Numerical investigations on a transpiring wall reactor for supercritical water oxidation

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**Numerical Investigations on a Transpiring Wall Reactor for Supercritical Water Oxidation**

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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2003
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Finally, I wish to gratefully acknowledge the financial support by the Swiss National Science Foundation, project number 21-58645.93 and 2000-66497.01, having made this work possible.

Kai
Summary

Supercritical water oxidation (SCWO) is a high pressure, high temperature process for the purification of waste water. Supercritical water \((p > 221 \text{ bar}, t > 374^\circ \text{C})\) is an advantageous solvent for oxidation reactions. It is completely miscible with organics and with oxygen. Hence, there is no limiting interfacial mass transfer resistance. This leads together with the high temperatures (approx. \(400 – 800^\circ \text{C}\)) to fast reaction rates, i.e. complete conversion at small residence times. The SCWO process aims for the purification of hazardous and persistent waste waters that often contain salts. At high but subcritical temperatures salt containing water is very corrosive. At supercritical temperatures water is a poor solvent for salts. When salty water is heated up above the critical temperature, the salts will precipitate and may plug the used reactor. Several concepts have been proposed in the pertinent literature to cope with the challenges of corrosion and plugging. At the ETH, the concept of a transpiring wall reactor (TWR) featuring a hydrothermal flame is investigated. The present work has been done to gain more insight into the reactor and to optimize its operation.

In the first part, a dimensionless model and inert computational fluid dynamic (CFD) simulations have been used to do a parametric analysis of a simplified transpiring wall reactor used for supercritical water oxidation. The analysis is done in order to find optimal flow conditions that prevent deposition of salt particles at the wall and that result in a favorable temperature field in the reactor. The parameters are temperature and flux of the bulk flow, as well as transpiration temperature and intensity. The protection at the wall is quantified by the thermodynamically allowable salt inlet mass fraction not leading to precipitation. This mass fraction can be calculated for any location in the reactor. Natural convection effects and non-linear properties diminish the protective boundary layer. Still, the transpiration temperature is to be chosen as low as possible for best wall protection from salt sedimentation. The analysis shows
that a high bulk temperature, a large bulk flow rate as well as a considerable transpiration intensity provide a more favorable flow field needed to maintain adequate kinetics for the waste destruction chemistry. Natural convection effects are always present in the range of operating conditions.

In a second part, experiments have been run to provide a data source for the validation of the CFD calculations. After evaluating the feasibility and the suitability of measuring various experimental values, the temperature field in the reactor and the residence time distribution (RTD) of the fuel inlet were selected. For the determination of the RTD, a special sensor that is able to withstand the harsh environment at the sensor location (salty supercritical water at 250 bar and 520°C) has been designed, constructed, and incorporated into an existing reactor. The experiments yielded valuable informations, not only for the validation of the CFD simulations but also for a better understanding of the phenomena occurring in the reactor.

In the third part, reactive CFD simulations are performed including the whole complexity of the geometry, as well as several species with an overall reaction. As boundary conditions, the measured operating conditions from the experiments were used. The comparison of the calculated with the experimentally measured values showed generally a good agreement. A mismatch of the temperature behavior near the transpiring wall helped to reveal a deficiency of the model to describe the transfer to the wall correctly.

All in all, a basis has been set to the CFD modelling of the flow field in a SCWO reactor. Experimental data has been provided on which CFD simulations can be tested and thereby validated. Reactive CFD simulation have been run and new modelling challenges are discussed.
Zusammenfassung


Im ersten Teil wurden ein dimensionsloses Modell sowie inerte Strömungsberechnungen (CFD) angewendet, um eine Parameteranalyse durchzuführen an einem vereinfachten Schwitzwandreaktor (engl. TWR). Die Analyse wurde gemacht, um die optimalen Strömungsbedingungen zu finden, welche eine Ablagerung von Salzpartikeln verhindern und ein günstiges Temperaturfeld im Reaktor erzeugen. Die varierten Parameter sind Temperatur und Flux der Hauptströmung sowie Schwitzwassertemperatur und Intensität. Der Schutz an der Wand wird quantifiziert durch den thermodynamisch erlaubten Salzmassenan-

In einem zweiten Teil wurden Experimente durchgeführt, um Daten zu erhalten, die als Grundlage einer Validierung der CFD Berechnungen dienen. Nachdem die Machbarkeit und die Eignung, verschiedene experimentelle Größen zu messen, ausgewertet wurde, ist eine Temperaturfeldmessung im Reaktor sowie eine Bestimmung der Verweilzeitverteilung (engl. RTD) ausgewählt worden. Für die Bestimmung der RTD musste ein spezieller Sensor, welcher fähig ist, der aggressiven Umgebung beim Einbauort (salziges überkritisches Wasser bei 250 bar und 520°C) zu widerstehen, ausgelegt, konstruiert und in einen existierenden Reaktor eingebaut werden. Die Experimente lieferten wertvolle Informationen, nicht nur für die Validierung der CFD Simulationen, sondern auch, um das Verständnis über die Vorgänge im Reaktor zu fördern.


Gesamthaft gesehen wurde eine Grundlage gelegt, um ein Strömungsfeld in einem SCWO Reaktor zu modellieren. Experimentelle Daten wurden bereitgestellt, um CFD Berechnungen zu testen und somit zu validieren.
Reaktive CFD Berechnungen wurden ausgeführt und neue Modellherausforderungen sind diskutiert.
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Nomenclature

Abbreviations

CFD  computational fluid dynamics
CSTR continuously stirred tank reactor
CW  cooling water
dft discrete fourier transformation
EoS equation of state
fft fast fourier transform
FI flow indication
GCI grid convergence index
HPLC high-pressure liquid chromatography
HTO hydrothermal oxidation
HWA hot wire anemometry
I-A tag of intensity variation experiment (table 5.1)
I-B tag of intensity variation experiment (table 5.1)
I-C tag of intensity variation experiment (table 5.1)
LES large-eddy simulation
ox oxygen
PFR plug flow reactor
PI pressure indication
PIC pressure indication and control
PR Peng-Robinson
PRVT Peng-Robinson with constant volume translation
QA quality assurance
RANS Reynolds-averaged Navier-Stokes
RTD residence time distribution
RTD-NF tag of intensity variation experiment (table 5.4)
RTD-WF tag of intensity variation experiment (table 5.4)
SCW supercritical water
SCWO supercritical water oxidation
SRK  Soave-Redlich-Kwong
TIA  temperature indication and alarm
TIC  temperature indication and control
T-A  tag of intensity variation experiment (table 5.2)
T-B  tag of intensity variation experiment (table 5.2)
T-C  tag of intensity variation experiment (table 5.2)
TW   transpiring water
TWR  transpiring wall reactor
VLE  vapor-liquid equilibrium
WW   waste water

Greek letters

\( \alpha \) [-]  temperature dependency of attraction term
\( \epsilon \) \([m^2/s^3]\)  dissipation of the turbulent kinetic energy
\( \epsilon \) [-]  void fraction
\( \epsilon \) [-]  external emissivity coefficient
\( \eta \) \([kg/m \cdot s]\)  dynamic viscosity
\( \gamma \) [-]  magnitude parameter in linear filter
\( \kappa \) [-]  parameter appearing in Eq. 3.13
\( \kappa \) [-]  ratio of solid and liquid void fraction
\( \lambda \) \([m^2/s]\)  thermal conductivity
\( \mu \) \([m^2/s]\)  kinematic viscosity
\( \mu \) \([\text{debye}]\)  dipole moment
\( \phi \) var. units  scalar
\( \rho \) \([kg/m^3]\)  density
\( \sigma \) \([S/cm]\)  specific conductivity
\( \sigma \) var. units  standard deviation
\( \sigma \) \([W/m^2K^4]\)  Stefan-Boltzmann constant
\( \tau \) \([N/m^2]\)  stress
\( \tau \) \([s]\)  time interval
\( \tau \) \([s]\)  mean residence time
\( \omega \) [-]  acentric factor
## Latin letters

<table>
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<tr>
<th>Symbol</th>
<th>Unit</th>
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<td>$A$</td>
<td>$[m^2]$</td>
<td>area</td>
</tr>
<tr>
<td>$b$</td>
<td>$[m^3/mol]$</td>
<td>covolume</td>
</tr>
<tr>
<td>$C$</td>
<td></td>
<td>var. units constant</td>
</tr>
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<td>$C_c$</td>
<td>$[1/cm]$</td>
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<td>$C$</td>
<td>$[mol/m^3]$</td>
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<td>$[mol/m^3]$</td>
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<td>heat capacity at constant pressure</td>
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<tr>
<td>$D$</td>
<td>$[m]$</td>
<td>distance or diameter</td>
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<td>$D_{ij}$</td>
<td>$[m^2/s]$</td>
<td>diffusion coefficient of species $i$ in $j$</td>
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<td>$[S]$</td>
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<td>$[m/s^2]$</td>
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<td>flux</td>
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</tr>
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<td>mass</td>
</tr>
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<td>$[kg/mol]$</td>
<td>molecular mass</td>
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<td>$N$</td>
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<tr>
<td>$n$</td>
<td>[-]</td>
<td>exponent</td>
</tr>
<tr>
<td>$P$</td>
<td>$[bar]$ or $[MPa]$</td>
<td>pressure</td>
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<tr>
<td>$Pr$</td>
<td>[-]</td>
<td>Prandtl number</td>
</tr>
<tr>
<td>$p$</td>
<td>[-]</td>
<td>probability</td>
</tr>
<tr>
<td>$p$</td>
<td>[-]</td>
<td>order of integration method</td>
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<tr>
<td>$Q$</td>
<td>$[J/s]$</td>
<td>heat flow</td>
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Nomenclature

\( q \) [J/m\(^2\) s] heat flux
\( R \) [m] radius
\( R \) [Ω] resistivity
\( R \) [J/mol K] universal gas constant
\( Re \) [-] Reynolds number
\( Ri \) [-] Richardson number
\( r \) [-] refinement ratio
\( \vec{r} \) [m] position vector
\( S \) var. units source
\( Sc \) [-] Schmidt number
\( St \) [-] Stanton number
\( T \) [K] absolute temperature
\( t \) [°C] temperature
\( t \) [s] time
\( U \) [V] potential difference
\( u \) [m/s] velocity
\( VT \) [m\(^3\)/mol] volume translation
\( v \) [m\(^3\)] volume
\( w \) [kg/kg] weight fraction
\( x \) [m] direction in space
\( x \) [m] transpiration length
\( y^+ \) [-] dimensionless normal distance from the wall

Sub- and superscripts

bulk bulk flow property
c cell
c critical
c coarse based on the coarse grid
eff effective
ext external
fine based on the fine grid
HW hot-wire
id ideal gas
in at the inlet
κ kinetic theory
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<tr>
<td>l</td>
<td>liquid</td>
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<tr>
<td>loss</td>
<td>getting lost</td>
</tr>
<tr>
<td>m</td>
<td>mass</td>
</tr>
<tr>
<td>no tr</td>
<td>without transpiration</td>
</tr>
<tr>
<td>out</td>
<td>at the outlet</td>
</tr>
<tr>
<td>p</td>
<td>pressure</td>
</tr>
<tr>
<td>pc</td>
<td>pseudo-critical</td>
</tr>
<tr>
<td>r</td>
<td>reduced (normalized with the critical value)</td>
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<tr>
<td>relax</td>
<td>relaxation</td>
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<tr>
<td>res</td>
<td>residual</td>
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<tr>
<td>s</td>
<td>solid</td>
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<td>salt</td>
<td>of the salt</td>
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<tr>
<td>sol</td>
<td>solubility</td>
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<td>sp</td>
<td>species</td>
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<td>t</td>
<td>turbulent</td>
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<td>tr</td>
<td>transpiration fluid property</td>
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<td>wall</td>
<td>at the wall</td>
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<td>wt.</td>
<td>weight</td>
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<td>x</td>
<td>based on the plate length</td>
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<td>∞</td>
<td>at infinity</td>
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<td>·</td>
<td>averaged</td>
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<td>fluctuating part</td>
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Chapter 1

Introduction

1.1 Structure of the presented work

This work starts with an introduction to supercritical water oxidation in which its advantages and challenges are discussed. Then the concept of the investigated reactor is derived accounting for the challenges of the process.

In the following modelling part all used models are described and explained. This acts together with the properties part as the basis of the numerical investigations that are one of the two main objectives of this work. The numerical investigations start with a parameter study using a simplified model and geometry. This investigation is compared with inert CFD simulations which incorporate the effects of gravity. An experimental part is then performed to get more insight in the flow field and to have some data for validation. In the succeeding part specific reactive CFD simulations have been performed allowing a comparison with the experiments. The results from the reactive simulations allow a better understanding of the temperature field in the reactor. Following the conclusions an outlook is given on proposed future investigations. Special emphasis is thereby given to the modeling of the process.

1.2 Supercritical Water Oxidation

Dense supercritical high pressure fluids are of rapidly growing interest in science. The number of applications of supercritical fluids in chemistry,
chemical reaction engineering and separation processes increases continuously, e.g. supercritical fluid chromatography and extraction or the rapid expansion from a supercritical solution. The thermophysical properties of supercritical fluids make them attractive as media for chemical reactions. Work on processes, e.g. separation processes, and chemical reaction in and with supercritical fluids is reviewed in articles of Hutchenson and Foster (1995), Savage et al. (1995), (1999) and Ding et al. (1996). An emerging technology in the environmental field is that of the oxidative destruction of organic wastes in supercritical water. This process is known as supercritical water oxidation (SCWO) or as hydrothermal oxidation (HTO). Newer reviews on SCWO include the works of Yesodharan (2002), Abeln et al. (2001), Kritzer and Dinjus (2001), Tester and Cline (1999), and Schmieder and Abeln (1999).

**Figure 1.1**: The supercritical region is defined by having a pressure and a temperature above the critical one \((t_c, p_c)\).

SCWO is a high pressure process for disposal of toxic and hazardous organic waste waters. The first works that are of great importance date back to the middle of the seventies [e.g. review of Tester et al., 1993a]. The process parameters pressure and temperature are higher than the critical data of pure water \((t_c = 374^\circ C, p_c = 221 \text{ bar})\). Near and above the critical point, the properties of water are quite different from those
at ambient conditions and the solvent characteristics change drastically. Above the critical state conditions, water that is polar in the liquid phase becomes non-polar [e.g. Hirth and Franck, 1993]. Therefore, organic compounds and gases such as oxygen and nitrogen are miscible with supercritical water in all proportions.

![Figure 1.2: Solubility of various salts in supercritical water. $p = 250$ bar.](image)

In contrast to the high solubility of organics, many inorganics (e.g. salts) having high solubilities in liquid subcritical water, dissolve extreme poorly in supercritical water [Martynova, 1973; Armellini and Tester, 1993] (Fig. 1.2). Under supercritical conditions, the reaction system is comprised in a single fluid phase. Because of this, many of the inherent transport resistances that exist in multi-phase contacting are absent, e.g., there is no inhibition for the mass transfer of oxygen from the gas phase into the liquid phase. The monophase system and the considerably high temperatures ($400 – 800^\circ C$) are prerequisites for the superior final conversion and volume specific conversion efficiencies compared to other disposal processes. SCWO is an excellent low emission alternative to incineration. For aqueous solutions containing between 1
and 20 wt.-% organics, SCWO may be more economical than controlled incineration or activated carbon treatment and more efficient than wet oxidation [Tester et al., 1993a; Svensson, 1995]. Oxidation in supercritical water is applicable to a wide range of feed mixtures and is not limited to aqueous organics. An amazing variety of materials have already been oxidized: contaminated soil [Kronholm et al., 2002], garbage [Jin et al., 2001], PET industry effluents [Cocero et al., 2000], contaminated sludges [Crain et al., 2000; Cooper et al., 1997], sewage sludge [Shanableh and Shimizu, 2000], printed circuit board wastes [Chien et al., 2000], even tire waste [Park et al., 1999]. A further advantage of the aqueous reaction medium is the exclusion of dioxins or furanes in the exhaust gas since the SCWO is operated at temperatures where these compounds are not formed.

1.2.1 Unsolved challenges of the process

Until the end of the eighties all attempts to use the SCWO technique to treat industrial salt containing waste water failed. The process was inhibited by two major technical problems preventing a successive continuous operation: First, the inner wall of the reactor must be made of material which must withstand not only the high temperature (≈ 600–800°C) and pressure conditions but also a very corrosive fluid mixture. The technique ran into problems as soon as concentrations of ions and salts exceeded limiting values. The corrosion damaged the load-bearing vessel walls [e.g. Boukis et al., 1997; Fill and Tiltscher, 1997]. Mitton et al. (1995) report both general corrosion as well as pitting and stress corrosion cracking in high-nickel alloys. Reviews on this topic are given by Wagner et al. (1999), Mitton et al. (2000) and by Han (2000).

The second problem emerged from the low solubility of salts in the supercritical water (Fig. 1.2). Armellini and Tester (1991) and (1994) examined the rapid precipitation of salts (NaCl and NaSO₄) in the course of the supercritical water oxidation process. The sedimentation and adherence of the precipitated salt particles to the walls led to plugging of the reactor. The corrosion and plugging due to sticky salts is called the "dual problem" of supercritical water oxidation [La Roche, 1996]. The plugging of the reactor will not be prevented by using materials which
1.3 Transpiring wall concept

The knowledge of the dual problem leads to the conclusion that, in a promising process, no wall in the whole setup should ever be in contact with waste water that has a temperature above a critical value given by the nature of the waste water (e.g. salt content). Therefore, any preheater which is used should not exceed the temperature limit either. This implies that the reactor must be able to deal with an inlet temperature of the waste water stream lower than the critical value.

![Diagram of transpiring wall concept]

**Figure 1.3:** Transpiring wall concept: the transpiring water entering the reactor through the wall and is supposed to form a layer of cold water that protects the wall from the hot and corrosive bulk flow.

The most promising solution of the dual problem within the su-
1. Introduction

A supercritical reactor lies in the prevention of the salt deposition by fluid dynamic means. Three different concepts have been applied to the SCWO process: film cooling, transpiration cooling, and the MODAR type salt settling chamber [Barner et al., 1992, Fig. 1.4]. Film cooling is realized by introducing a cold flow at the wall parallel to the feed. The concept of transpiration cooling is based on a porous wall through which a protective cooling fluid enters the reactor. This transpiring fluid is supposed to form an inert layer on the wall. In the MODAR reactor the salt containing waste water flows down the center of the rather large vessel and the precipitated salt particles are meant to fall into a brine at the bottom of the reactor. The other products flow back up along the walls and leave at the outer top. The challenge of the wall-contact-free heating up of the educt stream to reaction temperature has only been overcome with great losses up to now. Ahluwahlia (1996) and Crooker et al. (2000) use pure hot supercritical water as transpiring fluid and as additional auxiliary flow entering the reactor. It is obvious that the amount needed of this auxiliary pure supercritical water stream is huge. Other publications of research groups working with a transpiring wall reactor include Abeln et al. (2001) and Haroldsen et al. (1996).

![Figure 1.4: Schematic of the MODAR reactor.](image)

In a former research project at the process engineering lab of ETH, a SCWO pilot plant was built. The design was based on a continuous hydrothermal flame (Fig. 1.5) in a film cooled radial and coaxial burner [La Roche, 1996; La Roche et al., 1997; Weber and Trepp, 1996; Weber, 1997; Weber et al., 1999]. Important experience was gained. A spontaneous start of the reaction can be achieved in the reactor. The flame burned steadily even when the feed inlet temperature is lowered below 100°C. The same experiments were run with fuel that contained salts. Therefore, the required low inlet temperatures were reached satisfac-
Figure 1.5: Hydrothermal flame using a coaxial burner at an operating pressure of 250 bar.

Recently, a similar reactor type has been investigated by Sato et al. (2001). Yet, in contrast to the ETH reactor, they only succeeded in having a short steady flame (up to 11 s), whereas the flame in the ETH reactor burns steadily (duration of the experiment is not limited).
1.4 Concept of the investigated reactor

The considerations mentioned up to now have led to the development of new concept of a reactor at ETH (Fig. 1.6). It is built in a project parallel to the present one [Wellig et al., 2002; Wellig, 2003] and tries to account for the following points to allow a continuous operation: The inlet temperature of the waste water stream should be below 90°C, as above this temperature Cl⁻-ions lead to corrosion [Weber, 1997]. Hence, also no wall should be in contact with the hot waste water above 90°C. The flow direction is from top to bottom to limit natural convection effects emerging from the density difference between the cold outlet and the hot reaction zone. The temperature in the reaction zone is aimed to be kept at a value high enough ($\gtrsim 600^\circ$C) for complete conversion given the residence time through the mass flow and the reactor geometry.

![Concept of reactor at ETH.

The waste water is injected directly into the hot environment that is provided by the exhaust gases of a hydrothermal flame. The hydrothermal flame is run by a pure water and organic (methanol) mixture that
acts as fuel, and pure oxygen. Additional oxygen may be provided by a separate inlet to allow to run the flame at optimal conditions for stability. The reactive mixture flows down a tube that is protected by an inert fluid layer coming through the tube itself (transpiring wall concept from above). A large amount of cold water is injected near the bottom of the tube to cool down the mixture below a temperature at which it does no more harm to the wall and to the pressure relief valve.
Chapter 2

Modeling

Computational fluid dynamics (CFD) and process simulation are important tools for the design and optimization of chemical processes. Process simulation is already a well-established tool in process industry, being used to study individual unit operations, whole processes, or even entire plants. The latest generation of process simulation tools is extremely flexible, being able to represent a very wide range of multicomponent, multiphase and reactive systems. It can also deal with both steady-state and dynamic models. However, most of the models used by process simulation tools either ignore all spatial variations of properties within each unit operation, e.g. invoking the ”perfectly mixed” assumption in the continuously stirred tank reactor CSTR, or are limited to simple idealized geometries, e.g. a plug flow reactor PFR. Moreover, even in models that represent mass and heat transfer phenomena to a high degree of detail, the treatment of fluid mechanics is usually quite rudimentary. As a result, process simulation may offer only an incomplete and unsatisfactory description of processes in which local interactions between mixing and other phenomena, and the way in which these interactions are influenced by equipment geometry, are significant.

CFD is a particularly powerful tool for the study of fluid dynamics and mixing processes within individual items of process equipment. The aim is often to avoid expensive experimentation and to use the information and the gained insight to obtain a better design of the unit. The ability of CFD to handle complex equipment geometry and non-constant properties is especially important in this context. CFD simulation has already made valuable contributions to a wide range of process applications. Nonetheless, despite many recent improvements, CFD’s ability
to describe the physics involved in several application areas and to solve the underlying numerical problems is still limited. Such areas include, among others, the important classes of complex reactive systems and multiphase processes with multicomponent phase equilibria. Moreover, CFD is currently primarily used for steady state simulations. Performing realistic dynamic simulations is often problematic due to excessive computational times and difficulties with the description of some of the discontinuities that typically occur in dynamic processes.

### 2.1 Computational Fluid Dynamics

The equations of fluid dynamics can be solved numerically with the aid of computers. The set of techniques and procedures to achieve this has led to the development of what is known as computational fluid dynamics (CFD). Although it is not possible to leave out real experiments, numerical experiments using CFD allow the determination of certain trends and give an insight into the physics of complex problems that would be impractical to study experimentally, i.e. confined to high experimental costs or even impossible to measure. The subject has now advanced to the point where commercial packages are available and can be used to simulate or predict complex fluid dynamics problems. The technique is very powerful and spans a wide range of industrial and nonindustrial application area.

### 2.2 Basic equations

The main problem of fluid dynamics is the determination of the velocity components and state of the fluid (comprising temperature, pressure and species concentration) subject to certain imposed conditions. In addition to the fluid dynamics problem, consideration is given to the case when several species are present and chemical reactions occur. The underlying equations that allow the solution of the most general problem of a multicomponent, reacting, fluid mixture with depending properties are the following:
Conservation of Mass (Continuity)

\[ \frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_j} (\rho u_j) = 0 \]  \hspace{1cm} (2.1)

where

- \( t \) = time
- \( x_j \) = \( j^{th} \) coordinate direction
- \( u_j \) = fluid velocity component in the \( j \)-direction
- \( \rho \) = fluid density

Conservation of Momentum (Navier-Stokes)

\[ \frac{\partial}{\partial t} (\rho u_i) + \frac{\partial}{\partial x_j} (\rho u_i u_j) = - \frac{\partial p}{\partial x_i} + \frac{\partial \tau_{ij}}{\partial x_j} + F_i \]  \hspace{1cm} (2.2)

where

- \( i = 1, 2, 3 \)
- \( p \) = pressure
- \( \tau_{ij} \) = stress tensor
- \( F_i \) = surface or body force, e.g. = \( \rho g_i \)
- \( g_i \) = acceleration due to gravity

Conservation of Energy

\[ \frac{\partial (\rho h_{tot})}{\partial t} + \frac{\partial (\rho u_j h_{tot})}{\partial x_j} = \frac{\partial}{\partial x_j} \left( \lambda \frac{\partial T}{\partial x_j} \right) + \frac{\partial p}{\partial t} + \frac{\partial (u_j \tau_{ij})}{\partial x_j} + S_h \]  \hspace{1cm} (2.3)

where \( h_0 \) is the total enthalpy defined as:

\[ h_{tot} = \sum_{i=1}^{N_{sp}} w_i h_i + \frac{1}{2} (u_1^2 + u_2^2 + u_3^2) \]  \hspace{1cm} (2.4)
with

\[ h_i = \Delta h_{f,i}^0 + \int_{T_0}^{T} c_{P,i}(T) dT \] (2.5)

where

- \( h_{f,i}^0 \) = standard formation enthalpy of species \( i \)
- \( N_{sp} \) = total number of species
- \( T_0 \) = standard state temperature
- \( c_{P,i} \) = specific heat of species \( i \)
- \( \lambda \) = thermal conductivity
- \( p \) = static pressure
- \( \tau_{ij} \) = viscous stress tensor

### Conservation of Species

\[
\frac{\partial (\rho w_i)}{\partial t} + \frac{\partial (\rho u_j w_i)}{\partial x_j} = \frac{\partial}{\partial x_j} \left( D \frac{\partial w_i}{\partial x_j} \right) + S_{w_i}
\] (2.6)

where

- \( i = 1 \ldots N_{sp} - 1 \)
- \( w_i \) = mass fraction of species \( i \)
- \( D \) = diffusivity
- \( S_{w_i} \) = source term of species \( i \), e.g. due to reaction

Equations (2.1)-(2.6) constitute a set of \( N_{sp} + 4 \) equations with \( N_{sp} + 5 \) unknowns, which may be taken to be the \( N_{sp} \) weight fractions \( w_i \), the pressure \( p \), the total enthalpy \( h_{tot} \) and the three velocity components \( u_i \). The density, \( \rho \), and the specific heat, \( c_P \), are found using some kind of equation of state (see chapter 3). The knowledge that the sum over all mass fraction must always equal unity closes the set of equations:

\[
\sum_{i=1}^{N_{sp}} w_i = 1
\] (2.7)

It should be noted that the above equations are written for a cartesian coordinate system. Simplification of the above equations is possible for certain particular cases.
2.3 Turbulence

A complete transient solution of the exact Navier-Stokes equations for turbulent flows in complex geometries at high Reynolds numbers is unlikely to be obtainable in the near future. Two popular methods are employed to transform the Navier-Stokes equations in such a way that the small scale turbulent fluctuations do not have to be calculated: Reynolds averaging and filtering. Both of these transformations lead to a closure problem, i.e., there are less equations than unknowns. In order to close the set of equations additional model equations, e.g., turbulence models, need to be applied to be able to get a solution to the posed problem.

The Reynolds-averaged Navier-Stokes (RANS) equations represent transport equations for the mean flow quantities only, with all the scales of the turbulence being modeled. The approach of permitting a solution for the mean flow variables greatly reduces the computational effort.

In a large-eddy simulation (LES) the large eddies are computed in an always time-dependent (transient) simulation that uses a set of spatially filtered equations. Filtering transforms the exact time-dependent Navier-Stokes equations to remove the eddies that are smaller than the size of the mesh. Mean flow properties are extracted from the LES by statistically analyzing the transient simulation results. The attraction of LES is that, by modeling a smaller part of the turbulent kinetic energy spectrum (and solving more), the error induced by the turbulence model will be reduced. Also, the small scales at least are supposed to be isotropic and therefore easier to model. Moreover, there still remain unresolved conceptual problems with LES like energy transfer from small to large scales, matching important quantities across the spatial filtering interface, etc.

The Reynolds-averaged approach is generally used for practical engineering calculations, especially combined with the $k-\epsilon$ turbulence model and its variants.
2.3 Turbulence

2.3.1 Reynolds Averaging

In Reynolds averaging, the solution variables in the instantaneous Navier-Stokes equations are decomposed into the mean (ensemble-averaged or time-averaged) and fluctuating components. For the velocity components:

\[ u_i = \bar{u}_i + u_i' \]  

(2.8)

where \( u, \bar{u}_i \) and \( u_i' \) are the instantaneous, the mean and the fluctuating velocity components \( (i = 1, 2, 3) \).

Likewise, for pressure and other scalar quantities:

\[ \phi_i = \bar{\phi}_i + \phi_i' \]  

(2.9)

where \( \phi \) denotes a scalar such as pressure, energy, or species concentration.

2.3.2 Favre Averaging

In Favre or density weighted averaging, the solution variables in the instantaneous Navier-Stokes equations are decomposed into the density weighted mean and fluctuating components. For the velocity components:

\[ u_i = \tilde{u}_i + u_i'' = \frac{\rho u_i}{\hat{\rho}} + u_i'' \]  

(2.10)

where \( \tilde{u}_i \) and \( u_i'' \) are the weighted mean and instantaneous velocity components \( (i = 1, 2, 3) \).

Likewise, for pressure and other scalar quantities:

\[ \phi = \tilde{\phi} + \phi'' = \frac{\rho \phi}{\hat{\rho}} + \phi'' \]  

(2.11)

where \( \phi \) denotes a scalar such as pressure, energy, or species concentration.

Substituting expressions of this form for the flow variables into the instantaneous continuity and momentum equations and taking a time (or
ensemble) average (and dropping the tilde on the weighted mean velocity, $\tilde{u}_i$) yields the ensemble-averaged momentum equations. They can be written as (shown for Favre averaging):

\[
\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_j}(\rho u_j) = 0 \tag{2.12}
\]

where $u_j$ represents the density weighted mean fluid velocity component in the $j$-direction.

\[
\frac{\partial (\rho u_i)}{\partial t} + \frac{\partial (\rho u_i u_j)}{\partial x_j} = -\frac{\partial p}{\partial x_i} + \frac{\partial}{\partial x_j} \left[ \mu \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \delta_{ij} \frac{\partial u_l}{\partial x_l} \right) \right] + \frac{\partial}{\partial x_j} \left( -\rho \tilde{u}_i \tilde{u}_j \right) + F_i \tag{2.13}
\]

where

\[-\rho \tilde{u}_i \tilde{u}_j = "Reynolds stresses"
\]

\[\delta_{ij} = \text{Kroenecker Delta-Function:}
\]

\[\begin{align*}
0, & \quad \text{if } i \neq j \\
1, & \quad \text{if } i = j
\end{align*}\]

Equations 2.12 and 2.13 are called Reynolds averaged Navier-Stokes (RANS) equations (sometimes the momentum equations alone are called Navier-Stokes equations). They have the same general form as the Navier-Stokes equations (Eq. 2.1 and 2.2), but with the velocities and other solution variables now representing averaged values. For variable density flows, it is more appropriate to interpret Equations 2.12 and 2.13 as Favre averaged Navier-Stokes equations, with the velocities representing density weighted averaged values. As such, they can be applied to density-varying flows [Libby and Williams, 1993]. Favre averaging contains the effects of a fluctuating density, but it does not eliminate the appearance of extra variables in the basic conservation equations, i.e., the so called closure problem. The additional terms in the momentum equations represent the effects of turbulence. These are called Reynolds stresses and must be modeled in order to close the set of equations (2.12 and 2.13).
2.3.3 Closure

The Reynolds and Favre approach to turbulence modeling requires that the Reynolds stresses in Equation 2.13 be appropriately modeled. A common method employs the Boussinesq hypothesis to relate the Reynolds stresses to the mean velocity gradients:

\[-\rho \overline{u'_i u'_j} = \mu_t \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) - \frac{2}{3} \left( \rho k + \mu \frac{\partial u_i}{\partial x_i} \right) \delta_{ij} \]  

(2.14)

where \( \mu_t \) is the so-called turbulent viscosity. In the case of the \( k - \epsilon \) models, two additional transport equations (for the turbulent kinetic energy, \( k \), and the turbulence dissipation rate, \( \epsilon \)) are solved, and \( \mu_t \) is computed as:

\[ \mu_t = C_\mu \rho \frac{k^2}{\epsilon} \]  

(2.15)

with \( C_\mu = 0.09 \). The disadvantage of the Boussinesq hypothesis as presented is that it assumes \( \mu_t \) is an isotropic scalar quantity, which is not strictly true. The Boussinesq assumption leads to effective properties of the form:

\[ \mu_{\text{eff}} = \mu + \mu_t \]  

(2.16)

\[ \lambda_{\text{eff}} = \lambda + \lambda_t \ , \quad \lambda_t = \frac{\mu_t c_p}{Pr_t} \]  

(2.17)

\[ D_{\text{eff}} = D + D_t \ , \quad D_t = \frac{\mu_t}{Sc_t} \]  

(2.18)

where \( Pr_t \) and \( Sc_t \) are the turbulent Prandtl and Schmidt number respectively.

For wall bounded flows turbulence models require the application of damping functions which ensure that the turbulent quantities vanish at the wall. There are two approaches to damping function: universal wall functions that were determined for high Reynolds-number flows; and low Reynolds-number turbulence models allowing for viscous effects with which the equations can be integrated all the way into the viscous sublayer of the wall. Wall functions transfer the wall boundary conditions to the near wall grid points located in the fully turbulent flow. The
advantage of this approach is its low computational costs, i.e. required memory size and computational time. Yet most of the wall transfer functions have been derived from simple, steady (for example channel-type) flows. Low Reynolds-number turbulence models require many grid points in the near-wall layer so as to resolve the steep gradients that prevail there. So that despite of the success of the wall function approach, there are many flow situations where its use may be unsuitable, e.g. flows with large pressure gradients at the wall, flows with mass transfer at the wall, and flows with large property variations in the near wall region.

2.3.4 Turbulence-Chemistry Interaction

A chemical reaction can only occur when the educts of the reaction are mixed on a molecular level. Therefore, the reaction progress is influenced by the mixing time and by the reaction rate. The fluid inside a grid cell is not perfectly mixed. The level of turbulence-chemistry interaction depends on the time scales involved, namely, the turbulent time scale and the chemical reaction time scale. When the chemical reaction time scale is very large (compared with the turbulent time scale), then the reactants will mix relatively quickly while the reaction proceeds relatively slowly, and the reaction rate can be approximated by the kinetic reaction rate calculated using mean values. When the chemical reaction time scale is very small (compared with the turbulent time scale), the controlling mechanism is the mixing of the reactants, and the reactions can be assumed to reach equilibrium instantaneously. There have been several attempts to obtain a turbulence-controlled reaction rate under these circumstances, notably eddy-break-up models and models based on probability density functions. Unfortunately, in many engineering applications the situation is between these two extremes, which makes the modelling even more complicated.

Eddy Break-up model

In the eddy break-up model, the reaction rates are calculated from an Arrhenius expression and from a eddy dissipation model. The limiting
(slowest) rate is used as the reaction rate, and the contribution to the source terms in the species conservation equations are calculated from this reaction rate. In turbulent flows, this mixing time is dominated by the eddy properties, and therefore, the rate is proportional to a mixing time that is a function of the turbulent kinetic energy $k$ and its dissipation $\epsilon$.

2.4 Determination of the Residence Time Distribution

There are at least two ways of retrieving the residence time distribution (RTD) from a flow by use of CFD simulations, transient simulation and a stochastic streamline tracking (random walk) method. Running a transient simulation requires substantial computational time. Streamline tracking on the other hand only makes use of a single converged steady state solution of the flow problem. The integration times of the streamlines, weighted by the mass flow that they represent, give a picture of the RTD. If the flow field is turbulent, the turbulent mixing must be accounted for. This can be done by stochastic analysis. From the 2 investigated models [Shuen et al., 1983; Baxter and Smith, 1993], finally the one from Shuen et al. (1983) was chosen due to its simplicity and comparable accuracy. A good review of this topic is given by MacInnes and Bracco (1992).

2.4.1 Effect of mixing on the mean residence time

If only regular streamlines are used for the calculation of the RTD, then the calculation neglects the effects of turbulent mixing. Yet turbulent mixing is important as shown in the following example. Consider a vessel with 2 inlets and 1 outlet. For non-constant density the overall mean residence time is given as:

$$
\tau = \frac{\sum_{i=1}^{N_{\text{inlets}}} M_i}{\sum_{i=1}^{N_{\text{inlets}}} J_{m,i}}
$$

(2.19)
where $M_i$ is the mass of fluid in the reactor that entered the reactor through inlet $i$. The mean residence time for inlet flow $i$ ($J_{m,i}$) is given as:

$$\tau_i = \frac{M_i}{J_{m,i}} \quad (2.20)$$

First, let us consider the case of total segregation in the vessel where the velocities of the two fluids stay segregated throughout the vessel (Fig. 2.1).

![Figure 2.1: Total segregation of two flows for their entire passage through the vessel.](image)

In this case, equation 2.20 is easily applied to each fluid. If one of the $M_i$ gets larger (and therefore the other one gets smaller) then its mean residence time gets smaller and the one from the other inlet gets longer.

In the perfectly mixed case (Fig. 2.2), the effective velocity of the faster fluid will be lowered and the effective velocity of the slower fluid will be accelerated. Both fluids have the same mean residence time.

![Figure 2.2: The two inlet flows mix immediately in the vessel.](image)

In this case the mean residence time can be estimated by equation 2.19. In all, mixing has an equalizing effect on the mean residence times of the various inlets.
2.4 Determination of the RTD

2.4.2 Stochastic particle tracking

The model was taken from Shuen et al. (1983). Several streamlines are integrated using the converged steady state flow field. In the laminar case there are no velocity fluctuations and the streamlines can be calculated by:

\[ dx_i = \overline{u_i} \, dt \]  \hspace{1cm} (2.21)

where \( \overline{u_i} \) represent the mean velocity in \( i \)-direction. (In laminar flows there are actually no fluctuation, so that \( \overline{u_i} = u \). The use of \( \overline{u_i} \) is done to better compare Eq. 2.21 with later equations.) The data needed for the integration is taken from a fully converged CFD simulation with a \( k-\epsilon \) turbulence model (the procedure may also be used with other turbulence models). The integration times of the streamlines are then weighted according to the mass flow they represent. For turbulent streamlines the turbulence must be considered too. The velocity in the RANS equations divided into a mean and a fluctuating part (Eq. 2.10), i.e. in the turbulent case streamlines can be calculated by:

\[ dx_i = (\overline{u_i} + u_i') \, dt \]  \hspace{1cm} (2.22)

In the \( k-\epsilon \) model the fluctuating part is taken into account by solving a transport equation for the turbulent kinetic energy \( k \) which is defined as:

\[ k = \frac{1}{2} \left( \overline{u_1'^2} + \overline{u_2'^2} + \overline{u_3'^2} \right) \]  \hspace{1cm} (2.23)

where \( \overline{u_i'^2} \) are the time averages of the square of the fluctuating velocities in 3 coordinate directions. Inherent in the \( k-\epsilon \) model lies the assumption that the turbulence is isotropic meaning that the fluctuation velocities in all directions are of the same magnitude. Therefore one can write

\[ \overline{u_i'^2} = \frac{2}{3} k \]  \hspace{1cm} (2.24)

In order to retrieve the fluctuation part of the velocity from the kinetic energy, a distribution has to be assumed. This distribution is taken to be Gaussian. Then the probability \( p(u_i') \) of \( u_i' \) is

\[ p(u_i') = \frac{1}{\sqrt{2\pi\sigma^2}} \exp \left( -\frac{u_i'^2}{2\sigma^2} \right) \]  \hspace{1cm} (2.25)
where
\[ \sigma = \sqrt{\frac{2}{3} k} \]  
(2.26)

The value of the standard deviation \( \sigma \) results from a comparison of the integral of all stochastic fluctuation velocities squared weighted with their probability and the normalized integral of the fluctuation velocities over time (Eq. 2.24).

\[
\overline{u_i'^2} = \int_{-\infty}^{\infty} u_i'^2 p(u_i') \, du_i' = \frac{2}{3} k
\]  
(2.27)

The fluctuation velocity is kept constant during an average eddy lifetime defined by equation 2.28. Then new fluctuation velocities and a new eddy life time is determined from the local turbulence values.

\[
\tau_{relax} = C_D \frac{k}{\epsilon}
\]  
(2.28)

Several values for the constant \( C_D \) are found in literature:

\[
C_D = \sqrt{\frac{3}{2} C_\mu^{3/4}} \approx 0.134 \quad \text{[Shuen et al., 1983]} \quad (2.29)
\]

where \( C_\mu \) is a constant (\( = 0.09 \)) appearing in the \( k - \epsilon \) turbulence model, or

\[
C_D \approx 0.30 \quad \text{[Fluent, 2001]} \quad (2.30)
\]

### 2.5 Solving the set of equations

The equations mentioned above are transformed into a set of algebraic equations that are usually be solved iteratively. The procedure of committing a CFD simulation, consists of the following:

1. **Formulate the flow problem:** The first step of the analysis process is to formulate the flow problem by checking the answers to the following questions:
2.5 Solving the set of equations

- what is the objective of the analysis?
- what geometry should be included?
- what dimensionality of the spatial model is required? (2D, 2D axisymmetric, 3D)
- is steady state modeling appropriate?
- what is the nature of the flow? (laminar, turbulent)
- how should the fluid properties be modeled?
- which terms of the general N-S equations may be neglected?

2. Grid generation: Approximations of the geometry and simplifications may be required to allow an analysis with reasonable effort. At this point, decisions are made as to the extent of the finite flow domain in which the flow is to be simulated. Portions of the boundary of the flow domain coincide with the surfaces of solid objects, e.g. reactor wall. Other surfaces are free boundaries over which flow enters or leaves. The flow domain is discretized into a grid. The grid should exhibit some minimal grid quality as defined by measures of orthogonality (especially at the boundaries), relative grid spacing (15% to 20% stretching is considered a maximum value), grid skewness, etc... Further the grid spacing should be consistent with the desired resolution of important features (possible use of adaptive gridding).

3. Establishing the boundary and initial conditions: Since a finite flow domain is specified, physical conditions are required on the boundaries of the flow domain (temperature, composition, velocities). The simulation generally starts from an initial solution and uses an iterative method to reach a final flow field solution.

4. Perform the simulation: The simulation is performed with various options, e.g., under-relaxation, and solver type. As the simulation proceeds, the solution is monitored to determine if a "converged" solution has been obtained.

5. Post-process the simulation to get the results: Post-processing involves extracting the desired flow properties from the computed
flow field. The computed flow properties are to be compared to results from analytic, computational, or experimental studies to establish the validity of the computed results.

6. *Repeat the process to examine sensitivities:* The sensitivity of the computed results should be examined to understand the possible differences in the accuracy of results and/or performance of the computation with respect to such things as: dimensionality (2D/3D), boundary conditions, grid density, turbulence model.

### 2.5.1 Convergence problems

Under-relaxation factors can help to stabilize the solution and hence aid convergence by controlling the degree to which solutions are permitted to change from one iteration to the next. A common way to apply under-relaxation is linear under-relaxation:

\[
\theta_{i+1, \text{relax.}} = \lambda \theta_{i+1, \text{no relax.}} + (1 - \lambda) \theta_i
\]  

(2.31)

where \(\theta_i\) is the value of a variable at iteration \(i\) and \(\lambda\) is the amount of under-relaxation (\(\lambda = 1 \rightarrow \) no under-relaxation). The used software package CFD-ACE+ provides applies 2 kinds of under-relaxation. One is the just mentioned linear under-relaxation, and the other is the so-called false time-step (or inertial) relaxation [CFDRC, 2002].

Natural convection problems are known to be a challenge for convergence. No general rule have been set up till now on how to choose under-relaxation factors. Table 2.1 lists two sets of under-relations factor as they were mostly used in the simulations. Using these factors stable convergence was observed. Convergence was judged by the 3 following criterions:

**Residuals** Residual values for each variable must fall by several magnitudes through the course of the run. For all results presented here at least four orders of magnitude reduction in the residuals are observed.
2.5 Solving the set of equations

<table>
<thead>
<tr>
<th>variable</th>
<th>type of relaxation</th>
<th>parameters resulting in ( \text{fast convergence} )</th>
<th>parameters resulting in ( \text{stable convergence} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>velocities</td>
<td>false time-step</td>
<td>0.5</td>
<td>2</td>
</tr>
<tr>
<td>pressure correction</td>
<td>false time-step</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>enthalpy</td>
<td>false time-step</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>turbulence</td>
<td>false time-step</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>species</td>
<td>false time-step</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>pressure</td>
<td>linear</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>density</td>
<td>linear</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>viscosity</td>
<td>linear</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>temperature</td>
<td>linear</td>
<td>0.1</td>
<td>0.01</td>
</tr>
</tbody>
</table>

*Table 2.1: Listing of the usually used under-relaxation factors for the simulations.*

**Variables** The values of all variables throughout the domain must not change if additional iterations are performed.

**Conservation of scalars** The imbalance term from the balances of mass, energy and species over any subdomain need to be negligibly small.

### 2.5.2 ”Bugs” in the specific CFD code

In general, the used software (CFD-ACE+ 6.4) performed reliably and proofed to be user friendly. Yet some inconsistencies between the manual and the code were found. The elaboration of these inconsistencies has been quite time consuming. 4 points shall be reported here in order that consecutive worker do not have to spend time to discover them again: turbulent transport properties, model in porous media for transport properties, wrongly specified units for the source term, and species transport in the energy equation.
Transport properties

When the Reynolds averaged Navier-Stokes equations are solved, effective viscosity, the thermal conductivity, and the diffusivity values are applied (Eq. 2.16). The *user defined subroutine* feature and the *porous media module* of the used software in the used versions have some inconsistencies with these variables. It is advised that one checks whether molecular or effective properties are received, set, and depicted (in CFD-VIEW).

Porous media module

A porous media module has been implemented in Version 6.6. The module takes care of adoptions of the transport properties in porous media. Due to the changes that have been done by CFDRC after my reporting of the transport property inconsistency, this module has been wrongly implemented. The transport properties in it do account for turbulence effects which they should not as it is already included in the effective transport coefficients (see chapter 3.4). The only work-around to this problem is to not use the porous media module.

Units of source term

The software allows to set a source term for energy and species by a user subroutine. It has to be checked carefully which units are to be used when setting such sources. Experience showed that is best not to use any source term for species mass fraction for its implementation is doubtful.

Species Transport in the Energy Equation

If the Lewis number,

\[ Le_i = \frac{\lambda}{\rho c P D_{i,m}} = \frac{Sc}{Pr} \]

(2.32)
for any species is far from unity, the transport of enthalpy due to species diffusion should not be neglected:

\[
\nabla \cdot \left[ \sum_{i} h_i \bar{J}_i \right]
\]

(2.33)

Otherwise, the term can lead to significant errors in the enthalpy field [Fluent, 2001]. Since the molecular Lewis number of water is different from unity near the critical region, it was checked if the term is incorporated in the software. Test simulations showed that this is not the case for it reproduces physically impossible temperature fields if the flow is laminar. For a turbulent flow, turbulence dominates the transport of scalar. There, \( Le \) usually equals unity since the same value is given the turbulent Schmidt and Prandtl number (Eq. 2.32).

### 2.6 Error estimation of grid based calculations

In common English the words *verify, validate, and confirm* all have the same meaning. When used as technical terms it is important that such quality determining terms are exactly defined. The following definitions date back to Boehm (1981) and Blottner (1990) and have been set as a standard by Roache (1998) that is widely accepted in the field of quality assurance (QA) in CFD.

**Calibration:** The process of adjusting numerical or physical modeling parameters in the computational model for the purpose of improving agreement with experimental data.

**Verification:** The process of determining that a model implementation accurately represents the developer’s conceptual description of the model and the solution of the model.

**Validation:** The process of determining the degree to which a model is an accurate representation of the real world from the perspective of the intended uses of the model.
For a trustful CFD simulation several steps of quality assurance are needed: The used model needs to be shown that it represents the nature of the problem, the code needs to be shown that it solves the model correctly, and the single simulation needs to be shown that it is a close approximation to the exact solution of the model. Table 2.2 gives a overview of these needs.

<table>
<thead>
<tr>
<th>term</th>
<th>goal</th>
<th>responsibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Verified simulation</td>
<td>Solution has negligible iterative and grid based uncertainty</td>
<td>code user</td>
</tr>
<tr>
<td>Verified solver</td>
<td>Solver calculates correct solutions of analytical and benchmark problems</td>
<td>code developer</td>
</tr>
<tr>
<td>Validated model</td>
<td>Model represents physics</td>
<td>model developer</td>
</tr>
</tbody>
</table>

Table 2.2: Needs for a verified simulation.

The emphasis in the following discussion is put on the verification of single calculations, and on the validation of the combination of models used.

2.6.1 Verification of Calculations

Before the uncertainty can be calculated, the objective value of the problem needs to be known, e.g. figure 2.3 shows the approximated solution of the function \( f(x) \). If the behavior of the function at large values of \( x \) is of interest even the most coarse integration step \( (dx = 1) \) gives a reasonable approximation.

On the other hand if the value of the roots \( (f(x) = 0) \) is of interest (cf. Fig. 2.4) only the finest integration step yields an acceptable result.
2.6 Error estimation of grid based calculations

Figure 2.3: Example function $f(x)$ approximated by Euler integration using various integration steps $dx$.

Figure 2.4: Example function $f(x) = x(x-1.5)(x-2.2)(x-3.3)(x-4)$ approximated by Euler integration using various integration steps $dx$.

Richardson extrapolation

This procedure is based on the assumption that the code itself has already been verified for the same class of problems, and that code errors
are not an issue. The discrete solutions $f(x)$ are assumed to have a series grid representation of the grid spacing $h$:

$$f(x) = f_{\text{exact}} + g_1 h + g_2 h^2 + g_3 h^3 + \ldots$$  \hspace{1cm} (2.34)

where $f_{\text{exact}}$ is the exact solution, and $g_i$ are continuous functions that do not depend on any discretization.

The exact solution can be extrapolated ($h \to 0$) using 2 solutions from differently coarse grids (assuming an at least second order method ($g_1 = 0$)).

$$f_{\text{exact}} = f_{\text{fine}} + \frac{f_{\text{fine}} - f_{\text{coarse}}}{r^p - 1}$$  \hspace{1cm} (2.35)

where $f_{\text{fine}}$ and $f_{\text{coarse}}$ are the solutions from the fine and coarse grid respectively, $r = h_{\text{fine}}/h_{\text{coarse}}$, and $p$ is the order of the integration method [Richardson, 1910, 1927].

The Richardson extrapolation is applied to the approximation of $\pi$ [Richardson, 1927; Roache, 1997], to demonstrate its power. $\pi$ is defined by:

$$\pi = \frac{\text{circumference}}{\text{diameter}} \text{ of a circle}$$  \hspace{1cm} (2.36)
2.6 Error estimation of grid based calculations

The circle is approximated by regular inscribed polygons, with 4 and 6 sides (Fig. 2.6). Eq. (2.36) yields for these 2 grids $\pi_4 = 2\sqrt{2}$ and $\pi_6 = 3$. Now $\pi_\infty$ can be approximated by Eq. (2.35) as 3.1373, whose relative deviation to the exact $\pi$ is less than 2\%.

**Grid convergence index (GCI)**

The idea behind the grid convergence index (GCI) is to decouple the estimated relative error from 2 different grids from the refinement ratio $r$ and the order $p$ of the integration method (spatial or temporal). Doing this, a uniform measure of the grid convergence of a problem is received.

\[
GCI_{\text{fine}} = F_s \frac{\left| f_{\text{fine}} - f_{\text{coarse}} \right|}{f_{\text{fine}} r^p - 1} \tag{2.37}
\]

and

\[
GCI_{\text{coarse}} = F_s r^p \frac{\left| f_{\text{fine}} - f_{\text{coarse}} \right|}{r^p - 1} \tag{2.38}
\]

where $F_s = 3$ is a safety factor [Roache, 1998].
Figure 2.7: Grid convergence index of the example problem vs. integration step.

2.6.2 Validation of Physical Models

The prime recommended guideline for the validation of a model is to compare it with measurements, whose experimental uncertainties are known and their levels are acceptable [Mehta, 1996]. Thereby, the goal is to identify and quantify the uncertainty of the simulation. The required accuracy of the validation depends on the application. Most important in the validation process is that the trends are predicted by the numerical tools since most design changes are incremental over a baseline [AIAA, 1998].
Chapter 3

Properties

The advantage and the disadvantage of a supercritical fluid reaction media lies in its thermochemical and phase-change-related properties. By adjusting the temperature and the pressure the properties can be selected. Close to the critical (resp. pseudo-critical) point the properties vary strongly with temperature. Since the temperatures in this range are already considerably high and the dependency on it is large, good control of the temperature field is needed. In the considered reactor concept the temperature range is from room temperature (cooling water) up to $\approx 1500^\circ\text{C}$ (in the flame). The reactor concept discussed in chapter 1.4 gives the possibility to control the temperature field in the reactor by selecting specific operating conditions. One of the goals of the present work is to help select these operating conditions by checking their influences on the temperature and flow field. It is done by calculating the flow in the reactor by means of computational fluid dynamics. For the CFD description of the flow there are basically 5 different fluid properties needed:

- density $\rho$
- enthalpy $h$ or isobaric heat capacity $c_P$
- thermal conductivity $\lambda$
- dynamic viscosity $\mu$
- diffusion coefficient $D_{ij}$ of species $i$ in species $j$

The search and evaluation of properties and their descriptions is therefore concentrated to these properties.
3.1 Physical properties of pure Water

Since water is used in many industries, e.g. steam power industry, great effort has been undertaken to exactly measure and model its properties. An international non-profit association (IAPWS) of national organizations has been founded whose only concern is with the thermophysical properties of water and steam. Accurate formulations are developed and tested by IAPWS. The current proposed formulation is the *IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam* also known as IAPWS-IF97 or steam tables [Wagner and Kruse, 1998]. The properties of pure water are all based on this formulation except for the self-diffusion coefficient that is not part of the formulation.

![Figure 3.1: Density $\rho$ of pure water vs. temperature $t$ at various pressures.](image)

**Figure 3.1:** Density $\rho$ of pure water vs. temperature $t$ at various pressures.
3.1 Physical properties of pure Water

3.1.1 Density

Figure 3.1 shows a plot of the density of water versus the temperature at various pressures. At a pressure of 1 bar water evaporates at 100°C. Thereby, the density drops in a discontinuous fashion from the high liquid density (960 kg/m$^3$) to the low steam density (0.59 kg/m$^3$). With increasing pressure the evaporation occurs at higher temperature and the change in density gets smaller since the liquid density varies stronger with temperature than the density of steam. At the critical pressure ($t_c = 374^\circ$C, $p_c = 221$ bar) or above, there is no more evaporation but the transition from liquid like densities to gas like densities is continuous. Near the critical resp. pseudo-critical point there is still a sharp gradient in the density. As long as temperature is not in the near-critical region the density of the supercritical fluid behaves much like an ideal gas (e.g. $t > 600^\circ$C at 250 bar). This behavior is not only valid for the density but also for most other properties.

3.1.2 Enthalpy

Figure 3.2: Enthalpy $h$ of pure water vs. temperature $t$ at various pressures.
The enthalpy shows a similar behavior as the density (Fig. 3.2). At 1 bar the evaporation at 100°C causes a discontinuity in the enthalpy (heat of evaporation). At higher pressures the discontinuity is at a higher temperature and smaller. At and above the critical pressure there is a smooth transition from the liquid state to the gaseous state. Again, there is still a sharp gradient near the critical point at which the gradient reaches infinity. At pressures much higher than the critical one the transition from liquid to gaseous becomes less and less distinct.

3.1.3 Heat Capacity

![Graph of heat capacity vs. temperature at various pressures.](image)

**Figure 3.3:** The heat capacity $c_P$ of pure water vs. temperature $t$ at various pressures.

The heat capacity is the partial derivative of the enthalpy with respect to temperature at constant pressure (Fig. 3.3). At the critical pressure and below it has an infinite value at the evaporation point. Above but still near the critical pressure the heat capacity features a distinct peak. The temperature corresponding to this peak is defined as the pseudo-critical
temperature $t_{pc}$. For very high temperatures the heat capacity goes for all pressures towards the heat capacity of the ideal gas [taken from Reid et al., 1987].

### 3.1.4 Thermal conductivity

![The thermal conductivity $\lambda$ of pure water vs. temperature $t$ at various pressures.](image)

**Figure 3.4:** The thermal conductivity $\lambda$ of pure water vs. temperature $t$ at various pressures.

The thermal conductivity features a characteristic maximum at the critical point (Fig. 3.4). At the pseudo-critical points this maximum is much less distinct even for pressures close to the critical pressure. The thermal conductivity is about an order of magnitude smaller in the gaseous and supercritical region than in the liquid region. A smaller thermal conductivity hinders the molecular heat transfer across the fluid.
3.1.5 Viscosity

The kinematic viscosity $\eta$ (Fig. 3.5) is high in the liquid phase but low in the gaseous phase and in the supercritical phase (Note the log-scale on the left axis of figure 3.5). A low viscosity means that the mixing is fast (high momentum transfer rate) since the viscosity act as a resistance to the mixing.

**Figure 3.5:** The kinematic viscosity $\eta$ of pure water vs. temperature $t$ at various pressures.

3.1.6 Diffusion coefficient


$$D \rho = 1 \cdot 10^{-4} \left( A + B \rho_{mol} \ln \rho_{mol} + C \rho_{mol} + E \rho_{mol}^{0.3613} \right)$$  \hspace{1cm} (3.1)
3.1 Physical properties of pure Water

with:

\[ \rho_{\text{mol}} = 1 \cdot 10^{-6} \rho / M \]  
(\text{unit conversion kg/m}^3 \text{ to mol/cm}^3)

\[ A = 7.59322 \cdot 10^{-7} T^{0.45456} \]
\[ B = 1.42704 \cdot 10^{-3} + 0.223153/T - 0.24277 \cdot 10^{-5} T \]
\[ C = 0.85568 \cdot 10^{-2} + 0.859735/T - 0.12813 \cdot 10^{-4} T \]
\[ E = -0.018153 + 0.029224 \cdot 10^{-3} T - 0.0083486 \cdot 10^{-6} T^2 \]

A comparison between the self-diffusion coefficient calculated by this correlation and the dynamic viscosity calculated by Wagner and Kruse (1998) is depicted in figure 3.6. For gases at ordinary conditions, the Schmidt number, i.e., the ratio between the kinematic viscosity and the self diffusivity, is usually around 0.7 – 1. The Schmidt number of water in the supercritical state is also in this range.

Figure 3.6: The dynamic viscosity \( \mu \) and the self-diffusion coefficient of pure water vs. temperature \( t \) at various pressures.
3.2 Physical properties of mixtures

For the numerical flow description (CFD) it is important that the property models used are as accurate as possible yet not computationally costly. The choice of the models is of great importance. Since correlations are only valid in a defined range the knowledge of this range is stringent. In the present case the temperature range extents from room temperature (where water is in liquid state) to high temperatures in the flame (where water is a gas). In order to receive properties of mixtures there are 2 main approaches: calculating the mixture properties by weighting the pure properties according to there mass or molar fraction or weighting of the parameters entering the correlations. It is worth noting that in the second approach all single species properties must be described by the same correlation. In the first approach different correlations for the single species properties can be used.

3.2.1 Density

The density $\rho$ and the enthalpy $h$ resp. heat capacity $c_P$ are calculated by an equation of state (EoS). An EoS can be a simple function fit to experimental data (also $\rho = 1000 \text{ kg/m}^3$ is an EoS) or a complex function based on physical models, e.g. model of attraction and repulsion forces. A review on EoS is given by Sandler et al. (1994). Several classes of EoS exist that are suitable for special purposes:

So called exact EoS are usually large polynomial functions fit to a large amount of experimental data, e.g. the equation of Wagner and Kruse (1998) discussed above for the pure water properties. Due to their size the evaluation is costly. They are valid only for the species for which they have been developed.

Model based EoS can be divided into subgroups: cubic EoS and non-cubic EoS. The non-cubic EoS are EoS that feature more complicated dependency of the pressure from the molar volume than a cubic polynomial. They are based on chemical theories, quasichemical theories, perturbation theories, and alike [Economou and Donohue, 1996; Muller and Gubbins, 2001]. Equations of this kind have become popular to
model nonpolar monoatomic fluids, polar associating fluids, chain-like macromolecules and electrolyte solutions. Examples of such EoS are the perturbed-hard-chain-theory (PHCT) [Beret and Prausnitz, 1975; Donohue and Vimalchand, 1988], associated-perturbed-anisotropic-chain-theory (APACT) [Ikonomou and Donohue, 1986; Economou and Donohue, 1992], Panayiotou-Sanchez-Lacombe [Sanchez and Lacombe, 1977; Panayiotou and Sanchez, 1991], the statistical-associating-fluid-theory (SAFT) [Huang and Radosz, 1990, 1991; Chapman et al., 1989, 1990], and many others. A crossover (CR) modification can be implemented into a EoS to make sure that the universal scaling laws hold which apply near the critical point [Kiselev, 1997; Kiselev and Rainwater, 1998; Kiselev and Friend, 1999; Kiselev et al., 2001]. This modification if applied to a cubic EoS makes the EoS non-cubic in nature especially near the critical point [Kiselev, 1998]. The near-critical region where the asymptotic scaling laws are valid is said to be quite small [Tang and Sengers, 1991].

For the reactive calculations in the present work a cubic EoS is selected mainly because of their wide ability for many substances, the fast evaluation and the comparable accuracy in density prediction if not use in a total predictive way. Sometimes more complex forms, e.g. the modified Carnahan-Starling EoS, do not even present any advantage for the calculation of volumetric data [Zabaloy and Vera, 1998].

**Cubic equations of state**

The cubic EoS of van der Waals (1873) was the first to give a qualitative description of both phases. It consists of an attraction term and a repulsion term:

\[
P = \frac{RT}{(v - b)} - \frac{a}{v^2}
\]  

(3.2)

The parameter \( b \) in the repulsion term represents the excluded volume, i.e. the volume that is occupied by other molecules. The attraction term models the attractive forces in liquids. For the temperature going towards
infinity, cubic EoS go asymptotically towards the ideal gas law. The parameters in a cubic EoS can either be fit to real density or enthalpy data or they can be set to fulfill two important necessary conditions at the critical point, i.e.:

\[
\left(\frac{\partial P}{\partial v}\right)_{T=T_c} = 0 \tag{3.3}
\]

\[
\left(\frac{\partial^2 P}{\partial v^2}\right)_{T=T_c} = 0 \tag{3.4}
\]

The second approach is preferred if the EoS is to be valid over a wide range and not just within the region where the experimental data has been collected.

**Modification of the attraction term**

There have been many corrections to the attraction term. The form of Redlich and Kwong (1949) was the first to reproduce the vapor-liquid equilibria well for which EoS are used often [Ghosh, 1999]. This is especially true when using the temperature dependency of the attraction term introduced by Soave (1972).

\[
P = \frac{RT}{(v-b)} - \frac{a_c \alpha}{v(v+b)} \tag{3.5}
\]

where \(\alpha\) is a function of the acentric factor \(\omega\) introduced by Pitzer et al. (1955):

\[
\alpha = \left[1 + (0.48 + 1.57 \omega - 0.176 \omega^2)(1 - \sqrt{T_r})\right]^2 \tag{3.6}
\]

The acentric factor \(\omega\) and the reduced temperature \(T_r\) are defined as:

\[
\omega = -\log \frac{P(T_r = 0.7)}{P_c} - 1.0 \quad \text{and} \quad T_r = \frac{T}{T_c} \tag{3.7}
\]
3.2 Physical properties of mixtures

$a_c$ and $b_c$ result from the above mentioned condition at the critical point (Eq. 3.3 and 3.4). For the Soave-Redlich-Kwong (SRK) they are:

\[
a_c = 0.42748 \frac{R^2 T_c^2}{P_c} \quad (3.8)
\]

\[
b_c = 0.077796 \frac{R T_c}{P_c} \quad (3.9)
\]

Peng and Robinson (1976) came up with a different basic form of the attraction term. The accuracy for vapor-liquid equilibrium calculations of this form is similar to the one of the SRK EoS, but is better for the calculation of liquid densities. Since the liquid density is an issue in the present investigation the Peng-Robinson form has been used.

\[
P = \frac{R T}{(v - b)} - \frac{a_c \alpha}{v(v + b) + b(v - b)} \quad (3.10)
\]

with

\[
a_c = 0.45724 \frac{R^2 T_c^2}{P_c} \quad (3.11)
\]

\[
b_c = 0.077796 \frac{R T_c}{P_c} \quad (3.12)
\]

\[
\alpha = \left[ 1 + \left( 0.37464 + 1.54226 \frac{\omega}{\kappa} - 0.26992 \omega^2 \right)(1 - \sqrt{Tr}) \right]^2 \quad (3.13)
\]

**Modification of the repulsion term**

The calculation of liquid densities remains to be the real test for an EoS. Allowing that the covolume $b$ in the repulsion term is temperature dependent improves this calculation [Xu and Sandler, 1987], but may lead to "unphysical" properties like negative $c_P$ values [Trebble and Bishnoi, 1986]. Volume translation ($VT$) is an other promising method of further improving the liquid densities calculation of cubic EoS. Several different forms have been presented: constant, Gaussian shape, and others. Volume correction were done by Peneloux et al. (1982) and Ji and
Lempe (1997) for the SRK EoS and Proust et al. (1993) and Mathias et al. (1989) for the PR EoS. A temperature dependent VT lead to negative $c_P$ values in the present work in case of water when the parameters appearing in the EoS were fit only to the density but not to density and enthalpy simultaneously. Using a constant volume translation on the other hand has been shown to be thermodynamically consistent [Peneloux et al., 1982], and in the present work it matched the data as good as more complicated forms.

Finally, a PR EoS was chosen with a constant VT. According to Poling et al. (2001) accuracy will probably be best for polar and associating substances with fitted, not generalized functions for $\alpha(T)$. Therefore, the parameters in the PRVT EoS were all fit to exact densities of the pure species at 250 bar. The exact densities were calculated according to the sources given in table 3.1.

<table>
<thead>
<tr>
<th>compound</th>
<th>exact EoS</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>steam tables</td>
<td>Wagner and Kruse (1998)</td>
</tr>
<tr>
<td>methanol</td>
<td>IUPAC / BWR</td>
<td>Reuck and Craven (1993)/</td>
</tr>
<tr>
<td>oxygen</td>
<td>BWR</td>
<td>Wilding and Rowley (1986), (1987)</td>
</tr>
</tbody>
</table>

**Table 3.1:** List of sources of the exact property values of density and enthalpy of the pure compounds. The method by Wilding and Rowley (1986), (1987) yields more accurate density predictions for methanol than the similar methods of Golobic and Gaspersic (1994) or Wu and Stiel (1985).
3.2 Physical properties of mixtures

Figure 3.7: Comparison of the densities of water, methanol, oxygen, and carbon dioxide at 250 bar vs. temperature calculated by the exact equations of state and by the chosen Peng-Robinson EoS with constant volume translation (PRVT). The parameters in the PRVT were fit to match the densities from the exact EoS. For methanol the fit has been done for the range 300-800°C, since there is no methanol at any location in the reactor where the temperature is below this range.
### 3.2.2 Enthalpy

According to Walas (1985) (p. 502) the residual enthalpy $h_{res}$ can be calculated from a pressure explicit equation of state $p = p(v, T)$ by

$$\Delta h_{res} = h_{id} - h = - \int_{\infty}^{v} \left[ T \left( \frac{\partial P}{\partial T} \right)_v + v \left( \frac{\partial P}{\partial v} \right)_T \right] dv$$

$$= RT - pv + \int_{\infty}^{v} \left[ P - T \left( \frac{\partial P}{\partial T} \right)_v \right] dv \quad (3.14)$$

where

- $P = \text{absolute pressure}$
- $h_{id} = \text{enthalpy of the ideal gas}$
- $h = \text{enthalpy of the real gas}$
- $v = \text{molar volume of the real gas}$
- $T = \text{absolute temperature}$

The used Peng-Robinson equation of state with constant volume translation is:

$$P = \frac{RT}{v + VT - b} - \frac{a}{(v + VT)^2 + 2b(v + VT) - b^2} \quad (3.15)$$

where $a = a_c \alpha$ and $b = b_c$ are determined by Eqn. 3.11 to 3.13. The residual enthalpy is calculated as:

$$h_{res} = - \frac{v(-a^2(v + VT - b) + RT(v^2 + 2v VT + VT^2 + 2b v + 2b VT - b^2))}{(v^2 + 2v VT + VT^2 + 2b v + 2b VT - b^2)(v + VT - b)}$$

$$+ RT - \frac{\sqrt{2} \text{artanh} \left( \frac{(v + VT + b)\sqrt{2}}{2b} \right) a (-a + 2T \frac{\partial a}{\partial T})}{2b} \quad (3.16)$$

There is a speciality with the artanh appearing in the above equation: it is only defined in the domain $D = [-1, 1]$ which can be seen by looking at its definition:

$$\text{artanh}(x) = \frac{1}{2} \ln \frac{1 + x}{1 - x} \quad (3.17)$$

For the calculation of the enthalpy (Eq. 3.16) the definition for artanh is used (Eq. 3.17), in which for values outside the domain of artanh the denominator is exchanged by its absolute value.
3.2 Physical properties of mixtures

Figure 3.8: Comparison of the enthalpies of water, methanol, oxygen, and carbon dioxide at 250 bar vs. temperature calculated by the exact equations of state and by the chosen Peng-Robinson EoS with constant volume translation (PRVT). The parameters in the PRVT were fit to match the densities from the exact EoS except for water where they have been refit. For methanol the fit has been done for the range 300-800°C, since there is no methanol at any location in the reactor where the temperature is below this range.
3.2.3 Viscosity

For the transport properties not as many equations have been proposed as regarding the other properties mentioned above. They are more difficult to model than state variables. Also measured data is rare. Chapman and Enskog have proposed the dense gas theory in 1961. Since then several modification appeared in literature. Out of these correlation the one by Chung et al. (1984), (1988) is said to be the most accurate one in a large range [Reid et al., 1987].

For water the parameters in this modified version of the Chapman Enskog theory have been refitted to experimental data.

\[ \eta = \eta_\kappa + \eta_p \]  
(3.18)

where

\[ \eta_\kappa = \eta_0 [G_2^{-1} + A_6 Y] \]  
(3.19)

\[ \eta_0 = 4.0785 \cdot 10^{-5} \frac{(MT)^{1/2}}{V_c^{2/3} \Omega^*} F_c \]  
(3.20)

\[ F_c = 1 - 0.275 \omega + 0.059035 \mu^4 + \kappa \]  
(3.21)

\[ \Omega^* = 1.16145 T^{*-0.14874} + 0.52487 / \exp(0.77320 T^*) \]  
\[ + 2.16178 / \exp(2.43787 T^*) - 6.435 \cdot 10^{-4} T^{*-0.14874} \]  
\[ \cdot \sin(18.0323 T^{*-0.76830} - 7.273771) \]  
(3.22)

\[ T^* = T_r / 1.2593 \]  
(3.23)

\[ G_2 = \frac{A_1 [1 - \exp(-A_4 Y)]]}{Y + A_2 G_1 \exp(A_5 Y) + A_3 G_1} \]  
\[ \frac{A_1 A_4 + A_2 + A_3}{A_1 A_4 + A_2 + A_3} \]  
(3.24)

\[ G_1 = \frac{1 - 0.5 Y}{(1 - Y)^3} \]  
(3.25)
3.2 Physical properties of mixtures

Figure 3.9: Viscosities of water, methanol, oxygen, and carbon dioxide at 250 bar vs. temperature calculated by the correlation by Chung et al. (1984). \( \kappa \) and \( \mu \) enter Eq. 3.21, 3.28, and 3.29. The parameters for water have been fit to the exact correlation by Wagner and Kruse (1998).

\[
Y = \frac{\rho V_c}{6}
\]  

(3.26)
\[ \eta_p = A_3 Y^2 G_2 \exp(A_8 + A_9/T^* + A_{10}/T^{*2}) \]
\[ \times \left[ \frac{36.344 \cdot 10^{-6} \sqrt{MT_c}}{V_c^{2/3}} \right] \]  
\hspace{1cm} (3.27)

\[ A_i = a_0(i) + a_1(i) \omega + a_2(i) \mu_r^4 + a_3(i) \kappa \quad i = 1, 10 \]  
\hspace{1cm} (3.28)

\[ \mu_r = \frac{131.3 \mu}{(V_c T_c)^{1/2}} \]  
\hspace{1cm} (3.29)

<table>
<thead>
<tr>
<th>( i )</th>
<th>( a_0(i) )</th>
<th>( a_1(i) )</th>
<th>( a_2(i) )</th>
<th>( a_3(i) )</th>
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<td>-0.72663</td>
</tr>
</tbody>
</table>

**Table 3.2:** Coefficients to calculate \( A_i \) (3.28). These coefficients were wrongly reproduced in some literature reviews.

In Fig. 3.9 a comparison is shown of the experimental viscosity data found with the fitted viscosity correlation. In the case of water the comparison is done with the numerically costly correlation proposed by Wagner and Kruse (1998).
3.2.4 Thermal conductivity

The thermal conductivity $\lambda$ is determined according to the same source as the viscosity [Chung et al., 1984, 1988]. Its equations are:

$$\lambda = \lambda_\kappa + \lambda_p$$  (3.30)

where

$$\lambda_\kappa = \lambda_0 [(1/H_2) + B_6 Y]$$  (3.31)

$$\lambda_0 = 7.452 (\eta_0/M) \Psi$$  (3.32)

$$\Psi = 1 + \alpha \frac{0.215 + 0.28288 \alpha - 1.061 \beta + 0.26665 Z}{0.6366 + \beta Z + 1.061 \alpha \beta}$$  (3.33)

$$\alpha = \frac{c_v}{R} - \frac{3}{2}, \beta = 0.7862 - 0.7109 \omega + 1.3168 \omega^2, Z = 2 + 10.5 T_r^2$$  (3.34)

$$H_2 = \frac{(B_1/Y) [1 - \exp(-B_4 Y)] + B_2 G_1 \exp(B_5 Y) + B_3 G_1}{B_1 B_4 + B_2 + B_3}$$  (3.35)

$$B_i = b_0(i) + b_1(i) \omega + b_2(i) \mu_\tau^4 + b_3(i) \kappa \quad i = 1, \ldots 7$$  (3.36)

<table>
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<th>$b_2(i)$</th>
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Table 3.3: Coefficients to calculate $B_i$ (Eq. 3.36). These coefficients were wrongly reproduced in some literature reviews.
Figure 3.10: Conductivities of water, methanol, oxygen, and carbon dioxide at 250 bar vs. temperature calculated by the correlation by Chung et al. (1984). $\kappa$ and $\mu$ enter Eq. 3.36 and 3.29 respectively. The parameters for water have been fit to the exact correlation by Wagner and Kruse (1998).
3.2.5 Diffusion coefficient

Diffusion in CFD is usually treated according to Fick’s law. The diffusion coefficient in the Fick’s law is calculated as the sum of the molecular and the turbulent diffusion coefficients. In the main part of the reactor the diffusion process is dominated by turbulence but at some locations molecular diffusion is the dominant factor. The diffusion coefficient that depends on diffusing compound and on the composition of the mixture is simplified. The mixture is taken as pure water since water is the main component. This is justified by the fact that molecular diffusion is not important in large parts of the reactor and a more complicated model would increase the computational cost disproportionally. Most correlations for the molecular diffusion coefficient found in literature are valid only for liquid or gas state and not for both. For all species but water a correlation valid for supercritical fluids has been taken [He, 1997]:

\[ D_{12} = \left[ 0.61614 + 3.0902 \exp\left( -0.87756 \sqrt{10^3 \frac{M_1 V_{c1}}{p_{c1}/10^5}} \right) \right] \cdot 10^{-10} (V_1^k - 23.0) \sqrt{T/(1000 M_2)} \]  

(3.37)

with

\[ k = \begin{cases} 
1 & \text{for } \rho_r \geq 1.2 \\
1 + \rho_r - 1.2 & \text{for } \rho_r < 1.2 
\end{cases} \]  

(3.38)

For water the self-diffusion coefficient discussed in chapter 3.1.6 has been used.

3.3 Reaction kinetics in supercritical fluids

In the present work only the oxidation reaction of methanol (Me or CH₃OH) is considered since all experiments were run with methanol. The overall reaction equation of the methanol oxidation is:

\[ CH_3OH + \frac{3}{2} O_2 \longrightarrow CO_2 + 2 H_2O \]  

(3.39)
For the reaction rate $-r$ the common Arrhenius Equation is used:

$$-r = c_{Me}^n c_{O_2}^m A \exp \left( \frac{-E_a}{RT} \right)$$  \hspace{1cm} (3.40)

where $c$ stands for concentrations, $A$ is the pre-exponential factor, $E_a$ is the activation energy, and $R = 8.3144 \text{ J/mol K}$ is the universal gas constant. At the considered operating conditions the temperature in the reactor is relatively high. It has been stated that if the educts mix then they react rather instantly [Weber, 1997], i.e. an exact kinetic is not needed but rather a good mixing model which is actually one of the main reasons why a CFD study is done on the reactor.

Reaction kinetic measurements are mostly done at temperatures around $400^\circ\text{C}$ where the rates have moderate values. Still, the differences in measured reaction kinetics found in the literature are quite large (Fig. 3.11). For methanol several kinetics are available (cf. table 3.4). When extrapolated to temperatures of interest ($700 – 1500^\circ\text{C}$) even larger deviations among different data are predicted. For the present study the overall reaction kinetic of Tester et al. (1993b) has been selected arbitrarily.

<table>
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<tr>
<th>reference</th>
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<th>$E_a / \text{J/mol}$</th>
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<td>Webley and Tester (1989)</td>
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<td>Tester et al. (1993b)</td>
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<td>Brock et al. (1996)</td>
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</tr>
<tr>
<td>Rice and Steeper (1998)</td>
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<td>85900</td>
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</table>

Table 3.4: List of references for the compared reaction kinetics of methanol with parameter entering Eq. 3.40, $n = 1$, $m = 0$. 
3.4 Properties in porous media

3.4.1 Heat transport

The heat transport is treated according to Fick’s law in the commercially available CFD solver that is used. The single adaptive parameter in this equation is the effective thermal conductivity \( \lambda_{\text{eff}} \). \( \lambda_{\text{eff}} \) in regular Reynolds or Favre averaged turbulent flow models is the sum of the molecular (“laminar”) and the turbulent thermal conductivity. Inside a porous media (= zone with stationary solid parts, that are smaller than the grid scale, and fluid in between) the heat transport is a combination of conduction through the solid and transport through the fluid. The superficial velocities in porous zone are normally small due to the large pressure drop. Since the effects influencing the transport are smaller than the grid size a model is needed. For \( \lambda_{\text{eff}} \) several correlations can be found in literature. They are functions of the porosity \( \epsilon = \text{void fraction} \), the thermal conductivity of the fluid \( \lambda_l \), and the thermal conductivity of the
solid $\lambda_s$:

Volume averaged:

\[ \lambda_{\text{eff}} = \epsilon \lambda_l + (1 - \epsilon) \lambda_s \] (3.41)

Gurau et al. (1998):

\[ \lambda_{\text{eff}} = -2 \lambda_s + \frac{1}{\epsilon/(2 \lambda_s + \lambda_l) + (1 - \epsilon)/(3 \lambda_s)} \] (3.42)

Krupiczka (1967):

\[ \lambda_{\text{eff}} = \lambda_l \kappa^{0.280 - 0.757 \log_{10}(\epsilon) + 0.057 \log_{10}(\kappa^{-1})} \] (3.43)

where

\[ \kappa = \frac{\lambda_s}{\lambda_l} \] (3.44)

Kunii and Smith (1960) (for $0.26 < \epsilon < 0.476$):

\[ \lambda_{\text{eff}} = \lambda_l \left( 1 - \sqrt{1 - \epsilon} + \frac{2\kappa \sqrt{1 - \epsilon}}{\kappa - B} \left[ \frac{(1 - \kappa^{-1}) B}{(1 - \kappa^{-1} B)^2} \ln(\kappa/B) - \frac{B + 1}{2} - \frac{\kappa (B - 1)}{\kappa - B} \right] \right) \] (3.45)

where

\[ B = 1.25 \left( \frac{1 - \epsilon}{\epsilon} \right)^{10/9} \] (3.46)

Woodside and Messmer (1961) for $\epsilon \to 1$:

\[ \lambda_{\text{eff}} = \lambda_l \frac{2 \epsilon + \kappa (3 - 2 \epsilon)}{3 - \epsilon + \kappa \epsilon} \] (3.47)

Zehner and Schlünder (1970):

\[ \lambda_{\text{eff}} = \lambda_l \left( \epsilon + \frac{3 \kappa (1 - \epsilon)}{3 \kappa \epsilon + 2} \right) \] (3.48)
Koch and Brady (1985):

\[ \lambda_{\text{eff}} = \lambda_l \left( 1 + 3 (1 - \epsilon) \frac{\kappa - 1}{\kappa + 2} \right) \]  

(3.49)

In the investigated problem the choice of the correlation results in quite different effective thermal conductivities inside the porous wall (Fig. 3.12). The void fraction \( \epsilon = 0.17 \) is taken from the producer of the sintered porous tube\(^1\) and the thermal conductivity of the solid \( \lambda_l = 9.285 + 0.015544 (t + 273.15) \) is taken from a producer of alloy 625\(^2\).

\[ \text{Figure 3.12: Effective thermal conductivity } \lambda_{\text{eff}} \text{ according to several different correlations.} \]

\(^1\)GKN Sinter Metals Filters GmbH, Radevormwald, Germany
\(^2\)Wiggin Alloys Limited, Hereford, England
3.4.2 Species transport

Figure 3.13: Variation of effective mass diffusivity $D_{\text{eff}}$ with respect to the void fraction $\epsilon$, for $D_s = 0$. The prediction of Neale and Nader (1973) and Ryan et al. (1980), along with the experimental results from Ryan et al. (1980), are shown [from Kaviany, 1995].

The correlation to adjust the diffusion coefficient to the porous environment is taken from Neale and Nader (1973). There are not many correlations for this adoption yet the presented one seems to match experimental results quite well (Fig. 3.13).

$$D_{\text{eff}} = D_l \frac{2\epsilon}{3 - \epsilon} \quad \text{for } D_s = 0$$  \hspace{1cm} (3.50)
Chapter 4

Inert Simulations

The investigation discussed in this chapter has been started before the reactor was in operation. The exact geometrical design of the inlet was not set at that time. Because of that, and to be more general, the investigation is based on a simplified geometry of the reactor and also on a simplified model described later on. The geometry has been taken as the one of a simple vertical tube, and the model is inert in the sense that all properties have been taken as the ones of pure water at 250 bar, no reactions are accounted for, and the heat of the flame is approximated by hot water. The discussion about the model is given in the outlook (chapter 7.3).

4.1 State of Art

Many aqueous industrial wastes contain salts or acids, or such may form during SCWO, e.g. when acids are neutralized by conversion into salts. Salt-containing water gets very corrosive when heated and salt particles themselves can be highly corrosive at elevated temperatures. Salts have a substantial solubility at subcritical temperatures but, above the pseudo-critical temperature, the solubility is very low (Fig. 1.2). At pressures of interest for SCWO (e.g. 250 bar), this leads to precipitation of salt particles from the supercritical mixture. Special design measures are needed to prevent corrosion, fouling, and plugging of SCWO reactors. One approach is to use a design for which only pure water is in contact with the reactor wall. Prevention of wall contact by salt is a subject
of investigation with a transpiring wall reactor (TWR) at Sandia Na-
tional Laboratory, Ca (USA) [Haroldsen et al., 1996; Rice et al., 1997],
at the Forschungszentrum Karlsruhe, Germany [Abeln and Kluth, 2002],
University of Valladolid, Spain [Cocero and Santos, 2002], at the Com-
missariat à l’Energie Atomique in France [Fauvela et al., 2002], and with
a transpiring wall reactor at the Swiss Federal Institute of Technology
Zurich (ETH). The following investigation focuses on the reactor at the
ETH. The aim of this study is to develop models which allow one to assess
the TWR concept and to determine optimal operating conditions. Two
models are discussed. One is a simple analytical representation which
uses lumped parameters such as heat and mass transfer coefficients. The
other model uses computational fluid dynamics (CFD) in an effort to
explore the details of the process. A simplified SCWO reactor system is
shown in figure 4.1. The porous inner tube of the ETH reactor has an
inner diameter of 22 mm and a length of up to 350 mm.

![Figure 4.1: Schematic of a tubular transpiring wall reactor. Bulk
inlet at the top, transpiring water through the porous wall, and outlet
at the bottom. The variable transpiration length $x$, which is reported
in later figures, is the length from beginning of transpiration down-
wards.](image)

The properties of pure water are used for the calculations. Density, en-
thalpy, viscosity, and thermal conductivity are obtained from the steam
tables [Wagner and Kruse, 1998, chapter 3].
Salt in the bulk phase will, at high temperatures (> 400°C), mainly be in particulate form (real waste water often contains salt that is in ionic or particulate form depending on composition and temperature). A comparison of measured particle diffusion values from the literature [Protopopov et al., 1994] (only a publication citing the reference and plotting the results has been found [Jiang et al., 1995]) with the self-diffusion coefficient of water from Liu and Macedo (1995) shows that the self-diffusion coefficient is considerably larger than the particle (0.01µm) diffusion coefficient. This is also intuitively reasonable because particles are large compared to molecules dissolved in the liquid phase and therefore ”diffuse” more slowly. Since the sizes of the salt particles in the flow are unknown and since some salt might be in dissolved form, the self-diffusion coefficient of pure water was used. This is a worst case assumption (or conservative assumption) because the resulting concentration at the wall would be smaller if the smaller particle diffusion coefficient were used.
4.2 Analytical model

For a turbulent boundary layer on a smooth flat plate, Kays and Crawford (1993) give a correlation for the Stanton numbers with and without transpiration. They assume a laminar incoming flow, constant properties (except density), and a constant free stream velocity \( u_\infty \) (velocity far away from the plate).

\[
St_m = St_{m, no tr} \left( \frac{\rho_{bulk}}{\rho_{tr}} \right)^{-0.4} \ln(1 + B) \frac{B}{B}
\]  
(4.1)

and

\[
St_{m, no tr} = \frac{0.0287 \, Re_x^{-0.2}}{0.169 \, Re_x^{-0.1} (13.2 \, Sc - 8.66) + 0.85}
\]  
(4.2)

with

\[
St_m = \frac{h_m}{u_\infty}
\]  
(4.3)

where \( h_m \) is the mass transfer coefficient, \( (\rho_{bulk}/\rho_{tr})^{-0.4} \) accounts for the density variation and \( \ln(1 + B)/B \) for the effects of transpiration. The properties are taken at bulk conditions. \( B \) is defined as:

\[
B = \frac{\text{intensity}}{St_m}
\]  
(4.4)

where the intensity is defined as the ratio of the transpiration mass flux and the bulk mass flux:

\[
\text{intensity} = \frac{J_{tr}}{J_{bulk}}
\]  
(4.5)

From the definitions of the mass transfer coefficient \( h_m \) and the Stanton number, it is possible to calculate the mass fraction of the transpired species at the wall \( w_{tr,wall} \):

\[
J_{tr} \, w_{tr,in} = J_{tr} \, w_{tr,wall} + h_m \, \rho \, (w_{tr,wall} - w_{tr,bulk}),
\]

or

\[
w_{tr,wall} = \frac{B \, w_{tr,in} + w_{tr,bulk}}{B + 1}
\]  
(4.6)
where $w_{tr}$ stands for the mass fraction of a species entering through the transpiring wall. From this simple model, the mass fraction and the temperature (derivation not shown) at the transpiring wall can be predicted.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.2.png}
\caption{Prediction from the analytical model. $J_{bulk} = 5.26\, \text{kg/(m}^2\text{s)},$ varying intensity, $t_{bulk} = 700^\circ\text{C}, t_{tr} = 400^\circ\text{C}.$}
\end{figure}

Even for intensities as small as 1%, good thermal and chemical (shielding from the bulk species) protection is predicted (Fig. 4.2) except at the immediate leading edge where the boundary layer is just about being built. Salt concentration at $x = 0.2\, \text{m},$ for instance, will be reduced by about an order of magnitude when intensity $= 1\%$. Kays and Crawford (1993) state a rule-of-thumb that, above this value, a so-called ”blow-off” of the boundary layer may occur. This leads to an enhanced turbulent mixing and therefore degradation of the protection. It is important to note that, for the dimensions of the ETH reactor, the transpiration mass flow rate and the reactor inlet mass flow rate are equal when the intensity is 1.6%. A value of 1% is therefore quite reasonable. The purpose of the transpiring water is to keep the wall cool and the salt particles away from the wall. If the temperature of the transpiring water is low enough,
it can also redissolve salt particles. Therefore, it is important to know the dependence of the protection behavior on the temperature $t_{tr}$ of the transpiration flow.

The analytical model predicts better chemical protection for high transpiration temperatures (Fig. 4.3). This results mainly from the property variation term in equation (4.1). As expected, the temperature at the wall depends greatly on the transpiration temperature. At temperatures below the pseudo-critical temperature the dependence is minor (cf. $w_{tr,wall}$ at 300°C and 100°C).

The trend of increasing protection with increasing bulk mass flux (Fig. 4.4) results from increases in the Reynolds number, which in turn decreases the Stanton number.

The dependence on the bulk temperature has also been investigated (Fig. 4.5). The influence on the chemical protection is minor. The resulting change of the wall temperature is close to the change in the bulk temperature at the leading edge, but is smaller at larger values of $x$. 

**Figure 4.3:** Prediction from the analytical model. $J_{bulk} = 5.26\, \text{kg}/(\text{m}^2\text{s})$, intensity = 0.2%, $t_{bulk} = 700°C$, varying $t_{tr}$. 

The analytical model predicts better chemical protection for high transpiration temperatures (Fig. 4.3). This results mainly from the property variation term in equation (4.1). As expected, the temperature at the wall depends greatly on the transpiration temperature. At temperatures below the pseudo-critical temperature the dependence is minor (cf. $w_{tr,wall}$ at 300°C and 100°C).

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**Figure 4.3:** Prediction from the analytical model. $J_{bulk} = 5.26\, \text{kg}/(\text{m}^2\text{s})$, intensity = 0.2%, $t_{bulk} = 700°C$, varying $t_{tr}$. 

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The trend of increasing protection with increasing bulk mass flux (Fig. 4.4) results from increases in the Reynolds number, which in turn decreases the Stanton number.
Figure 4.4: Prediction from the analytical model. Varying $J_{\text{bulk}}$, intensity $= 0.2\%$, $t_{\text{bulk}} = 700^\circ C$, $t_{\text{tr}} = 400^\circ C$.

Figure 4.5: Prediction from the analytical model. $J_{\text{bulk}} = 5.26 \text{ kg/(m}^2\text{s)}$, intensity $= 0.2\%$, varying $t_{\text{bulk}}$, $t_{\text{tr}} = 400^\circ C$. 
4.3 CFD Simulations

The entire reactor has been modeled using computational fluid dynamics. The transpiring wall is modeled as a second fluid zone with a large momentum resistance. In this zone, heat transfer results from a combination of conduction through the metal and convection. For the computations of this zone, the effective thermal conductivity is evaluated according to Koch and Brady (1985) and the diffusivity is corrected according to Neale and Nader (1973). Pressure drop was represented in accordance with data from the manufacturer of the sintered tube\textsuperscript{1}. The conditions at the wall (where the transpiring wall zone and the bulk zone meet) result from the interactions of the flow through the transpiring wall zone and in the bulk flow zone. The interface is not quite a surface of no slip but the velocities parallel to the wall are very small. The boundary conditions are listed in table 4.1.

<table>
<thead>
<tr>
<th>bulk inlet</th>
<th>wall of the reactor</th>
<th>transpiration inlet</th>
</tr>
</thead>
<tbody>
<tr>
<td>temperature fixed</td>
<td>conservation of energy flux, continuity of temperature</td>
<td>temperature fixed</td>
</tr>
<tr>
<td>flow rate fixed</td>
<td>conservation of mass flux, continuity of concentration, and shear stress</td>
<td>flow rate fixed</td>
</tr>
</tbody>
</table>

Table 4.1: Boundary conditions used in the simulations.

The calculations are performed using the CFD-ACE+ v6.4 flow solver software package\textsuperscript{2}. It solves the mass balance, the species balance, one momentum balance in each direction (Navier-Stokes equations), and the total enthalpy balance. The low Reynolds number $k$-$\epsilon$ model from Chien (1982) is used to model turbulence. The special feature of the low Reynolds number model lies in the boundary treatment. The integration of the governing equations is carried out all the way to the wall without invoking the use of wall functions. Wall functions, i.e. assumed dimensionless velocity profiles, are useful for high Reynolds number, constant

\textsuperscript{1}GKN Sinter Metals, MI, USA

\textsuperscript{2}developed by CFD Research Corporation, Huntsville, Alabama (USA)
property flows; but are not well suited to the low Reynolds number, variable property conditions of the present application. A 500 mm flow development section is located upstream of the 350 mm long main zone and a 100 mm long outlet zone is located downstream of it. An axisymmetric \((20 + 45 + 10) \times 30\) structured grid was used to resolve the main flow field in combination with a \(45 \times 15\) structured grid for the porous wall zone. The cells were clustered near the wall to capture the drastically changing physical properties and because the low Reynolds number turbulence model needs a fine grid near the wall with \(y^+ < 1\). Although these features make the computations more expensive as compared to the standard \(k-\epsilon\) turbulence model, a low Reynolds number model is the model of choice for flows in the supercritical regime [Youn and Mills, 1993; Zhou et al., 1994]. Grid independence is tested by a grid convergence study (chapter 2.6.1). This study has been based on the length of the recirculation zone of the base case simulation mentioned below. This length is a distinctive value for the flow field since it characterizes a mixed convection flow field. \(GCI_{fine} = 0.012\) and \(GCI_{coarse} = 0.089\) result correspondingly. The fluid is modeled as pure water at 250 bar with a Newtonian viscosity. The two inlet fluids (bulk and transpiring wall) are modeled as different components, transpiration water and bulk (inlet feed) water. This division, plus the solution of the transport equation for the two species, allows the fraction of the bulk component to be determined for any location in the reactor vessel. All simulations were done with a second order differencing scheme. Grid independence was tested by a grid convergence study [Roache, 1998]. The large dependency of the properties on temperature near the critical point poses a challenge to the numerical convergence. In order to validate the model, isothermal CFD simulations were undertaken in order to compare the predicted mass fraction of the transpiring species at the wall to the one predicted by the analytical correlation described above (Fig. 4.6).

A comparison between the analytical model and the CFD simulations shows that the concentration levels are about the same, but the variation with position is significantly different (Fig. 4.6). Particularly at large \(x\), this calls into question the fidelity of the boundary layer model for this particular flow geometry and turbulence intensity (the flow is only mildly turbulent). The observed decrease of protection close to the end of the
plate \((x = 0.34 \text{ m})\) is due to the abrupt change of the wall-normal velocity from a finite value to zero. This causes an enhanced mixing. For most of the reactor length, the CFD model predicts very good wall protection at an intensity level as defined in Eq. 4.5 of 1%.

### 4.4 Results from CFD simulations

A parametric analysis has been performed to elucidate effects of bulk and transpiration conditions on wall temperature and concentration. Bulk mass flux was varied from 2.63 to 15.78 kg/(m²s), bulk temperature from 600 to 800°C, transpiration temperature from 370 to 700°C,
4.4 Results from CFD simulations

and transpiration intensity from 0.5 to 2%.

4.4.1 Base case

As a base case, operating conditions were chosen to coincide with those expected in the ETH transpiring wall reactor. The operating conditions are given in the caption of figure 4.7. The bulk inlet mass flux corresponds at a temperature of 700°C to a velocity of 0.087 m/s. The transpiration and the bulk fluid mix rather quickly. This leads to continuous cooling of the bulk flow (Fig. 4.7, left). The temperature gradient is steep near the wall and flat near the axis. The temperature gradient is steep near the wall and flat near the axis. The stream function plot (Fig. 4.7, right) shows that two natural convection eddies form in the reactor between which there is a ”dead zone” of slowly flowing fluid. The upper eddy starts at approximately 2 diameters below the top edge of the transpiring wall. Because of the back-flowing fluid, the isotherms and the composition isolines (Fig. 4.7, middle) are bent upwards at the axis in the eddy. The second recirculation zone near the bottom of the transpiration zone is not of major importance for the behavior of the reactor.

A popular material for building SCWO reactors is alloy 625 because of its high strength at elevated temperatures and its ability to withstand corrosive attack. The porous wall of the ETH reactor is a sintered tube of this alloy. The maximum allowable working temperature for alloy 625 at a pressure of 250 bar, is 600°C. Sufficient cooling is achieved in the base case to maintain the wall temperature below this limit. In order to avoid corrosion, however, the concentration of ions at the wall is decisive. The limiting salt concentration to inhibit corrosion is not known. Yet the base case simulation predicts only a small dilution of the bulk mixture at the wall. Therefore, the protection from corrosion does not seem to be adequate. The base case simulation predicts a wall temperature above 400°C and a mass fraction of the transpiring species $w_{tr}$ of $\cong 0.4$. Therefore, considerable salt will be present and protection from adherence will not be assured.
Figure 4.7: Prediction from the CFD simulations (inlet and outlet zones not shown, porous wall gray). Left: temperature contours; middle: $w_{\text{bulk}}$ contours; right: stream function contours. 2 recirculation zones exist between which there is a "dead zone" of slowly flowing fluid. $J_{\text{bulk}} = 5.26\,\text{kg}/(\text{m}^2\text{s})$, intensity = 1%, $t_{\text{bulk}} = 700^\circ\text{C}$, $t_{\text{tr}} = 370^\circ\text{C}$.
4.4.2 Effects of the temperature of the transpiring water

The analytical model showed a rather modest effect of transpiration temperature (Fig. 4.3). But the analytical model is valid only for high Reynolds numbers and nearly constant properties. In addition, natural convection effects are neglected. The CFD simulation predicts a rather different behavior (Fig. 4.8).

![Figure 4.8](image)

**Figure 4.8:** Prediction from the CFD simulations. $J_{\text{bulk}} = 5.26 \text{ kg}/(\text{m}^2\text{s})$, intensity = 1%, $t_{\text{bulk}} = 700^\circ\text{C}$, varying $t_{\text{tr}}$.

As the transpiration temperature is decreased, the density difference relative to the bulk flow increases. Below $t_{\text{tr}} \approx 600^\circ\text{C}$ a natural convection eddy forms in the bulk flow. This eddy enhances the mixing and destroys the favorable protective boundary layer. A new boundary layer forms downstream of the natural convection eddy, but $w_{\text{tr,wall}}$ remains rather low. Also, the strongly varying properties and the finite radius seem to play a role since simulations neglecting gravity showed a similar
yet less distinct behavior (Fig. 4.9).

**Figure 4.9:** Prediction from the CFD simulations to check to influence of gravity. $J_{\text{bulk}} = 5.26 \text{ kg/(m}^2\text{s)}$, intensity = 1%, $t_{\text{bulk}} = 700^\circ\text{C}$, $t_{\text{tr}} = 370^\circ\text{C}$, gravity considered / ignored.

Protection against deposition can result either from keeping the bulk fluid away from the wall or by keeping the wall temperature at a low temperature at which salt is quite soluble (about $370^\circ\text{C}$). The temperature at the wall depends strongly on the transpiration temperature. Low transpiration temperatures cool the wall efficiently but, at the present intensity, a subcritical temperature at which salts are redissolved was not achieved. For all transpiration temperatures, the required cooling for material integrity is met. If good protection is needed, low transpiration temperatures must be chosen. But this will cause natural convection effects that destroy the favorable cool and inert boundary layer.
### 4.4.3 Effects of the bulk flow temperature

One option to increase conversion is to raise the bulk inlet temperature since the reaction rate increases exponentially with increasing temperature (assuming that the usual Arrhenius dependency applies). The mean residence time in the reactor is quite short (on the order of 2 s in the base case until the temperature is supercritical). To capture the influence of the bulk temperature on the flow field, simulations with lower and higher bulk temperatures were run (Fig. 4.10).

![Figure 4.10: Prediction from the CFD simulations.](image)

In order to achieve a considerable destruction during this short residence time, the lower bulk temperature limit is taken as 600°C. The upper limit is set by the unwanted production of NO$_x$ which occurs at temperatures above 1800 K [Fluent, 2001], although material integrity (e.g., if transpiration should be temporarily disrupted) is also a factor. Still, this upper limit might be set at an even higher value. With a higher bulk inlet temperature, the natural convection eddy starts further down...
In the reactor and it covers a smaller area both radially and axially. Apparently, radial mixing decreases with increasing bulk temperature. The bulk species mass fraction shows this effect of enhanced mixing at lower bulk temperatures (Fig. 4.10, bottom), but the effect is quite weak. The temperature at the wall correlates with the bulk temperature (Fig. 4.10, top). Heat transfer is responsible for this effect. The temperature difference, being the driving force of heat transfer, is about twice as high for $t_{\text{bulk}} = 800^\circ\text{C}$ as for $t_{\text{bulk}} = 600^\circ\text{C}$. For all conditions, the required cooling was achieved in the sense of material integrity ($t < 600^\circ\text{C}$) but not in the sense of salt re-dissolution ($t$ below 400$^\circ\text{C}$).

4.4.4 Effects of the total mass flows

The natural convection eddy seems to play a major role in destroying the favorable boundary layer. Optimum total mass flows (of bulk and transpiration) might therefore be expected at a Reynolds number for which the bulk flow is strong enough to hinder natural convection effects. To understand the influence of the total flow, simulations were run with the transpiration intensity fixed but with different total flow rates. The thermal and species mixing are greatest at small flow rates (Fig. 4.11, top). It is possible that an even higher flow rate would totally suppress the formation of a natural convection eddy. There is no natural convection eddy at the highest mass flow rates ($J_{\text{bulk}} = 15.78 \text{ kg/m}^2\text{s}$), but there is still a decrease of the axial downward velocity on the axis and an enhanced mixing compared to simulations that were run at the same conditions but with gravity turned off.

These results clearly show a positive influence of large mass flow rates. But sufficient protection was achieved in none of these simulations, i.e. salt particles would not get re-dissolved if they reached the wall and the concentration of bulk fluid at the wall is relatively high.

4.4.5 Effects of the transpiration intensity

To make sure that the chosen transpiration intensity is not above the critical value for "blow-off", the base case intensity was halved and dou-
The results from these runs show that increasing the intensity does increase the protection of the wall (Fig. 4.12). Therefore, despite the limit of 1% intensity for boundary layer “blow-off” given by Kays and Crawford (1993), a higher intensity may be advantageous.

### 4.4.6 Towards optimal conditions

If it is assumed that salt acts as a passive tracer with a diffusivity equal to that of water, then salt concentration can be inferred from the distribution of the bulk water, provided that all of the salt enters with bulk water (i.e. none is generated within the reactor). The maximum allowable concentration of salt in the feed stream can then be calculated from:

\[ w_{sol}(t) \geq w_{bulk}(\vec{r}) \cdot w_{salt,in} \]  

\[ (4.7) \]
where \( w_{sol} \) is the solubility of the salt considered that depends on the temperature \( t \), \( w_{bulk} \) is the mass fraction of the bulk mixture at a given location in the reactor (\( \vec{r} \) being the position vector) and \( w_{salt,in} \) is the weight fraction of the salt in the bulk inlet. Note that the maximum salt concentration occurs at the reactor inlet, and everywhere else it is less than this value owing to dilution of the bulk flow by transpiration water. Note also that \( w_{bulk} \) can be thought of as the dimensionless mass concentration relative to the inlet concentration. Sodium sulfate (Na\(_2\)SO\(_4\)) has been chosen as the model salt. Its solubility in hydrothermal media has been well studied. At 250 bar, its solubility is rather large for subcritical temperatures below 350°C, but then decreases very strongly with increasing temperature up to at least 400°C (Fig. 1.2). The correlation for calculating the maximum solubility on a weight fraction basis is taken from Rogak and Teshima (1999). They compared measurements from several publications and their own work to obtain the following
correlation:

\[
w_{\text{sol}}(t) = \begin{cases} 
-3.49612 \ln \left( \frac{t - 337.70602}{49.11281} \right) & 337.7 \leq t \leq 385.8^\circ C \\
10^{323.3458 - 0.605186 t} & 385.8 \leq t \leq 388.5^\circ C \\
32.19 (t - 385.645) \ln(1000 t^{1.2}) & 388.5 \leq t \leq 400.0^\circ C 
\end{cases}
\]

(4.8)

By rearranging equation (4.8), the maximum inlet mass fraction \(w_{\text{salt in, wall}}\) of salt to just avoid salt precipitation can be calculated. This gives a more meaningful measure of the success achieved by the TWR. From the parametric study above, one might propose the operating conditions given in the caption of figure 4.13.

**Figure 4.13:** Prediction from the CFD simulation with optimized operating conditions. \(J_{\text{bulk}} = 15.78 \text{ kg/(m}^2\text{s)}, \text{ intensity} = 2\%, t_{\text{bulk}} = 800^\circ C, t_{\text{tr}} = 350^\circ C.\)

Even with these operating conditions, the temperature at the wall is not
below the pseudo-critical (Fig. 4.13, top). However, the mass fraction of the transpiring species shows that the shielding is considerably better than at any of the previous operating condition (Fig. 4.13, middle). Even so, good protection is not predicted. The wall temperature and composition allow to calculate the salt inlet concentration that does not lead to precipitation; and does not reach values needed for good protection (Fig. 4.13, bottom).

### 4.5 Conclusions

A parametric study has been performed to elucidate the effects of the operating conditions on the chemical and thermal protection of a transpiring wall tubular SCWO reactor. An analytical model predicts good protection for modest transpiration intensities. A CFD model of the reactor capable of capturing spatial effect in some detail revealed the negative influence of natural convection and of strongly varying properties. Due to the large radial density differences, a natural convection eddy forms in the reactor at the selected operating condition. A variation in the operating conditions within a reasonable range did not reveal any case with sufficient protection. At transpiration temperatures needed to re-dissolve salt particles that may approach the wall, there is a natural convection eddy that largely destroys the favorable effect of the boundary layer. Large bulk mass flow rates diminish the natural convection effects but, due to the large property variations there is still an enhanced radial mixing. The results of this study suggest that the cold transpiring water (subcritical) is to be chosen for good protection. The natural convection effects can be reduced by designing the inlet geometry in a way that the impulse is stronger at the axis.
Chapter 5

Experimental

5.1 Plant setup

The design (Fig. 5.1) and the construction of the transpiring wall reactor and the whole pilot plant setup has been done in a parallel project [Wellig, 2003]. The whole system has been designed to withstand an operating pressure of 400 bar. The pressure in the reactor, that was 250 bar in all experiments, is controlled by a pneumatic control value. At all inlets of the TWR the temperature and the mass flow rate are measured. The inlet temperatures are controlled by an electrical heating system (except cooling water, waste water, and oxygen). All important measurement data are simultaneously transmitted to a computer. The plant features 4 different storage facilities (O₂ gas bottles, N₂ gas bottles, fuel mixture tank, waste water tank) plus access to the desalinated water piping system of the building to feed the reactor. The setup of the piping is such that the fuel and waste water inlets can be supplied with either water, waste water, or fuel mixture. At the liquid outlet samples can be withdrawn for analysis.

In order to ignite the flame the fuel mixture inlet was heated up to self-ignition temperature (around 400-500°C). Cool-down was achieved by flushing the reactor with a large amount of unheated water. Experiments have been run with and without the transpiring wall inserted in the reactor. More information about the setup and the experiments will be found in Wellig (2003).
Figure 5.1: Pilot plant with the TWR [Wellig, 2003].

5.2 Choice of validation measurements

A measurement procedure was to be chosen to validate the CFD calculations. The measurement would have to be feasible, reasonably accurate, and describe an important feature of the flow significantly. The first choice was the use of a hot wire anemometer to measure fluctuating flow quantities. Since the feasibility of an exact measurement was uncertain and the relevance of the measurement in the case of the investigated
flow was dubious other means of validation were searched and evaluated. These include the measurement of the chemical potential over the transpiring wall and the heat flux through the wall. Finally, the temperature field in the reactor and residence time distribution of the fuel inlet were chosen to be measured for reasons described below.

5.2 Choice of validation measurements

5.2.1 State of the art

The most preferable way to validate CFD calculations is to compare them with measurements, whose experimental uncertainties are known and their levels are acceptable [Mehta, 1996]. In the field of SCWO there are only few publications on performed CFD calculations [Oh et al., 1995, 1996a, b, 1997]. The validation in these works was confined on a temperature comparison near the wall of a reactor. The location of this temperature comparison was close to the wall at which a constant temperature had been set as a boundary condition for the CFD simulations. Therefore, it does not surprise much that a comparable temperature had been found. Others compared the final conversion of a tubular reactor with their calculated results [Zhou et al., 2000].

5.2.2 Hot wire anemometry

A first idea for the validation was the use of hot wire anemometry (HWA). HWA has been used for more than 50 years and is a widely accepted validation tool for flows of gases and liquids.

A HWA sensor measures fluid velocity by sensing the heat loss from an electrically heated wire (or thin film) that is immersed in the fluid flow. The sensor is kept at a constant temperature using an electronic control circuit that adjusts the electrical current across the wire.

\[ Q_{\text{loss}} = A h (T_{HW} - T_{\text{fluid}}) = I^2 R \]  

Assuming a constant temperature difference \((T_{HW} - T_{\text{fluid}})\), the heat transfer coefficient \(h\) alone governs the heat loss. It depends on fluid properties, sensor geometry, and velocity relative to the sensor.
Advantages

Advantages, besides the long experience, are the high spatial and temporal resolution. HWA is suitable for the measurement of flows with very fast fluctuations at a point (high turbulence) combined with a spatial resolution down to sub-millimeter level. Velocities from a few cm/s to well above the speed of sound can be measured [Bruun, 1995].

Drawbacks

![Calculated calibration plot: Expected output voltage of HWA sensor vs. velocity for different temperatures. The expected velocity is 0.125 m/s, the wire temperature (750°C) is given by DANTEC (max. allowed temperature for best resolution). For the heat transfer coefficient the correlation of Kramers was used [Bruun, 1995, p. 20].](image)

HWA is a well known technique to measure velocities and velocity fluctuations mainly in isothermal flows. A calibration of the sensor needs to be done before each run because of the complexity of the heat loss coefficient correlation and due to fouling reasons. In case of a non-isothermal flow this calibration runs need to be done for the whole temperature range (Fig. 5.2).
The capability to measure in a steam environment could not be conclusively stated by the 2 producers of the sensors, which have been approached (Dantec\textsuperscript{1} and TSI\textsuperscript{2}).

\textbf{Figure 5.3:} Sensitivity of the output signal. The temperature measurement must have a resolution indicated by the line in order to have theoretically a resolution of 1% of turbulence. The ETH reactor will have a Reynolds number around 10’000 (estimated in the hot reactive zone) so there will be about 10% of turbulence.

In the context of former Ph.D. projects on a first generation SCW reactor [Weber, 1997; La Roche, 1996] a movie has been recorded of an upward flowing hydrothermal flame. This movie shows that the flame may not be steadily burning but rather feature a largely changing geometric extent. With the downwards flowing flame as investigated by this work the unsteadiness will be smaller but may not be non-existing. Therefore, the constant temperature difference assumption needed for the operation of a HWA may not be given. A second temperature sensing sensor would have to be mounted close to the hot wire. Due to the large temperature gradient the spatial distance between the 2 sensors has to be chosen as small as possible. From experience of mounting ther-

\textsuperscript{1}Dantec Dynamics A/S, Skovlunde, Denmark
\textsuperscript{2}TSI Incorporated, Shoreview, MN (USA)
mocouples in the reactor the mounting could probably be done with a 1 mm uncertainty (reactor diameter is 22 mm). Now, knowing that the temperature difference at the measurement height will be in the order of 400°C an uncertainty in the temperature measurement of about 40°C can be estimated \((1 \text{ mm}/(22 \text{ mm}/2) \times 400°C)\).

A sensitivity analysis can be done by comparing the temperature derivative of the output signal to the velocity derivative of the output signal and an uncertainty in the turbulence intensity measurement can be estimated (Fig. 5.3). It can be concluded that a measurement may most probably yield inaccurate results in case of highly non-isothermal flow locations which are the ones of interest.

5.2.3 Chemical Potential

A review of electrodes for potential measurements in aqueous systems at elevated pressures is given by Niedrach (1987). All temperature mentioned therein are in the subcritical range where Teflon® can be used for sealing. Therefore, these approaches are not suited for application in the current investigation.

Chemical potential sensor

If a piece of metal is in contact with a fluid there is a potential difference between the fluid and the metal. This potential depends on the nature of the fluid and the metal. If the same kind of metal is also in contact with a different fluid a potential difference can be measured between the 2 pieces of metal. If the fluid is salt containing water then the potential is a strong function of the ion concentration. The measurement of the potential can be exploited as a concentration measurement. Based on this idea a possible sensor design has been drawn (Fig. 5.4).

The sensor would measure the potential difference between the sensor in contact with the fluid layer right next to the transpiring wall and the desalinated water behind the transpiring wall resp. the reactor wall.
5.2 Choice of validation measurements

Advantages

One main reason why the transpiring wall is used is the protection from the corrosive bulk fluid. The measurement of the chemical potential is actually a measurement of the driving force of the corrosion. Therefore, one measures exactly what the transpiring wall is to achieve. Changing the transpiration flux will change the chemical potential and a minimal potential could be stated below which the corrosion remains insignificant.

Drawbacks

The measurement of the chemical potential needs to have a minimum electrical resistance between the 2 contact points of about $10^9 \Omega$. Also the temperature at the 2 contact points has to be the same since the potential depends on the temperature. Due to these 2 reasons, using this concept as a validation has been rejected.

Figure 5.4: Schematic of the chemical potential sensor.
5.2.4 Heat flux

Heat flux sensor

In most flows the heat and mass transfer analogy is valid (Chilton-Colburn analogy). Using this analogy one can state that there is no mass transfer if there is no heat transfer. If we can measure the heat transfer through the porous wall we then have a qualitative measurement of the mass transfer. Increasing the transpiration flux will lead to a decreased heat transfer. At the point where the heat flux vanishes (flat temperature profile) there will also be no mass transfer to the wall.

Figure 5.5: Schematic of the heat flux principle.

Advantages

With the measurement of the heat flux to the transpiring wall one would not only have a measured quantity to compare but also, because of the analogy between heat and mass transport, a quantity closely related to the variable to be optimized. Provided that the heat flux to the wall is
zero, the turbulent heat transport to the wall is zero, and there is no mass transport to the wall. Hence, no particles will be transported to the wall. The experimental setup would include several high precision (differential) temperature measurements across the transpiring wall.

**Drawbacks**

The measurement setup will be difficult to implement into the existing reactor. The Chilton-Colburn analogy may not be valid for precipitated salt particles or transport in or near a porous zone. The results are hard to quantify, e.g., it is not clear how small the heat flux has to be chosen. Due to these uncertainties the heat flux concept has been rejected.

### 5.3 Temperature field

The temperature field in a reactor depends on mixing, convection, conduction, and reactions. The temperature itself is the largest influence in all fluid properties, that in turn influence the flow field. Therefore, a given temperature field corresponds to a specific flow field. Even in a high pressure, high temperature environment temperature measurements are feasible with commercially available components.

#### 5.3.1 Setup

Access for measurement equipment has been provided during the design of the reactor (Fig. 5.6). Additional thermocouples have been implemented to determine the radial temperature profiles at 3 different planes using 4 measurement points over the radius (Fig. 5.7). The transpiring wall (TW) has been segmented into 4 parts for 2 main reasons: a) segmentation allows that different temperatures and flow rates can be set over the length of the transpiring wall, and b) the sealing between the chamber behind the transpiring wall and the inside of the transpiring wall at the place where the thermocouples are lead through could only be accomplished with a non-porous tube element. Solid rings of alloy
625 were inserted between the transpiring wall elements. These rings also seal between the single chambers behind the transpiring wall elements. Standard implementation of the thermocouples\(^3\) into the reactor is done by bearing a hole into a high pressure plug of alloy 625. Then the thermocouple is pushed through this hole and the seal is provided

\(^3\)Thermocouples type K from Thermocontrol GmbH, Switzerland.

**Figure 5.6:** TWR designed by [Wellig, 2003] with inlet flows and planes at which the radial temperature profiles were measured. WW = waste water, ox = oxygen, TW = transpiring wall inlet, CW = cooling water inlet, \(x\) = length along transpiring wall.
by tightening the high pressure screw. Once the screw is tightened the distance between the sealing position and the tip of the thermocouple cannot be altered. Therefore, the measurement location is fixed. The first tightening (fixation) has been done outside of the reactor in a device that allows to set the measurement location precisely (±1 mm).

5.3.2 Results

Once the thermocouples had been implemented, the temperatures on the different measurement planes were always recorded together with further experimental data.

Special emphasis has been put on 2 operation parameters: the transpiration intensity intensity and the transpiration temperature t_tr. In order to investigate their importance on the temperature field in the reactor, experiments have been run with fixed operating conditions except for operating parameter of interest.

In figure 5.8 measured radial temperature profiles are shown for different transpiration intensities. For intensities of 1 and 2% the temperature on
Figure 5.8: Radial temperature profiles in the transpiring wall reactor for different transpiration intensities.

The upper measurement plane ($x = 95\, \text{mm}$) is supercritical and for 5% it is close to pseudo-critical. Near the wall the temperature is subcritical on all measurement planes. Note, that there is an influence of the intensity on the temperature behind the uppermost transpiring wall element. The
Table 5.1: Compilation of the operating conditions of the simulations concerning the transpiration intensity variation, $p = 250$ bar. Mass flow rates in g/s, temperatures in °C. The transpiration flows correspond to an intensity of $\approx 1$, 2, and 5%.

Table 5.2: Compilation of the operating conditions of the simulations concerning the transpiration temperature variation, $p = 250$ bar. Mass flow rates in g/s, temperatures in °C. The transpiration flows were heated up to 75, 125, 250°C. transpiration flow rates correspond to an intensity of $\approx 2\%$.

Heat conduction through the reactor wall and the heat flux that is in the opposite direction of the transpiration flow are large enough to heat up the incoming transpiring water from 40°C up to 200°C (for intensity...
Figure 5.9: Radial temperature profiles in the transpiring wall reactor for different transpiration temperatures.

= 1%). The temperatures behind the transpiring wall elements are actually not measured on the same measurement height as the profiles. They are measured in the small inlet chambers behind the transpiring wall elements. On the middle and the low measurement planes (x = 155
resp. 215 mm) the temperature profile is subcritical over the whole radius. From the shapes of these 2 profiles it can be concluded that there is a natural convection eddy between these 2 measurement planes. It transports cold fluid up in the middle of the tube and hot fluid down near the wall. This natural convection eddy may not disturb the plug flow behavior in the upper part of the reactor.

Figure 5.9 shows measured radial temperature profiles for different transpiration temperatures. On the upper measurement plane ($x = 95$ mm) the temperature is supercritical in the core of the tube and subcritical near the wall. The transpiration temperature variation has a small influence on the temperature profile. The whole profile is lowered with lower transpiration temperature. From this it can be concluded that the transpiring water does mix to some extent with the bulk flow but does not change the flow field with the preferred cold fluid layer near the transpiring wall - at least on the height of the measurement plane. On the middle measurement plane ($x = 155$ mm) the temperature is still supercritical (close to pseudo-critical) in the core of the tube and is subcritical at the wall. On the low measurement plane ($x = 215$ mm) the temperature is subcritical over the whole radius. In these runs there seems to be no natural convection eddy in the lower part of the reactor. This may be due to the different concentrations in waste water and fuel inlet streams compared to the series discussed above which may lead to a more homogeneous expansion due to the temperature rise caused by the reaction. Note again, the strong influence of the bulk flow on the temperature behind the transpiring wall elements.

5.4 Residence time distribution

Residence time distributions (RTD) provide a convenient means for characterizing the overall flow behavior of reaction vessels. RTDs can be described analytically in only a few idealized cases, e.g. the plug flow reactor (with/without dispersion), the continuously stirred reactor and combinations thereof.

Figure 5.10 shows RTDs for a few idealized reactor cases. The knowledge of the RTD alone does not allow for reliable calculation of the conver-
In SCW reactors featuring a transpiring wall, natural convection may prevail if the operating conditions are selected inadequately. A reliable RTD can be used to shed light on the contribution of natural convection to the reactor flow field, and thus may provide guidance on the selection of operating conditions that lead to a favorable temperature field in the reactor, i.e. a long hot zone at the axis and a cold fluid layer at the wall.
5.4 Residence time distribution

5.4.1 Setup

In order to get an exact residence time distribution of an inlet a measurement of the concentration of a passive scalar, e.g. salt concentration right before and after the reactor is needed. Little can be found on sensors that are suited for a passive scalar measurement at the investigated process conditions. Ding and Seyfried (1996) investigated the use of a gold sensor for the \textit{in situ} determination of dissolved H$_2$ in deionized supercritical water. Liu and Macdonald (1995) used a relative resistance sensor to do the same thing. It is not clear if valuable measurement results would be recovered when measuring in a mixture as is presented in the investigated reactor. Macdonald and Kriksunov (2001) have developed a sensor by which it is possible to measure pH or chemical potential in the supercritical water environment. From the figures in the publication it can be concluded that the response time of this sensor is in the order of minutes. Therefore, this kind of sensor is not suited for the measurement of the raw data for the RTD.

The measurement concept has been newly developed in the frame of this work (Fig. 5.11). Salt solution that is used as the tracer is pumped through a loop connected to a 6-port valve. Switching the position of the valve sets the loop inline between a HPLC pump pumping desalinated water and the reactor feed. Right after this connection point the salt concentration is measured by an electrical conductivity sensor. At the outlet of the reactor a second sensor is mounted. Special high temperature and high pressure sensor had to be developed, designed and built for that. The sensor should measure temperature and electrical conductivity simultaneously. To meet the challenges of the hot and corrosive environment highly inert materials are to be used.

5.4.2 Conductivity sensor

Electric conductivity is obviously the ability of a material to conduct electric current. Since the charge on ions in solution facilitates the conductance of electrical current, the conductivity of a solution is a function of its ion concentration (linear for low ion concentrations).
Figure 5.11: Simplified schematic of the experimental setup used to get the data needed to determine the residence time distribution. Operating pressure of the SCWO reactor: 250 bar, temperature at sensor 1: up to 520°C (during ignition of the hydrothermal flame).

Calculation of the design of the sensor

The principle by which instruments measure conductivity is simple: two electrodes are placed in the fluid sample, a potential \( (U) \) is applied across the electrodes (normally a sine wave voltage in order to avoid polarization effects), and the current \( (I) \) is measured. Conductivity \( (G) \), the inverse of resistivity \( (R) \), is determined from the voltage and current values according to Ohm’s law (integral form).

\[
G = \frac{1}{R} = \frac{I}{U}
\] (5.2)
The basic unit of conductivity is Siemens [S], also called mho (inverse of ohm). Since cell geometry affects conductivity values, standardized measurements are expressed in specific conductivity units [S/cm] to compensate for variations in electrode dimensions and geometry. The specific conductivity \( \sigma \) is the product of measured conductivity \( G \) and the electrode cell constant \( C_c \).

\[
\sigma = G C_c = \frac{C_c}{R}
\]  

The usual ways to determine its value is by calibrating the sensor with a standard conductivity solution. Only for some idealized sensor geometries the cell constant can be analytically derived. This is desirable for an estimation the cell constant prior to its fabrication.

The total current \( I \) flowing through any area \( A \) is:

\[
I = \int_A \vec{i} d\vec{A}
\]  

where \( \vec{i} \) the area specific local current. The differential form of Ohm’s law is:

\[
i = \sigma \vec{E}
\]  

where \( \vec{E} \) is the potential field. The potential difference or voltage \( U \) equals the integral over any streamline \( L \) of the potential field from its starting point to its end point.

\[
U = \oint_{L_{\text{end}}}^{L_{\text{start}}} \vec{E} d\vec{l}
\]  

If the conductivity \( \sigma \) of the fluid is constant in the domain then the cell constant \( C_c \) results as:

\[
C_c = R \sigma = \frac{U}{I} = \frac{\oint_{L_{\text{end}}}^{L_{\text{start}}} \vec{E} d\vec{l}}{\int_A \vec{E} d\vec{A}}
\]  

Provided that the potential function is known and the integrals in equation 5.7 are solvable the cell constant can be calculated.
Cell constant of 2 flat plates

Most conductivity sensors consist of 2 flat plates. Provided that the plates are parallel to each other with distance $L$ between them and each one has an area of $A$ and assuming $\sqrt{A} \gg L$ then the potential field $\vec{E}$ between the plates is constant:

$$\vec{E}(x, y) = E_0$$  \hspace{1cm} (5.8)

The cell constant $C_c$ results from equation (5.7) as:

$$C_c = \frac{\oint_{L_{end}}^{L_{start}} \vec{E} \, dl}{\int_A \vec{E} \, d\vec{A}} = \frac{E_0 L}{E_0 A} = \frac{L}{A}$$  \hspace{1cm} (5.9)

Cell constant of 2 parallel pins

The second case considered is the cell constant of 2 parallel equal sized pins ($D$ distance between their axes, $R$ radius of the pins, and $L$ length). The energy field $\vec{E}(x, y)$ of the 2 pins is given by (assuming $L \gg D > R$, origin in the middle of the 2 pins, $x$ pointing towards the axis of one of the pins, $y$ perpendicular to $x$ and to the axes of the pins):

$$\vec{E}(x, y) = \frac{I}{2\pi L\sigma} \left( \frac{1}{\sqrt{(x - D/2)^2 + y^2}} + \frac{1}{\sqrt{(x + D/2)^2 + y^2}} \right)$$  \hspace{1cm} (5.10)

Integrating over the streamline at $y = 0$ gives the voltage $U$ between the pins

$$U = 2 \int_0^{D/2 - R} \vec{E}(x, y = 0) \, dx = \frac{I}{2\pi L\sigma} \ln \frac{D - R}{R}$$  \hspace{1cm} (5.11)

The cell constant $C_c$ is calculated as (Eq. 5.7):

$$C_c = \frac{1}{\pi L} \ln \frac{D - R}{R}$$  \hspace{1cm} (5.12)
Design of the conductivity sensor

The sensor is built from a standard high pressure plug\(^4\). In order to have a reasonable cell constant a 11/16” plug is used. It is modified according to figure 5.12.

![Figure 5.12: Construction drawing of the sensor.](image)

A blind hole in milled from each side into the plug leaving a 6 mm thick platform. 3 holes are drilled into this platform. 2 of the 3 holes are used to lead through 2 alloy 52\(^5\) pins that are coated with platinum. These pins act as the actual sensor. The pins are electrically insulated from the wall and from each other by glass sealing. Glass beads type EG 6000\(^6\) were used. A second bead (“sleeve”) insures that there is no short-circuiting

---

\(^4\)from SITEC Sieber Engineering AG, Maur, Switzerland

\(^5\)Alloy 52 consist mainly of \(\approx 50\%\) nickel and \(\approx 50\%\) iron, and has a very low thermal expansion which is important when working with glass sealings.

\(^6\)from Electro-Glass Products, PE, USA
through the wall of the plug. The third hole is used to lead through a high pressure tube (HC-22, \( \phi_{in} = 0.75 \text{ mm}, \ \phi_{out} = 1/16" \)) into which a thermocouple (type K) is hard-welded. This setup allows to measure temperature and conductivity at the same location.

![Scheme and photograph of the sensor.](image)

**Figure 5.13:** Scheme and photograph of the sensor.

Equation 5.12 was used to choose the geometric dimensions of the sensors. Once the sensors were built their cell constant was measured using a standard (NIST traceable) conductivity solution (3.9 mS/cm). The results are compared in table 5.3.

<table>
<thead>
<tr>
<th></th>
<th>cell constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>analytical solution (Eq. 5.12)</td>
<td>0.41 cm(^{-1})</td>
</tr>
<tr>
<td>measured cell constant sensor 1</td>
<td>0.46 cm(^{-1})</td>
</tr>
<tr>
<td>measured cell constant sensor 2</td>
<td>0.54 cm(^{-1})</td>
</tr>
</tbody>
</table>

**Table 5.3:** Calculated and measured cell constants of the built sensors.

### 5.4.3 Extraction of the RTD from the tracer data

A review on this subject is given by Torres and Oliveira (1998). The concentration of a tracer at an inlet \( c_{in} \) (Sensor 1 in Fig. 5.14) and the concentration at the outlet \( c_{out} \) (Sensor 2 in Fig. 5.14) are related
through a convolution integral:

\[
c_{out}(t) = \int_{0}^{t} E(\theta) c_{in}(t - \theta) d\theta
\]  \hspace{1cm} (5.13)

where \( E \) is the RTD. Due to the mathematical complexity of the convolution integral the extraction of the RTD function is not straightforward. Two popular approaches are found in the literature: convolution in the time domain and deconvolution in the frequency domain.

![Graph](image.png)

**Figure 5.14:** Raw data from the experiment (RTD-WF). Sensor 1 is located before the fuel inlet and sensor 2 is located right after the outlet.

**Time domain analysis**

In the convolution analysis a flow model has to be assumed which fixes the shape of the RTD. Flow models feature parameters that depend on the mean residence time \( \tau \) and the spreading of an ideal tracer peak in the reactor due to dispersion (the variance \( \sigma^2 \)). More complex model
can depend on higher moments too. The values of these parameters are either found using curve fitting with non-linear optimization (minimization of the sum of the squared differences between the calculated and the measured output concentration) or by numerically determining the needed moments from the experimental tracer data and calculating the model parameter from these values.

The numerical determination of $\tau$ (1st moment) and $\sigma^2$ (2nd moment) is as follows:

$$\tau = \frac{\int_0^\infty t \, c \, dt}{\int_0^\infty c \, dt} \approx \frac{\sum t_i c_i \Delta t_i}{\sum c_i \Delta t_i} \quad (5.14)$$

$$\sigma^2 = \frac{\int_0^\infty (t - \tau)^2 \, c \, dt}{\int_0^\infty c \, dt} \approx \frac{\sum (t_i - \tau)^2 c_i \Delta t_i}{\sum c_i \Delta t_i} \quad (5.15)$$

In case of a non-ideal input pulse at the inlet, the moments of the RTD are received by [Levenspiel, 1999; Torres and Oliveira, 1998]:

$$\tau_{RTD} = \tau_{out} - \tau_{in} \quad (5.16)$$

and

$$\sigma^2_{RTD} = \sigma^2_{out} - \sigma^2_{in} \quad (5.17)$$

respectively. For higher moments similar equations apply.

In the literature two flow models and combination of them are often used, the Plug Flow with Dispersion and the Tanks-in-Series model. The RTD of the Plug Flow model with Dispersion is (erroneous in Levenspiel (1999), correct in Levenspiel (1972)):

$$E(\theta) = \tau E(t) = \frac{1}{\sqrt{4\pi Pe \theta}} \exp \left[ -\frac{(1 - \theta)^2}{4Pe \theta} \right] \quad (5.18)$$

where $Pe = D/(uL)$ is the Peclet number ($u =$ superficial velocity, $L =$ length of the tube, $D =$ dispersion coefficient), and $\theta = t/\tau$ is the normalized residence time. $Pe$ is related to the variance $\sigma^2$ by:

$$\sigma^2 = \tau^2 (2Pe + 8Pe^2) \quad (5.19)$$
The RTD of the Tanks-in-Series model (a series of \(N\) continuously stirred tanks reactors) is [Levenspiel, 1999]:

\[
E(\theta) = \tau E(t) = N \frac{(N \theta)^{N-1}}{(N-1)!} \exp(-N \theta) \quad (5.20)
\]

where \(N\) is related to the variance \(\sigma^2\) by:

\[
\sigma^2 = \frac{\tau^2}{N} \quad (5.21)
\]

At large values of dispersion the Plug Flow with dispersion model is the model of choice due to the discreteness of the fitting parameter \(N\) in the Tanks-in-Series model.

Deconvolution in the time domain has not been considered based on the publication of Mills and Dudukovic (1989). It states that the matrix to be solved in this approach is ill-conditioned and too large to be solved when reasonable sampling rates are used, even on the largest computers at that time.

**Frequency domain analysis**

The main advantage of the deconvolution approach in the frequency domain is that the shape of the RTD does not have to be assumed \textit{a priori}. When the convolution integral (Eq. 5.13) is transformed into the frequency domain by applying Laplace or Fourier transformation a much simpler equation results (Fourier transformation will be used in this work due to the availability of \textit{fast fourier transformation} (fft) in the numerical codes used):

\[
C_{out}(s) = E(s) C_{in}(s) \quad (5.22)
\]

This equation is to be solved and back-transformed into the time domain. The problem is dominated by noise when discrete fourier transformation (dft) is applied [Mills and Dudukovic, 1989]. Therefore, a filtering method is to be used. Using the popular linear filter (regularization), the
5. Experimental

The transformed RTD is received as:

\[ E(s) = \frac{C_{out}(s)}{C_{in}(s)} \frac{1 + \gamma \frac{B(s) B^*(s)}{C_{in}(s) C_{in}^*(s)}}{1} \]  \hspace{1cm} (5.23)

where \( B(s) \) is the dft of smoothing formula coefficients \( b \) (size of \( b = \) size of \( c_{in} \)), e.g.

\[ b = [1, -2, 1, 0, \ldots, 0] \]  \hspace{1cm} (5.24)

The value of \( \gamma \) in Eq. 5.23 is bound in 0 and \( \infty \). Some technique to specify its optimal value is needed, e.g. the evolution of the moments (Eqs. 5.16 and 5.17) can be used as criteria.

Both frequency and time domain analysis have been performed to extract the RTD from the experimental data. Time domain analysis showed to result in more trustful results.

This is consistent with some publications, which describe the frequency analysis as prone to inaccuracies [Viitanen, 1994].

5.4.4 Results

The conductivity sensors showed good performance in a wide range of temperature and pressure. Temperatures at the upper sensor were as high as 520\(^\circ\)C for several minutes at a pressure of 250 bar.

The main goal of the measurements is to get a measure of the amount of back-mixing in the reactor. Since the absolute value of the backmixing is hard to interpret the reactor was run with the same operating conditions in steady state once with the hydrothermal flame burning and once without the flame burning. The RTD has been extracted by numerically determining the first and second moment of the RTD (Eqs. 5.14 – 5.17) and calculating the parameters of the Plug Flow with Dispersion model (Eqs. 5.18 and 5.19). The use of the Plug Flow with Dispersion model does not affect the results but serves well for visualization.
5.4 Residence time distribution

<table>
<thead>
<tr>
<th>tag</th>
<th>date</th>
<th>sample</th>
<th>$J_{\text{fuel}}$</th>
<th>$J_{\text{fuelox}}$</th>
<th>$J_{\text{WW}}$</th>
<th>$J_{\text{WWox}}$</th>
<th>$J_{T_{W1}}$</th>
<th>$J_{T_{W2}}$</th>
<th>$J_{T_{W3}}$</th>
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<tr>
<td>RTD-NF</td>
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<td>CD7a</td>
<td>1.53</td>
<td>0.60</td>
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<td>CD10a</td>
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<td>0.45</td>
<td>1.06</td>
<td>0.35</td>
<td>0.93</td>
<td>0.61</td>
<td>0.60</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>tag</th>
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<th>$w_{Me,\text{WW}}$</th>
<th>$t_{\text{fuel}}$</th>
<th>$t_{\text{fuelox}}$</th>
<th>$t_{\text{WW}}$</th>
<th>$t_{\text{WWox}}$</th>
<th>$t_{T_{W1}}$</th>
<th>$t_{T_{W2}}$</th>
<th>$t_{T_{W3}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RTD-NF</td>
<td>0.16</td>
<td>0.00</td>
<td>300</td>
<td>238</td>
<td>49</td>
<td>73</td>
<td>94</td>
<td>92</td>
<td>66</td>
</tr>
<tr>
<td>RTD-WF</td>
<td>0.16</td>
<td>0.00</td>
<td>329</td>
<td>283</td>
<td>307</td>
<td>270</td>
<td>273</td>
<td>253</td>
<td>175</td>
</tr>
</tbody>
</table>

Table 5.4: Compilation of the operating conditions of the simulations concerning the RTD comparison, $p=250\text{bar}$. Mass flow rates in g/s, temperatures in °C. The transpiration flows correspond to an intensity of $\approx 2\%$. 

Figure 5.15: Experimentally determined residence time distribution $E(t)$ with an extinct hydrothermal flame (RTD-NF).

The RTD of the feed inlet of the reactor without the hydrothermal flame burning (RTD-NF) has a mean residence time $\tau$ of 3.2 s and a dimensionless variance $\sigma^2/\tau^2$ of 12.25 (Fig. 5.15). Since the reactor features 8 inlets the interpretation of a RTD of one of the inlets is not straight for-
ward. The mean residence time of inlet $i$ is defined by (see also chapter 2.4.1):

$$\tau_i = \frac{M_i}{J_{m,i}}$$  \hspace{1cm} (5.25)

where $M_i$ is the mass of fluid in the reactor that entered the reactor through inlet $i$ and $J_{m,i}$ is the mass flow rate of inlet $i$. The amazingly short mean residence time $\tau$ can only be explained by a special flow field: The temperatures of the feed stream and the oxygen stream are both subcritical before entering the combustion chamber, i.e. the tube in which the flame is burning when ignited. When there is no flame burning then there are 2 phases. One is the oxygen and the other is the subcritical fuel mixture that flows through in a jet like behavior. Further down in the reactor the fuel mixture mixes with the transpiring and the cooling water and leaves the reactor through the bottom (see also chapter 2.4.1).

When the hydrothermal flame is burning (RTD-WF, Fig. 5.16) the mean residence time is 11.8 s and the dimensionless variance is 9.0. Since the temperature is higher in the reactor the density is much lower. Therefore,
there is less mass in the reactor which would actually mean that the mean residence time is shorter. On the other hand, due to the high temperature in the flame there is only one single supercritical phase present. That is why the jet existing in the RTD-NF case mixes much sooner with the surrounding fluid. This leads to a flat radial velocity profile, which more than counterbalance the density change. Referring to Eq. 5.25, the slower velocity leads to a larger mass of fluid in the reactor that entered through the fuel inlet.
Chapter 6

Reactive Simulations

6.1 State of art

Using a one-dimensional model Saur et al. (1993) calculated the combustion process of a counterflow diffusion flame in supercritical water at pressures up to 3000 bar. Except for the geometry the properties used in the simulation were exactly modelled. They were able to predict temperatures and conversion in the flame.

The first CFD simulation of a steady-state SCWO process has been done by Oh et al. (1995), (1996a), (1996b), and (1997). They have used some simplifying assumption in the evaluation of the heat capacity [Oh et al., 1997]. Their comparison with experimental data (3 points) is of little use since they compare the temperature close to the wall with measured values, yet they use a very similar temperature as boundary condition at the same wall.

Complete 2D and 3D CFD simulations with all important properties modelled are reported by [Zhou et al., 2000]. First they compared the calculated conversion for a simple tubular reactor. Then they investigated the influence of the gravity in a more complicated geometric setup. In the second case they did not have any experimental data to validate their calculations.
6.2 Model

All simulations were done on 2D axisymmetric grids. The standard $k-\epsilon$ turbulence model was used to account for the turbulence. Even though it is known that a low-Reynolds approach is to be used near the wall for supercritical fluids, regular wall function were applied. This was done to limit the computational costs of the simulations (since a coarser grid could be used). The fluid properties used are described in section 3.2. The reaction kinetics were taken from Tester et al. (1993b). The thermal conductivity in the porous region is adopted according to Krupiczka (1967). The equations were solved using a first order upwind scheme since higher order schemes did not converge. An average calculation took about 1 week to converge on 1 GHz processor workstation with 512 MB RAM.

6.3 Reactor without inserted transpiring wall

The system boundary has to be set in a way that on the whole boundary the temperature or the heat flux and the mass flux is known. In case of the reactor into which the transpiring wall has not been inserted, the whole reactor is included in the system. The used grid is depicted in figure 6.1. The heat transfer through the wall to the surrounding air is the most important phenomenon for the temperature profile along the axis of the reactor. This heat transfer is dominated by the radiative and the convective heat loss to the surroundings. The software allows to model the heat transfer through the solid reactor wall. At the outer edge of the wall the emissivity $\epsilon$ and a convective heat transfer coefficient $h$ can be set.

\[
q = h (T_{wall} - T_{ext}) + \sigma \epsilon (T_{wall}^4 - T_\infty^4) \tag{6.1}
\]
where

\[
\begin{align*}
  h &= \text{external heat transfer coefficient} \\
  T_{\text{ext}} &= \text{external temperature} \\
  \sigma &= \text{Stefan-Boltzmann constant} = 5.6696 \times 10^{-8} \text{ W/m}^2\text{K}^4 \\
  \epsilon &= \text{external emissivity coefficient} \\
  T_\infty &= \text{temperature of the radiation source or sink}
\end{align*}
\]

\textbf{Figure 6.1:} The grid that is used for the reactive CFD simulation of the TWR without the transpiring wall (out of scale by a factor of 5). The geometry includes reactor wall and the sophisticated head (left) with the several inlets. Near the outlet (right) of the reactor there is the cooling water inlet.

The emissivity is estimated as 0.63 [Green et al., 2000] and the external heat transfer coefficient due to natural convection in the surrounding air has been estimated [according to VDI, 1991] as 10 W/m\(^2\)K.
6.3 Reactor without inserted transpiring wall

6.3.1 Results

Experimental data are available for the temperature at the inside wall of the reactor with the hydrothermal flame burning [Wellig, 2003].

The calculated and measured temperature profiles do clearly not match well (Fig. 6.2, right). The flame is the only heat source in the system and the heat transfer to and through the wall is the only heat loss. Heat transfer to the wall is dominated by turbulence. Hence, the axial temperature profile shows a strong dependency on the heat loss through the wall. The ratio of the radiation part to the convective part (Eq. 6.1) at the outer wall is in the order of 2 to 5. For a better match, a more accurate description is needed of the turbulent mixing, the geometry of the
reactor, and the numerous influences affecting the heat loss (e.g. conduction into the supporting frame that holds the reactor in place). Another reason for a part of the mismatch of the data may be due to the not totally reached steady state during the experiment. The temperatures at the inner reactor wall were still somewhat increasing when the data was taken. In order to find the real deficiencies of the model, a simpler system with less influencing parameters has to be set up and more data is to be collected during the experiment [AIAA, 1998] (at the time of the experiment the thermocouples that radial temperature profiles were not implemented yet).

6.4 Reactor with inserted transpiring wall

6.4.1 Setup

The geometry of the TWR is depicted in figure 5.6. The system boundary has been set to include the transpiring wall elements yet not the pressure bearing reactor wall. The temperatures of all inlets are known from the experiments. Due to the huge radial temperature gradient there may be some heat loss in the opposite direction to the inward flowing transpiring flow. This heat loss has been accounted for in the calculations. The used grid is shown in figure 6.3. Grid independence is tested by a grid convergence study (chapter 2.6.1). This study has been based on the length of the supercritical zone of the RTD-WF simulation mentioned below as a criterion. This length is a distinctive value for the flow field. $GCI_{\text{fine}} = 0.057$ and $GCI_{\text{coarse}} = 0.170$ is received.

6.4.2 Intensity variation

The measured operating conditions from the intensity variation experiments were used (table 5.1). Comparing the calculated results (Fig. 6.4) with measured results (Fig. 5.8, page 90) the match of the overall behavior is satisfactory. The lengths of the region where the bulk fluid is supercritical are similar. These lengths are best being observed in the $c_p$
value fields since the distinct peak in the $c_P$ value represent the transition from super- to subcritical (Fig. 6.5). For an intensity of 1% (I-A) the supercritical region extents to below the second measurement plane. The streamline plots (Fig. 6.5) exhibit a small recirculation zone at and below the transition from super- to subcritical temperatures. This eddy is more distinct in case of the higher intensities (I-B and I-C on bottom of Fig. 6.5). In these two cases the lengths of the supercritical regions are smaller as expected. For an intensity of 5% the supercritical region does not even extent over the first measurement plane. In the other parts of the reactor all streamline plots indicate a rather plug flow like behavior. Only at the top of the last transpiration section, through which the large amount of cooling water enters the reactor, there is a small disturbance. This disturbance is probably a result of the relatively fast and cold cooling water and has no effect on the performance of the reactor.

The calculated profile are much flatter than the measured ones. Heat transport is dominated by turbulence. The turbulent heat transfer coefficient that results from the turbulent mixing is therefore apparently overestimated. Most significant is the mismatch of the temperature profiles close to the porous wall.
Figure 6.4: Calculated temperature profiles of the intensity variation runs at the positions of the measurement planes. The experimental results of these intensity variation operating conditions are depict in Fig. 5.8 and are given in table 5.1
Figure 6.5: Calculated property fields \((t, c_P)\) and streamlines of I-A (top, \(int = 1\%\)), I-B (bottom left, \(int = 2\%\)), and I-C (bottom right, \(int = 5\%\)). The experimental results of these intensity variation operating conditions are depict in Fig. 5.8 and are given in table 5.1.
6.4.3 Transpiration temperature variation

![Graph showing temperature profiles](image)

**Figure 6.6:** Calculated temperature profiles of the transpiration temperature variation runs at the positions of the measurement planes. The experimental results of these transpiration temperature variation operating conditions are depict in Fig. 5.9 and are given in table 5.2.

For the temperature variation runs again measured operating condition
were used as boundary conditions (table 5.2). Comparing the calculated results (Fig. 6.6) with measured results (Fig. 5.9, page 92) the match of the overall behavior is given. The length of the supercritical regions are similar. The expected trend of the length is reproduced (note the $c_P$ value fields in Fig. 6.7). As in the intensity variation comparison, the calculated radial temperature profile are much flatter than the experimental ones. The streamline plots (Fig. 6.7) show an even more distinct eddy shortly below the transition from supercritical to subcritical temperatures.
Figure 6.7: Calculated property fields \((t, c_P)\) and streamlines of T-A (top, \(t_{tr} = 125\,^\circ C\)), T-B (bottom left, \(t_{tr} = 200\,^\circ C\)), and T-C (bottom right, \(t_{tr} = 250\,^\circ C\)). The experimental results of these transpiration temperature variation operating conditions are depicted in Fig. 5.9 and are given in table 5.2.
6.4.4 Residence time distributions

Steady state simulation have been run using the measured boundary conditions given in table 5.4. The residence time distributions (RTD) have been extracted from the CFD calculations using the procedure described in chapter 2.4.2. For each RTD 1000 trajectories have been integrated (Eq. 2.22) and their integration times have been weighted by the mass flow they represent. A comparison between the different $C_D$ values from literature, that affect the relaxation time during which the fluctuating velocities are kept constant (Eq. 2.29 and Eq. 2.30), show a negligible influence in the investigated cases. Evaluation of $C_D$ was done according to Eq. 2.29.

![Figure 6.8: Temperature field and streamlines of the calculated flow field without (RTD-NF, left) and with (RTD-WF, right) the hydrothermal flame burning.](image)

The match of the mean residence time $\tau$ is very good in case of the hydrothermal flame burning and poor when the hydrothermal flame is
not burning (Figs. 6.9 and 6.10). The dispersion is underestimated in both cases. \( \tau \) is influenced by several parameters (chapter 2.4.1), which makes the interpretation of the results more difficult. The match of \( \tau \) for RTD-WF is amazing whereas for the RTD-NF case the big difference between the predicted and the measured \( \tau \) must be due to some fundamental error. The evolution of the tracer concentration is displayed online during the experiments. Already during the experiment the short \( \tau \) has been observed. The explanation for this is that the flow in the reactor is a 2-phase flow whereas the used standard CFD model is based on a single (supercritical) phase. Therefore, the CFD simulation cannot reproduce the flow adequately. The real flow field features a jet like behavior of the core fuel inlet a long length down into the reactor. As the CFD simulation prognoses a mixing (due to the single phase) of the jet sooner than in reality, a slower core velocity and a longer \( \tau \) results. To closer represent the physics in this case, a 2-phase model has to be applied which complicates the model by a great amount.

**Figure 6.9:** Calculated RTD from the CFD simulations. Cases: RTD-WF (right), and RTD-NF (left). The simulation of the RTD-NF case gives wrong results due the disregard of the two-phase nature of the flow at these conditions.
6.5 Discussion

The reactive simulations have to handle several challenges: First, the definition of the system boundary needs to be taken special care of. If an inappropriate system boundary is selected then the modeling error from geometric simplifications and necessary models and assumptions, e.g., the heat loss coefficients at the outside of the reactor, may add up to large discrepancies with the experimental results. At all system boundaries temperature and flows should be measured. Second, due to the immense temperature differences in the reactor, heat transport plays a major role. Also, the temperature resulting from the heat flux determines all properties of the fluid. The transition from super- to subcritical temperature goes together with a drastic change of all properties.

The results of the reactive CFD simulation show some effects that have been observed in similar fashion in the experiments. One such phenomenon is the occurrence of a recirculation zone at and below the region where the transition from super- to subcritical temperatures takes place.

Figure 6.10: Comparison of the measured and calculated response at the second sensor.
in the reactor. A possible explanation for this behavior is shown in figure 6.11. $Gr$ is a representation of the driving force of natural convection and the “local” Grashof number shows a huge maximum at these temperatures.

![Figure 6.11: The “local” Grashof number $Gr = \Delta \rho g l^3 / \rho \nu^2$ vs. temperature, where the density difference $\Delta \rho$ is based on a $1^\circ C$ temperature difference, and $l = 22\ mm$.](image)

The lengths of the supercritical region have been reproduced also in a quantitative manner. A main deficiency of the reactive simulations is that the radial temperature profiles are predicted too flat. A reason for this may be the limited capability of the used software to model a porous region. All transport properties are altered in the porous region to porous region models from the literature (see chapter 3.4). For best results the turbulence quantities should approach zero at the interface between the bulk fluid zone and the porous region fluid zone. Using a Low-Reynolds turbulence model the turbulent quantities have to be integrated all the way into the viscous sublayer at the liquid-liquid interface similar to the treatment at regular walls. This is not implemented in the used software. If this behavior is not modelled, there will be no true viscous sublayer at the porous wall which acts as a resistance to heat transfer and hence, would lead to a shape of the temperature profile that better resembles the
experimental one. A discussion about capabilities of other CFD software packages and another model that may provide more accurate results are given in the outlook (chapter 7.3.1).
Chapter 7

Conclusion

CFD in general and particularly for complex flows as in SCWO reactors needs validation in order to be routinely used for robust predictions. CFD calculations found in the literature in the field of SCWO usually do not contain a thorough comparison with experimental data. The main reason for this is the scarce availability of such data even for simpler reactors than the investigated transpiring wall reactor. In the present work an attempt has been made to build a CFD model including all important features and trends of the investigated flow. Various kinds of validation experiments have been thought through, and of these 2 kinds have been selected to be carried out. The needed additional equipment has been designed, built, and incorporated into an existing reactor. The experiments were run successfully. The experimental data is compared to the CFD results. Several phenomena are being explained by the CFD simulations. Remaining deficiencies of the model are elaborated and a proposed enhancement to the model is given.

7.1 Summary and Discussion of the Results

The present work can be split into 3 parts: First, an analytical model has been applied and inert CFD calculations were performed to investigate the influences of the operating conditions on the resulting flow field. Objectives of investigation in this part are the occurrence of a recirculation zone in the reactor due to the natural convection and a quantitative measure of the wall protection from salt sedimentation. The temperature
and the intensity of the transpiring flow showed the strongest influence on the flow field and on the protection. Natural convection effects lead to a less favorable flow field and protection, but with carefully selected operating conditions the reactor can have a good performance.

Second, a means of validation is looked for. The measurement of the radial temperature profiles on 3 heights in the reactor and the measurement of a tracer response were selected. From the measured tracer responses the residence time distribution has been extracted. The experiments yielded valuable data for validation. Explanations of the results are discussed.

In the third part reactive CFD simulation results are compared to the experimental findings. Several qualitative and some quantitative agreement are obtained. One of them is the length of the supercritical region in the reactor. Even though this length depends sensibly on all heat inputs and losses the match is satisfactory. One important deficiency remained: the match of the radial temperature profiles. These were not reproduced in a good fashion. An enhancement of this match is expected if a better model is used near the porous wall.

## 7.2 Scale-up considerations

CFD simulations are well suited for scale-up calculations provided that validated simulations exist. A transpiring wall reactor for supercritical water oxidation is not scaled-up in a straight forward way. Keeping the transpiration intensity constant is equivalent to saying that the protective layer at the wall is proportional to the inner radius $R$ of the porous tube. This is reasonable as the surface of the porous tube is proportional to $R$ too. The bulk flow rate, being the throughput, is, at constant velocity proportional to $R^2$. Natural convection effects on the other hand may cause an unfavorable flow field. The Grashof number $Gr$ is used to describe flows dominated by natural convection. For mixed convection flows the Richardson number $Ri$ is used:
Grashof number:

\[ Gr = \frac{\Delta \rho g l^3}{\rho v^2} = \frac{F_{\text{bouyant}}}{F_{\text{viscous}}} \]

Richardson

\[ Ri = \frac{\Delta \rho g l}{\rho u^2} = \frac{F_{\text{bouyant}}}{F_{\text{turbulent}}} \]

Provided that the radius \( R \) is the appropriate length scale and if a constant Richardson number is to achieve, then a increase of \( R \) must go together with a square root increase of the bulk velocity \( u \). A slightly different dependency on the prevalence of natural or convective forces is given by Aung (1987), (Fig. 7.1).

**Figure 7.1:** Map to prevailing flow regime in a tube [Aung, 1987]. The investigated flow is an opposed downward flow with \( Re \approx 5000 \) and \( Gr \ Pr \ D/L \approx 5 \cdot 10^8 \).

It should always be kept in mind that dimensionless numbers are only
valid for mildly changing properties. The selection of the temperature at which the properties are to be evaluated is not of great importance as they will be the same in the scaled-up reactor. All in all, analytical rules may be used for the scale-up but a check of the flow field in the reactor using CFD simulations is proposed. For these, as already mentioned above, a carefully validated model is a must.

7.3 Outlook

7.3.1 Enhancement to the existing CFD model

In the beginning of this work a selection of an appropriate commercial CFD software package was performed. Since other people at the Institute were using Fluent it was decided that it would be used for the present work too. Soon it was realized that the new Fluent (version 5.0 and higher) which is based on the C-programming language, does not allow to set the heat capacity $c_P$ by a user defined function. Therefore, the older Fluent version 4.5 was used. After some first results, a new CFD software package CFD-ACE+ Version 6.4 was chosen since a collaborating research group had worked with this software successfully.

After having worked with a software on a project one knows several drawbacks of it. In order that this knowledge gets not lost, the list of needed features of a CFD software for the investigated flow problem has been set up. The abilities of the newest versions of some well known CFD software packages have been checked on whether they could tackle all these challenges. The outcome of this investigation is summarized in table 7.1. The investigated flow contains highly non-linear properties which have to be accounted for. Commercial CFD software often allows this by compiling user defined functions with the code. Second, since the investigated flow is turbulent, yet not highly turbulent the choice of the turbulence model is important. Implementing new turbulent models in

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1 Fluent Incorporated, Lebanon, NH, USA
2 CFD Research Corporation, Huntsville, AL, USA
3 Group of Prof. J. W. Tester, Energy laboratory, Massachusetts Institute of Technology (MIT) in Cambridge, MA, USA
a commercial code at oneself is very time consuming and convergence problems exist with higher models. Therefore, the choice of the turbulence model is basically given by the existing models in the commercial code. All considered codes feature several $k-\epsilon$ turbulence models with wall functions and low-Reynolds approaches.

One known deficiency of the model used in the present work is the treatment of the turbulent quantities near the porous wall. Since the average pore-size of the used wall is 3 $\mu$m, there will be basically no turbulence in this region (The turbulent kinetic energy $k$, by which the turbulence is quantified in the $k-\epsilon$ turbulence model, is the mean time averaged of the fluctuating part of the velocity). The turbulence in the porous region does not alter flow properties since its influence in the fluid properties is explicitly not accounted for. There is some influence though at the interface between the porous zone and the regular fluid zone (bulk flow). At regular walls the turbulent kinetic energy and its dissipation tend towards zero. In the present model, since the turbulent values are not zero or negligibly small in the porous zone, this is not the case. This so called dampening near the wall would result in viscous sublayer near the porous wall that acts as a resistance to the mass and heat transfer to the porous wall (zone). The fact that the turbulent kinetic energy inside the porous media goes to zero may not be sufficient as the dampening is not correctly modeled. Therefore, the profiles of the turbulent quantities normal to the wall and the transfer resistances will be inaccurately reproduced. A special treatment is needed at this interface. None of the investigated CFD software packages (table 7.1) seems to allow to implement such a boundary condition. To implement such a boundary condition one should look for an open source code CFD solver.

Due to the presence of steep temperature and property gradients in the flow good spatial resolution is needed. Yet if the fine grid expands over the whole reactor then the computational costs are immense. To overcome this conflict solution adaptive gridding procedures are to be used. Adaptive gridding or meshing is a technique by which a mesh evolves in conjunction with the numerical solution of the problem. To use adaptive meshing effectively, it must be used in conjunction with the solver. The typical procedure for using any adaptive procedure is as follows:
7.3 Outlook

- Generate an initial coarse mesh.
- Compute an approximate solution using the solver.
- Determine where the mesh needs to be modified.
- Adapt the mesh by adding or removing cells.
- Recompute the solution using the solver.
- Determine if the solution is accurate, e.g. by some kind of error estimator.
- If not, return to step 3.

This procedure continues until the change in the solution is below some user-specified tolerance. Note that because the initial mesh is coarse and the convergence performance is enhanced, the overall solution time is reduced.

7.3.2 Idea of a new CFD model

The software used will only treat a wall or a fluid-solid interface, in a way that a correct viscous sublayer will build up. Based on this thought, a new idea of a CFD model has emerged (Fig. 7.2). It features a solid zone at the porous wall side of the interface. The model must take care to correctly describe the heat and mass transfer. For the heat transfer, this is done by adding 2 other zones behind the solid zone. The outermost zone has the same thickness and function as the original porous wall. The transpiring fluid enters this zone and flows towards the solid zone. In the small zone between this porous wall zone and the solid zone the whole mass flow is withdrawn by a sink term that has the same magnitude as the total transpiration mass flow. Doing so the heat transfer from the inside of the porous tube to the outside is approximated. The sink zone and the solid zone are both very thin, and the thermal conductivity of the both zones is taken to be very large in order that the influence of these zones on the heat transfer resistance is negligible. This can be tested in a simulation by checking the temperature difference across these zones.
Figure 7.2: Schematic of a CFD configuration that may lead to more exact results. The sink and the source term are equally large as the total of the transpiration inlet. The thickness of the sink, source, and solid zones is taken as small as possible and the thermal conductivity of the solid is taken to be very large so that the thermal resistance through the solid can be neglected.

In the porous zone the properties of the fluid are adapted to account for the material of which the porous wall is built. In order to account for the correct species transport, there is a thin zone on the bulk flow side of the interface. In this zone the transpiring water enters by the use of a source term. The composition of this source is pure (transpiring) water. A remaining assumption of this model is that the diffusivity is zero inside the porous wall. This assumption is not far off from reality but could also be relaxed by additional modelling.

First tests using this model have shown that convergence is hard to reach with such a geometrical arrangement of zones. The turbulent quantities in the porous wall zone reach nonphysical values.
Table 7.1: Features of some commercial CFD software packages needed for the modeling of the investigated flow.

<table>
<thead>
<tr>
<th>code</th>
<th>company</th>
<th>user defined properties</th>
<th>turbulence effects in the porous region</th>
<th>mesh adaption</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFD-ACE+ 6.4</td>
<td>CFD Research Corporation</td>
<td>conductivity, viscosity, density, enthalpy</td>
<td>momentum resistance, user defined properties, <strong>turbulent quantities unchangeable</strong></td>
<td>none</td>
</tr>
<tr>
<td>Fluent 6.0</td>
<td>Fluent Incorporated</td>
<td>conductivity, viscosity, density, enthalpy</td>
<td>momentum resistance, given adapted properties, turbulent quantities through user defined source terms</td>
<td>built-in</td>
</tr>
<tr>
<td>STAR-CD 3.10A</td>
<td>CD adapco Group</td>
<td>conductivity, viscosity, density, <strong>not enthalpy</strong></td>
<td>momentum resistance, user defined properties, turbulent quantities controllable</td>
<td>built-in (also to estimated error)</td>
</tr>
<tr>
<td>CFX-TASCflow 2.11</td>
<td>AEA Technology</td>
<td>conductivity, viscosity, density (circumstantial), enthalpy</td>
<td>momentum resistance, user defined properties (circumstantial), <strong>turbulent quantities unchangeable</strong></td>
<td>none</td>
</tr>
<tr>
<td>CFX-5.5.1</td>
<td>AEA Technology</td>
<td>conductivity, viscosity, density, enthalpy</td>
<td>momentum resistance, user defined properties, turbulent quantities through user defined source term</td>
<td>built-in</td>
</tr>
</tbody>
</table>
7.3.3 Particle Simulations

For calculating particle tracks from a steady state simulation several models exist. In some CFD software packages some are already implemented. The precipitation of particles is more complicated. Equilibrium data is needed together with the precipitation kinetics. In case of SCWO the precipitation is very fast, which is concluded from the fact that very small particles are built [Armellini and Tester, 1993; Haroldsen et al., 1996]. It may not be worth putting up the effort to model the precipitation itself but rather only to simulate the particle tracks and the deposition. Particle track simulations will never be better than the underlying steady state simulation. Therefore, it is proposed that the emphasis is put on the optimization of the steady state simulation in order to build a confident basis for any additional evaluations.

7.3.4 Turbulence Models

There are a variety of turbulence models available. Some are better suited to variable density flows than the used ones. But, as usual, the better the turbulence model the more computational intensive it is. A large eddy simulation (LES) is probably the model of choice. It would certainly be worth calculating the flow field using LES. The additional knowledge gained from such a simulation may not be tremendous but with the best accuracy that is possible today. Of course, it only makes sense to go towards more complicated turbulence models when all open issues are solved with the simpler model.
References


Curriculum Vitae

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