

The lag between micro- and macro-mixing in compressed fluid flows



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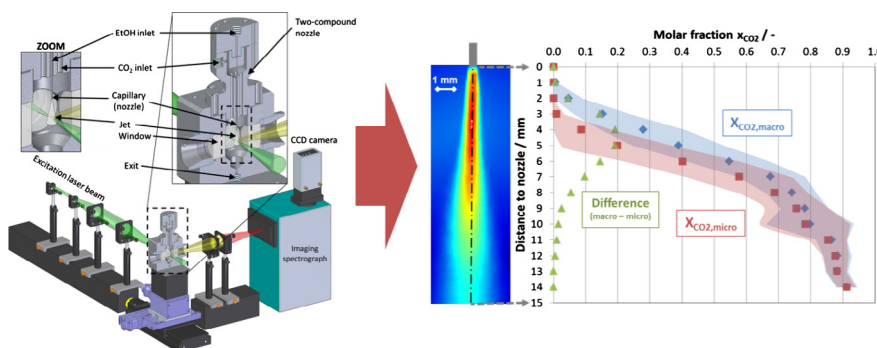
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HIGHLIGHTS

- Simultaneous remote composition analysis on micro- and macro-scale.
- Based on spat. and temp. resolved one-dimensional *in situ* Raman spectroscopy.
- Lag between macro- and micro-mixing quantified spatially resolved.
- Lag between macro- and micro-mixing quantified along a line.

GRAPHICAL ABSTRACT



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ABSTRACT

We report the application of a novel optical Raman-based measurement technique for the simultaneous determination of the progress of mixing on the micro- and on the macro-scale. The introduced measurement technique is applicable to mixing systems containing one compound, which potentially can form hydrogen bonds, such as water, alcohols or amines, and does not rely on the addition of traces of indicator compounds. Here we demonstrate its applicability by analyzing the lag of micro-mixing behind macro-mixing when liquid ethanol is injected into a supercritical bulk environment mainly composed of carbon dioxide (CO₂). While the degree of mixing on the macro-scale is determined from the ratio of the intensities of characteristic Raman signals of ethanol and CO₂, the degree of mixing on the micro-scale is determined from the shape of the O–H stretching vibration Raman signal of ethanol, which is a function of the development of hydrogen bonds.

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1. Introduction

Mixing is a crucial step for many process technologies. Reactions or precipitation mechanisms are governed by interactions between molecules and thus are largely determined by the degree

of mixing on a molecular level (micro-scale), which is not easily accessible with conventional measurement techniques. Therefore we here present a Raman-based measurement technique which simultaneously probes the degree of mixing on the micro- as well as on the macro-scale.

In rocket (Mayer et al., 2000; Roy et al., 2013) and internal combustion engines (Falgout et al., 2016; Wensing et al., 2015) as well as in hydrothermal flames (Meier et al., 2016) for spallation drilling (Rothenfluh et al., 2011) or waste water treatment (Wellig et al., 2009; Queiroz et al., 2015), the fuel and the oxidizer have to be

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mixed before the onset of the combustion. Different “particles-from-sprays” processes, which also take place at elevated pressure, rely on a fast mixing of either a solution with a blowing agent (Liparoti et al., 2015), a solution with an antisolvent (Braeuer et al., 2011) or an emulsion with an extraction agent (Kluge et al., 2009). For the generation of polyurethane foams the isocyanate and the carbon dioxide (CO₂) containing polyol have to be mixed homogeneously before the initialization of the polymerization and the solidification of the foam (Michaeli and Heinz, 2000). All these processes have in common that they take place at elevated pressure, up to 25 MPa. Considering the critical parameters of example pure compounds, which are for water 647.1 K & 22.1 MPa, for CO₂ 304.2 K & 7.4 MPa, for nitrogen 126.2 K & 3.4 MPa and for ethanol 514 K & 6.3 MPa, it becomes obvious that these compounds and mixtures of them are treated at conditions at which they feature a considerable compressibility and thus at elevated pressures can be said to be compressed.

Compressed fluids – here we use the wording “fluid” as we do not want to specify the fluid’s state as either gaseous, supercritical or eventually liquid – feature a kinematic viscosity ν which regarding its value exceeds that of the mass diffusivity D . Therefore the dimensionless Schmidt number

$$Sc = \frac{\nu}{D} \quad (1)$$

of compressed fluids is usually between $Sc \approx 1$ for non-compressed gases and $Sc > 100$ for liquids. The Schmidt number of a fluid in the vicinity of its critical point is usually $Sc \approx 10$. Physically, the Schmidt number relates the thickness of the hydrodynamic mixing layer to the thickness of the mass transfer layer. While the thickness of the hydrodynamic mixing layer is proportional to the kinematic viscosity, the thickness of the mass transfer layer is proportional to the diffusivity. The hydrodynamic mixing layer is the layer containing the velocity gradient between two fluids A and B flowing with different velocities. The mass transfer layer is the layer containing the composition gradient between two fluids A and B of different composition. Turbulent hydrodynamic mixing layers break down into eddies, which again break down into smaller and smaller eddies (Richardson, 1922), until a smallest size scale, the so called Kolmogorov scale, is reached at which the eddy’s rotational energy is dissipated (Kolmogorov, 1941; Davidson, 2004). As long as eddies rotate, the thickness of the hydrodynamic mixing layers between the eddies and the surrounding fluid is still determined by the viscosity. At the time when the eddies cease to rotate, the velocity gradient between the previous eddy structure and the surrounding fluid becomes zero and thus also the hydrodynamic mixing layer disappears, while the mass transfer layer remains. Assuming the hypothetical case that there is no mass diffusion during the flow-driven macro-mixing, then the smallest eddy structures would still contain solely fluid A and would be surrounded by fluid B. Such a state we refer to as macroscopically mixed, but microscopically not-mixed. Macroscopic mixing is determined by the viscosity and by the flow, while microscopic mixing is solely governed by the mass diffusivity and homogenizes the mixture on a molecular level. Summarizing, for many non-compressed gases, for which $Sc \approx 1$ we therefore can assume that at the time when the fluids A and B are mixed on a macro-scale, they are also mixed on a micro-scale. Such a system would not feature composition heterogeneities on a micro-scale, when it is already homogeneous on a macro-scale. This is different for liquids, where $Sc > 100$ describes that mass diffusion is still ongoing at times when macroscopic mixing is already over. Such a system would feature long-living composition heterogeneities on a micro-scale when it is already homogeneous on the macro-scale. For compressed fluids the situation is in between. The lifetime (time-scale) of the obtained micro-scale heterogeneities can be longer than the reaction time in diesel

combustion or the nucleation time in precipitation processes. This implies that reactions or particle nucleation can start in systems which are not yet homogeneously mixed on the micro-scale. Then the prevailing composition heterogeneities on the micro-scale, which spread over the entire mixture, make homogeneous reaction or nucleation conditions impossible, which influences also the reaction products and the generated particles. There will be regions in which fluid A and B are mixed on a molecular level, regions in which they are not yet mixed and regions in which the mixture state is in between. In other words, the micro-scale heterogeneities can in principle be translated into the heterogeneities of the products made with any high pressure process containing compressed fluids, if the product formation starts in a system still heterogeneous on the micro-scale.

Fig. 1 shows the detection section of a typical planar laser diagnostics experiment for the analysis of the mixing processes taking place in a hypothetical jet-mixing experiment. Here a “black” fluid is injected as a jet into a “white” bulk fluid. In the jet mixing zone downstream the nozzle the black and the white fluids mix. The cross section of the jet, which is irradiated by the planar light sheet is imaged via one lens onto a charged coupled device (CCD)-detector. One pixel of the CCD-chip is enlarged as an insert and decorated with a question mark in Fig. 1. The pixel is filled grey which is supposed to indicate that at this location in the illuminated cross section of the jet, one can find 50% of the black fluid and 50% of the white fluid, together resulting in grey.

Unfortunately, due to the limited spatial resolution of measurement techniques, no information can be extracted on the degree of mixing below the spatial resolution limit. The hypothetical mixing states I to VI in Fig. 1 all represent scenarios where one would find equal portions of black and white fluid. But only state I shows a scenario in which the two fluids are really mixed. States II to VI represent scenarios which are macroscopically mixed, but are not yet mixed on a micro-scale. State VI can for example represent a structure of a previous Kolmogorov scale eddy which is still visible just because diffusion is so slow that the relaxed eddy structure still contains only the black fluid.

Therefore the spatial resolution of measurement techniques, which usually is above the scale of the micro heterogeneities, makes a direct investigation into micro-mixing impossible. In fact, techniques which potentially can analyze micro-mixing must rely on probing phenomena taking place beyond their spatial resolution, so on the molecular scale. Thus, known methods rely on the addition of substances acting either as pH-indicator (Koochesfahani and Dimotakis, 1986; Lehwald et al., 2010), as energy transfer indicator (Yip et al., 1994; Braeuer et al., 2011) or as educts for consecutive competing reactions (Baldyga and Bourne, 1989; Kling and Mewes, 2004; Bałdyga and Bourne, 1999). Unfortunately this is not an option for processes operated close to the critical parameters of the fluids treated in them, as these processes are rather sensitive towards minor modifications. The addition of traces of indicator-substances could heavily affect the thermodynamics, the fluid properties and with this mixing and mass transfer.

On this purpose we developed a non-invasive tracer-free and remote measurement technique which *in situ* probes simultaneously the degree of micro- and macro-mixing in an example turbulent jet mixing experiment. The jet mixing configuration is in the style of that of the supercritical antisolvent (SAS) technique for the generation of fine particles from compressed fluid systems (Braeuer et al., 2011); certainly here without the formation of particles, as micro- and macro-mixing is in the focus of this study instead of particle formation. The decisive advantage of the here presented Raman method is that no indicator-substance has to be added to the fluids. The degree of micro-mixing is extracted from the probed development of hydrogen bonds, an interaction

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