The Collaborative Research Centre "Oxyflame"

1

Reinhold Kneer, Viktor Scherer, Heinz Pitsch, Andreas Dreizler, Anna Maßmeyer, Stefan Pielsticker and Benjamin Gövert

Contents

R. Kneer (✉) · A. Maßmeyer · S. Pielsticker · B. Gövert
Institute of Heat and Mass Transfer, RWTH Aachen University, Aachen, Germany
e-mail: kneer@wsa.rwth-aachen.de

A. Maßmeyer
e-mail: massmeyer@wsa.rwth-aachen.de

S. Pielsticker
e-mail: pielsticker@wsa.rwth-aachen.de

B. Gövert
e-mail: goevert@wsa.rwth-aachen.de

V. Scherer
Department of Energy Plant Technology, Ruhr-Universität Bochum, Bochum, Germany
e-mail: scherer@leat.rub.de

H. Pitsch
Institute for Combustion Technology, RWTH Aachen University, Aachen, Germany
e-mail: h.pitsch@itv.rwth-aachen.de

A. Dreizler
Institute of Reactive Flows and Diagnostics, Technische Universität Darmstadt, Darmstadt, Germany
e-mail: dreizler@rsm.tu-darmstadt.de

R. Kneer et al. (eds.), *Clean Energy Conversion*,
https://doi.org/10.1007/978-3-031-98956-8_1

Abstract

To combat climate change, it is imperative to reduce anthropogenic CO_2 emissions to net-zero by approximately 2055, especially in solid fuel combustion processes. In the present book, the focus is placed on the detailed investigation of the oxy-fuel process, where the combustion air is replaced with a mixture of oxygen, carbon dioxide, and water vapour, facilitating near carbon-neutral combustion. Research conducted within the presented research centre *Oxyflame* encompasses a diverse array of fuel types, spanning from pulverised fossil fuels such as bituminous coal and lignite to renewable biomass sources including walnut shells, beech wood or miscanthus. Substantial advancements in the experimental characterisation of reaction kinetics, particle dynamics, flame behaviour, and radiation effects in combustion environments of different scales are presented. The results yield into the development of robust models for combustion and transport phenomena as well as efficient simulation methodologies for designing combustion chambers, paving the way for efficient oxy-fuel systems capable of effectively reducing greenhouse gas emissions in alignment with global climate protection goals.

1.1 Introduction

To limit global warming to 1.5 °C above pre-industrial levels, as outlined in the *Paris Agreement* [1], anthropogenic carbon dioxide (CO_2) emissions must be reduced to net zero by roughly 2055 [2]. At present, 79% of global CO_2 emissions are caused by the power generation and industry [2–4]. Therefore, the major contribution to reduce CO_2 emissions has to come from these sectors [2,3].

Noting that current predictions for primary energy demand do not see a rapid decline in the consumption of fossil fuels—be it solid, liquid, or gaseous—up to 2040 [4], an essential part of technical solutions to reduce CO_2 emissions will be the application of carbon capture, utilisation, and storage (CCUS) technologies. A prerequisite for achieving CCUS technologies is the transformation of existing energy conversion processes for large-scale power generation or in industrial applications. One advanced method to achieve CCUS in combustion systems is the oxy-fuel process.

Here, the term "oxy-fuel" refers to a combustion atmosphere consisting of oxygen (O_2), carbon dioxide (CO_2), and water vapour (H_2O), which replaces air in conventional combustion systems. The major advantage of this process is that the flue gas is composed almost exclusively of CO_2 and H_2O. Water vapour is easily removed from the exhaust stream by condensation, leaving CO_2 in high concentrations. This enables CO_2 to be efficiently captured for storage and use. The combination of the oxy-fuel process with CCUS enables near carbon-neutral combustion of fossil fuels. In addition, using biomass as a fuel for CCUS (BECCUS) can create a net carbon sink [5,6].

Due to the different properties of the combustion atmosphere compared to air, the chemical reactions as well as heat and mass transfer phenomena occurring on and

around the particles can no longer be described using the approaches developed for air combustion. Chemical reactions are particularly influenced by the high partial pressure of CO_2, which significantly affects both, the heterogeneous and gas-phase reactions. In heterogeneous reactions, the gasification of the remaining carbon solids (char) or diffusion inside the char pores can alter reaction dynamics. In homogeneous gas-phase reactions, high CO_2 concentrations increase the importance of the reverse of the main radical-producing reaction $O_2 + H \rightarrow OH + O$. Further, heat and mass transfer in a CO_2-containing atmosphere are affected in multiple ways. The CO_2 has a significantly higher molar heat capacity than the main air component N_2, thereby withdrawing more energy from the reaction zones. At high temperatures, CO_2 (and H_2O) are highly radiative molecules. The changed heat transfer directly impacts the heat-up process of the fuel particles, which affects the release of combustible gas species (pyrolysis) and the ignition behaviour. In contrast to O_2 and N_2, which have an effective Lewis number (defined as the ratio of thermal conductivity to diffusion coefficient) of approximately one, CO_2 has a significantly higher Lewis number. This can be particularly relevant for small-scale processes near the particle surface. The underlying coupled reaction-transport processes, particularly in the boundary layer of solid fuel particles, are currently only partially understood and, consequently, not fully considered in current state-of-the-art modelling approaches.

To close the existing knowledge gaps, the oxy-fuel combustion of solid fuels was investigated in the Collaborative Research Centre 129 "Oxyflame" funded by the *German Research Foundation* (DFG). The *Oxyflame* team comprises researchers from the fields of solid fuel and gas combustion, chemistry, thermodynamics, and fluid mechanics from the three participating locations: *RWTH Aachen University*, *Ruhr-Universität Bochum*, and *Technische Universität Darmstadt*.

1.2 Goals of Oxyflame

The effective and reliable design of large-scale oxy-fuel combustion systems requires a detailed understanding of the relevant chemical and physical processes across multiple orders of magnitude, i.e. from single molecular reactions over particles up to the entire combustion chamber. The need for this detailed understanding defines the scientific goals of *Oxyflame*:

- Development of a comprehensive understanding of all relevant mechanisms involved in the combustion of solid, pulverised fuels in an oxy-fuel atmosphere primarily composed of O_2, CO_2, and H_2O.
- Development of valid generalised models for combustion and transport phenomena in an oxy-fuel atmosphere, while accounting for all relevant effects at each scale.
- Development of physics-based, efficient simulation methods for the layout of oxy-fuel combustion chambers to allow for model-based design, optimisation, and sensitivity analysis.

As mentioned above, replacing air by a mixture of O_2, CO_2, and H_2O significantly alters combustion behaviour. This can result in modified chemical conversion rates, flame instabilities, or even local flame extinction and reignition. This also affects all relevant transport processes, which occur across length scales ranging from atomic scale $\mathcal{O}\left(10^{-10}\,\mathrm{m}\right)$ to typical furnace dimensions $\mathcal{O}\left(10^{1}-10^{2}\,\mathrm{m}\right)$. Related time scales range from chemical reactions $\mathcal{O}\left(10^{-9}\,\mathrm{s}\right)$ to the fuel residence time in large boilers, which is of the order of several seconds $\mathcal{O}(1\,\mathrm{s})$. To identify the dominant mechanisms underlying the coupled reaction-transport processes, this range of scales has been addressed within *Oxyflame*, both through generic laboratory-scale experiments and through larger-scale validation experiments of pulverised solid fuel combustion. Modelling approaches covering different scales have been considered ranging from molecular dynamics simulations over approaches that partially or even fully resolve turbulence all the way to a multi-physics and multi-scale description at the system-scale with large eddy simulation (LES).

1.3 Examined Fuels

To consider the effect of fuel type in experiments and model development within *Oxyflame*, fuels of different rank and elemental composition have been selected. The van Krevelen diagram in Fig. 1.1 depicts the fuel range by comparing the molar H/C ratio against the O/C ratio. The fuel spectrum covers coals as well as biomass in raw and torrefied state.

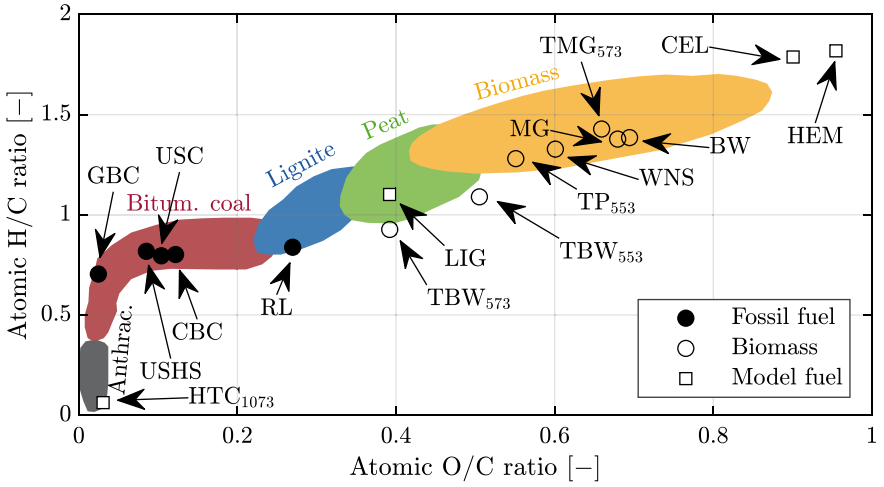

Fig. 1.1 Van Krevelen diagram of fuels used within *Oxyflame*. Fuel codes are listed in Tab. 1.1

Fossil fuels from various origins and ages served as a starting point in the experimental and modelling cycles and a reference to already existing research data. Two bituminous coals from the German Prosper-Haniel colliery (GBC) on the northern edge of the Ruhr area and the Minas Norte region in Colombia (CBC) serve as representatives of the oldest geological age. One US reference coal (USC) has been added for targeted comparisons and one high-sulphur fuel (USHS) allowed the investigation of pollutant formation. Rhenish lignite (RL) from the Hambach opencast mine is a representative of the younger geological age.

The selected raw biogenic fuels include one woody biomass (beech wood (BW)), one fast-growing energy plant (miscanthus × giganteus (MG)) and one agricultural residue (walnut shells (WNS)), all cultivated in Europe. These fuels exhibit diverse structural characteristics (woody or straw-like) and significantly different proportions of biomass structural components. Selected raw biomasses have been pre-treated by torrefaction at various temperatures and residence times. Torrefied biomasses possess properties comparable to "young" fossil fuels (e.g. Rhenish lignite), making them a suitable renewable alternative.

The fuel spectrum is supplemented by artificial fuels including extracted biomass components (cellulose (CEL), hemicellulose (HEM), and lignin (LIG)) and model fuels produced by hydrothermal carbonisation. The latter were used in experiments to study the catalytic activity of minerals by doping the base fuel with constituents such as Fe, K, and Na. Properties from proximate and ultimate analysis are listed in Table 1.1 for all fuels.

As the focus of *Oxyflame* was on pulverised solid fuel combustion, all fuels were milled and, in most cases, sieved to multiple size fractions typically spanning the overall range of 90–200 µm. Two exemplary particle size analyses for the fuels RL and WNS are provided in Fig. 1.2.

It is worth noting that research on waste-based fuels and larger particles was part of an *Oxyflame* spin-off. However, these findings are not included in this book but are documented in other sources [7–9].

Table 1.1 Properties of fuels investigated in *Oxyflame*. All values in mass-%

Code	Fuel name	Proximate analysis*			Elemental analysis•					
		Ash	Volat.	Fixed C◇	C	H	N	S	Cl	O◇
CBC	Colombian bit. coal (Minas Norte)	7.0	40.5	52.5	78.7	5.26	2.11	1.10	0.01	12.8
GBC	German bit. coal (Prosper-Haniel)	8.5	31.2	60.2	89.6	5.26	1.73	0.37	0.06	2.9
RL	Rhenish lignite (Hambach)	5.8	52.1	42.1	68.9	4.81	1.28	0.27	0.02	24.8
USHS	US high sulphur bit. coal	9.3	37.3	53.4	80.4	5.48	1.38	3.32	2.80	9.1
USC	US reference bit. coal (Pittsburgh #8)	12.3	37.5	50.2	81.3	5.39	1.64	0.38	–	11.3
TBW_{553}	Torrefied beech wood (553 K)	0.7	71.2	28.1	56.5	5.13	0.32	0.00	–	38.0
TBW_{573}	Torrefied beech wood (573 K)	1.0	58.6	40.5	62.3	4.81	0.35	0.01	–	32.6
TMG_{573}	Torrefied miscanthus (573 K)	4.1	63.0	32.9	49.9	5.94	0.21	0.00	–	43.9
TP_{553}	Torrefied poplar wood (553 K)	0.6	78.1	21.3	54.2	5.78	0.21	0.02	0.00	39.8
BW	Beech wood	0.4	85.3	14.3	48.9	5.64	0.23	0.02	–	45.2
MG	Miscanthus × giganteus	1.3	83.4	15.3	49.3	5.66	0.38	0.00	–	44.7
WNS	Walnut shells	0.4	81.1	18.5	52.1	5.77	0.28	0.02	0.29	41.8
CEL	Cellulose	0.3	95.2	4.5	42.4	6.32	0.30	0.00	–	50.9
HEM	Hemicellulose	3.7	84.7	11.6	41.1	6.23	0.21	0.10	–	52.3
LIG	Lignin	1.3	68.2	30.5	60.7	5.57	1.22	0.81	–	31.7
HTC_{1073}	Hydrothermally carbonised cellulose (1073 K)	0.0	3.0	97.0	95.6	0.50	0.00	0.00	–	3.9

∗: dry, •: dry and ash-free; ◇: by difference

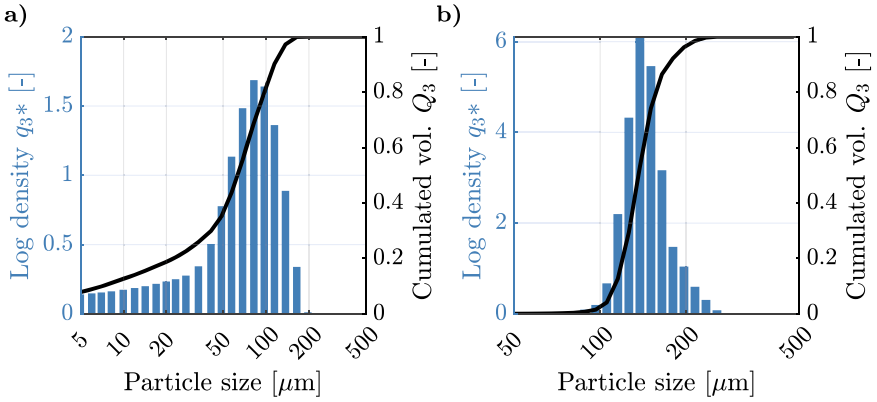

Fig. 1.2 Exemplary particle size analyses for **a**) unsieved Rhenish lignite (RL) and **b**) walnut shells (WNS) sieved by the manufacturer

1.4 Major Results of Oxyflame

The major results of *Oxyflame* are reported in this book, with a very brief overview given here, also outlining the chapter-wise content:

Parts I and II: Reaction Kinetics Measurements and Modelling
Flame and flow field development in the combustion chamber depend largely on volatile release and char combustion characteristics of the utilised solid fuel. To improve model approaches for oxy-fuel kinetics of pyrolysis and char conversion, a novel and extensive experimental database has been established. This database includes data gathered under realistic high heating rates for a wide variety of fuels and a broad range of different oxy-fuel atmospheres. Data comprise results from solid sampling and gas-phase analysis as well as data from optical measurements, such as single particle temperatures, size and shape evolution, for both ignited and non-ignited particles. The influence of catalytically active minerals such as Fe, K, and Na on pyrolysis-gas yields and char conversion was investigated. The findings confirmed that the catalytic activity of these minerals is relevant for the high heating rates under oxy-fuel conditions. Experimental analyses also included the study of sorption processes occurring on the fuel particles, leading to the development of a novel pore-structure-dependent sorption model that goes beyond current approaches. Regarding system-relevant corrosive effects, the release of minority species such as sulphur and chlorine was also examined.

The reactions and processes taking place in the carbon matrix were described on an atomic and molecular basis, particularly for the char burnout phase. It was shown that this allows to provide kinetic data that are based on defined molecular compositions and, thus, transferable between different solid fuels independent of their origins. For a knowledge-based design, fast and predictive models that depend on the chemical structure of the fuels are required for CFD simulations. Hence, the

well-known CPD model for pyrolysis has been transferred into a modular object-oriented formulation that allows for flexible coupling with different particle and reactor models. The modified CPD model was able to replicate all boundary conditions of the experimental test rigs within *Oxyflame*. It also has been successfully tested with data sets of extracted biomass components. Furthermore, the popular CCK code has been extended by a novel model for thermal annealing of biomass. To finally provide a seamless model for LES that covers pyrolysis and char burnout kinetics simultaneously, a more holistic approach was pursued, which is based on the CRECK-S model from *Politecnico di Milano*. This model has been calibrated based on the experimental results of *Oxyflame*.

For the gas-phase kinetics, detailed measurements have been performed in counterflow-diffusion flames using time-of-flight mass spectrometry. Different fuel blends representing volatile gases have been investigated in air and oxy-fuel atmosphere. Furthermore, the impact of different oxygenated and nitrogen-containing aromatic compounds on combustion and pollutant formation was studied in the same setup as tar representatives with particular relevance for biomass combustion. These data were used to develop well-validated detailed and reduced kinetic models for the gas-phase kinetics of volatiles from coal and biomass.

Part III: Particle Flow Interactions

For examining the coupled reaction-transport processes occurring on the meso-scale, the particle-laden two-phase flow assuming typical conditions of solid fuel flames was investigated using both, canonical experiments and DNS modelling. The DNS modelling for non-reacting conditions using up to 70,000 fully resolved particles in isotropic turbulence gave new insights into the interaction of flow field and the motion of spherical and elliptical particles. These results were used, e.g. to derive drag correlations for point-particle approaches. Experimental studies of individual particles and small particle groups in a laminar flow field revealed the changes in flame topology when progressing from individual particle combustion to particle group combustion. For measurements on particles moving in turbulent jets, an advanced high-speed measurement technique was developed and successfully used as a counterpart to respective DNS studies. On the modelling side, DNS for single particles in air and O_2/CO_2 environments showed that elevated CO_2 concentrations consume H radicals during devolatilisation, leading to a slowdown in chain-branching reactions and consequently to a destabilisation of the combustion process.

Part IV: Flame Studies

Regarding the investigations of flames and respective flow fields in large-scale combustion chambers, multiple unique data sets were compiled by means of cascaded experiments. Parameters for these investigations were oxidiser atmosphere, oxygen concentration, and fuel. Detailed investigation of the near-burner environment in a fully optically accessible combustor, operated with a supporting gas flame to compensate for the associated heat losses due to the large windows, produced unique data sets that are useful not only for validating solid fuel flame models but also for supporting the interpretation of results obtained in larger combustors with less opti-

cal access. Using similar burners in a pilot-scale combustion chamber, and operating it purely with solid fuel, the effects of various O_2/CO_2 mixtures on the flame shape could be investigated in detail. To bring the results closer to typical industrial scales, the burner design has been scaled up and was employed for an application-oriented validation of the results, using a combustion chamber with a thermal output of up to $1\,MW_{th}$.

Part V: Radiation
Another physical effect that comes into play mostly for larger combustors is thermal radiation, especially when the gas phase contains high concentrations of H_2O and CO_2. For this reason, the gas phase radiation has been modelled using correlated-k approaches, including particle radiation. This modelling approach was supported by detailed numerical investigations of the effect of particle shape and composition as well as on particle volume concentration. Various measurement setups were developed to compensate for the lack of biomass refractive index data. In addition, measurements of particle emissivity changes during char burnout provided valuable input for the particle radiation modelling.

Part VI: Full-Scale Modelling
The primary research objective of *Oxyflame* is to investigate, understand, and predict oxy-fuel combustion, spanning from small-scale laboratory configurations to semi-industrial applications. To achieve a comprehensive combustion modelling of various solid fuels, the scientific challenges can be categorised into four key areas: 1) solid fuel conversion, 2) gas-phase turbulence-chemistry interaction, 3) turbulent flow, mixing, and particle dynamics, and 4) radiation. Groundbreaking advancements have been achieved in these fields, both in depth and breadth.

Building on this understanding, the 3-D computational fluid dynamics (CFD) framework *OxySim-129* has been developed and is the focus of Chap. 19. *OxySim-129* extends the open-source CFD code OpenFOAM®, offering unprecedented predictive capabilities for the combustion of pulverised carbonaceous solid fuels under both oxy-fuel and standard air conditions at various reactor scales. Advanced detailed kinetic models for the solid phase have been seamlessly coupled with the turbulent reacting gas phase. Additionally, novel flamelet models have been developed and integrated into large eddy simulations (LES) of turbulent multiphase gas flows. The framework also incorporates fully coupled radiation models for the gas phase, particles, and their interactions, ensuring a comprehensive and highly accurate predictive tool.

Committed to the principles of open science, *Oxyflame* follows the FAIR data principles: Research data and software must be findable, accessible, interoperable, and reusable. In alignment with this philosophy, the *OxySim-129* software package will be released as open-source, providing access to both the scientific community and interested industrial partners.

Acknowledgements This work has been funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation)—215035359—SFB/TRR 129 'Oxyflame'.

References

1. United Nations Framework Convention on Climate Change. *Paris Agreement*. United Nations. 2015.
2. Intergovernmental Panel on Climate Change. *Global Warming of* 1.5 °C: *An IPCC Special Report on the Impacts of Global Warming of* 1.5 °C *Above Pre-Industrial Levels and Related Global Greenhouse Gas Emission Pathways, in the Context of Strengthening the Global Response to the Threat of Climate Change, Sustainable Development, and Efforts to Eradicate Poverty*. 2018.
3. Intergovernmental Panel on Climate Change. *Climate Change 2023: Synthesis Report: A Report of the Intergovernmental Panel on Climate Change*. Intergovernmental Panel on Climate Change (IPCC), 2023. https://doi.org/10.59327/IPCC/AR6-9789291691647.
4. International Energy Agency. *World Energy Outlook 2019*. 2019.
5. Gough, C., Thornley, P., Mander, S., Vaughan, N. and Falano, T., eds. *Biomass Energy and Carbon Capture and Storage (BECCS): Unlocking Negative Emissions*. Hoboken, New Jersey, USA: John Wiley & Sons, 2018.
6. Tanzer, S. E. and Ramírez, A. "When Are Negative Emissions Negative Emissions?" *Energy & Environmental Science* 12.4 (2019), 1210–1218. https://doi.org/10.1039/C8EE03338B.
7. Streier, R., Veckenstedt, I., Deck, T., Lampe, K. and Scherer, V. "Analysis of the Impact of RDF Combustion on Cement Clinker Quality in a Superstoichiometric Oxy-Fuel Atmosphere by CFD Simulations". *Combustion Science and Technology* online (2023), 1–19. https://doi.org/10.1080/00102202.2023.2239463.
8. Streier, R., Wirtz, S., Aleksandrov, K., Gehrmann, H.-J., Stapf, D., Zhang, M., Vogelbacher, M., Matthes, J. and Scherer, V. "Determination of the Statistical Distribution of Drag and Lift Coefficients of Refuse Derived Fuel by Computer Vision". *Fuel* 352 (2023), 128847. https://doi.org/10.1016/j.fuel.2023.128847.
9. Solana Gómez, R., Streier, R., Pielsticker, S., Scherer, V. and Kneer, R. "Experimentelle Bestimmung der Pyrolysekinetik von Ersatzbrennstoffen". *31. Deutscher Flammentag*. Berlin, Germany, 2023.