\text{O}_2 \) fuel cell, assumed 65 %. State-of-the-art stationary SOFC fuel cells feature energy conversion efficiencies in the range 55-60 % when fed with natural gas, and in the range 65-70 % when fed directly with hydrogen since the relative loss in the reformer is in the order of 10 % [20].

**Conventional route**

Box D of Fig. 2.4 features the conventional Rankine cycle, fueled by coal. Its work output \( W_{RC} \) and heat rejected \( Q_{RC} \) are given by

\[
\Delta H_{RC} = (\dot{h}_{H_2,0,RC} + \dot{h}_{CO_2,RC} h_{CO_2,T_a}) - \left( \dot{h}_{O_2,RC} h_{O_2,T_a} + \dot{m}_{coal} h_{coal,T_a} \right)
\]

\[ W_{RC} = \eta_{RC} \Delta H_{RC} \]  

(2-30)

\[ Q_{RC} = (1 - \eta_{RC}) \Delta H_{RC} \]

where \( \eta_{RC} \) denotes the conversion efficiency of a coal fired Rankine cycle, assumed 35 %.

**Exergy Efficiency**

The exergy efficiency for each of the power generation routes is defined as the ratio of the work output (either by the combined cycle (CC), fuel cell (FC), or Rankine cycle (RC)) to the total thermal power input into the process by solar energy and by the heating value of the reactants

\[ \eta_{ex,CC} = \frac{W_{CC}}{Q_{\text{solar}} + \dot{m}_{coal} \text{LHV}_{coal}} \]

\[ \eta_{ex,FC} = \frac{W_{FC}}{Q_{\text{solar}} + \dot{m}_{coal} \text{LHV}_{coal}} \]  

(2-31)

\[ \eta_{ex,RC} = \frac{W_{RC}}{\dot{m}_{coal} \text{LHV}_{coal}} = \eta_{RC} \]

where \( \text{LHV}_{coal} \) is the low heating value of coal, reported in Table 2.1. Note that Eqs. (2-31) are not exergy efficiencies in the literal way, since the terms in the denominators are not exergy, but energy. As defined above, they are a measure of how much of the invested thermal energy is transferred to useful work, i.e. exergy.
Specific electric output

The specific electric output shows the amount of electricity that can be produced per kg of coal feed, it is defined as following for the three routes

\[
EO_{cc} = \frac{\dot{W}_{cc}}{\dot{m}_{coal}}, \quad EO_{rc} = \frac{\dot{W}_{rc}}{\dot{m}_{coal}}, \quad EO_{rc} = \frac{\dot{W}_{rc}}{\dot{m}_{coal}}
\]  

(2-32)

Electric Gain Factor

Another important indicator of the process performance is the Electric Gain Factor (EGF), defined as the ratio of the electric output of the process to that obtained when using the same amount of coal in a 35%-efficient Rankine cycle.

\[
EGF_{cc} = \frac{\dot{W}_{cc}}{\dot{W}_{rc}}, \quad EGF_{rc} = \frac{\dot{W}_{rc}}{\dot{W}_{rc}}
\]  

(2-33)

The EGF for the conventional route is obviously 1.

Specific Emissions

The specific CO$_2$ emission is the amount of CO$_2$ emitted per electrical output for each route

\[
Em_{CO_2,cc} = \frac{(M_c + 2M_b)\dot{n}_{CO_2,cc}}{\dot{W}_{cc}}
\]

\[
Em_{CO_2,rc} = \frac{(M_c + 2M_b)\dot{n}_{CO_2,rc}}{\dot{W}_{rc}}
\]

(2-34)

Solar contribution to mix

The solar contribution to mix is the ratio of the solar power input to the total thermal power input to the process (solar power + heating value of coal).

\[
\eta_{SCM} = \frac{\dot{Q}_{solar}}{\dot{Q}_{solar} + \dot{m}_{coal}LHV_{coal}}
\]  

(2-35)

It indicates the solar contribution to the input energy mix.
Verification by comparison to ideal closed material cycle

The irreversibility calculation is verified by evaluating the maximum achievable exergy efficiency (Carnot efficiency) for an ideal closed material cycle in which the products recombine in an ideal fuel cell to give the original reactants. The available work is calculated as the sum of the ideal fuel-cell work and the lost work due to irreversibilities in the solar reactor, the heat exchanger, and during quenching. This maximum efficiency must be equal to that of a Carnot heat engine operating between 1350 and 300 K. Thus,

\[
\eta_{\text{max}} = \frac{W_{\text{fc,cc}} + T_o \cdot (\text{irr}_{\text{reactor}} + \text{irr}_{\text{heat}} + \text{irr}_{\text{quench}})}{Q_{\text{solar}}} \approx \eta_{\text{Carnot}} = 1 - \frac{300K}{1350K} = 78\% \tag{2.36}
\]

2.4 Results and discussion

Tables 2.2 and 2.3 show the complete energy balance and efficiencies calculation. Values for power are normalized to a coal mass flow rate \(m_{\text{coal}}\) of 1 g·s\(^{-1}\). Three routes for generating electricity are considered, and are depicted by the boxes A+B, A+C, and D of Fig. 2.4. Calculations have been carried out using the following baseline parameters: \(T_1 = T_o = 300K\), \(T_3 = 1350K\), \(p = \text{bar}\), \(\eta_{\text{cc}} = 55\%\), \(\eta_{\text{ic}} = 65\%\), \(\eta_{\text{fc}} = 35\%\), \(I = 1kW\cdot m^{-2}\), and \(C = 2000\). Table 2.2 presents the results for the case when the heat exchanger of box A is employed for producing steam at \(T_2 = 1250K\), that is, steam is fed to the solar reactor at 1250 K, coal is fed to the solar reactor at 300 K, and the products of the solar reactor are cooled in the heat exchanger from \(T_3 = 1350K\) to \(T_4\), before entering the quencher. Table 2.3 presents the results for the case when the heat exchanger of box A is excluded, that is, the reactants enter the solar reactor at \(T_1 = T_o = 300K\) and the products are quenched from \(T_3 = T_4 = 1350K\) to \(T_4 = 300K\). In both cases of Tables 2.2 and 2.3, the heat exchange of box C, with \(\eta_{\text{heat-exchanger}} = 62\%\) is employed to preheat the reactants to the water-gas shift reactor from 300 to 600 K.
Table 2.2. Thermodynamic analysis of the solar steam-gasification of coal using the process schematic shown in Fig. 2.4. Table 2.2 shows the case that employs the heat exchanger of box A, for preheating the feed of steam to $T_s$ before it is fed to the solar reactor. Values for power are normalized to a coal mass flow rate of 1 g·s⁻¹.

<table>
<thead>
<tr>
<th>Coal type</th>
<th>Eq.</th>
<th>Units</th>
<th>peat</th>
<th>lignite</th>
<th>bituminous</th>
<th>anthracite</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{solar}$</td>
<td>(2-11)</td>
<td>kW</td>
<td>7.17</td>
<td>9.15</td>
<td>11.79</td>
<td>12.36</td>
</tr>
<tr>
<td>$Q_{irradiation}$</td>
<td>(2-15)</td>
<td>kW</td>
<td>0.68</td>
<td>0.86</td>
<td>1.11</td>
<td>1.16</td>
</tr>
<tr>
<td>$Q_{reactor,net}$</td>
<td>(2-12)</td>
<td>kW</td>
<td>6.49</td>
<td>8.29</td>
<td>10.68</td>
<td>11.19</td>
</tr>
<tr>
<td>$Q_{net}$</td>
<td>(2-17)</td>
<td>kW</td>
<td>1.02</td>
<td>1.71</td>
<td>2.38</td>
<td>2.77</td>
</tr>
<tr>
<td>$T_s$</td>
<td>(2-17)</td>
<td>K</td>
<td>1053</td>
<td>946</td>
<td>889</td>
<td>839</td>
</tr>
<tr>
<td>$Q_{quench}$</td>
<td>(2-20)</td>
<td>kW</td>
<td>2.39</td>
<td>2.53</td>
<td>2.81</td>
<td>2.70</td>
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<tr>
<td>$I_{r,reactor}$</td>
<td>(2-14)</td>
<td>W·K⁻¹</td>
<td>16.5</td>
<td>20.6</td>
<td>25.5</td>
<td>27.0</td>
</tr>
<tr>
<td>$I_{r,ref}$</td>
<td>(2-19)</td>
<td>W·K⁻¹</td>
<td>2.3</td>
<td>4.0</td>
<td>5.6</td>
<td>6.6</td>
</tr>
<tr>
<td>$I_{r,quench}$</td>
<td>(2-21)</td>
<td>W·K⁻¹</td>
<td>11.9</td>
<td>12.9</td>
<td>14.5</td>
<td>14.1</td>
</tr>
<tr>
<td>$W_{CC}$</td>
<td>(2-22)</td>
<td>kW</td>
<td>15.08</td>
<td>18.73</td>
<td>22.88</td>
<td>24.15</td>
</tr>
<tr>
<td>$Q_{CC}$</td>
<td>(2-22)</td>
<td>kW</td>
<td>12.34</td>
<td>15.33</td>
<td>18.72</td>
<td>19.76</td>
</tr>
<tr>
<td>$W_{IC}$</td>
<td>(2-28)</td>
<td>kW</td>
<td>13.90</td>
<td>17.28</td>
<td>21.17</td>
<td>22.29</td>
</tr>
<tr>
<td>$Q_{IC}$</td>
<td>(2-29)</td>
<td>kW</td>
<td>1.26</td>
<td>1.57</td>
<td>1.92</td>
<td>2.02</td>
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<tr>
<td>$W_{BC}$</td>
<td>(2-30)</td>
<td>kW</td>
<td>8.23</td>
<td>9.98</td>
<td>11.90</td>
<td>12.50</td>
</tr>
<tr>
<td>$Q_{BC}$</td>
<td>(2-30)</td>
<td>kW</td>
<td>15.28</td>
<td>18.53</td>
<td>22.10</td>
<td>23.21</td>
</tr>
<tr>
<td>$\eta_{absorption}$</td>
<td>(2-11)</td>
<td></td>
<td>0.91</td>
<td>0.91</td>
<td>0.91</td>
<td>0.91</td>
</tr>
<tr>
<td>$\eta_{inlet}$</td>
<td>(2-18)</td>
<td></td>
<td>0.30</td>
<td>0.40</td>
<td>0.46</td>
<td>0.51</td>
</tr>
<tr>
<td>$\eta_{inlet}$</td>
<td>(Box A)</td>
<td></td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
</tr>
<tr>
<td>$\eta_{inlet}$</td>
<td>(Box C)</td>
<td></td>
<td>0.49</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>$\eta_{ex,CC}$</td>
<td>(2-31)</td>
<td></td>
<td>0.45</td>
<td>0.46</td>
<td>0.46</td>
<td>0.46</td>
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<tr>
<td>$\eta_{ex,IC}$</td>
<td>(2-31)</td>
<td></td>
<td>0.35</td>
<td>0.35</td>
<td>0.35</td>
<td>0.35</td>
</tr>
<tr>
<td>$EO_{CC}$</td>
<td>(2-32)</td>
<td>kWh/kg</td>
<td>4.19</td>
<td>5.20</td>
<td>6.35</td>
<td>6.71</td>
</tr>
<tr>
<td>$EO_{IC}$</td>
<td>(2-32)</td>
<td>kWh/kg</td>
<td>3.86</td>
<td>4.80</td>
<td>5.88</td>
<td>6.19</td>
</tr>
<tr>
<td>$EO_{BC}$</td>
<td>(2-32)</td>
<td>kWh/kg</td>
<td>2.28</td>
<td>2.77</td>
<td>3.31</td>
<td>3.47</td>
</tr>
<tr>
<td>$EGF_{CC}$</td>
<td>(2-33)</td>
<td></td>
<td>1.83</td>
<td>1.88</td>
<td>1.92</td>
<td>1.93</td>
</tr>
<tr>
<td>$EGF_{IC}$</td>
<td>(2-33)</td>
<td></td>
<td>1.69</td>
<td>1.73</td>
<td>1.78</td>
<td>1.78</td>
</tr>
<tr>
<td>$Em_{CO_{2},CC}$</td>
<td>(2-34)</td>
<td>kg CO₂/kWh</td>
<td>0.52</td>
<td>0.51</td>
<td>0.49</td>
<td>0.51</td>
</tr>
<tr>
<td>$Em_{CO_{2},IC}$</td>
<td>(2-34)</td>
<td>kg CO₂/kWh</td>
<td>0.56</td>
<td>0.55</td>
<td>0.53</td>
<td>0.55</td>
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<tr>
<td>$Em_{CO_{2},BC}$</td>
<td>(2-34)</td>
<td>kg CO₂/kWh</td>
<td>0.95</td>
<td>0.96</td>
<td>0.94</td>
<td>0.99</td>
</tr>
<tr>
<td>$\eta_{SCM}$</td>
<td>(2-35)</td>
<td></td>
<td>0.23</td>
<td>0.24</td>
<td>0.26</td>
<td>0.26</td>
</tr>
</tbody>
</table>
Table 2.3. Thermodynamic analysis of the solar steam-gasification of coal using the process schematic shown in Fig. 2.4. Table 2.3 shows the values that change for the case without the heat exchanger of box A, i.e. when steam enters the solar reactor at $T_s = T_r$.

<table>
<thead>
<tr>
<th>Coal type</th>
<th>Eq.</th>
<th>Units</th>
<th>peat</th>
<th>lignite</th>
<th>bituminous</th>
<th>anthracite</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{solar}$</td>
<td>(2-11)</td>
<td>kW</td>
<td>8.29</td>
<td>11.04</td>
<td>14.41</td>
<td>15.41</td>
</tr>
<tr>
<td>$Q_{radiation}$</td>
<td>(2-15)</td>
<td>kW</td>
<td>0.78</td>
<td>1.04</td>
<td>1.36</td>
<td>1.45</td>
</tr>
<tr>
<td>$Q_{reactor,net}$</td>
<td>(2-12)</td>
<td>kW</td>
<td>7.51</td>
<td>10.00</td>
<td>13.06</td>
<td>13.96</td>
</tr>
<tr>
<td>$Q_{HE}$</td>
<td>(2-17)</td>
<td>kW</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>$T_s$</td>
<td>(2-17)</td>
<td>K</td>
<td>1350</td>
<td>1350</td>
<td>1350</td>
<td>1350</td>
</tr>
<tr>
<td>$Q_{quench}$</td>
<td>(2-20)</td>
<td>kW</td>
<td>3.41</td>
<td>4.24</td>
<td>5.18</td>
<td>5.46</td>
</tr>
<tr>
<td>$irr_{reactor}$</td>
<td>(2-14)</td>
<td>W*K$^{-1}$</td>
<td>19.2</td>
<td>25.1</td>
<td>31.7</td>
<td>34.2</td>
</tr>
<tr>
<td>$irr_{quench}$</td>
<td>(2-21)</td>
<td>W*K$^{-1}$</td>
<td>16.2</td>
<td>20.1</td>
<td>24.6</td>
<td>25.9</td>
</tr>
<tr>
<td>$\eta_{HE}$ (Box A)</td>
<td>(2-18)</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\eta_{excc}$</td>
<td>(2-31)</td>
<td>-</td>
<td>0.47</td>
<td>0.47</td>
<td>0.47</td>
<td>0.47</td>
</tr>
<tr>
<td>$\eta_{exPC}$</td>
<td>(2-31)</td>
<td>-</td>
<td>0.44</td>
<td>0.44</td>
<td>0.44</td>
<td>0.44</td>
</tr>
<tr>
<td>$\eta_{SM}$</td>
<td>(2-35)</td>
<td>-</td>
<td>0.26</td>
<td>0.28</td>
<td>0.30</td>
<td>0.30</td>
</tr>
</tbody>
</table>

The maximum exergy efficiency amounts to 50% for route A+B and 46% for route A+C, when anthracite coal is feedstock and when using a heat exchanger between reactants and products of the solar reactor. For the other three types of coal, the exergy efficiency is slightly inferior but still exceeds 49% for route A+B and 45% for route A+C. Thus, both solar gasification routes offer significantly higher exergy efficiencies than the conventional 35%-efficient route via the coal-fired Rankine cycle. The path to H₂ and its use in high-efficient fuel cells (route A+C) is thermodynamically less favorable than using syngas directly in a combined cycle (route A+B), due to the energy consumption in the processing of H₂ from syngas, especially during the H₂/CO₂ separation. Hydrogen and its use in fuel cells may be the preferable path for mobile and/or decentralized applications. In contrast, syngas may be the desired final fuel for centralized power generation, or for applications in the chemical industry, e.g. synthesis of methanol and Fischer-Tropsch chemicals.

An important source of irreversibility is associated with the re-radiation losses from the solar reactor. More than 9% of the input solar power is lost by re-radiation. One can reduce the re-radiation losses by increasing the solar concentration ratio. For example, the exergy efficiency is increased by 2% when the solar concentration ratio is increased to 5000, as a result of being able to use a smaller solar reactor’s aperture to intercept the same amount of solar power and, consequently, reduce re-radiation losses and
increase the absorption efficiency (see Eq. (2-11)). However, solar flux concentrations ratios at the level of 5000 require high precision optical components that incurred higher investment costs. A mean solar concentration ratio varying in the range 1500-2000 corresponds to stagnation temperatures between 2268 and 2437 K, and delivers appropriate solar power fluxes for processes operating in the range 1200-1500 K, provided conduction and convection losses are kept to low levels. Note that, for a given solar concentration ratio, smaller apertures intercept a reduced fraction of the incoming solar power. Consequently, the optimum aperture size becomes a compromise between maximizing solar radiation capture and minimizing re-radiation losses [21]. Re-radiation losses may also be diminished to some extent by implementing selective windows with high reflectivity in the infrared spectrum around 2.15 μm where the Planck's spectral emissive power for a 1350 K blackbody peaks (from Wien's displacement law, Eq. (5-41)). The major source of irreversibility is, however, associated with the quenching of syngas exiting the reactor. As indicated in Table 2.3 for the four types of coal, between 35 and 41% of the solar power input is lost by quenching the syngas from 1350 to 300 K, resulting in a decrease of the exergy efficiency to 47% for route A+B, and to 44% for route A+C. The use of a heat exchanger for recovering part of the sensible heat of the syngas seems justifiable.

The exergy efficiency of an energy conversion process is an important criterion for judging its relative economic potential. For a solar process it is particularly important: the higher the exergy efficiency, the lower is the required solar collection area for producing a given amount of fuel, and, consequently, the lower are the costs of the solar concentrating system which usually correspond to about half of the total investments for the entire solar plant [22]. Thus, high exergy efficiency implies favorable economic prospects.

If coal and solar energy are separately used for electricity generation, the combined total exergy efficiency will range between 25% for solar thermal power plants to 35% for coal-fired Rankine cycles. While coal can be stored and transported to meet customers' electricity demands, the direct solar thermal power generation is intermittent and limited to regions of high solar insolation. The chemical storage of solar energy, as proposed via the hybrid solar coal gasification process, overcomes these drawbacks and further offers higher exergy efficiencies. Solar thermal electricity systems can feature on-site thermal storage capabilities (e.g., using molten salt as the
heat transfer medium [16]) to allow for solar electricity dispatchability after sunset. Transmission of solar electricity from regions of high insolation may be a viable option; its cost will need to be compared with the cost of electricity from solar-processed chemical fuels.

The EGF for the two electricity generation routes A+B and A+C are indicated in Table 2.2, along with the specific CO₂ emissions. As expected, the EGF is highest for route A+B and reaches values varying in the range between 1.83 for peat coal to 1.93 for anthracite. The EGF is relatively high also for route A+C, reaching values between 1.69 and 1.78, depending on the coal. Thus, both solar gasification routes offer a remarkable net gain in the electrical output, averaging about double specific electric output vis-à-vis the direct use of coal for fueling a 35%-efficient Rankine cycle. Doubling the specific electric output implies reducing by half the specific CO₂ emissions, which average 0.50 kg CO₂/kWhₑ for the combined cycle route and 0.55 kg CO₂/kWhₑ for the fuel cell route. Finally, the solar contribution to the input energy mix \( \eta_{SCM} \) is about 1/4 when using a heat exchanger, and slightly higher when excluding a heat exchanger.

### 2.5 Summary and Conclusions

A 2nd-law analysis has been carried out for the solar steam-gasification of coal, followed by either a syngas-fueled 55%-efficient combined cycle or by a hydrogen-fueled 65%-efficient fuel cell. The potential has been demonstrated to double the specific electrical output and, consequently, reduce by half the specific CO₂ emissions, vis-à-vis a coal-fueled 35%-efficient Rankine cycle. The proposed coal/solar hybrid chemical process conserves coal and reduces emissions. It further converts intermittent solar energy into a storable and transportable chemical fuel, to meet customer’s energy demands whenever and wherever needed. At the same time, coal is solar-upgraded to a cleaner fluid fuel that can be used for electricity generation in highly efficient combined cycles or fuel cells. In contrast to the gasification, using process heat derived from the internal coal combustion, the solar-driven gasification produces high quality syngas that is not contaminated by the products of combustion. Syngas can be further processed to separate streams of H₂ and CO₂. If the latter is sequestered, the proposed process becomes a decarbonization process that converts coal to hydrogen without release of CO₂ to the atmosphere.
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3 Solar Steam Gasification Experiments

3.1 Introduction

This chapter presents the experimental setup and the analysis of the experimental data, for the steam gasification of charcoal in a laboratory scale quartz tubular reactor, containing a fluidized bed of charcoal particles, directly exposed to an external source of concentrated radiation.

3.2 Solar Chemical Reactor and Experimental Setup

The chemical reactor used in this study consists of a 25 mm-outer diameter, 22 mm-inner diameter, 25 cm-height quartz tube containing a charcoal/steam fluidized bed directly exposed to high flux irradiation. Fig. 3.1 shows a schematic of the reactor parts and dimensions. Such a reactor concept is characterized by its uniform irradiation, temperature, and gas-solid contacting surface scheme over the reaction domain, to provide efficient heat and mass transport, and also to serve as a suitable tool for measuring interfacial kinetics [34].

![Figure 3.1. Schematic and dimensions of the tubular quartz reactor.](image)
Tests were conducted at the ETH’s high-flux solar simulator [31]. This facility provides a rapid external source of intense thermal radiation that approaches the heat transfer characteristics of highly concentrating solar systems. It consists of a high-pressure argon arc enclosed in a 27 mm-diameter, 200 mm-length water-cooled quartz envelope. The arc is close-coupled to a precision elliptical trough reflector, with one of the linear foci coinciding with the arc. The focal plane of the solar simulator is thus defined as the horizontal plane containing the second linear focus. The elliptical mirror is truncated 9.2 cm above the focal plane to permit external access. With this arrangement, up to 75 kW of continuous radiative power at peak fluxes exceeding 4250 kW/m² are attained at the focal plane, mostly at visible wavelengths with additional power in the near infrared and ultraviolet regions of the spectrum, and confined within a 45° rim angle. Power, power fluxes, and temperatures can be adjusted to meet the specific requirements by simply varying the electrical input power to the arc electrodes.

Figure 3.2. Experimental set-up at ETH’s High-Flux Solar Simulator.

The experimental set-up is shown in Fig. 3.2. The tubular reactor is positioned at the focal plane of the solar simulator and subjected to lateral and top irradiation. Using the
Monte-Carlo ray tracing technique (see chapter 5), the incident power flux irradiation at the top of the reactor is estimated to be 1300 kW/m² and at the quartz walls 180 kW/m², resulting in a total incident power of 2.6 kW.

The nominal fluidized-bed temperature is measured by pyrometry and by a thermocouple Type S, inducted to the reaction area through the gas outlet and submerged into the fluidized bed, i.e. it is not directly exposed to the incoming irradiation. The incoming Ar flow is controlled using a Bronkhorst HI-TEC flow controller. The H₂O feed is adjusted by a pump, preheated and then evaporated in a steam generator. After exiting the reactor, the product gases are quenched to room temperature and analyzed on-line by gas chromatography (High speed Micro GC G2890A by Agilent Technologies, equipped with Molecular Sieve 5A and HaySep A capillary columns). The excess water is condensed and collected. The consumption of water was determined by weighting fed water upstream and condensed water downstream, and further verified by the O₂ and H₂ mass balances of the gases measured by the GC.

During a typical experiment, a batch of solid reactants is first heated to the desired temperature under an Argon flow and subjected to an H₂O-Ar flow under isothermal conditions.

**Particle properties**

All experiments were conducted with activated charcoal in the form of pressed pellets, with mean properties listed in Table 3.1.

<table>
<thead>
<tr>
<th>Table 3.1. Mean properties of activated charcoal particles used as reactants.</th>
</tr>
</thead>
<tbody>
<tr>
<td>diameter</td>
</tr>
<tr>
<td>length</td>
</tr>
<tr>
<td>sphericity</td>
</tr>
<tr>
<td>effective diameter</td>
</tr>
<tr>
<td>bulk density</td>
</tr>
<tr>
<td>apparent density (pellet)</td>
</tr>
<tr>
<td>total specific surface</td>
</tr>
<tr>
<td>external specific surface</td>
</tr>
<tr>
<td>total pore volume</td>
</tr>
</tbody>
</table>
Pore size distribution, determined by BET measurements (Hg for small pores, N₂ for larger pores), is shown in Fig. 3.3.

Figure 3.3. Pore size distribution of activated charcoal.

### 3.3 Steam Gasification of Charcoal in a Fluidized Bed

The fluidized bed parameters measured for the transition regime from fixed to fluidized bed, and for a fully developed regime, are listed in Table 3.2, using a typical loading of 6 g charcoal. Estimates of mass and heat transfer within the fluidized bed was made using the correlations extracted from [37]. For typically $Re_p \sim 70$, $Sh_p \sim 56$, and $Nu_p \sim 8$, $k_m \sim 0.6 \text{ m/s}$ and $h \sim 200 \text{ W/m}^2\text{K}$.

Table 3.2. Fluidized bed parameters.

<table>
<thead>
<tr>
<th>Regime</th>
<th>Transition</th>
<th>Fully developed</th>
</tr>
</thead>
<tbody>
<tr>
<td>volume of fixed bed</td>
<td>17 cm³</td>
<td>23 – 30 cm³</td>
</tr>
<tr>
<td>void fraction</td>
<td>35%</td>
<td>50 – 65%</td>
</tr>
<tr>
<td>superficial velocity $u_o$</td>
<td>11 cm/s</td>
<td>20 – 60 cm/s</td>
</tr>
<tr>
<td>$Re_p$</td>
<td>~ 30</td>
<td>~ 40 – 90</td>
</tr>
<tr>
<td>gas residence time $\tau$</td>
<td>0.16 s</td>
<td>0.09 – 0.15 s</td>
</tr>
</tbody>
</table>
The steam-gasification of charcoal can be represented by Eq. (2-1), setting the H/C ratio $x$, and the O/C ratio $y$, to 0, thus

$$C_{\text{gr}} + H_2O = CO + H_2$$  \hspace{1cm} (3-1)

The equilibrium composition of the system C + H$_2$O at 1 bar is similar to the one shown in Fig. 2.1, but yielding an equimolar mixture of H$_2$ and CO, at above 1200 K.

Experimental runs were conducted in the temperature range 1000-1500 K. The experimental data is given in Table 3.3.

<table>
<thead>
<tr>
<th>Exp</th>
<th>Input</th>
<th>Output</th>
<th>$l$</th>
<th>Temperatures</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$C$</td>
<td>$H_2O$</td>
<td>$Ar$</td>
<td>$H_2$</td>
</tr>
<tr>
<td>#</td>
<td>g/min</td>
<td>l/min</td>
<td></td>
<td>%</td>
</tr>
<tr>
<td>1</td>
<td>5.08</td>
<td>0.40</td>
<td>4</td>
<td>7.20</td>
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<td>2</td>
<td>4.78</td>
<td>0.40</td>
<td>4</td>
<td>8.02</td>
</tr>
<tr>
<td>3</td>
<td>4.46</td>
<td>0.40</td>
<td>4</td>
<td>8.42</td>
</tr>
<tr>
<td>4</td>
<td>4.14</td>
<td>0.40</td>
<td>4</td>
<td>8.70</td>
</tr>
<tr>
<td>5</td>
<td>3.82</td>
<td>0.40</td>
<td>4</td>
<td>8.58</td>
</tr>
<tr>
<td>6</td>
<td>3.52</td>
<td>0.40</td>
<td>4</td>
<td>8.56</td>
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<tr>
<td>7</td>
<td>6.42</td>
<td>0.87</td>
<td>3</td>
<td>0.17</td>
</tr>
<tr>
<td>8</td>
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<td>0.87</td>
<td>3</td>
<td>0.24</td>
</tr>
<tr>
<td>9</td>
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</tr>
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</tr>
<tr>
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<td>3</td>
<td>0.24</td>
</tr>
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<td>3</td>
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</tr>
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</tr>
<tr>
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<td>5.01</td>
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<td>3</td>
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<td>4.88</td>
<td>0.87</td>
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<td>2</td>
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</tr>
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<td>2</td>
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</tr>
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<td>2</td>
<td>16.16</td>
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<tr>
<td>23</td>
<td>5.28</td>
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<td>2</td>
<td>14.02</td>
</tr>
<tr>
<td>24</td>
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<td>2</td>
<td>14.88</td>
</tr>
<tr>
<td>25</td>
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<td>0.62</td>
<td>2</td>
<td>15.06</td>
</tr>
<tr>
<td>26</td>
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<td>0.62</td>
<td>2</td>
<td>15.19</td>
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<td>21.52</td>
</tr>
<tr>
<td>28</td>
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<td>0.62</td>
<td>1</td>
<td>22.39</td>
</tr>
<tr>
<td>29</td>
<td>3.46</td>
<td>0.62</td>
<td>1</td>
<td>21.76</td>
</tr>
</tbody>
</table>
temperatures $T_{\text{bed}}$ of data sets 32-41 were missing due to a TC failure, and have been calculated by correlation $T_{\text{pyr}}$ vs. $T_{\text{bed}}$.

### 3.4 Data Analysis

The fractional water conversion is defined as the ratio of the molar flow rate of water consumed to that of water fed to the reactor.

$$X_{H_2O} = \frac{\dot{n}_{H_2O}^{\text{out}} - \dot{n}_{H_2O}^{\text{in}}}{\dot{n}_{H_2O}^{\text{in}}} \quad (3-2)$$

The experimentally measured $X_{H_2O}$ is shown in Fig. 3.4 as a function of temperature. As expected, conversion increases with temperature.

![Figure 3.4. Experimentally measured fractional water conversion as a function of temperature.](image-url)
Assuming steady state conditions, the mass balance yields

\[
\left(n_{H_2O}^{out} - n_{H_2O}^{in}\right) = n_{CO}^{out} + 2n_{CO_2}^{out} = n_{H_2}^{out}
\]  

(3-3)

The validity of Eq. (3-3) is examined in Fig. 3.5 where the molar rate of CO+2CO₂ is plotted vs. the one of H₂. The solid line represents the exact stoichiometric behavior whereas the dashed line is the result of a least-square linear fitting of all measured data points. The good agreement between the two lines supports the assumption of steady state conditions.

Figure 3.5. Stoichiometric behavior of molar product flow rates.

The gas product composition measured by GC is shown in Fig. 3.6, and consists of H₂, CO, and CO₂. Omitted is Ar, the carrier gas, and excess steam, which has been condensed downstream. There is clear experimental evidence that the CO₂/CO molar ratio decreases with temperature, which is consistent with the Boudouard equilibrium. Above 1400 K, the syngas mixture consists primarily of an equimolar mixture of H₂ and CO, as predicted by thermodynamic equilibrium.
The quality of the syngas is described by the $\text{H}_2/\text{CO}$ and $\text{CO}_2/\text{CO}$ molar ratios. The $\text{H}_2/\text{CO}$ molar ratio can be adjusted by the water-gas shift reaction to meet the requirements for the post-processing of syngas to hydrogen, ammonia, methanol, or Fischer-Tropsch’s chemicals. The $\text{CO}_2/\text{CO}$ molar ratio is a measure of the contamination and should be kept preferable as low as possible. Fig. 3.7 shows the experimentally measured variation of these two molar ratios with temperature. Both values appear to be exponentially decreasing, approaching 1 for $\text{H}_2/\text{CO}$ and 0 for $\text{CO}_2/\text{CO}$.

Figure 3.6. Variation of the product gas composition (measured by GC) as a function of the fluidized bed temperature.

Figure 3.7. Temperature dependence of syngas quality indicators.
3.5 Summary

The steam gasification of charcoal have been investigated for a fluidized bed reactor directly exposed to an external source of concentrated thermal radiation. Such a reactor concept features efficient heat and mass transport. High quality syngas containing an equimolar mixture of H₂ and CO and less than 5 % CO₂ was produced at above 1400 K, i.e. the potential of the solar steam-gasification to produce high quality syngas from charcoal was experimentally verified. This syngas is notably superior than the one typically obtained in autothermal reactors, besides the additional benefit of the upgraded calorific value. The LHV (low heating value) of the products, assuming complete conversion, is 530 kJ/mol and 34 % higher than that of the original feedstock. The solar gasification further eliminates the need for pure oxygen as feedstock.
Seite Leer / Blank leaf
4 Kinetic Analysis

4.1 Introduction

This chapter describes the kinetic analysis of the steam-gasification of charcoal. The rate laws are formulated based on the analysis of elementary reaction mechanisms describing reversible adsorption/desorption processes and irreversible surface chemistry. The rate constants are computed by matching theoretical and experimental results obtained from the experimental study presented in chapter 3, and their temperature dependence is determined by imposing an Arrhenius-type rate law.

4.2 Reaction mechanism

Several elementary reaction mechanisms have been proposed for describing the coal gasification with steam [7,36,38,39]. The model presented here is based on Müller [73], but has been further improved by Trommer [74]. Two distinct phenomena are considered.

(1) Reversible sorption of gaseous species onto the carbon surface,

\[ \text{H}_2\text{O} + \Theta_v \xleftrightarrow[k_1]{k_3} \Theta_{\text{OH}} \]  
\[ \text{CO} + \Theta_v \xleftrightarrow[k_1]{k_4} \Theta_{\text{CO}} \]  
\[ \text{CO}_2 + \Theta_v \xleftrightarrow[k_1]{k_3} \text{CO} + \Theta_o \]  
\[ \text{H}_2 + \Theta_v \xleftrightarrow[k_1]{k_4} \Theta_{\text{H}_2} \]

where, \( \Theta_i \) represents the fraction of active carbon sites occupied by specie \( i \), and \( \Theta_v \) is the fraction of vacant sites. Thus,

\[ \Theta_v = 1 - (\Theta_o + \Theta_{\text{O}_2\text{H}} + \Theta_{\text{CO}} + \Theta_{\text{H}_2}) \]  

---

2 Material from this chapter has been published in Mueller R, v. Zedtwitz P, Wokaun A, Steinfeld A. Kinetic investigation on steam gasification of charcoal under direct high flux irradiation. *Chemical Engineering Science*, 2003, 58, 5111-5119. The kinetic analysis has been performed within the framework of the Diplomarbeit of R. Müller [73].
(2) Irreversible reactions among adsorbed species and with molecules in the gas phase, described by

\[ \Theta_{\text{OH}} \xrightarrow{k_i} \Theta_0 + \Theta_{i_1} \]  
\[ \Theta_0 + nC_i \xrightarrow{k_i} \text{CO} + n\Theta_{i_1} \]  
\[ \text{CO}_2 + \Theta_{\text{CO}} \xrightarrow{k_i} 2\text{CO} + \Theta_0 \]

where \( C_i \) are inactive carbon sites. Eq. (4-8) accounts for CO formation at high partial pressures of CO and \( \text{CO}_2 \), and can be neglected at the pressure range used in this study [74].

Note: less than 0.1 \% of methane was detected experimentally among the gaseous products (Table 3.3), despite its prediction at thermodynamic equilibrium (e.g. 2 \% at 1000 K, as indicated in Fig. 2.1). As a consequence, \( \text{CH}_4 \) production was neglected, and reactions (2-3) and (2-4) have not been considered in the model of the reaction mechanism.

Reaction rates for the species involved in the gas phase and for the absorbed surface species are then formulated as

\[ r_{\text{H}_2} = -k_{1\text{H}_2}\Theta_{\text{H}_2} + k_{-1}\Theta_{\text{OH},\text{H}} \]  
\[ r_\text{H}_2 = k_{-4}\Theta_{\text{H}_2} - k_{4\text{H}_2}\Theta_{i_1} \]  
\[ r_{\text{CO}} = (k_{5\text{CO}} - k_{2\text{CO}})\Theta_{\text{CO}} + (k_{6} - k_{-2\text{CO}})\Theta_0 + k_{-2}\Theta_{\text{CO}} \]  
\[ r_{\text{CO}_2} = -k_{5\text{CO}_2}\Theta_{\text{CO}} + k_{3\text{H}_2}\Theta_{\text{CO}} \]  
\[ r_{\Theta_{\text{OH},\text{H}}} = k_{1\text{H}_2}\Theta_{\text{OH},\text{H}} - (k_{-1} + k_{5})\Theta_{\text{OH},\text{H}} \]  
\[ r_{\Theta_0} = k_{2\text{CO}}\Theta_{\text{CO}} - k_{-2}\Theta_{\text{CO}} \]  
\[ r_{\Theta_{i_1}} = k_{4\text{H}_2}\Theta_{i_1} - k_{-4}\Theta_{\text{H}_2} + k_{2}\Theta_{\text{OH},\text{H}} \]  
\[ r_{\Theta_0} = k_{5}\Theta_{\text{OH},\text{H}} - k_{6}\Theta_0 + k_{3}\Theta_{\text{CO}} + k_{-2}\Theta_{\text{CO}} \]

Assuming steady state, i.e. \( r_{\Theta_0} = 0 \), balancing production and consumption of surface species leads to a system of linear equations, Eq. (4-13)-(4-16), and (4-5). Its solution yields \( \Theta_0 \) as a function of elementary \( k_i \) and partial pressures. Substituting the
solutions found for $\Theta_i$ and further neglecting any inhibiting effects due to low pressures, Eq. (4.9)-(4.12) can be re-formulated in terms of complex rate constants $K_i$,

$$K_i = \frac{k_1 k_3}{k_1 + k_3} \quad K_2 = k_3 \quad K_3 = \frac{k_4}{k_6}$$

(4-17)

as

$$r_{\text{H}_2\text{O}} = -k_1 p_{\text{H}_2\text{O}} - k_3 p_{\text{H}_2\text{O}} p_{\text{CO}}$$

(4-18)

$$r_{\text{CO}} = k_2 p_{\text{H}_2\text{O}} + 2k_3 p_{\text{CO}} - k_3 p_{\text{H}_2\text{O}} p_{\text{CO}}$$

(4-19)

$$r_{\text{CO}_2} = -k_2 p_{\text{CO}} + k_1 p_{\text{H}_2\text{O}} p_{\text{CO}}$$

(4-20)

$$r_{\text{H}_2} = k_3 p_{\text{H}_2\text{O}} + k_3 p_{\text{H}_2\text{O}} p_{\text{CO}}$$

(4-21)

Since the $r_i$ describe surface reactions, they are expressed in units of mol/(m$^2$s).

### 4.3 Arrhenius type rate law

The two-phase fluidized-bed model of Davidson and Harrison [26], in which rising bubbles exchange mass with the particulate phase, was applied assuming plug flow behavior. In the temperature range considered, heat and mass transport processes are assumed to occur much faster than the chemical reactions and, consequently, not to be rate controlling. This assumption is justified by the high values obtained for the rate of heat and mass transfer when multiplying their corresponding coefficients (as estimated from the Nu and Sh numbers, respectively) times the external pellets surface area and the temperature/concentration gradient, respectively. Therefore, in the analysis that follows, heat and mass transfer processes have been neglected. However, as it will be shown later, mass transfer resistance appears to become predominant at above 1300 K.

Mass balance for each species $i$ over a differential element of either surface area or particle mass (multiplied by the specific surface area $a$) along the reactor axis yields,

$$dh_i = r_i dA = r_i adm_c$$

(4-22)

where $r_i$ are the reactions rates defined by Eq. (4-18)-(4-21). The partial pressures required for the kinetic expressions can be calculated assuming ideal gases.
\[ p_i = p_f \sum_j \frac{\dot{n}_i}{\dot{n}_j}. \]  

(4-23)

The system of four coupled differential equations is solved numerically by Runge-Kutta and by iterating on the values of \( K_i \) to minimize the residuum between theoretically calculated and experimentally measured molar flow rates of products. The residuum was defined as

\[ \varepsilon_{\text{res}} = \sqrt{\sum_i \log^2 \left( \frac{\dot{n}_{\text{sim}}^i}{\dot{n}_{\text{exp}}^i} \right)} \]  

(4-24)

where \( \dot{n}_{\text{sim}}^i \) and \( \dot{n}_{\text{exp}}^i \) are the simulated and experimental molar product flows, respectively.

The model was applied for the experimental data that was obtained in the gasification experiments, described in chapter 3.

Fig. 4.1 shows theoretically modeled vs. the experimentally measured product flow rates for the four relevant species: H\(_2\)O, H\(_2\), CO, and CO\(_2\). The solid line represents perfect match. The root mean square deviation (RMS) is 0.99 for H\(_2\)O, CO, and CO\(_2\), and 0.97 for H\(_2\).

Figure 4.1. Experimentally measured vs. theoretical modeled product flow rates.
The temperature dependence of each $K_i$ is determined by imposing an Arrhenius-type rate law,

$$K_i(T) = K_{i0} \cdot \exp\left(\frac{-E_{Ai}}{R_iT}\right)$$  \hspace{1cm} (4-25)

Arrhenius plots for $K_{iA}$, $K_{i2A}$, and $K_3$ are shown in Fig. 4.2(a), (b), and (c), respectively. The apparent activation energies and corresponding frequency factors are shown in Table 4.1.

Table 4.1. Kinetic parameters for Arrhenius rate law.

<table>
<thead>
<tr>
<th>$K_i$</th>
<th>$E_{Ai}$</th>
<th>$K_{i0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{iA}$</td>
<td>250.2 kJ/mol</td>
<td>$6.07 \times 10^4$ mol/(kg·s·Pa)</td>
</tr>
<tr>
<td>$K_{i2A}$</td>
<td>-74.2 kJ/mol</td>
<td>$2.47 \times 10^4$ mol/(kg·s·Pa)</td>
</tr>
<tr>
<td>$K_3$</td>
<td>-323.5 kJ/mol</td>
<td>$3.78 \times 10^{18}$ Pa$^{-1}$</td>
</tr>
</tbody>
</table>
Figure 4.2. Arrhenius plots for $K_p$, $K_{pa}$ and $K_r$. 
Since the $K_i$ represent complex reaction mechanisms rather than elementary steps, a negative value for the apparent activation energy, as in the case of $E_{A_3}$, does not necessarily imply inconsistency with the transition state theory. Rather, it implies that the activation energy of the elemental reaction rate $k_6$ has to be higher than the one for $k_{-3}$, which is justified by the different kind of reactions described. The negative value of $E_{A_2}$ can not be explained likewise, but might be caused by the relatively small absolute value of the respective term compared to the term $K_i$, so that a small change of the parameters of $K_i$ have a relatively big influence on $K_i$, this assumption is supported by the statistical spread of the experimental data in Fig. 4.2b. But eventually, as will be seen later in Chapter 6.4, the model can predict the experimental data considerably well. The activation energies obtained can not be directly compared with the values reported in literature [36,39], since different kinetic models have been used in these studies to describe the gasification process. Fig. 4.2a-c further show a convex trend at temperatures above about 1300 K (depicted as dashed line), indicative of mass transfer resistance for diffusion of the gaseous species through the gas boundary layer surrounding the carbon particle, and for diffusion of gaseous species inwards and outwards through the solid porous layer [34].

4.4 Summary and conclusions

The reaction kinetics of the steam gasification of charcoal have been investigated using the data from the gasification experiments with the fluidized bed reactor directly exposed to concentrated thermal radiation. Rate law expressions were formulated based on elementary reaction mechanisms of reversible sorption of gaseous species onto the carbon surface, and irreversible reactions of the adsorbed species among them and with molecules in the gas phase. After some algebraic manipulation, the system of elemental rate constants could be condensed into three complex kinetic constants. Assuming plug flow conditions, these complex rate constants are computed by matching theoretical and experimental results. Their temperature dependency is determined by imposing an Arrhenius-type rate law. The apparent activation energies obtained are 250, -74, and -323 kJ/mol.

A problem identified while analyzing the experimental data of the kinetic study is the accurate measurement of the bed temperature in the fluidized bed reactor. The kinetic
model can reproduce the experimental molar flow composition for each single experiment very accurately, as depicted in Fig. 4.1, but when connected to the measured bed temperatures, the data is rather spread, as can be seen in the Arrhenius plots, Fig. 4.2. A kinetic study using thermogravimetry might overcome this drawback. The kinetic model can predict the charcoal gasification reasonably well, however, the parameter obtained are only valid for the particles used for the study. For application for a different feedstock, the specific parameters have to be determined previously. The validity for the gasification of petroleum coke has already been demonstrated in a subsequent study [77].

The mass transfer limitation at high temperatures has not been addressed in detail, since it seems reasonable, in regard to develop an efficient process, to run the reaction at temperatures below mass transfer limitation.
5 Chemical Reactor Modeling

5.1 Introduction

This chapter presents the numerical model that has been developed to describe the steam gasification of coal in a tubular quartz reactor containing a fluidized/packed bed directly exposed to concentrated solar radiation. The focus was set on the radiation heat transfer, but all other modes of heat transfer have also been considered. Two approaches are examined to describe the radiative transfer within fluidized and packed beds for large particles of size parameter greater than 10. In the first approach, the bed is modeled as a continuous medium, using spectral absorption and scattering coefficients based on measured spectral reflectivity, and scattering phase functions for diffuse reflecting spherical particles. In the second approach, the bed is modeled as a cloud of randomly positioned spherical particles, with diffuse spectral reflection, absorption, and emission taking place at the particle surface. The bed region is divided into elemental disks in axial direction. Mass and energy conservation equations that account for radiation, conduction, convection, reaction, particle-mixing, and enthalpy change are applied in each element and solved numerically to calculate temperature profiles throughout the bed for particles, gas phase, and quartz tube.

5.2 Geometrical configuration

The solar reactor configuration has been presented in chapter 3, and is shown schematically in Fig. 5.1. The radiation source is the ETH's high-flux solar simulator [31]. The tubular quartz reactor containing a packed bed or fluidized bed of coal particles is positioned vertically below the reflector, perpendicular to the focal plane. The system of coordinates is selected with the origin at the center of the trough elliptical mirror.

For the purpose of discretization, the particle/gas suspension in the bed region is divided into $n$ disks, and the quartz walls enclosing the bed region into $n$ rings, of height $d_x = (x_{bt} - x_{bb})/n$, as illustrated in Fig. 5.1 for the bed region. The properties of particles, quartz and gas are assumed constant within each element. A 2-dimensional

---

grid was used for the quartz wall below and above the bed region (axial, circumferential), and for the top and bottom layers (radial, circumferential), only radiative exchange was considered for these elements.

(a) (b)

Figure 5.1. Geometrical configuration (a) ETH's High-Flux Solar Simulator with tubular quartz reactor, (b) elements of tubular quartz reactor and bed region.

5.3 Global iteration

Fig. 5.2 shows a global flow sheet of the modeling. The model consists mainly of two modules:

(1) application of the Monte Carlo (MC) ray tracing method for determining the radiative transfer

(2) application of mass and energy conservation equations for determining temperatures and product gas composition

The results of the MC ray tracing are necessary to calculate the mass and energy balances. Since the radiative properties used in the MC are temperature dependent, the two modules are solved iteratively until convergence. The convergence criterion is defined in Eq. (5-4). Initially, all temperatures relevant for radiative heat transfer are set to 1000 K. Then a complete MC ray-tracing is performed to compute the radiative fluxes, which are input to the mass/energy balances. Finally, the conservation
equations are solved to obtain the new temperature distribution. This procedure is repeated until the convergence criterion, which is based on the difference of emitted energy in all elements from two subsequent ray tracing runs, is small enough.

5.4 MC analysis

The Monte Carlo (MC) ray-tracing method is a powerful numerical technique that allows the treatment of problems beyond the reach of analytical techniques, and is flexible enough to remove diffuse-gray-isothermal-isotropic simplifying assumptions for treating non-diffuse, non-gray, non-isothermal, anisotropic problems involving complex 3D geometries [57].

Ray properties

Each ray is defined by its origin \( r_p \), direction \( \hat{u} \), associated power \( w \), and wavelength \( \lambda_p \). The origin and direction are defined on emission, and changed due to intersection with the different elements of the model, according to the ray tracing described below. The ray's associated power is constant, and calculated from the total power \( P_{arc} \) emitted by the Ar arc and for a MC run of \( n_{rays} \) rays as

\[
\text{set parameters, calculate particle distribution,}
\text{set start temperatures for quartz/particles (1000K)}
\]

\[
\text{reset counters,}
\text{calculate emission limits}
\]

\[
\text{perform ray tracing for } n_{rays} \text{ rays emitted from the Ar arc,}
\text{resulting counters represent the radiative heat transfer,}
\text{radiative properties are temperature dependent}
\]

\[
\text{apply mass and energy conservation for particles, gas and quartz,}
\text{resulting are the temperature distributions for gas, particles and quartz}
\]

\[
\text{check for convergence for mean of emission limit differences}
\text{for two subsequent iteration steps}
\]

Figure 5.2. Flow sheet of modeling showing the global iteration loop. The MC blocks are further detailed in chapter 5.4, the mass and energy conservation block in chapter 5.5.
\[ w = \frac{p_{\text{arc}}}{n_{\text{rays}}} \]  

(5-1)

The ray's associated wavelength \( \lambda_e \) is also defined on emission, according to the spectral distribution of emitting element or medium, and stays constant until the ray is absorbed.

**MC loop**

Before the start of each MC run all ray counters are set back to 0, this includes the absorption counters (quartz, bed region), the counters for surface flux, and all other counters that refer to a run of \( n_{\text{rays}} \) rays.

For the bed region and the quartz cylinder, the emission limits have to be calculated. They give the number of rays to be emitted according to the element's emitted power, thus they are defined as

\[ N_{\text{em,p}} = \frac{\hat{Q}_{\text{em,p}}}{w} \]  

(5-2)

\[ N_{\text{em,q}} = \frac{\hat{Q}_{\text{em,q}}}{w} \]  

(5-3)

where \( \hat{Q}_{\text{em,p}} \) and \( \hat{Q}_{\text{em,q}} \) is the emitted power of particles and quartz, calculated at the elements temperature \( T_p^i \) or \( T_q^i \), respectively, and given in Eqs. (5-89), (5-90), and (5-91).

The convergence criterion for the global iteration loop is defined by the expansion of the emission limits, i.e.

\[
\frac{1}{n} \left| \sum N_{\text{em,p}}^{i(m)} - N_{\text{em,p}}^{i(m-1)} \right| \to 0 \quad \frac{1}{n} \left| \sum N_{\text{em,q}}^{i(m)} - N_{\text{em,q}}^{i(m-1)} \right| \to 0
\]  

(5-4)

where the superscript \( (m) \) denotes the global iteration step. Note that no absolute value has been taken from the emission limit differences. This is necessary due to the stochastic noise caused by the MC technique, i.e. it is a way to compensate the minor fluctuations of emission limits for subsequent MC runs.

Also, for all the quartz elements outside the bed region, the local temperatures are updated considering only radiative exchange, i.e.
where \( w \) is the power carried by a single ray, \( N_q \) and \( dV_q \) are the counter of absorptions and the volume of the specific quartz element, \( \sigma \) is the Stefan-Boltzmann constant, and \( \alpha_{q,a} \) is the Planck mean absorption coefficient for the quartz, calculated below in Eq. (5-35), and evaluated at the elements temperature. Eq. (5-5) was solved iteratively using the Newton algorithm.

**Beam emission from Ar arc**

The radiation source is a high-pressure argon arc, modeled as a cylindrical volume of radius \( r_{arc} \) and length \( l_{arc} \) emitting a total power of \( P_{arc} \). Its axis lies in the upper focal line of the elliptical mirror; it is parallel to the \( z \) axis, and the displacement in \( x \) direction is equal \( x_{arc} \). The origin of emission within the cylinder is chosen randomly, according to

\[
\begin{align*}
z_0 &= (3R_{a} - 0.5)l_{arc} \\
\varphi_0 &= 2\pi \cdot R_{\varphi} \\
r_0 &= r_{arc} \cdot \sqrt{R_{\varphi}}
\end{align*}
\]  

(5-6)

where \( R \) is a random number chosen from a uniform set \([0,1]\). The vector to the ray's origin is then

\[
\hat{r}_0 = \left[ r_0 \cdot \cos \varphi_0 + x_{arc} \quad r_0 \cdot \sin \varphi_0 \quad z_0 \right]^T.
\]  

(5-7)

The direction of emission is assumed isotropic. Thus, the direction of a generic ray is given by the unit vector

\[
\hat{u} = \left[ \sin \theta \cos \varphi, \quad \sin \theta \sin \varphi, \quad \cos \theta \right]^T
\]  

(5-8)

randomly determined by the cone angle and circumferential angle \((\varphi, \theta)\),

\[
\begin{align*}
\varphi &= 2\pi \cdot R_{\varphi} \\
\theta &= \cos^{-1}(1 - 2R_{\theta})
\end{align*}
\]  

(5-9)

The equation of the generic ray is finally

\[
\hat{r} = \hat{r}_0 + t \cdot \hat{u}
\]  

(5-10)
where \( t \) is the distance that the ray travels from its origin, and, by definition, \( t \geq 0 \).

For the selection of the wavelength of the emitted ray, two spectral distributions of the emitted radiation are employed: (1) Planck’s distribution for a 5780 K blackbody, to simulate the solar spectrum, and (2) the spectral distribution for the Ar arc [31], provided by the manufacturer and shown in Fig. 5.3. For Planck’s distribution, the associated wavelength is found from

\[
\lambda_b = \frac{F_0^{-1} (\mathcal{R}_\lambda)}{T}
\]

for \( T = 5780 \) K. \( F_0^{-1} \) is the inverse of the blackbody fraction function \( F_0 \). \( F_0^{-1} \) gives the fraction of the radiation emitted by a blackbody at temperature \( T \) that lies within the interval \([0, \lambda T]\). For the Ar arc, \( \lambda_\alpha \) is found from

\[
\mathcal{R}_\lambda = \frac{\int_\lambda^\infty i_\lambda d\lambda}{\int_0^\infty i_\lambda d\lambda}
\]

with \( i_\lambda \) given in Fig. 5.3. Fig. 5.4 shows the associated wavelength as a function of the random number for both spectral distributions.

![Figure 5.3. Spectral intensity of emitted radiation by the Ar arc.](image-url)
Figure 5.4. Ray's wavelength in function of the random number, Eq. (5-11) and (5-12).

**Ray tracing within arc mirrors**

Fig. 5.5 shows the flow sheet of the first part of the MC loop. After emission, the ray proceeds along its path until it hits one of the reflector elements.

![Flowchart](Image)

Figure 5.5. The first part of MC loop flow chart depicts ray emission and the ray tracing until the reactor intersection. See Fig. 5.7 for the 2nd part of the flow chart.
These elements, depicted in Fig. 5.1, are the arc mirror, the elliptical mirror, the vertical mirror walls, the angular mirror walls, and the reflector exit. The equations of these elements are given below, the dimensions are depicted in Fig. 5.6.

- **Arc mirror:**
  \[
  (x - x_{arc})^2 + y^2 = r_{arc}^2 \quad x < x_{am} 
  \]  
  \( (5-13) \)

- **Elliptical mirror:**
  \[
  \frac{x^2}{a_{mir}^2} + \frac{y^2}{b_{mir}^2} = 1 
  \]  
  \( (5-14) \)

- **Vertical wall mirrors:**
  \[
  z = \pm \frac{d_{mir}}{2} 
  \]  
  \( (5-15) \)

- **Angular wall mirrors:**
  \[
  y = \pm \left( \frac{b_{mir} - y_{ex}}{x_{mir} - x_{ex}} (x - x_{mir}) + b_{mir} \right) 
  \]  
  \( (5-16) \)

- **Reflector exit:**
  \[
  x = x_{ex} 
  \]  
  \( (5-17) \)

![Diagram](image)

Figure 5.6. Solar simulator reflector dimensions.

The quartz envelope of the Ar arc, the arc itself, and the air in the reflector are assumed non-participating media, i.e. the beam passes through them without interaction.

The next intersection of the generic ray with the above elements is found by solving the system of equations (5-10) and (5-13), (5-14), (5-15), (5-16), or (5-17), to find the smallest positive path length to intersection \( t \). No real solution implies no intersection.

When the ray hits one of the mirror elements, Eq. (5-13)-(5-16), it is reflected in the intersection point, and the direction of the reflected ray \( \hat{u} \), is calculated using a combined model for diffuse/specular reflection that incorporates an angular error for surface imperfections [65]. For a beam incident on a mirror element, a random number...
is compared to the diffuse fraction $f_d$ to decide whether the reflection is diffuse, or specular with error.

$$R_d \in \left[ \left[ 0, f_d \right], \left[ f_d, 1 \right] \right] \rightarrow \begin{cases} \text{diffuse} & \text{specular with error} \\ & \end{cases} \tag{5-18}$$

For diffuse reflection, the direction is chosen randomly from a set that is weighted according to Lambert's cosine law, i.e.

$$\varphi = 2\pi R_\varphi \quad \theta = \sin^{-1} \sqrt{R_\theta} \tag{5-19}$$

The direction of the reflected beam is then

$$\hat{u} = \sin \theta \left( \cos \varphi \cdot \hat{e}_x + \sin \varphi \cdot \hat{e}_y \right) + \cos \theta \cdot \hat{n} \tag{5-20}$$

where $\hat{n}$ is the surface normal unit vector in the point of reflection, and $(\hat{e}_x, \hat{e}_y, \hat{n})$ is a local Cartesian coordinate system.

The model for specular reflection with error takes into account that the surface is not geometrically perfect, which leads to small errors in the direction of a perfectly specular reflected beam $\hat{u}_s$, given by

$$\hat{u}_s = \hat{u} - 2 \left( \hat{n} \hat{u} \right) \hat{n} \tag{5-21}$$

The (small) angular errors $(\delta_x, \delta_y)$ are distributed according to a two-dimensional Gaussian distribution.

$$\begin{align*}
\delta_x &= \sqrt{2} \sigma_x \text{erf}^{-1} \left( 2R_1 - 1 \right) \\
\delta_y &= \sqrt{2} \sigma_y \text{erf}^{-1} \left( 2R_2 - 1 \right) \tag{5-22}
\end{align*}$$

where $\sigma_x$ is the standard deviation and $\text{erf}^{-1}$ the inverse error function. The resulting error vector is then

$$\hat{u}_\text{err} = \sin \delta_x \cdot \hat{e}_x + \sin \delta_y \cdot \hat{e}_y \tag{5-23}$$

where $(\hat{e}_x, \hat{e}_y, \hat{u}_s)$ is a local Cartesian coordinate system adjusted at the direction for perfect specular reflection. The beam direction after reflection is then
\[
\hat{u} = \frac{\hat{u}_i + \hat{u}_{err}}{|\hat{u}_i + \hat{u}_{err}|} \tag{5-24}
\]

If the incoming ray hits the surface at a rather flat angle, it can happen that the resulting vector after reflection is directed into the surface, i.e. the ray would propagate into the surface. To prevent this from happening, the dot product of surface normal and beam direction after reflection must be positive, i.e.

\[\hat{n} \cdot \hat{u} > 0 \tag{5-25}\]

If this is not the case, the direction after reflection is recalculated using a new set of angular errors \(\delta_1, \delta_2\).

The emitted rays undergo none, single, or multiple reflections at the mirror elements until they hit the rectangular exit, defined by Eq. (5-17), and leave the reflector.

Fig. 5.7 shows the 2\textsuperscript{nd} part of the MC ray tracing flow sheet, that encompasses the MC ray tracing within the quartz tubular reactor and the bed region.

Figure 5.7. The 2\textsuperscript{nd} part of MC loop flow chart depicts the complete ray tracing within the quartz tubular reactor and the bed region. Arrows that end up in a 'new beam' field are going back to the first MC flow chart, see Fig. 5.5.
Tubular quartz reactor (intersection)

When a ray leaves the reflector, it is checked whether it hits the reactor. The outer surface of the tubular quartz reactor is given by

\[ x^2 + y^2 = r_q^2 \quad x_{rb} < x < x_{rt} \quad \text{wall} \]

\[ x = x_{rt} \quad x^2 + y^2 < r_q^2 \quad \text{top} \]

\[ x = x_{rb} \quad x^2 + y^2 < r_q^2 \quad \text{bottom} \]

When the ray hits the tubular reactor, it is either reflected or refracted at the quartz/air boundary, when it does not hit the reactor, it is considered to be lost. To account for a displacement of the reactor axis from its ideal position, the ray's origin on the exit can be moved by an offset, i.e.

\[ \tilde{r}_p = \tilde{r}_p + \tilde{r}_{\text{offset}} \]

before the intersection with the tubular quartz reactor is calculated.

Figure 5.8. Fractions of emitted energy incident (a) on the total reactor surface, (b) on the reactor top, (c) on the reactor wall above bed bottom, and (d) on the wall below bed bottom for a horizontal displacement of the reactor. Values are given in percentage (%) of the total emitted arc power. For coordinate (0,0) the reactor axis is congruent to the x-axis. The flux distribution is symmetric at the \( y = 0 \) and \( z = 0 \) planes.
Fig. 5.8 shows contour plots for the fractions of emitted energy (by the Ar arc) that is incident (a) on the total reactor surface, (b) on the reactor top, (c) on the reactor wall above bed bottom, and (d) on the wall below bed bottom, for a horizontal displacement of the reactor. It can be observed that the fraction of the radiation incident on the wall above the frit, is about 70% of the total incident radiation, about 20% is incident on the top, and the remainder of 10% on the lower wall section.

Quartz/air boundary

A ray that hits the quartz walls of the tubular reactor is either reflected or refracted. Total reflection occurs when the angle between the incoming ray and the surface normal, \( \theta_i \), is greater than \( \theta_{\text{max}} = \sin^{-1}(n_1/n_2) \), where \( n_1 \) and \( n_2 \) are the refractive indices of the medium it exits and enters, respectively. For the two media being quartz and air, total reflection only occurs for beams that leave the quartz layer to the air. Otherwise, if \( \theta_i < \theta_{\text{max}} \), the probability of reflection is given by Fresnel’s equation for the directional-hemispherical specular reflectivity [57]

\[
\rho_s(\lambda, \theta_i) = \frac{1}{2} \frac{\sin^2(\theta_i - \theta_r)}{\sin^2(\theta_i + \theta_r)} \left[ 1 + \frac{\cos^2(\theta_i + \theta_r)}{\cos^2(\theta_i - \theta_r)} \right] \tag{5-28}
\]

where \( \theta_r \) is the angle between the refracted ray and the (inner) normal to the surface, calculated by Snell’s law

\[
\theta_r = \sin^{-1} \left( \frac{n_1 \sin \theta_i}{n_2} \right) \tag{5-29}
\]

If \( \rho_s > R_p \), the ray is reflected. In both cases of reflection, the direction of the reflected ray is determined using Eq. (5-21). Rays that are reflected on the outer surface of the reactor are considered to be lost. If the ray is not reflected, it will be refracted in the direction

\[
\hat{\mathbf{u}}_r = \left[ \cos(\theta_i) \frac{n_1}{n_2} - \cos(\theta_2) \right] \cdot \hat{n} + \frac{n_1}{n_2} \cdot \hat{\mathbf{u}} \tag{5-30}
\]

and proceed on its path in the medium it enters, rays that cross the quartz/air boundary to the outside are considered to be lost. Fig. 5.9 shows the fraction of emitted energy lost by reflection on the outer quartz surface.
Figure 5.9. Fractions of energy lost by reflection on the outer quartz surface. Values are given in percentage (%) of total emitted arc power.

Quartz layer

The quartz layer is modeled as a 3D non-isothermal non-gray, absorbing, emitting, non-scattering participating medium. When a ray enters the quartz layer, the path length $t_a$ to the probable point of attenuation inside the quartz is determined by [57]

$$t_a = \frac{\ln \mathcal{R}_1}{a_{\lambda}}$$  \hspace{1cm} (5-31)

where $a_{\lambda}$ is the quartz absorption coefficient, band-approximated using measured data [66] and given in Table 5.1.

<table>
<thead>
<tr>
<th>wavelength interval [\mu m]</th>
<th>quartz absorption coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[0, \lambda_1]$ = $[0, 0.17]$</td>
<td>$a_1 = 2.99 \text{ cm}^{-1}$</td>
</tr>
<tr>
<td>$[\lambda_1, \lambda_2]$ = $[0.17, 3.0]$</td>
<td>$a_2 = 0.03 \text{ cm}^{-1}$</td>
</tr>
<tr>
<td>$[\lambda_2, \infty]$ = $[3.0, \infty]$</td>
<td>$a_3 = 2.99 \text{ cm}^{-1}$</td>
</tr>
</tbody>
</table>

The path length to the next boundary $t_b$ is calculated by intersection of the ray's path (5-10) with the reactor's outer surface (5-26), and with its inner surface, given by

$$x^2 + y^2 = (r_q - d_w)^2 \quad (x_{rb} + d_i) < x < (x_{rt} - d_i) \quad \text{wall}$$

$$x = (x_{rt} - d_i) \quad x^2 + y^2 < (r_q - d_w)^2 \quad \text{top}$$

$$x = (x_{rb} + d_i) \quad x^2 + y^2 < (r_q - d_w)^2 \quad \text{bottom}$$

(5-32)

where $d_w$ and $d_i$ specify the thickness of the reactor wall and the reactor top/bottom, respectively. If $t_a$ is smaller than $t_b$, the ray is absorbed, a count is recorded at the
location of absorption, and its history is terminated. When the total number of absorbed rays is still lower than the local emission limit, Eq. (5-3), a new ray is isotropically emitted from the same location, to comply with the emission term of the local energy balance. The direction of the new emitted ray is calculated using Eq. (5-8) and (5-9), and its wavelength found by solving the implicit equation

$$\mathcal{R}_\lambda = \frac{\int_{\lambda} a_\lambda e_{\text{bb}}(\lambda, T) d\lambda}{\int_{0} a_\lambda e_{\text{bb}}(\lambda, T) d\lambda}$$ (5-33)

where $e_{\text{bb}}(\lambda, T)$ is the spectral blackbody emissive power, evaluated at the temperature of the location of emission. Eq. (5-33) is solved by applying the band approximation for the 3 spectral intervals of Table 5.1, yielding

$$\lambda_b = \begin{cases} \frac{F_{0-\lambda T} (\mathcal{R}_c a_p / a_1)}{T} & \text{for } \mathcal{R}_\lambda \leq \mathcal{R}_{\lambda_1} \\ \frac{F_{0-\lambda T} \left( (\mathcal{R}_c a_p - (a_1 - a_2) F_{\lambda T}^{\lambda_1}) / a_1 \right)}{T} & \text{for } \mathcal{R}_\lambda < \mathcal{R}_c \leq \mathcal{R}_{\lambda_1} \\ \frac{F_{0-\lambda T} \left( (\mathcal{R}_c a_p - (a_1 - a_2) F_{\lambda T}^{\lambda_2} - (a_2 - a_3) F_{\lambda T}^{\lambda_3}) / a_3 \right)}{T} & \text{for } \mathcal{R}_{\lambda_1} < \mathcal{R}_\lambda \end{cases}$$ (5-34)

where $a_p$ is the Planck mean absorption coefficient,

$$a_p(T) = a_1 F_{0-\lambda_1 T} + a_2 (F_{\lambda T}^{\lambda_1 - \lambda_2}) + a_3 (1 - F_{\lambda T}^{\lambda_2})$$ (5-35)

$a_1$, $a_2$, and $a_3$ are the values of the absorption coefficients in the 3 spectral intervals, respectively, given in Table 5.1, and $\mathcal{R}_c$ and $\mathcal{R}_{\lambda_1}$ are the random numbers corresponding to the wavelengths $\lambda_c = 0.17 \mu m$, and $\lambda_1 = 3.0 \mu m$, respectively

$$\mathcal{R}_c = \frac{a_1 F_{0-\lambda_1 T}}{a_p}, \quad \mathcal{R}_{\lambda_1} = \frac{(a_1 - a_2) F_{\lambda T}^{\lambda_1} + a_2 F_{\lambda T}^{\lambda_2}}{a_p}$$ (5-36)

Fig. 5.10 shows a contour plot for the resulting wavelength (in $\mu m$) as a function of temperature and random value. It shows that most of the emitted radiation is in a range of 3.0-15 $\mu m$ for a quartz temperatures 800-1400 K.
Once the direction and wavelength of the new emitted ray are known, new path lengths $t_a$, to the next (probable) point of attenuation, and $t_b$, to the next boundary, are calculated for the new ray.

If $t_b$ is smaller than $t_a$, the ray proceeds to the next boundary, where it is either reflected or refracted at the quartz/air boundary, according to the procedure described earlier. If the ray is reflected, the path length to attenuation is reduced by $t_b$

$$t_a = t_a - t_b,$$  \hspace{1cm} (5-37)

and compared to the new path length $t_b$ resulting from the intersection of the ray's new origin and direction after reflection with the reactor's outer and inner surfaces. If the ray is leaving the quartz layer to the outside it is assumed to be lost. A ray leaving the quartz layer to the inside enters the bed region $[x_{bb}, x_{bt}]$, the upper $[x_{bt}, x_{nt} - d_i]$, or the lower $[x_{nt} + d_i, x_{bb}]$ void region.

**Void region**

For consideration of an increased opacity and contamination of the quartz wall in the freeboard region above the bed, as it was observed during the experiments, a fraction
of the rays is absorbed on the inner surface of the quartz wall, on entering the upper void region, according to

\[ R_a \in [0, \rho_f] \rightarrow \text{absorption} \]
\[ [\rho_f, 1] \rightarrow \text{no absorption} \]  \hspace{1cm} (5-38)

If absorbed, a new ray is emitted isotropically from the same location, to ensure radiative equilibrium. The direction of emission is determined by Eqs. (5-8) and (5-9). The emitted ray propagates in the void region or in the quartz layer, according to the direction of emission, i.e.

\[ \hat{n} \cdot \hat{u} > 0 \rightarrow \text{void region} \]
\[ \hat{n} \cdot \hat{u} < 0 \rightarrow \text{quartz} \]  \hspace{1cm} (5-39)

where \( \hat{n} \) is the normal on the inner wall surface, and \( \hat{u} \) is the direction of the newly emitted ray.

If not absorbed, or after emission to the void region, or in the lower void region, the ray propagates to the to the bed region, or the next quartz boundary, where - for the upper void volume - again surface absorption/emission is considered.

Fig. 5.11 shows plots for (a) the fraction of energy emitted by the Ar arc that is entering the quartz layer, (b) the fraction of energy emitted by the Ar arc that is entering the bed region, (c) the fraction of energy emitted by the quartz that is entering the bed region, and (d) the fraction of energy that is leaving the quartz layer to the outside. The difference between Fig. 5.11(a) and 5.8(a) is due to reflection on the outer quartz surface, Fig. 5.9. By comparison of Fig. 5.11(a), (b), and (c) can also be observed that only about 20 % of the radiation entering the quartz eventually ends up entering the bed region, and that the emission from the quartz accounts for about 25 % of the total radiation incident on the bed region (the fraction of rays emitted from the bed and reentering the bed region after reflection in the quartz layer is below 0.02 % of emitted Ar power, or about 1.5 % of the total flux incident on the bed region. Fig. 5.11(d) is the fraction of energy lost by reemission, about 85 % of the energy that is entering the quartz layer.
Figure 5.11. Fractions of energy emitted (a) by the Ar arc that is entering the quartz layer, (b) by the Ar arc that is entering the bed region, (c) by the quartz that is entering the bed region, and (d) the fraction of energy that is leaving the quartz layer to the outside. Values are given in percentage (%) of total emitted arc power.

MC in bed region

Two MC approaches are applied: (i) a pseudo-continuous MC model that assumes a homogeneous medium and computes its absorption/scattering coefficients and scattering phase function, and (ii) a particle-discrete MC model that assumes an ensemble of randomly placed particles and traces the interaction of radiation with the surface of each particle.

The particles are assumed opaque, isothermal (a good approximation for \( Bi \ll 1 \)), spherical (a generally good assumption for most irregularly shaped randomly oriented particles), and having independent scattering, as justified by referring to independent/dependent scattering regime map shown in Fig. 5.12, for the range of particle volume fractions, \( \varepsilon_r = (0.3-0.7) \), and size parameters used in this study [67]. The size parameter is a dimensionless number connecting the particle size to the wavelength

\[
\xi = \frac{\pi d_p}{\lambda}
\]  

(5.40)
The wavelength interval used in this study is calculated using Wien's displacement law
\[ \lambda_{\text{max}} T = 2897.8 \mu m K \]  
where \( \lambda_{\text{max}} \) is the wavelength for maximum spectral hemispherical emissive power \( e_{ab}(\lambda, T) \) of a blackbody at temperature \( T \). For the temperatures of arc emission, 5780 K, and surrounding, 300 K, \( \lambda_{\text{max}} \) is 0.5 and 100 \( \mu m \), and for an average particle diameter \( d_p \) of 1 mm, the size parameter ranges between 300 and 6000. For simplification, the gas phase is taken to be a non-participating medium; its contribution to the radiative transfer has been estimated to be less than 5% [62].

![Diagram](image_url)

**Figure 5.12. Independent/dependent scattering regime map.** Particle volume fraction and size factor used are 0.3-0.7, and 300-600 respectively. Graph extracted from [67].

**Bed region as continuous participating media**

In approach (i), the bed region is modeled as a 3D non-isothermal, non-gray, absorbing, emitting, and anisotropically scattering participating medium, which is justified by the size parameter range [57]. Radiative properties are computed using geometrical optics for large particles. Particle properties are assumed constant within each disk.

The scattering and absorption coefficients, and the scattering phase function for large \( (\xi > 5) \) diffusely reflecting spheres are [57].
where $N_p$ is the particle number density, $r_p$ is the particle radius, $\theta$ is the angle between the directions of the incoming and scattered rays, and \( \rho_\lambda \) is the spectral hemispherical reflectivity of coal, obtained from measurements [68] and shown in Fig. 5.13.

The extinction coefficient for large spheres is then given by

$$\kappa_b = \sigma_\lambda + a_\lambda = \rho_\lambda^2 \pi \cdot N_p = \frac{3 \epsilon_s}{4 r_p}. \quad (5-44)$$

It is not dependent of the wavelength, because, for large particles, it is linked to the free path length that the ray travels in the bed without interaction. Note that the extinction coefficient is connected to the local mean solid fraction $\epsilon_s$, which is calculated later for each disk in the bed region.

Now, when a beam enters the bed region, the path length $t_o$ to the probable point of attenuation inside the bed is calculated from

$$t_o = -\ln(3\epsilon_s)/\kappa_b \quad (5-45)$$
Similar to the procedure in the quartz layer, $t_a$ is compared to the path length the ray travels to the next boundary $t_b$. Since $\kappa$ is constant only within the local disk, here $t_b$ is the distance the ray travels to the local disk boundary. When the ray reaches the boundary before extinction, i.e. $t_a > t_b$, it leaves the bed to the void region, gets to the air/quartz boundary, or enters another disk with a different extinction coefficient.

For a ray leaving the bed to the void region, the ray's direction $\hat{u}$ does not change, and the ray propagates in the void region. For a ray incident on the quartz surface, reflection/refraction is considered as described earlier, and when it is reflected, the path length to attenuation is reduced by $t_b$, i.e. $t_a = t_a - t_b$. When the ray enters another disk, the path length to attenuation is reduced to

$$ t_a = (t_a - t_b) \frac{\kappa_i}{\kappa_b} \tag{5-46} $$

with $\kappa_i$ and $\kappa_b$ being the extinction coefficient of the layer the beam leaves and enters, respectively. $t_a$ is then compared to the path length to the next disk boundary.

When the ray is attenuated ($t_a < t_b$), another random choice, depending on the albedo

$$ \Omega_1 = \frac{\sigma}{\kappa_b} = \rho_1, \tag{5-47} $$

determines, whether the ray is either absorbed or scattered. $\Omega_1$, is the probability of scattering, evaluated at the ray's wavelength. If the ray is scattered, i.e. $\mathcal{R}_a < \Omega_1$, its direction forms an angle with the incident direction, obtained by numerically solving

$$ \mathcal{R}_a = \frac{1}{2} \left[ \Phi(\theta, \psi) \sin \theta \cdot d\theta = \frac{2}{3\pi} \left[ \theta - \frac{3}{4} \sin(2\theta) + \frac{1}{2} \theta \cos(2\theta) \right] \right] \tag{5-48} $$

using the Newton algorithm. The scattering phase function $\Phi$, Eq. (5-43), gives, in statistical terms, the probability of scattering in a certain direction, and is derived from the integration of the angle between incident and reflected ray over half the surface of a diffuse reflecting sphere, see Fig. 5.14a for the phase function, and Fig. 5.14b for the distribution of the resulting scattering angle.
The azimuthal angle $\psi$ of the scattered ray is randomly chosen between $0$ and $2\pi$ because $\Phi$ is independent of $\psi$ for spherical particles. The direction of the scattered ray is then

$$\hat{u}_\sigma = \sin \theta_o \left( \cos \phi_o \hat{e}_x' + \sin \phi_o \hat{e}_y' \right) + \cos \theta_o \hat{u}$$

(5-49)

where $(\hat{e}_x', \hat{e}_y', \hat{u})$ is a local Cartesian coordinate system, calculated by

$$\hat{e}_x' = \hat{e}_x \times \hat{u} / \sin(\cos^{-1}(\hat{u}^T \hat{e}_x))$$

$$\hat{e}_y' = \hat{u} \times \hat{e}_x'$$

(5-50)

Since the scattering is assumed elastic, the wavelength of the scattered ray remains unchanged.

If the ray is absorbed, a count is recorded at the location of absorption, and its history is terminated. When the number of absorbed rays is still lower than the emission limit, Eq. (5-2), a new ray is isotropically emitted from the same location, to ensure no energy accumulation in radiative equilibrium. The direction of isotropic emission is randomly determined by Eqs. (5-8) and (5-9). The new ray is emitted by the non-gray medium at a wavelength found by solving Eq. (5-33), with the absorption coefficient given by Eq. (5-42). Using
\[ a_x = (1 - \rho_x) \kappa_b \]  
(5-51)

and the surface spectral absorptivity

\[ a_x = (1 - \rho_x) \]  
(5-52)

Eq. (5-33) can be written as

\[ R_x = \frac{\int_0^{\lambda_p} \alpha_x e_{ab}(\lambda, T) d\lambda}{\int_0^{\lambda_p} \alpha_x e_{ab}(\lambda, T) d\lambda} \]  
(5-53)

evaluated at \( T_p \) of the location of emission. The reflectivity outside the given wavelength interval of the reflectivity data \([\lambda_{\text{min}}, \lambda_{\text{max}}] = [0.3, 2.6] \mu m\) (Fig. 5.13) has been assumed equal to its values at the interval boundary. The denominator of Eq. (5-53) can then be written as

\[ a^0 + \int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} \alpha_x e_{ab}(\lambda, T) d\lambda + a^a T^* (1 - F_0 - \alpha_{\text{wm}} T) \]  
(5-54)

The integral \( \int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} \alpha_x e_{ab}(\lambda, T) d\lambda \) has been integrated numerically for a range of temperatures of interest \( T = [300, 3000] K \) with a differential \( d\lambda = 10^{-5} \mu m \). The data was saved in a matrix \( I_\Delta \) with data intervals of \( \Delta \lambda = 0.1 \mu m \) and \( \Delta T = 10 K \), so that

\[ I_\Delta(i, i_r) = \int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} \alpha_x e_{ab}(\lambda, T) d\lambda \]  
(5-55)

To simplify the notation we define \( I(T) = \int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} \alpha_x e_{ab}(\lambda, T) d\lambda \), the value \( I(T) \) can then be found by linear interpolation as

\[ I(T) = I_\Delta(257, i_r) + \frac{I_\Delta(257, i_r + 1) - I_\Delta(257, i_r)}{\Delta T} (T - 300K - (i_r - 1)\Delta T) \]  
(5-56)

\[ i_r = \text{int}(i + (T - 300K)/\Delta T) \]

With Eq. (5-54) we get the Planck mean absorptivity and the Planck mean absorption coefficient as
\[ \alpha_p = \frac{1}{\sigma T^4} \int_0^\infty \alpha_\lambda e_{\lambda b}(\lambda, T) d\lambda \]

\[ a_p = \frac{1}{\sigma T^4} \int_0^\infty s_\lambda e_{\lambda b}(\lambda, T) d\lambda = \kappa_c \alpha_p \]  

The random number boundaries are defined as

\[ R_{\lambda_{min}}(T) = \frac{\alpha_{\lambda_{min}} F_{0 \rightarrow \lambda_{min}T}}{a_p} \]

\[ R_{\lambda_{max}}(T) = \frac{\alpha_{\lambda_{max}} F_{0 \rightarrow \lambda_{max}T} + I(T) / \sigma T^4}{a_p} \]  

and the wavelength of emission is found from

\[ \lambda_b = \frac{F_{0 \rightarrow \lambda_{min}} (R_{\lambda} \alpha_p / \alpha_{\lambda_{max}})}{T} \quad \text{for } R_{\lambda} < R_{\lambda_{min}}(T) \]

\[ \lambda_b = \int_{\lambda_{min}}^{\lambda_{max}} \alpha_\lambda e_{\lambda b}(\lambda, T) d\lambda = (\alpha_\lambda R_{\lambda} - \alpha_{\lambda_{min}} F_{0 \rightarrow \lambda_{min}T}) \sigma T^4 \quad \text{for } R_{\lambda_{min}}(T) < \lambda_{\lambda} < R_{\lambda_{max}}(T) \]

\[ \lambda_b = \frac{F_{0 \rightarrow \lambda_{max}} (1 - (\alpha_\lambda R_{\lambda} - \alpha_{\lambda_{max}} F_{0 \rightarrow \lambda_{max}T} - I(T) / \sigma T^4) / \alpha_{\lambda_{max}})}{T} \quad \text{for } R_{\lambda_{max}}(T) < \lambda_{\lambda} \]

\( \lambda_b \) is found from linear interpolation for the value of \( \int_{\lambda_{min}}^{\lambda_{max}} \alpha_\lambda e_{\lambda b}(\lambda, T) d\lambda \) in \( I_\delta(i_x, i_y) \).

Fig. 5.15 shows a contour plot for the resulting wavelength (in \( \mu m \)) as a function of temperature and random value. It shows that the emitted radiation is mostly in a range of 1.5-10 \( \mu m \) for particle temperatures 800-1400 K.
Once the direction and wavelength of the new emitted ray or of the old scattered one are known, the ray is tracked to determine the new location of extinction.

**Bed region as discrete particles**

In approach (2), the fluidized bed is modeled as a set of randomly-positioned spherical particles with (or without) a Gaussian particle size distribution. Two different algorithms are used to determine the discrete particle distribution: (a) the free random placement (FRP), and (b) the packed bed algorithm (PBA).

In algorithm (a), for every particle to be placed a set of random coordinates is generated within the bed region and it is checked that there is no overlapping with already placed particles. This is repeated until the mass of placed particles equals the total mass of particles in the reactor. Due to geometrical limitations the maximum solid fraction that can be reached with the free random placement algorithm lies around 0.3.

In algorithm (b) for each particle a random start location is defined at the top of the reactor. The particles are then falling down into the bed region, and after interaction with already placed particles and/or the reactor wall and bottom they finally reach a fixed position that does not allow further downward movement. The so generated
packed bed has a solid fraction around 0.6, and the bed height obtained for a fixed (measured) maximum height lies within 2% of the one measured experimentally.

A varying solid fraction within the bed region can be accounted for by an underlying part wise linear stretching function for the packed bed algorithm.

The discrete particle method also allows the consideration of a particle size distribution. A Gaussian type distribution with limited minimum and maximum size has been implemented for the selection of the random radius of each new spherical particle.

The algorithms connected with the discrete particle placement are described in detail in Appendix A.

The MC technique follows a generic ray that interacts with the ensemble of particles. When a ray enters the bed region, the closest intersection with one of the placed particles is calculated.

The rays origin is given by \( \hat{r}_p \), it's direction by \( \hat{u}_b \). Each spherical particle is defined by its center point \( \hat{r}_l \) and radius \( r_l \), for \( l = 1..n_p \).

The ray's path is given by

\[
\hat{r}(t) = \hat{r}_p - t \cdot \hat{u}_b \tag{5-60}
\]

Fig. 5.16 shows a schematic of a ray that intersects a spherical particle.

The distance of the sphere center to the ray \( d_{iu} \) is given by

\[
d_{iu} = \sqrt{(\hat{r}_m - \hat{r}_l)^2 - t_{pl}^2}
\]

\[
t_{pl} = \hat{u}_b \cdot \hat{r}_l
\]

Figure 5.16. Intersection of a ray with a spherical particle.
For intersection, the sphere radius has to be smaller than $d_{lu}$, and the sphere has to be in positive ray direction, i.e.

$$d_{lu} < t_{ri} \land t_{ri} > 0$$  \hspace{1cm} (5-62)

The path length to intersection is then

$$t_s = t_{ri} - \sqrt{r_i^2 - d_{lu}^2}$$  \hspace{1cm} (5-63)

Eqs. (5-60)-(5-63) are evaluated for all spheres to find the closest distance to intersection.

When a ray hits a particle, a random choice determines whether the ray is either absorbed or reflected at the particle's surface, depending on the surface spectral absorptivity $\alpha_x = (1 - \rho_x)$, evaluated at the ray's wavelength. If the ray is reflected, the direction of diffuse reflection is chosen randomly from a set that is weighted according to Lambert's cosine law, Eqs. (5-19) and (5-20), where $\hat{n}$ is the surface normal at the point of incidence, and $(\hat{e}_x', \hat{e}_y', \hat{n})$ is a local Cartesian coordinate system.

If the ray is absorbed, a similar procedure is applied as for the continuous media model. A count is recorded at the location of absorption, and the ray's history is terminated. A new point of emission is selected randomly on the particle's surface, according to

$$\hat{r}_e = \hat{r}_i + (\cos \theta \cdot \hat{e}_x + \sin \theta (\cos \varphi \cdot \hat{e}_y + \sin \varphi \cdot \hat{e}_z)) \hat{r}_i$$  \hspace{1cm} (5-64)

with $(\varphi, \theta)$ calculated by Eq. (5-9). If the absorption counter for the point of emission is still lower than the local emission limit, Eq. (5-2), a new ray is emitted with a direction according to Eqs. (5-19) and (5-20), with $\hat{n}$ being the surface normal unit vector in the point of emission.

Eventually, each ray originated in the radiation source (Ar-arc) that is incident in the reactor, or each ray emitted in the quartz layer or by the fluidized bed medium, would undergo scattering/absorption by the participating media and reflection/refraction at the quartz boundaries. The history of a generic ray is then a complete random sequence, which terminates when it is absorbed by either the fluidized bed or the quartz walls, or lost to the surroundings. This procedure is repeated for a large number of rays for obtaining statistically meaningful results.
5.5 Fluid dynamics

In order to get the solid mixing rate $\dot{n}_{c,\text{mix}}$ and the mean solid fraction distribution $\varepsilon'$ throughout the bed region, the fluid dynamic behavior of the bed has to be taken into account.

Three approaches are considered: (1) perfect mixing, (2) no mixing, and (3) partial mixing.

**Perfect mixing**

In approach (1) the particles are assumed to be mixed perfectly, i.e. $\dot{n}_{c,\text{mix}} \to \infty$. This implies that the particles are all at the same temperature, and the solid fraction distribution is constant for the whole bed, and given by

$$\varepsilon_s = \frac{m_c}{\rho_c} \frac{1}{x_b A_b} \quad (5.65)$$

where $m_c$ and $\rho_c$ are the mass and density of the particles, and $x_b$ and $A_b$ are the fluidized bed height and reactor cross section area of the bed region, respectively. Perfect mixing refers to a bed with strong fluidization, as it has been observed during the experiments for the kinetic study.

**No mixing**

In approach (2) the particles are not mixed, i.e. $\dot{n}_{c,\text{mix}} = 0$, which refers to a packed bed. The solid fraction distribution is also given by Eq. (5.65), with $x_b$ being the height for the packed bed.

**Partial mixing**

In approach (3) the half volume fraction of moving particles $\phi_i'$ is defined for every layer in the bed, it is the volume fraction of particles that is exchanged between layers $i$ and $i+1$. The solid fraction in the not moving fraction of the layer $(1-2\phi_i')$ is assumed equal to a packed bed, and here given by

$$\varepsilon_k = \frac{m_c}{\rho_c} \frac{1}{A_b x_k} \quad (5.66)$$
where \( x_h \) is the height of the packed bed, measured before the experiments. The solid fraction in the moving fraction is assumed constant throughout the bed, and is calculated as

\[
\varepsilon_m = \frac{m_c / \rho_c - \varepsilon_i V_{dx} \sum (1 - 2 \phi_b')}{V_{dx} \sum 2 \phi_b'}
\]  

(5-67)

where \( V_{dx} \) is the volume of one layer. The mean solid fraction distribution in the bed is then given as

\[
\varepsilon_i' = 2 \phi_b' \varepsilon_m + (1 - 2 \phi_b') \varepsilon_i
\]  

(5-68)

and the mass per layer as

\[
m_{dx} = V_{dx} \rho_i \varepsilon_i'
\]  

(5-69)

The velocity of the particles that are carried up the bed is for a bubbling fluidized bed given by the bubble velocity, since the particles are carried up the bed in the bubble wakes. A correlation from the literature [69,70] was used to calculate the bubble velocity, it is

\[
u_b = (u_o - u_{mf}) + 0.711 \sqrt{g d_b}
\]  

(5-70)

were \( u_o \) is the mean superficial velocity, and \( u_{mf} \) the minimum fluidization velocity.

The mean superficial gas velocity is calculated using the ideal gas law

\[
u_o' = \frac{n_i R_u T_g'}{P_i A_b}
\]  

(5-71)

where \( n_i' \) is the total molar flow, \( R_u \) is the universal gas constant, \( P_i' \) is total pressure, and \( T_g' \) is the gas temperature.

At minimum fluidization conditions the drag force of the upward moving gas equals the weight of the particles, using the Ergun equation for the frictional pressure drop in a packed bed, this leads to [69,70]

\[
\frac{1.75}{(1 - \varepsilon_i')^3 \phi_i} Re_{p,mf}^2 + \frac{150 \varepsilon_i}{(1 - \varepsilon_i')^3 \phi_i^2} Re_{p,mf} = Ar
\]  

(5-72)
where $\phi$ is the sphericity, defined as ratio of the surface area of a sphere to the surface area of a particle with both having the same volume. $Ar$ is the Archimedes number

$$Ar = d_p^3 \rho_g (\rho_s - \rho_g) g / \mu_g^2$$  \hfill (5-73)

and $Re_{p,mf}$ the Reynolds numbers at minimum fluidization

$$Re_{p,mf} = u_{o,mf} d_p \rho_g / \mu_g.$$  \hfill (5-74)

$\rho_g$ and $\mu_g$ are the density and the dynamic viscosity of the gas mixture, given by Eqs. (5-82) and (5-80), respectively.

Solving (5-72) for the superficial minimum fluidization velocity finally leads to

$$u_{o,mf} = \frac{\mu_g}{d_p \rho_g} \left( \sqrt{K_1^2 + K_2 Ar} - K_1 \right)$$  \hfill (5-75)

where $K_1$ and $K_2$ stand for

$$K_1 = \frac{150 \varepsilon_i}{3.5 \phi_i} \quad K_2 = \frac{(1-\varepsilon_i)^3}{1.75} \phi_i.$$  \hfill (5-76)

Finally, the solid mixing rate, defined as the molar flow of particles that is exchanged between layer $i$ and $i+1$ in both directions is

$$\dot{n}_{c,mix}^i = \frac{u_{o,A} \phi_i \varepsilon_m \rho_c}{M_c (1-\varepsilon_m)}$$  \hfill (5-77)

**Pressure drop in the fluidized and the packed bed**

The Ergun equation [69,70] is used to calculate the frictional pressure drop per layer ($d_x$) in the packed bed

$$\frac{p_i^{i-1} - p_i^i}{d_x} = 150 \left( \frac{\varepsilon_i^2}{(1-\varepsilon_i)^3} \right) \frac{\mu u_o}{(\phi d_p)^2} + 1.75 \frac{\varepsilon_s}{(1-\varepsilon_i)^3} \frac{\rho_s u_o^2}{\phi d_p}$$  \hfill (5-78)

where the gas properties are calculated at the gas temperature $T_g^i$.

When the gas velocity exceeds the minimum fluidization velocity, i.e. when the bed is fluidized, the pressure drop per $dx$ equals the weight of particles within the layer
Properties of the gas mixture

The dynamic viscosity of the gas mixture is calculated using the method of Wilke [72]

\[ \mu_g = \sum_i \frac{y_i \mu_i}{\sum_j y_j \phi_{ij}} \]  \hspace{1cm} (5-80)

where \( y_i \) is the mole fraction, \( \mu_i \) the kinematic viscosity, and \( M_i \) the molar weight of species \( i \) in the gas phase. \( \phi_{ij} \) is called interaction parameter, given by

\[ \phi_{ij} = \frac{(1 + (\mu_i/\mu_j)^{y_i} (M_i/M_j)^{y_i})^2}{(8(1+M_i/M_j))^{y_i}} \]  \hspace{1cm} (5-81)

The thermal conductivity of the gas mixture \( k_g \) is calculated analogous by substituting \( k_i \) for \( \mu_i \) in eqs. (5-80) and (5-81), as suggested by Mason and Saxena [72].

The gas mixture is considered to be an ideal gas, so its density is

\[ \rho_g = \frac{p_t}{\bar{n}_t R_g T_g} \sum_i M_i \bar{n}_i \]  \hspace{1cm} (5-82)

5.6 Mass and energy conservation

As already mentioned earlier, the quartz tube is divided into \( n \) rings, and the particle suspension in the bed is divided into \( n \) disks, for the purpose of discretization, as illustrated in Fig. 5.1. The elements are denoted with superscript \( i = 1..n \). The subdivisions serve as control volumes for particles and gas phase, defining particle properties with index \( i \) as state of the particles in disk \( i \), and gas properties with index \( i \) as state of the gas flow leaving disk \( i \) and entering disk \( i+1 \), see Fig. 5.17. The boundary conditions are the temperature, molar composition, and total pressure of the incoming gas flow

\[ T_g^0, \bar{n}_{H_2O}^0, \bar{n}_H^0, \bar{n}_CO = \bar{n}_{CO_2} = \bar{n}_H_2 = 0, p_t^0 \]  \hspace{1cm} (5-83)
Figure 5.17. Definition of temperatures and subdivisions in the bed region.

Steady-state mass/energy conservation is applied to particles, quartz and gas phase, yielding

for particles
\[ \dot{Q}_{abs,p} = \dot{Q}_{em,p} + \dot{Q}_{pg} + \dot{Q}_{chm} + \dot{Q}_c + \dot{Q}_{cd,p} + \dot{Q}_{mix} \]  
(5-84)

for gas
\[ \dot{Q}_{chm} + \dot{Q}_{pg} + \dot{Q}_{ag} = \dot{H}_{out}' - \dot{H}_{in}' \]  
(5-85)

for quartz
\[ \dot{Q}_{abs,q} = \dot{Q}_{em,q} + \dot{Q}_{ag} + \dot{Q}_{aq} + \dot{Q}_{cd,q} \]  
(5-86)

The terms for absorbed radiation of the quartz and particles are found by MC

\[ \dot{Q}_{abs,p} = w \cdot N_p' \]  
(5-87)

\[ \dot{Q}_{abs,q} = w \cdot N_q' \]  
(5-88)

\( w \) is the power carried by a single ray, Eq. (5-1), and \( N_p' \) and \( N_q' \) are the counters of absorptions for particles and quartz, respectively.

For the terms of emitted power, emission from a volume [57] is applied for the quartz

\[ \dot{Q}_{em,q} = 4a_{p,q}T_q'^4dV_q \]  
(5-89)

and for the pseudo-continuous MC model

\[ \dot{Q}_{em,p} = 4a_{p,p}T_p'^4dV_p \]  
(5-90)

whereas for the particle-discrete MC model it is emission from a surface.
\[
\dot{Q}_{em,p}^i = A_{dx}^i \alpha_p \sigma T_p^{i4}
\]

where \(dV\) is the volume of the respective emitting element, \(A_{dx}^i\) is the total particle surface in element \(i\), calculated for the generated discrete particle distribution, and \(\alpha_p\) and \(\alpha_p\) are the Planck mean absorption coefficient and the Planck mean absorptivity, respectively, given in Eq. (5-35) for the quartz, and in Eqs. (5-57) for the bed.

The conduction terms for the quartz rings and for the bed are

\[
\dot{Q}_{cd,q}^i = -A_q k_q \left( T_q^{i+1} - 2T_q^i + T_q^{i-1} \right) / d_x
\]

and

\[
\begin{align*}
\dot{Q}_{cd,b}^i &= -(1-2\phi_b^i) A_b k_{eff} \frac{T_p^i - T_q^i}{d_x} \\
&= -(1-2\phi_b^i) A_b k_{eff} \frac{T_p^{i+1} - T_p^i}{d_x} - (1-2\phi_b^{i-1}) k_{eff} \frac{T_p^i - T_p^{i-1}}{d_x} \\
&= (1-2\phi_b^{i-1}) A_b k_{eff} \frac{T_p^{i-1} + T_p^i}{d_x}
\end{align*}
\]

for \((i = 1)\)

\[
\begin{align*}
\dot{Q}_{cd,b}^i &= -(1-2\phi_b^i) A_b k_{eff} \frac{T_p^i - T_q^i}{d_x} \\
&= -(1-2\phi_b^i) A_b k_{eff} \frac{T_p^{i+1} - T_p^i}{d_x} - (1-2\phi_b^{i-1}) k_{eff} \frac{T_p^i - T_p^{i-1}}{d_x} \\
&= (1-2\phi_b^{i-1}) A_b k_{eff} \frac{T_p^{i-1} + T_p^i}{d_x}
\end{align*}
\]

for \((i = 2..n-1)\) (5-93)

\[
\dot{Q}_{cd,b}^n = (1-2\phi_b^{i-1}) A_b k_{eff} \frac{T_p^{i-1} + T_p^i}{d_x}
\]

for \((i = n)\)

with \(A_b\) and \(A_q\) being the bed and the quartz cross sectional areas, \(k_q\) the thermal conductivity for the quartz, of the and \(k_{eff}\) the effective thermal conductivity for a packed bed, given by [75]

\[
\frac{k_{eff}}{k_g} = \frac{1 + 2\beta e_i + (2\beta^3 - 0.1\beta) e_i^2 + 0.05e_i^3 \exp(4.5\beta)}{1 - \beta e_i}
\]

\[
\beta = \frac{k_c}{k_g}
\]

where \(k_c\) and \(k_g\) are the thermal conductivities of particles and gas phase, respectively, and \(e_i\) is the volume fraction of particles. \((1-2\phi_b^i)\) is the volume fraction of the layer that is not mixed, i.e. conduction is only considered in the packed bed. For a fully packed bed, the volume fraction of mixing is set to \(\phi_b^i = 0\).
The term for particle mixing is given by

\[
\dot{Q}_{\text{mix}}^i = n_{i,\text{mix}} \cdot (h_{c,i} - h_{c,i+1}) \quad \text{for } (i = 1)
\]

\[
\dot{Q}_{\text{mix}}^i = n_{i,\text{mix}} \cdot (h_{c,i} - h_{c,i+1}) + n_{i,\text{mix}} \cdot (h_{c,i} - h_{c,i+1}) \quad \text{for } (i = 2, n-1)
\]

\[
\dot{Q}_{\text{mix}}^n = n_{n,\text{mix}} \cdot (h_{c,n} - h_{c,n+1}) \quad \text{for } (i = n)
\]

where \( n_{i,\text{mix}} \) is the molar exchange of particles between disk \( i \) and \( i+1 \) in both directions, Eq. (5-77), and \( h_{c,T} \) is the specific enthalpy of \( C \) at temperature \( T \).

The term for convection from particles to gas is

\[
\dot{Q}_{pq}^i = A_{pq}^i h_{pq} (T_p^i - T_g^i) \quad (5-96)
\]

\( A_{pq}^i \) is the mean particles-gas contact surface, given by

\[
A_{pq}^i = \frac{3\pi V_{ph}}{r_p \phi_p} \quad (5-97)
\]

\( h_{pq}^i \) is the mean heat transfer coefficient, calculated as

\[
h_{pq}^i = \frac{k_g}{d_p} \left( Nu_{pq,m} \frac{\varepsilon_m}{\varepsilon_3} (1 - 2\phi_b) + Nu_{pq,k} \frac{\varepsilon_k}{\varepsilon_3} 2\phi_b \right) \quad (5-98)
\]

using the following correlations for convective heat transfer between particles and gas in a fluidized bed [69]

\[
Nu_{pq,m} = \frac{h_{pq,m} d_p}{k_g} = 0.03 Re_p^{0.3} \quad (5-99)
\]

and in a packed bed [70]

\[
Nu_{pq,k} = \frac{h_{pq,k} d_p}{k_g} = 2 + 1.1 Pr g^{y3} Re_p^{0.6} \quad (5-100)
\]

The term for convection from quartz to the gas-particle emulsion is

\[
\dot{Q}_{aq}^i = A_{aq}^i h_{aq} (T_q^i - T_g^i) \quad (5-101)
\]

\( A_{aq} \) is the particles-gas contact surface, given by

\[
A_{aq} = \pi d_q d_x \quad (5-102)
\]
\( h' \) is the mean heat transfer coefficient, calculated as

\[
h' = k \left( \frac{Nu_{aq,m}}{d_p} \left( 1 - 2\phi_b \right) + \frac{Nu_{aq,k}}{d_b} 2\phi_b \right)
\]  

(5-103)

using the following correlations for convective heat transfer between quartz and the gas-particle emulsion in a fluidized bed [70]

\[
Nu_{aq,m} = \frac{h_{aq,m} d_p}{k_g} = 0.525 Re_p^{0.75}
\]  

(5-104)

and in a packed bed [70]

\[
Nu_{aq,k} = \frac{h_{aq,k} d_b}{k_g} = 2.26 Re_p^{0.8} Pr_g^{0.33} e^{-d_p/\lambda_b}
\]  

(5-105)

Finally, the term for convection from quartz to surrounding air is

\[
\dot{Q}_{aq} = A_{aq} h'_{aq} (T_q - T_a)
\]  

(5-106)

\( A_{aq} \) is the particles-gas contact surface, given by

\[
A_{aq} = \pi d_q d_x
\]  

(5-107)

and \( h'_{aq} \) is the heat transfer coefficient between the outer quartz surface and the surrounding air, calculated using [71]

\[
Nu_{aq} = \frac{h_{aq} d_x}{k_o} = \left[ 0.825 + \frac{0.387 Ra_{aq} \gamma^6}{\left( 1 + (0.492/Pr_o)^{9/16} \right)^{8/27}} \right]^2
\]  

(5-108)

\( k_o, Ra_{aq}, \) and \( Pr_o \) are the thermal conductivity, the Rayleigh, and the Prandtl numbers of air, respectively, evaluated at film temperature.

The chemistry term for the reaction of the gas phase at the particle surface is

\[
\dot{Q}_{chm} = \sum_i \dot{n}_{i,j} h_{j,T}
\]  

(5-109)

where \( h_{j,T} \) is the specific enthalpy of species \( j \) at temperature \( T \) (\( j = H_2, H_2O, CO, \) and \( CO_2 \)), and \( \dot{n}_{i,j} \) is the mole number increase due to reaction, given by
\[ \dot{n}_{r,j} = m_{dx}^{i} r_{j}^{a} \]  
(5-110)

with \( m_{dx}^{i} \) being the coal mass in disk \( i \), given by Eq. (5-69), \( r_{j}^{a} \) are the rates for surface reaction, Eq. (4-18)-(4-21), and \( a \) is the mass specific surface area. \( a \) is not known explicitly, but has been considered directly in the pre-exponential factor of the Arrhenius rate law, Table 4.1. The particle temperature \( T_{p}^{i} \) has been used for calculation of the (complex) kinetic parameters \( K_{i}(T) \), Eq. (4-25). For consideration of the mass transfer limitation for high temperatures as indicated by the dashed line in Fig. 4.2, a maximum temperature \( T_{K,\text{max}} \) has been defined for the calculation of the kinetic parameter \( K_{i} \), i.e. for all \( T_{p}^{i} > T_{K,\text{max}} \), \( K_{i}(T_{p}^{i}) \) is equal \( K_{i}(T_{K,\text{max}}) \).

The heat loss due to consumption of particles is

\[ \dot{Q}_{C}^{i} = -\dot{n}_{r,c}^{i} \left( h_{c,r_{p}}^{i} - h_{c,r_{s}}^{i} \right) \]  
(5-111)

with the mole number change of C due to reaction

\[ \dot{n}_{r,c}^{i} = -\left( \dot{n}_{r,CO}^{i} + \dot{n}_{r,CO_{2}}^{i} \right) \]  
(5-112)

The terms for the enthalpy flow in and out of the control volume are

\[ \dot{H}_{\text{out}}^{i} - \dot{H}_{\text{in}}^{i} = \sum_{j} \dot{n}_{j}^{i} \cdot h_{j,r_{p}}^{i} - \sum_{j} \dot{n}_{j}^{i-1} \cdot h_{j,r_{p-1}}^{i-1} \]  
(5-113)

with the mole number of the outgoing flow \( \dot{n}_{j}^{i} = \dot{n}_{j}^{i-1} + \dot{n}_{r,j}^{i} \). Note that the mole flow \( \dot{n}_{j}^{0} \) entering disk \( i = 1 \) is given by the boundary conditions.

**Iterations**

Fig. 5.18 shows the flow sheet and the different iterations that are required to solve the system of non-linear Eqs. (5-84)-(5-86) for all elements in the bed region.
Two nested iteration loops are used to iterate on the particle, gas, and quartz temperatures for the whole bed region. In the inner loop, the conservation equations are solved keeping the temperatures of adjacent elements, \((i-1), (i+1),\) constant. The Newton algorithm was applied, using numerically calculated partial derivatives \((\Delta T = 1K)\), and a convergence criterion of \(\varepsilon_f = 10^{-5} W\). Five iterations were needed to reach convergence, i.e. a difference less than \(10^{-5} W\) between the two sides of each of the energy balances, Eqs. (5-84)-(5-86).

The outer iteration loop accounts for the terms in the heat balances that are dependent on the temperature of adjacent elements, as the conduction and the mixing terms. The convergence criterion for the outer loop was defined as

\[
\frac{1}{2n} \sum_i \left| T_p^{i,(m)} - T_p^{i,(m-\nu)} \right| + \left| T_q^{i,(m)} - T_q^{i,(m-\nu)} \right| \leq 10^{-2} K
\]  

(5-114)

where the superscript \((m)\) denotes the outer iteration step. The outer iteration needs rather long to converge at the beginning, but gets faster for subsequent global iteration steps due to the progressive global convergence, i.e. due to the better starting values for quartz and particle temperatures.
5.7 Summary and Conclusions

A numerical model has been formulated to simulate a directly-irradiated fluidized-bed or packed bed of coal particles undergoing steam gasification. The model incorporated the Monte Carlo (MC) ray-tracing method for solving the 3D radiative exchange within an absorbing-emitting-refracting quartz tube and within an absorbing-emitting-scattering particulate bed. Langmuir-Hinshelwood type rate laws have been used to describe the reaction kinetics. The energy equation that couples heat transfer and chemical kinetics was solved numerically to yield temperature distributions, product gas compositions, and reaction extent, which were validated with experimentally measured data. Two modeling approaches are applied: (1) a quasi-continuous model that assumes an homogeneous medium and utilizes its macroscopic radiative properties (absorption and scattering efficiencies and scattering phase function), and (2) a particle-discrete model that assumes an ensemble of randomly-positioned particles and traces the interaction of radiation with each particle by geometrical optics. The former approach is superior in the computational time efficiency, while the latter approach provides a mean of verification of the radiative treatment of a suspension of particles as a continuous media. The model can be applied for computing the radiative heat transfer in high-temperature packed-bed or fluidized-bed reactors, involving directional and spectral dependent optical properties.
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6 Validation

6.1 Introduction

This chapter presents the validation of the model described in the last chapter with experimental data. First the experimentally measured flux distribution at the focal plane of the solar simulator reflector is compared to the flux distribution generated by modeling. For the 2nd part, the temperature distribution in packed and fluidized bed has been measured experimentally at 5 axial points in the bed region for a fluidized and for a packed bed, and has been compared to the temperature profile calculated numerically. In the 3rd part the model is validated using the experimental data from the gasification experiments described in chapter 3 to check product gas composition, and reaction extent.

6.2 Radiative power flux distribution

A Kendall radiometer was used to measure the incoming radiative power flux in the focal plane below the solar simulator reflector at various positions and for different power settings [76]. To get an equivalent flux distribution from the modeling a plane has been defined at the same x-position below the reflector model. The plane has been discretized, and the rays hitting the differential plane areas have been counted in a matrix $N_{ij}$.

The resulting flux for a differential area $dA_j$ is then

$$q_j = \frac{N_j w}{dA_j} \quad (6.1)$$

where $N_j$ are the number of hits on $dA_j$, and $w$ is the power per ray, given by Eq. (5-1).

From Eq. (6.1) can be seen that $q_j$ is directly proportional to the arc power $P_{arc}$, i.e. a change of the arc power will not change the shape of the flux distribution in the focal plane. The parameters that influence the shape of flux distribution are the arc radius $r_{arc}$, the fraction of diffuse/specular reflection $f_d$, Eq. (5-18), and the standard deviation $\sigma_\theta$ used for the angular error for specular reflection, Eq. (5-22). The values of these parameters have been found by minimizing the sum of differences between
experimentally measured and numerically calculated power fluxes at equivalent positions

$$\sum |\dot{q}_{i,\text{exp}} - \dot{q}_{i,\text{calc}}| \rightarrow 0$$

(6.2)

Figure 6.1 shows the experimentally measured data points and the numerically calculated curve for an arc current of 100, 200, and 300 A along the focal line (z-coordinate, Fig. 6.1a), and perpendicular to the focal line (y-coordinate, Fig. 6.1b). The agreement between the MC calculated values and the experimental ones is within 0.01% ± 7.2% (mean difference ± standard deviation). Fig. 6.2 shows a contour plot of the focal plane at 300 A. The parameter values used for these calculations were $f_d = 0.1$, and $\sigma_d = 1.5 \times 10^{-3}$.

![Figure 6.1](image)

**Figure 6.1.** Radiative power flux distribution at the focal plane, (a) along the focal line, and (b) perpendicular to the focal line. The data points correspond to the experimentally measured values by an absolute point radiometer. The curves correspond to the numerically calculated values by Monte Carlo for arc currents of 100, 200, and 300 A.
6.3 Temperature profile

Measurement of the temperature distribution along the quartz tubular reactor axis has been carried out for a fluidized bed and for a packed bed of coal particles, having only Ar flowing through the bed.

The same experimental setup has been used as for the gasification experiments, described in chapter 3, and shown in Fig. 3.2. The bed temperature has been measured at 5 axial positions in the center of the bed by thermocouples Type K inducted into the reactor through the gas inlet, and to the bed region through the frit of the reactor. The position of the thermocouples was adjusted before every experiment, so that they were not directly exposed to the incoming irradiation. Also, the reactor has been recorded during experiments to observe the fluidization behavior of the bed. The reactor’s position relative to the solar simulator reflector was measured accurately for proper reproduction in the modeling. Ar was fed at ambient temperature and at a mass flow rate of 3.0-7.7 l/min and 0.12-0.3 l/min for the fluidized and packed bed, respectively. The gas chromatograph was used to check for no remaining air in the reactor before the start of the experiments. The experiments were conducted with the activated charcoal pellets of the same type that have been used for the gasification experiments, their mean properties are listed in Table 3.1. Table 6.1 lists the set of parameters obtained from each experiment and used as input for the numerical modeling and for validation. 10 data sets have been obtained for a fluidized bed, and 7 for a packed bed.
Table 6.1. List of parameters obtained from experiments for temperature profile measurements.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>fluidized bed</th>
<th>packed bed</th>
</tr>
</thead>
<tbody>
<tr>
<td>distance reflector to reactor top</td>
<td>5-8 mm</td>
<td>5-8 mm</td>
</tr>
<tr>
<td>mass of coal in reactor</td>
<td>6.4-7.5 g</td>
<td>13.8-14.5 g</td>
</tr>
<tr>
<td>bed height packed</td>
<td>42-48 mm</td>
<td>70-76 mm</td>
</tr>
<tr>
<td>bed height in operation</td>
<td>50-60 mm&lt;sup&gt;a&lt;/sup&gt;</td>
<td>70-76 mm</td>
</tr>
<tr>
<td>arc power</td>
<td>100-300 A</td>
<td>100-300 A</td>
</tr>
<tr>
<td>distance of thermocouples from frit</td>
<td>7 - 53 mm</td>
<td>8 - 72 mm</td>
</tr>
<tr>
<td>temperature measured by TC in steady state</td>
<td>see Fig. 6.4b</td>
<td>see Fig. 6.4a</td>
</tr>
<tr>
<td>Ar flow</td>
<td>3.0 - 7.7 l/min</td>
<td>0.12 - 0.3 l/min</td>
</tr>
<tr>
<td>half volume of mixing</td>
<td>from recordings</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>a</sup> mean height observed from video recording

Figure 6.4 shows the experimental results at approximate steady-state conditions for the packed (a) and fluidized (b) beds exposed to radiation arc currents of 100, 200, and 300 A (see Fig. 6.1 for corresponding radiative power fluxes). As expected for the packed bed, the temperature increases monotonically from bottom to top and reaches 1450 K for the highest power flux at 300 A arc current. The rate of temperature increase is approximately constant because the internal radiative exchange approaches a conduction-like heat transfer within the bed. For the fluidized bed, the temperature increases significantly in the first quarter of the bed and then reaches an almost constant value, reaching 1300 K at 300 A arc current. This is consistent with the video-recording observation of a mostly packed-bed behavior in the lower bed region and a strongly bubbling fluidization in the upper bed region, because, as the gas flows upwards and is further heated, its volume expands and the fluidization increases. The half volume fraction of moving particles $\phi_b^i$ has been set based on observation from the video recording at the exact time of the data sample. Two x-values $x_{\phi_1}, x_{\phi_2}$ are chosen that define the region where $\phi_b^i$ changes from 0 to 0.5, by an underlying function

$$\phi_b^i = 0.5 \sin^2 \left( \frac{\pi}{2} \frac{x - x_{\phi_1}}{x_{\phi_2} - x_{\phi_1}} \right)$$

(6-3)

Fig. 6.3 shows $\phi_b^i$ for $x_{\phi_1} = 0$ mm, and $x_{\phi_2} = 30$ mm, as well as the resulting mean solid fraction distribution.
Also shown in Fig. 6.4(a) and (b) are the calculated temperatures of particles and gas under thermal equilibrium. For the packed bed, the gas is heated up to the particle temperature almost instantly at the entrance of the bed, as a result of the slow gas velocity and the high contact area between gas and particles.

The agreement between the calculated particle temperature values and the experimentally measured ones is within 1.1 % ± 3.2 % for the packed bed, and 1.1 % ± 5.6 % for the fluidized bed.

Figure 6.3. Half moving fraction and mean solid fraction distribution for $X_{\phi_1} = 0$ mm, and $X_{\phi_2} = 30$ mm, and for a total bed height of 60 mm.
Figure 6.4. Temperature distribution along the reactor axis for (a) packed bed, and (b) fluidized bed. The data points correspond to the experimentally measured values; the curves correspond to the numerically calculated values for particles (solid curve) and gas (dashed curve). The parameter is the arc current: 100, 200, and 300 A (see Fig. 6.1 for the corresponding radiative power fluxes).
6.4 Chemical composition

The experimental data obtained by gasification experiments (Chapter 3) has been used to validate the model involving the chemical reaction. The experimental setup is shown in Fig. 3.2. The product's chemical composition had been measured by the GC for the fluidized-bed reactor using a steam mass flow rate in the range 0.34 - 0.87 g/min, and an Ar/H₂O molar ratio in the range 1.3 - 8.3. Temperatures were controlled by varying the arc current in the range 200 - 500 A.

For the modeling, perfect mixing of particles has been assumed, since it corresponded well to the experimental observations for the strongly bubbling fluidized bed. The molar feed of H₂O and Ar, as well as the mass of particles in the reactor m_c was adjusted in order to account for the dependence of the bed's fluidization behavior at different bed temperatures, using a correlation that was found from the experimental data, considering only the data sets with a mass load m_c > 5.1 g, shown in Fig. 6.5.

Figure 6.5. Molar feed of Ar (n_Ar) and H₂O (n_H₂O) and mass load (m_c) vs. bed temperature. The data points show the experimentally measured values (for particle mass > 5.1 g). The lines are linear fits to the data points and correspond to the values used for the experiments obtained by the respective equations.

Figure 6.6 shows the experimentally measured data points and numerically calculated curves for the relative mole fractions of H₂, CO, and CO₂ in the product gases, i.e. the remaining H₂O and Ar molar fractions are here neglected. The data points correspond to the experimentally measured values given in Table 3.3; the filled points correspond
to the boundary conditions of molar feed and mass of particles indicated in Fig. 6.5. The agreement between experimentally measured data and numerically calculated curves is reasonably good for both types of data points, since the relative production of H₂, CO, and CO₂ is not dependent on the total coal mass. The mole fractions of CO₂ and CO approach zero and 0.5 at above 1450 K, respectively, which is consistent with the Boudouard equilibrium. At above 1450 K, the product composition consists of an equimolar mixture of H₂ and CO, as predicted by thermodynamic equilibrium.

![Figure 6.6. Product composition as a function of temperature. The data points correspond to the experimentally measured values by GC ('n' for H₂, 'A' for CO, 'o' for CO₂, given in Table 3.3, filled for the boundary conditions according to Fig. 6.5). The curves correspond to the numerically calculated values, using the boundary conditions given in Fig. 6.5.]

For the experimental conditions of Fig. 6.6, the energy balance yielded \( Q_{\text{ehm}} = 0.005 Q_{\text{inp}} \), \( Q_{\text{pg}} = 0.22 Q_{\text{inp}} \), \( Q_{\text{abs,}\text{p}} = 87.2 Q_{\text{inp}} \), \( Q_{\text{em,}\text{p}} = 84.5 Q_{\text{inp}} \), where \( Q_{\text{inp}} \) is the incident radiative power on the quartz reactor, 7.85 kW for an arc current of 400 A. Thus, most of the absorbed radiation is re-emitted and lost to the surroundings.

The water conversion, \( X_{\text{H₂O}} \), is, in the simulation, calculated by

\[
X_{\text{H₂O}} = 1 - \frac{n_{\text{H₂O}}}{n_{\text{H₂O}}^0}
\]  

(6.4)
For the experimental data, it is obtained from the oxygen mass balance using the product gas flows $\dot{n}_{CO}$, $\dot{n}_{CO_2}$ (calculated from GC measurements and feed gas flows), and $\dot{n}_{H_2O}$ (measured by the water pump), as

$$X_{H_2O} = \frac{\dot{n}_{CO} + 2\dot{n}_{CO_2}}{\dot{n}_{H_2O}} \quad (6.5)$$

The variation of $X_{H_2O}$ as a function of temperature is shown in Fig. 6.7, for the experimental measured (data points) and numerical calculated values (curve). The data points correspond to the experimentally measured values given in Table 3.3; the filled points correspond to the boundary conditions of molar feed and mass of particles indicated in Fig. 6.5. The agreement is notably better for the filled data points, since the water conversion is directly dependent on the total coal mass in the reactor.

![Figure 6.7. H$_2$O chemical conversion as a function of temperature. The data points ('o') correspond to the experimentally measured values given in Table 3.3, filled for the boundary conditions according to Fig. 6.5. The curves correspond to the numerically calculated values, using the boundary conditions given in Fig. 6.5.](image)

The rate of charcoal consumption, $\dot{X}_c$, is obtained from the carbon mass balance as

$$\dot{X}_c = \frac{\dot{n}_{CO} + \dot{n}_{CO_2}}{m_c/M_c} \quad (6.6)$$
where \( m_c \) denotes the initial amount of carbon in the bed. Since \( \dot{X}_c \) varied in the range 0.03-0.2 % s\(^{-1}\) for the experimental data, the assumption of steady state is reasonable, and the term \( \dot{Q}_c' \) in Eq. (5-84) is negligible.

The calculated rate of charcoal consumption, plotted in Fig. 6.8, increases to a maximum at a temperature of 1380 K, and then decreases for higher temperatures. From Fig. 6.7 can be seen that the reaction is complete for temperatures over 1380 K, i.e. all \( \text{H}_2\text{O} \) is converted to \( \text{CO}, \text{H}_2\text{O} \) and \( \text{CO}_2 \). Also, the molar ratio of \( \text{CO} \) to \( \text{CO}_2 \) in the output is already 10 and further increasing above 1380 K, therefore, the coal consumption approaches the \( \text{CO} \) production, which, on the other hand, is limited by the feed of \( \text{H}_2\text{O} \).

![Figure 6.8](image)

Figure 6.8. The solid line is the calculated rate of charcoal conversion \( \dot{X}_c \), the term \( \dot{n}_{\text{CO}} M_c / m_c \) is the part of \( \dot{X}_c \) caused by the \( \text{CO} \) production, \( \dot{n}_{\text{H}_2\text{O}} M_c / m_c \) represents the possible rate of charcoal conversion if all \( \text{H}_2\text{O} \) fed would react to \( \text{CO} \).

Using a radiation source with either a Planck's spectral distribution of a 5780 K blackbody or the actual Ar-arc spectral distribution did not result in noteworthy differences in the calculated curves of Figs. 6.1-6.7.
7 Summary and Outlook

This chapter gives a summary of the conducted research and the results achieved, and an outlook with suggestions how the work might be continued and improved.

The steam-gasification of coal into syngas was investigated using concentrated solar energy as the source of high-temperature process heat. A second-law analysis was carried out determining the maximum exergy efficiency and for identifying the major sources of irreversibility. The analysis established the thermodynamic base of the complete process and demonstrated its CO₂ mitigation potential by considering two technically viable routes for electricity generation from the gasification product: (1) syngas to be used to fuel a 55% efficient combined Brayton-Rankine cycle; and (2) syngas is further processed to H₂ (by water-shift gas reaction followed by H₂/CO₂ separation) which is used to fuel a 65% efficient fuel cell. The maximum exergy efficiency that was defined as the ratio of electric power output to the total thermal power investment, i.e. the solar power needed to run the gasification reaction plus the heating value of the reactants, reaches 50% for the combined cycle route and 46% for the fuel cell route. Both of these routes offer a net gain in the electrical output by a factor varying in the range 1.7-1.9, depending on the coal type and the power generation route, vis-à-vis the direct use of coal for fueling a 35%-efficient conventional Rankine cycle. Specific CO₂ emissions amount to 0.49-0.56 kg CO₂/kWhₑ, which is about half as much as the specific emissions discharged by the conventional cycle. In contrast to the conventional gasification, using process heat derived from the internal coal combustion, the solar-driven gasification produces high quality syngas that is not contaminated by the products of combustion. For the fuel cell route, the process becomes a decarbonization process if after separating the streams of H₂ and CO₂ the latter is sequestered, i.e. coal was converted to hydrogen without any release of CO₂ to the atmosphere.

A solar chemical reactor and experimental set-up have been designed and fabricated for investigating the solar thermal steam gasification of charcoal. The solar reactor features a quartz tube containing a fluidized/packed bed directly exposed to an external source of concentrated thermal radiation. For a typical experimental run, a batch of charcoal particles was heated to the desired temperature under an Argon flow and then subjected to a controlled H₂O-Ar flow under isothermal conditions. The product gases were analyzed by gas chromatography, this resulted in 41 data sets.
obtained in the temperature range 1000-1500 K. The data was analyzed for various aspects. The study also demonstrated the potential to produce high quality syngas with less than 5% CO₂ at temperatures above 1400 K, with an upgraded calorific value (34%), compared to the feedstock. The quality of the syngas is notably superior than the one typically obtained in autothermal reactors (with internal combustion of coal for process heat).

The reaction kinetics of the steam gasification of charcoal have been investigated using the data from the gasification experiments with the tubular quartz reactor. Rate law expressions were formulated based on elementary reaction mechanisms describing reversible adsorption/desorption processes and irreversible surface chemistry. Assuming plug flow conditions and steady state, the rate constants have been computed by matching theoretical and experimental results and their temperature dependence was determined by imposing an Arrhenius-type rate law.

A numerical model has been developed to describe the steam-gasification of coal or charcoal in a fluidized-bed or a packed-bed chemical reactor, directly exposed to an external source of concentrated radiation. The Monte Carlo (MC) ray tracing method is used to determine the radiation heat transfer from the source to the reactor, through the reactor quartz layer, and within the fluidized bed. Two approaches are examined to describe the radiative transfer within the fluidized bed for large particles of size parameter > 10, in the first approach, the bed is modeled as a continuous medium, using spectral absorption and scattering coefficients based on measured spectral reflectivity, and scattering phase functions for either specular or diffuse reflecting spherical particles. In the second approach, the bed is modeled as a cloud of randomly-positioned spherical particles, with spectral reflection (diffuse or specular), absorption, and emission taking place at the particle surface. The former approach is superior in the computational time efficiency, while the latter approach can provide a mean of verification of the radiative treatment of the particle-gas suspension as a continuous medium. Mass and energy balances that account for radiation, convection, conduction, chemical reaction, particle-mixing, and enthalpy change are applied in each element and solved numerically to calculate temperature profiles throughout the bed for particles, gas phase, and quartz tube. The model has been validated by comparing the numerically computed flux distribution, temperature profiles, product gas composition, and reaction extent with data obtained experimentally. The model can be applied for
computing the radiative heat transfer in high-temperature packed-bed or fluidized-bed reactors, involving directional and spectral dependent optical properties. The numerical model provides a tool for pre-design and optimization of fluidized and packed bed reactors subjected to high flux irradiation, it can be used to predict the solar reactor's performance under various operational conditions.

For the modeling, the gas phase has been assumed to be non-participating in the radiative exchange, but it can be easily implemented. The one-dimensional grid in the bed region is a reasonable assumption for the gas phase, assuming plug flow conditions, but it is a non ideal assumption for the radiative exchange, since most of the radiation is absorbed at a rather short distance from the bed's surface. This effect has less impact for a fluidized bed, since the particles are mixed vigorously, but for the packed bed the implied error becomes rather big. Therefore a three dimensional grid should be considered in the bed region. The fluid dynamic behavior of the bed was described by a simplified approach based on the assumption of two phases within the bed region, a resting phase with not moving particles and a solid fraction equal to a packed bed, and a moving phase, that involves the fraction of particles moving up and down the bed, whereas the mixing velocity is given by the bubble velocity. The respective area fractions have been validated by visual observation. However, to apply the model for the prediction of an up-scaled reactor, improvements have to be done in the prediction of the fluid dynamics. For the quartz layer, fully spectral properties could be applied instead of the band approximation used in this study.

The potential to double the specific electrical output in comparison with a conventional cycle has been demonstrated for the solar steam gasification of coal, by a thermodynamic analysis of an ideal system. High quality syngas was produced during gasification experiments in a laboratory scale fluidized bed chemical reactor exposed to highly concentrated thermal radiation. A model of the reaction kinetics has been developed for the steam gasification of coal, and the rate constants were computed using the experimental data obtained for a directly irradiated fluidized bed, validating its applicability when the heat of reaction is supplied by radiation. A numerical model was built to simulate the steam gasification of coal in a fluidized or packed bed of coal or charcoal particles in a solar chemical reactor. The focus was set on the radiative heat exchange by applying the MC ray tracing method that allowed the consideration of directional and spectral dependent optical properties, but all other modes of heat and
mass transfer have also been considered. The model was validated with experimental data. In summary, this dissertation contributes to the advancement of the chemical reactor engineering applied to novel high-temperature thermochemical processes for the production of solar fuels.
References


Appendix A

In this section the different algorithms are described that are used when the bed region is modeled as a set of discrete particles.

A.1 Gaussian particle size distribution

The discrete particle approach allows the consideration of a particle size distribution. A Gaussian distribution for the particle radius was applied,

\[ \Gamma(r) = \frac{1}{\sqrt{2\pi} \sigma_r} \int_{-\infty}^{\infty} \exp\left(-\frac{(u - \mu_r)^2}{2\sigma_r^2}\right) du \] (A-1)

where \( \mu_r \) is the mean value, and \( \sigma_r \) is the standard deviation. Fig. A.1 shows the Gauss distribution for \( \mu_r = 0.5 \text{ mm} \), and \( \sigma_r = 0.1 \text{ mm} \).

With the substitution \( z = (u - \mu_r) / \sqrt{2} \sigma_r \), Eq. (A-1) becomes

\[ \Gamma(z) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-z^2} du \] (A-2)

For the random selection of a radius, \( \Gamma(z) \) is set equal to a random number \( \mathcal{R}_z \). Due to symmetry of the Gauss distribution, Eq. (A-2) can then be written
For \( R_z \in [0,1] \), \( z \) varies in between \( \pm \infty \), and the resulting \( r_i \) can thus become negative. Therefore a maximum deviation \( \delta r_{\text{max}} = |r_i - \mu| \) is defined as an additional parameter of the particle distribution. The equivalent maximum difference of \( z \) is then
\[
\delta z_{\text{max}} = \delta r_{\text{max}} / \sqrt{2} \sigma_r .
\]

The integral in Eq. (A-3) is integrated numerically
\[
I_i(z = i \cdot \delta z_{\text{max}} / n) = \frac{\delta z_{\text{max}}}{n} \sum_{j=1}^{i} \exp \left(-\left(\frac{(j-0.5) \delta z_{\text{max}}}{n}\right)^2\right) \tag{A-4}
\]

The random numbers that correspond to \( \pm \delta z_{\text{max}} \) are then
\[
R_{\delta z_{\text{max}}} = 0.5 + I_i / \sqrt{\pi} \\
R_{\delta z_{\text{min}}} = 0.5 - I_i / \sqrt{\pi} \tag{A-5}
\]

For the selection of a random radius, a random number is selected and, if it lies within \([R_{\delta z_{\text{min}}}, R_{\delta z_{\text{max}}}]\), the respective equation of Eq. (A-3) is evaluated to yield \( z \), using linear interpolation between the discrete values of Eq. (A-4) to approximate the integral. The random radius is \( r_i = \mu_r + \sqrt{2} \sigma_r z \).

For a constant particle size, the number of spherical particles to be placed is given by
\[
n_p = \frac{m_c / \rho_c}{4 \pi r_p^3 / 3} \tag{A-6}
\]
but for a particle size distribution, new spheres (each with a random radius) are generated until the cumulative particle mass reaches the total mass of \( C \) in the reactor, i.e.
\[
\frac{4 \pi}{3} \rho_c \sum_i r_i^3 \leq m_c \tag{A-7}
\]
This defines the total number of particles \( n_p \) as the last index \( i \).
Note that the total number of particles is lower for the Gaussian particle size distribution than for a constant particle size that is equal to the distribution's mean \( \mu \), since the particle's volume is proportional to \( r^3 \).

For an equivalent number of total particles, the random particle size would have to be based on a Gaussian distribution for the particle volume instead.

### A.2 Free random placement (FRP)

In the FRP algorithm, for every spherical particle to be placed a set of random coordinates is generated in the bed region as a possible location of that particle.

\[
\begin{align*}
\vec{x} &= x_0 \vec{R}_x \\
\varphi &= 2\pi \vec{R}_\varphi \\
r &= \sqrt{\vec{R}_r} (r_j - r_i) \\
\vec{r}_i &= (x_{bb} + x) \cdot \hat{e}_x + r \cdot (\cos \varphi \cdot \hat{e}_y + \sin \varphi \cdot \hat{e}_z)
\end{align*}
\]  

(A-8)

Then it is checked if there is no intersection with already placed particles \( j = 1..i-1 \). The condition for no intersection is

\[
(\vec{r}_j - \vec{r}_i) \cdot (\vec{r}_j - \vec{r}_i) > (r_i + r_j)^2
\]  

(A-9)

If this is true for all \( j = 1..i-1 \), the sphere is successfully placed. If it is not true, a new possible location is calculated using Eq. (A-8). This is repeated until all the particles \( i = 1..n_p \) are successfully placed.

The FRP algorithm has certain limitations. The random selection of coordinates does not take into account the number of particles still to be placed, and the particles are generally not in contact with each other or with the wall. This leads to a saturation of possible locations for new placed particles. Therefore the maximum solid fraction that can be achieved is about 0.3. However, this is reasonable placement algorithm for a fluidized bed with perfect mixing.

### A.3 Packed bed algorithm (PBA)

In the packed bed algorithm for each particle a random start location is defined at the top of the reactor. The particle is falling down into the bed region, and after interaction with already placed particles and/or the reactor wall it reaches a fixed position that
does not allow further downward movement. Fig. A.2 shows a flow schematic of the
Packed bed algorithm.

For case (1) to (4) of the PBA, the possible position of the sphere $i$ is defined in function
of a parameter, i.e.

$$\hat{r}_c(t), \hat{r}_c(\alpha)$$  \hspace{1cm} (A-10)

the subscript C (for candidate) was used to distinguish $\hat{r}_c$ from $\hat{r}_i$, the position of $i$ at
each case’s start position.

The following notation was used to simplify the equations:

- sphere indices $l, J, K, L$
- sum of radii of $l$ and $J$ $r_u = (r_l + r_J)$
- midpoint of sphere $l$ $\hat{r}_i = [x_i, y_i, z_i]^T$
- unit vector $\hat{e}_u = [x_u, y_u, z_u]^T$
- connection vector $l$ to $J$ $\hat{r}_u = \hat{r}_i - \hat{r}_j = [x_u, y_u, z_u]^T$
- distance between $l$ to $J$ $d_u = |\hat{r}_u|$
(0) set random starting point (height above bed) → (1)

(1) I falling
   (1.1) until hits bottom → (5)
   (1.2) until hits J (loop 1..-1) → (2)

(2) I rolls on J
   (2.1) until drop from J → (1)
   (2.2) until hits bottom → (5)
   (2.3) until hits wall → (4)
   (2.4) until hits K (loop 1..-1 \ J)
      (2.4.1) immediate drop from J and K → (1)
      (2.4.2) immediate drop from J, I rolls on K → (2)
      (2.4.3) rolls on J and K → (3)

(3) I rolls on J and K
   (3.1) until hits bottom → (5)
   (3.2) until drop from J and K → (1)
   (3.3) until drop from J or K, rolls on K or J → (2)
   (3.4) until hits wall → (5)
   (3.5) until hits L (loop 1..-1 \ I,J,K)
      (3.5.1) immediate drop from J and K, rolls on L → (2)
      (3.5.2) drop from J or K, rolls on K or J and L → (3)
      (3.5.3) final position → (5)

(4) I rolls on J and wall
   (4.1) until hits bottom → (5)
   (4.2) until drop from J → (1)
   (4.3) until hits K
      (4.3.1) I rolls on K → (2)
      (4.3.2) I rolls on J and K → (3)
      (4.3.3) I rolls on K and wall → (4)
      (4.3.4) final position → (5)

(5) I reached final position, height check, next sphere → (0)

Figure A.2. Flow sheet of the packed bed algorithm. I, J, K and L are sphere indices.

(o) set random starting point, set height above bed

Random coordinates are generated within the cylinder and the starting height is set above the bed's top.

\[
\varphi = 2\pi R_p^2 \cos \varphi, \\
r = R_p \left( r_0 - r_f \right) \\
\dot{r}_i = x_r \cdot \hat{e}_x + r \cdot \left( \cos \varphi \cdot \hat{e}_y + \sin \varphi \cdot \hat{e}_z \right)
\]

(A-11)

(1) I falling

The path of I falling down in the reactor is given by

\[
\dot{r}_i(t) = \dot{r}_i - t \cdot \hat{e}_x
\]

(A-12)

The parameter is \( t \) for the path length.

(1.1) Path length to bottom (frit) hit
\[ t_b = x_i - (x_{bb} + r_i) \] (A-13)

(1.2) Check for intersection with already placed spheres \( J = 1..(l-1) \)

The distance of \( J \) to the fall line of sphere \( i \) is
\[ d_{ij} = \sqrt{(y_i - y_i)^2 + (z_i - z_i)^2} \] (A-14)

Intersection occurs, if \( J \) is close enough to the fall line
\[ d_{ij} < r_i \land x_i > x_j \] (A-15)

Thus, the path length to intersection is
\[ t_j = (x_i - x_j) - (r_i^2 - d_{ij}^2) \] (A-16)

\( t_j \) is calculated for all spheres \( J = 1..(l-1) \). The smallest \( t_j \) is chosen from \((t_i, t_b)\) so that \( t_j \) is greater than 0.

(a) \( I \) rolls on \( J \)

The path on \( I \) rolling on \( J \) is given by
\[ \hat{e}_x = \frac{(y_j \cdot \hat{e}_y + z_j \cdot \hat{e}_z)}{\sqrt{y_j^2 + z_j^2}} \]
\[ \hat{r}_c(\alpha) = \hat{r}_j + r_i \cdot (\cos \alpha \cdot \hat{e}_x + \sin \alpha \cdot \hat{e}_y) \] (A-17)

The parameter value for the start position is found from
\[ \alpha_0 = \cos^{-1}\left(\frac{(x_i - x_j)/r_{ij}}{r_j}\right) \] (A-18)

(2.1) Drop from \( J \)
\[ \alpha_d = \pi/2 \] (A-19)

(2.2) Bottom (frit) hit (only if \( r_j < r_i \))
\[ \alpha_b = \cos^{-1}\left(\frac{(x_{bb} + r_j - x_j)/r_{ij}}{r_i}\right) \] (A-20)

(2.3) Wall hit
The distance to the wall in \( \hat{e}_x \) direction is found from solving
\[(r_b - r_t)^2 = (y_t + t \cdot y_{y'x})^2 + (z_t + t \cdot z_{y'x})^2 \]

Intersection occurs if \( t < r_u \), where \( t \) is the positive solution of (A-21). The parameter value for a wall hit is then

\[\alpha_w = \sin^{-1}\left(\frac{t}{r_u}\right)\]

(2.4) Intersection with already placed sphere \( K = 1..(l-1) \setminus J \)

Point \( P \) is the projection of \( K \) in the plane containing \( \hat{e}_x \) and \( \hat{e}_{y'x} \), see Fig. A.4.

\[
\begin{align*}
\hat{e}'_{y'} &= \hat{e}_x \times \hat{e}_{y'x} \\
d_{KP} &= \hat{r}_K \cdot \hat{e}_{y'} \\
\hat{r}_p &= \hat{r}_K - d_{KP} \cdot \hat{e}_x
\end{align*}
\]

No intersection occurs for \( r_{IK}^2 < d_{KP}^2 \), otherwise the radius of the circle of possible intersection of \( I \) with \( K \) in this plane is given by

\[d_{PC} = \sqrt{r_{IK}^2 - d_{KP}^2}\]
Intersection occurs, if
\[ d_{ip} < d_{pc} + r_{ij} \wedge d_{ip} > |d_{pc} - r_{ij}| \]  
(A-25)

From geometric considerations (see Fig. A.4) result two candidates for the angle of intersection

\[ \alpha_{x_{ij}} = \cos^{-1}\left(\frac{x_{ip}}{d_{ip}}\right) \pm \beta \]  
(A-26)

\[ \beta = \cos^{-1}\left(\frac{d_{pc}^2 - d_{ip}^2 - r_{ij}^2}{-2d_{ip}r_{ij}}\right) \]

\( \alpha_i \) is chosen from \( (\alpha_d, \alpha_K, \alpha_x, \alpha_w, \alpha_b) \), so that \( \alpha_i \) is greater than and closest to \( \alpha_0 \). The new position of \( l \) is calculated using Eq. (A-17). If \( \alpha_d, \alpha_w, \) or \( \alpha_b \) was selected, the algorithm continues with case (1), (4), or (5), respectively. If \( \alpha_K \) or \( \alpha_x \) has been selected, further examination is needed to decide if the algorithm continues with part (1), (2), or (3).

2.4.1) \( l \) drops drops from both \( J \) and \( K \), (2.4.2) \( l \) drops drops from \( J \), and rolls on \( K \), or (2.4.3) \( l \) rolls on \( J \) and \( K \).

The path of \( l \) on \( J \) and \( K \) is a circle \( PL \) that (1) stands perpendicular to the connection of \( J \) and \( K \), and (2) has a centre point \( P \) that is on the connection of \( J \) and \( K \).

\[ \hat{e}_{x_{ij}} = \frac{\hat{r}_x}{d_{ij}} \]
\[ \hat{r}_p = \hat{r}_j + (\hat{r}_j^T \cdot \hat{e}_{x_{ij}}) \hat{e}_{x_{ij}} \]  
(A-27)

The radius of the circle \( PL \) is then equal \( d_{pi} \).

The unit vectors \( \hat{e}_{x_{ij}}, \hat{e}_{y_{ij}} \) are

\[ \hat{e}_{y_{ij}} = \frac{\hat{e}_{x_{ij}} \times \hat{e}_x}{|\hat{e}_{x_{ij}} \times \hat{e}_x|} \]
\[ \hat{e}_{x_{ij}} = \frac{\hat{e}_{y_{ij}} \times \hat{e}_x}{|\hat{e}_{y_{ij}} \times \hat{e}_x|} \]  
(A-28)

and corrected for direction

\[ \hat{e}_{x_{ij}} = \text{sign}(\hat{r}_p^T \hat{e}_{x_{ij}}) \cdot \hat{e}_{x_{ij}} \]
\[ \hat{e}_{y_{ij}} = \text{sign}(\hat{r}_p^T \hat{e}_{y_{ij}}) \cdot \hat{e}_{y_{ij}} \]  
(A-29)

The path of \( l \) on \( J \) and \( K \) would be then
\[
\hat{r}_c(\alpha) = \hat{r}_p + d_n \cdot \left( \cos \alpha \cdot \hat{e}_{xx} + \sin \alpha \cdot \hat{e}_{yy} \right) \quad (A-30)
\]

For the position of \( l \) on this path

\[
\alpha_0 = \cos^{-1} \left( \frac{\hat{e}_{xx}^T \hat{r}_p}{d_n} \right) \quad (A-31)
\]

The inclination of the plane with the circle \( P_l \) to the vertical is

\[
y_x = \cos^{-1} x_{xx} \quad (A-32)
\]

The projection of the circle \( P_l \) in a horizontal plane \((x = \xi)\) is an ellipse with half-axes

\[
a = d_n \\
b = d_n \cdot \sin(y_x) \quad (A-33)
\]

\( q \) is the projection of the distance of \( P \) to the lower sphere \( J \) or \( K \), see Fig. A.5.

\[
q = d_p \cdot \cos(y_x) \quad x_j < x_k \\
q = d_{px} \cdot \cos(y_x) \quad x_j > x_k \quad (A-34)
\]

If \( q \) is smaller than \( b \), \( l \) would drop immediately from the higher sphere and continue to roll on the lower sphere.

If \( q \) is greater than \( b \), \( \alpha_0 \) has to be compared to the critical angle of drop.

To get this angle we lay a tangent through \( q \) on the ellipse \( ab \). The tangent represents the direction that \( l \) would roll on the lower sphere. The equation of the tangent and ellipse are given by

\[
y = mx + q \\
x^2/a^2 + y^2/b^2 = 1 \quad (A-35)
\]

where \( x \) and \( y \) are the coordinates in the projected plane, see Fig. A.5.
By eliminating $y$ from (A-35) we get a quadratic equation for $x$, the determinant of the solution for this equation has to be zero for the tangent, so $m$ becomes

$$m = -\frac{\sqrt{(q^2 - b^2)/a^2}}{\frac{b^2}{a^2} + m^2}$$  \hspace{1cm} (A-36)

and the $x$-coordinate of the tangential point

$$x_d = \frac{-mq}{b^2/a^2 + m^2}$$  \hspace{1cm} (A-37)

the critical angle of drop is then

$$\alpha_d = \sin^{-1}(x_d/d_n)$$  \hspace{1cm} (A-38)

If $\alpha_d$ is smaller than $\alpha_o$, I will drop from the higher sphere $J$ or $K$ immediately, and the algorithm will continue with case (2) (identifying the sphere that $I$ rolls on as sphere $J$), otherwise, $I$ will roll on $J$ and $K$, and the algorithm will continue with part (3). If $J$ and $K$ are on equal height, $\alpha_d$ is equal $\pi/2$, $I$ will drop from both spheres $J$ and $K$ immediately, and the algorithm will continue with part (1).

**3) $I$ rolls on $J$ and $K$**

The path of $I$ is given by Eqs. (A-27)-(A-30) and the value of $\alpha_o$ for the start position of $I$ by Eq. (A-31).

**3.1) Bottom hit**

Figure A.5. Projection of the path of $I$ on $J$ and $K$ in a horizontal plane. $K$ is the lower sphere, the tangent represents the path $I$ would roll on $K$ after reaching the critical angle of drop $\alpha_d$ on its path on $J$ and $K$. 
only if \( x_{bb} + r > x_p \)

\[ \alpha_b = \cos^{-1} \left( \frac{x_{bb} + r - x_p}{d_{pj} \cos \gamma_x} \right) \]  

(A-39)

where \( \gamma_x \) is given by Eq. (A-32).

(3.2) Drop from \( J \) and \( K \)

only if \( x_k = x_i \)

\[ \alpha_{d_i} = \pi/2 \]  

(A-40)

(3.3) Drop from \( J \) or \( K \), \( I \) rolls on \( K \) or \( J \)

The critical angle \( \alpha_{d_i} \) is calculated by Eqs. (A-35)-(A-38).

(3.4) Wall hit

The distance to the wall in function of \( \alpha \) is given by

\[ d_w(\alpha) = r_b - r_i - \sqrt{y_c^2 + z_c^2} \]  

(A-41)

where \( y_c, z_c \) are the components of \( \hat{r}_c \), Eq. (A-30).

The equation for a wall hit

\[ d_w(\alpha) = 0 \]  

(A-42)

is evaluated in the interval \([\alpha_0, \pi/2]\), it can have 0, 1, or 2 solutions within this interval.

The derivative of \( d_w \) is

\[ d'_w(\alpha) = \frac{d}{d\alpha} d_w = -\frac{y_c y'_c + z_c z'_c}{\sqrt{y_c^2 + z_c^2}} \]  

(A-43)

where \( y'_c, z'_c \) are components of

\[ \hat{r}'_c = \frac{d \hat{r}_c}{d\alpha} = d_p \left( -\sin \alpha \cdot \hat{e}_r \cdot \cos \alpha \cdot \hat{e}_r \right) \]  

(A-44)

\( d_w(\alpha) \) has a minimum within \([\alpha_0, \pi/2]\) for

\[ d''_w(\alpha_0) < 0 \wedge d''_w(\pi/2) > 0 \]  

(A-45)
If it has a minimum, it is found by solving \( d'_w(\alpha_m) = 0 \) for \( \alpha_m \) by iteration in the interval \([\alpha_o, \pi/2] \), and the solution for the angle of wall hit \( \alpha_w \) is then found by solving

\( d_w(\alpha_w) = 0 \) by iteration in the interval \([\alpha_o, \alpha_m] \).

For no minimum, and \( d_w(\pi/2) < 0 \) the angle of wall hit \( \alpha_w \) is found by solving

\( d_w(\alpha_w) = 0 \) by iteration in the interval \([\alpha_o, \pi/2] \).

Otherwise, there is no wall hit for \( \alpha \in [\alpha_o, \pi/2] \).

\((3.4)\) Intersection with already placed sphere \( L = 1..(l-1) \setminus J,K \)

The point \( Q \) is the projection of \( L \) in the plane of the circle \( P_l \)

\[
\begin{align*}
    d_{IQ} &= \hat{r}_n \cdot \hat{e}_{x^*} \\
    \hat{r}_Q &= \hat{r}_i - d_{IQ} \cdot \hat{e}_{x^*}
\end{align*}
\]  

(A-46)

No intersection for \( r_i^2 < d_{IQ}^2 \), otherwise is the radius of the circle of possible intersection of \( I \) with \( L \) in this plane given by

\[
d_{QC} = \sqrt{r_i^2 - d_{IQ}^2}
\]  

(A-47)

Intersection occurs, if

\[
d_{PQ} < d_{QC} + d_{PC} \land d_{PQ} > |d_{QC} - d_{PC}|
\]  

(A-48)

where \( d_{PC} \) is given by Eq. (A-24).

As before, two candidates are resulting for the angle of intersection

\[
\begin{align*}
    \alpha_{i} &= \cos^{-1}\left( \frac{\hat{r}_{PQ} \cdot \hat{e}_{x^*}}{d_{PQ}} \right) \pm \beta \\
    \beta &= \cos^{-1}\left( \frac{d_{QC}^2 - d_{PQ}^2 - d_{PC}^2}{2d_{PQ}d_{PC}} \right)
\end{align*}
\]  

(A-49)

\( \alpha_i \) is chosen from \( (\alpha_b, \alpha_d, \alpha_d, \alpha_w, \alpha_i, \alpha_t) \), so that \( \alpha_i \) is greater than and closest to \( \alpha_o \).

The new position of \( I \) is calculated using Eq. (A-30). For \( \alpha_b, \alpha_d, \alpha_d, or \alpha_w \), the algorithm continues with case (5), (1), (2) or (4), respectively. For \( \alpha_i \) or \( \alpha_t \), further examination is needed to decide if the algorithm continues with part (2), (3), or (5).
(3.5.1) \( I \) drops drops from both \( J \) and \( K \), and rolls on \( L \), (3.5.2) \( I \) drops from \( J \) or \( K \), and rolls on \( K \) or \( J \) and \( L \), (3.5.3) \( I \) reaches final position.

Fig. A.6 shows a projection of \( J \), \( K \), and \( L \) to a horizontal plane, and the four possible sections for the projection of \( I \).

![Figure A.6. Projection of \( J \), \( K \), and \( L \) to horizontal plane, different cases for \( I \) projection.](image)

(1) The projection of \( I \) lies within the triangle defined by the projections of \( J \), \( K \) and \( L \). Since the points of contact between the spheres are lying on the direct connection between the midpoints, \( I \) can not move further downwards in this position.

(2) Since \( I \) lies on the opposite side from \( J \) on the connection from \( K \) to \( L \). Since the path of \( I \) on \( K \) and \( L \) is a circle around this connection, it will move further downwards and drop from \( J \) in any case. In order to decide if \( I \) will continue on \( K \) and \( L \), or only on one of those, Eqs. (A-27)-(A-38) are evaluated accordingly, substituting \( L \) for \( J \).

(3) Analogous to (2), swap \( J \) and \( K \).

The position of the projection of \( I \) is identified by checking the angles in the projected area. For (1) \( \beta_{JKL} > \beta_{JK} \land \beta_{KL} > \beta_{KL} \), for (2) \( \beta_{KL} < \beta_{JK} \land \beta_{KL} > \beta_{KL} \), and for (3) \( \beta_{JK} > \beta_{JK} \land \beta_{KL} < \beta_{KL} \), where \( \beta_{JKL} \) is defined as the angle between the directions \( K \) to \( J \) and \( K \) to \( L \) in the plane of projection, calculated as

\[
\beta_{JKL} = \cos^{-1} \frac{y_{KL} \cdot y_{KL} + z_{KL} \cdot z_{KL}}{\sqrt{y_{KL}^2 + z_{KL}^2} \cdot \sqrt{y_{KL}^2 + z_{KL}^2}} \quad (A-50)
\]

(4) If \( I \) lies in this section, Eqs. (A-27)-(A-38) are evaluated for (a) \( J \) and \( L \), and for (b) \( K \) and \( L \). If (a) results in a drop from \( K \), and (b) in a drop from \( J \), then \( I \) will continue to roll only on \( L \), i.e. part (2). For (a) drop from \( J \) and (b) staying on \( K \) and \( L \), as well as for (a) staying on \( J \) and \( L \) and (b) drop from \( K \), the algorithm will continue with part (3) by exchanging...
the sphere specifiers accordingly. Note that a drop from $L$ is not possible for (a) or (b), since the path of $I$ on $K$ and $L$ just led to the intersection with $L$. Also the result that $I$ would stay on $J$ and $L$ as well as on $K$ and $L$ is not possible in this section.

(4) $I$ rolls on $J$ and wall

The path of $I$ on $J$ and the wall is an ellipse at the distance $r_j$ from the wall. Unit vectors are defined for the path description

$$\hat{e}_{yw} = \frac{y_j \cdot \hat{e}_y + z_j \cdot \hat{e}_z}{\sqrt{y_j^2 + z_j^2}}$$

$$\hat{e}_{zw} = \text{sign}(\hat{r}_J^T (\hat{e}_x \times \hat{e}_{yw})) \cdot \hat{e}_x \times \hat{e}_{yw}$$

(A-51)

The parameter is the angle $\alpha$ that defines the height of $I$ above $J$, $(\cos \alpha \cdot r_I)$, and the horizontal distance of $I$ to $J$, $(\sin \alpha \cdot r_I)$. The relative coordinates $y_w, z_w$ are found by intersection of a circle of radius $(\sin \alpha \cdot r_I)$ around $J$, with a circle of radius $(x_b - r_J)$ around the $x$-axis, yielding

$$\hat{r}_c = (x_j + \cos \alpha \cdot r_I) \cdot \hat{e}_x + \left(\sqrt{y_j^2 + z_j^2} + y_w\right) \cdot \hat{e}_{yw} + z_w \cdot \hat{e}_{zw}$$

$$y_w = \frac{(r_b - r_I)^2 - (y_j^2 + z_j^2) - \sin^2 \alpha \cdot r_I^2}{2\sqrt{y_j^2 + z_j^2}}$$

$$z_w = \sqrt{\sin^2 \alpha \cdot r_I^2} - y_w^2$$

(A-52)

The starting angle is given by

$$\alpha_0 = \cos^{-1} \frac{x_{bw}}{r_I}$$

(A-53)

(4.1) Bottom hit, only if $x_{bb} + r_I \geq x_j$

$$\alpha_b = \cos^{-1} \frac{x_{bb} + r_I - x_j}{r_I}$$

(A-54)

(4.2) Drop from $J$

$$\alpha_d = \pi / 2$$

(A-55)

(4.3) Intersection with sphere $K = 1..(I-1) \backslash J$

The equation for an intersection with a sphere $K$, given by
\[ d_{cx}(\alpha) = \sqrt{(\hat{r}_c - \hat{r}_c)^\top (\hat{r}_c - \hat{r}_c) - r_{ik}^2} = 0, \]  

(A-56)

is evaluated in the interval \([\alpha_0, \pi/2]\), as has been done in part (3.4) for Eq. (A-42). The derivative of Eq. (A-56) is

\[
d''_{cx}(\alpha) = \frac{d}{d\alpha} d_{cx} = \frac{\hat{r}_c^\top \hat{r}_c}{d_{cx}^2} + \frac{1}{d_{cx}^2} \frac{d}{d\alpha} (\hat{r}_c^\top \hat{r}_c) - \frac{r_{ik}}{d_{cx}}.
\]

(A-57)

\[
y_w' = -\frac{r_{ij}^3 \sin 2\alpha}{2 (y_j^3 + z_j^3)}
\]

\[
z_w' = -\frac{1}{2z_w^2} \sin 2\alpha \left( 1 + \frac{y_w'}{\sqrt{y_j^3 + z_j^3}} \right)
\]

\[d_{cx}(\alpha)\] has a minimum within \([\alpha_0, \pi/2]\) for

\[d''_{cx}(\alpha_0) < 0 \land d''_{cx}(\pi/2) > 0\]

(A-58)

If it has a minimum, it is found by solving \(d_{cx}(\alpha_m) = 0\) for \(\alpha_m\) by iteration in the interval \([\alpha_0, \pi/2]\), and the solution for the angle of intersection with \(K\) \(\alpha_k\) is then found by solving \(d_{cx}(\alpha_k) = 0\) by iteration in the interval \([\alpha_0, \alpha_m]\).

For no minimum, and \(d_{cx}(\pi/2) < 0\) the angle of intersection with \(K\) \(\alpha_k\) is found by solving \(d_{cx}(\alpha_k) = 0\) by iteration in the interval \([\alpha_0, \pi/2]\).

Otherwise, there is no intersection with \(K\) for \(\alpha \in [\alpha_0, \pi/2]\).

\(\alpha_i\) is chosen from \((\alpha_b, \alpha_d, \alpha_k)\), so that \(\alpha_i\) is greater than and closest to \(\alpha_0\). The new position of \(l\) is calculated using Eq. (A-52). For \(\alpha_b\), or \(\alpha_d\), the algorithm continues with case (5), or (1) respectively. For \(\alpha_k\) further examination is needed to decide if the algorithm continues with part (2), (3), (4), or (5).

(4.3.1) \(l\) rolls on \(K\), (4.3.2) \(l\) rolls on \(J\) and \(K\), (4.3.3) \(l\) rolls on \(K\) and wall, (4.3.4) \(l\) reaches final position.

Fig. A.7 shows a projection of \(J\), \(l\), and \(W\), which is the contact point of \(l\) at the wall, to a horizontal plane, and the three possible sections for the projection of \(K\). Point \(W\) is found from
\[ \hat{r}_w = x_i \cdot \hat{e}_x + \left( y_i \cdot \hat{e}_y + z_i \cdot \hat{e}_z \right) \sqrt{y_i^2 + z_i^2} \]  

(A-59)

Figure A.7. Projection of \( J, K, \) and contact point of \( I \) at the wall \( W \) to horizontal plane, different cases for \( I \) projection.

(1) \( K \) supports \( I \) against \( J \) and the wall, i.e. \( I \) reached a fixed position, and the algorithm will continue with part (5).

(2) For any movement away from \( K \), \( I \) will loose the contact from the wall. In order to decide if \( I \) will continue on \( K \) and \( J \), or only on \( K \), Eqs. (A-27)-(A-38) are evaluated accordingly, and the algorithm will continue with part (2) or (3).

(3) \( I \) will continue to move along the wall and on \( K \). The algorithm will continue with part (4), by replacing \( J \) for \( K \).

The position of the projection of \( K \) is identified by checking the angles in the projected area, for \( \beta_{\text{WK}} > \beta_{\text{WJ}} \wedge \beta_{\text{WK}} > \beta_{\text{WJ}} \), \( K \) lies in (1), otherwise, for \( \beta_{\text{WK}} < \pi/2 \) in (2), or otherwise in (3).

(5) \( I \) reached final position.

When \( I \) reached a fixed position, it is checked whether it lies within the maximum height of acceptance, given by the bed height \( x_{bt} \), i.e.

\[ x_i + r_i \leq x_{bt} \]  

(A-60)

This check is necessary in order to generate a bed with a given height, if Eq. (A-60) is not true, the PBA starts again, step (0), for the same particle index, otherwise, the position of \( I \) is saved and the algorithm continues with the next particle index.
The bed generated with the PBA has a solid fraction of about 0.6. The bed height obtained after particle placement lies within 2% of the one measured experimentally.

### A.4 Surface area and mass per layer

For the discrete particle distributions, the surface area per layer is calculated exactly, since the terms for emission and for convection are proportional to the particle surface area. Also, for the chemistry term, the mass per layer is calculated exactly.

Fig. A.8 shows a spherical particle separated by the layer boundaries.

![Figure A.8. Spherical particle with layer boundaries and the relevant dimensions for the calculation of surface area and mass per layer.](image)

The contribution to the layer's surface area is

\[
\begin{align*}
  dA &= 2\pi r_t \cdot \delta_t & \text{top layer} \\
  dA &= 2\pi r_x \cdot d_x & \text{middle layer} \\
  dA &= 2\pi r_b \cdot \delta_b & \text{bottom layer}
\end{align*}
\]

and to the layer's mass

\[
\begin{align*}
  dm &= \pi \delta_t^2 \rho_c \left( r_t - \delta_t/3 \right) & \text{top layer} \\
  dm &= \frac{\pi d_x \rho_c}{2} \left( \delta_x^2 + \delta_t^2 + d_x^2/3 \right) & \text{middle layer} \\
  dm &= \pi \delta_b^2 \rho_c \left( r_i - \delta_b/3 \right) & \text{bottom layer}
\end{align*}
\] 

The total surface area \( A'_{\alpha} \) and mass \( m'_{\alpha} \) per layer is calculated by summarizing the contribution of each particle to the respective layers, according to the particles position.
A.5 Distribution stretching

The maximal solid fraction that can be obtained with the FRP algorithm is about 0.3. For the PBA, the solid fraction is constant at about 0.6. To generate a varying solid fraction within the bed region, as required for the partial mixing model, an underlying part wise linear stretching function is defined in axial bed direction as an extension to the packed bed algorithm that allows to reduce the packed bed's solid fraction to the required value.

First, a distribution for a packed bed is generated using the packed bed algorithm, and the mass per layer is calculated for the distribution.

The local stretch factor is then defined by the ratio of the solid fraction resulting from the fluid dynamics to the one obtained from the particle distribution, and given by

\[
\frac{f_{j}^{l}}{f_{i}^{l}} = \frac{\rho_{c}A_{i}d_{x}}{m_{j}^{l}}
\]  
(A-63)

If \( f_{j}^{l} \) would be smaller than 1 in a layer, it is set equal to 1. This is necessary to ensure no intersection of particles after distribution stretching. Usually this only occurs in the lowest layer \( (i=1) \) of the packed bed, since there, the spherical particles are lying on the bottom of the bed and therefore give a comparably smaller contribution to the layer's mass.

The stretch factor is then defined as

\[
f_{i}^{l} = \frac{1}{\sum_{j=1}^{j} f_{j}^{l}}
\]  
(A-64)

It is used for the stretching of the bed in axial direction, i.e. the x-coordinate of each particle is recalculated to

\[
x_{i} = x_{bb} + f_{i}^{l} (x_{i} - x_{bb})
\]  
(A-65)

After stretching, all particles above the bed top \( (x_{i} + r_{i} > x_{bb}) \) are deleted, and the surface area and mass per layer is recalculated for the new distribution.
Curriculum vitae

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1990-1995 Kantonsschule Romanshorn, Matura Typus B.
1995-2000 Studies at ETH Zurich, Department of Mechanical and Process Engineering.
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