Catalysis Today 216 (2013) 104–110

Contents lists available at SciVerse ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Understanding the operation and preparation of diesel particulate filters using a multi-faceted nuclear magnetic resonance approach

N.P. Ramskill[a,*], L.F. Gladden[a], A.P.E. York[b], A.J. Sederman[a], J. Mitchell[a], K.A. Hardstone[b]

[a] Department of Chemical Engineering and Biotechnology, University of Cambridge, Cambridge CB2 3RA, UK
[b] Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH, UK

ARTICLE INFO

Article history:
Received 2 April 2013
Received in revised form 19 June 2013
Accepted 22 June 2013
Available online 24 July 2013

Keywords:
Diesel particulate filter
Structured catalysts
Drying
Transport phenomena
Fluid dynamics

ABSTRACT

In the present study, a range of magnetic resonance techniques have been applied to investigate two aspects associated with the preparation and operation of diesel particulate filters (DPFs). First, magnetic resonance techniques are used to investigate the evolution of the water distribution within a DPF during a drying process, typical of that associated with the preparation of a catalyzed DPF. For comparison, the drying characteristics of a flow-through monolith were also studied. In the flow-through monolith, which has impermeable walls, the drying front was observed to propagate from the very start of drying. Conversely drying in the DPF was characterized by uniform, axial drying up to a critical point, after which a drying front moved progressively through the DPF until it was fully dried. An explanation of this two-stage process, by taking into consideration the permeability of the channel walls, is suggested. Second, magnetic resonance imaging velocimetry was used to investigate the flow through a DPF. It is demonstrated that magnetic resonance imaging velocimetry is able to quantitatively and non-invasively characterize the flow fields in two DPF substrates, with asymmetric and symmetric channel geometries, respectively.

1. Introduction

Internal combustion engines, whether they use petrol or diesel fuel, produce a number of species harmful to health and the environment. The four main pollutants of concern are carbon monoxide (CO), nitrous oxides (NO_x), hydrocarbons (HC) and particulate matter (PM). All four of these pollutants are subject to increasingly stringent emission limit legislation such as the European, US and Japan Emission standards set by the respective governments [1]. Although, in recent years, automotive manufacturers have optimized the engine design to improve efficiency, on-board aftertreatment systems are required to ensure that compliance with the legislation is achieved. Nowadays the majority of new vehicles, both gasoline and diesel (light and heavy duty), are fitted with autocatalysts for the abatement of pollutants from the exhaust gas to render them at acceptable levels. This work will focus on DPFs which have been developed for the abatement of emissions from diesel engines.

At their simplest level DPFs are bare, and are made of a porous ceramic (cordierite, silicon carbide, aluminium titanate). However, in order to meet the increasingly stringent legislated limits, multifunctional systems incorporating a catalyst have been developed. For instance, the continuously regenerating trap (CRT®) which comprises of a diesel oxidation catalyst (DOC) upstream of a bare DPF substrate has been developed to include a catalyst over which NO is re-oxidized to NO_2 to enhance the filter regeneration performance; this system is referred to as the catalyzed CRT® (CCRT®) [2]. Multifunctional emissions abatement systems have also been developed in the interest of reducing packaging volume, space onboard the automotive and ultimately the cost for vehicle manufacturers. For instance, the SCRF® has been developed to combine the DPF and SCR by coating the NO_x abatement catalyst onto the DPF substrate [3]. The catalyst is applied in the form of a washcoat which is subsequently dried to remove the water. In the case of catalyzed DPF, drying is one of the final stages in the manufacturing process and can have a significant effect on the product quality. It has previously been shown [4,5] that non-ideal drying can result in the macroscopic redistribution of the catalyst resulting in an accumulation at the peripheries of the monolith. It has also been shown that catalyst migration in monoliths can occur on the microscale of the substrate wall and washcoat during drying. The capillary forces acting due to the difference in the pore size between the macropores of the substrate and the micropores of the washcoat, as determined by XPS measurements, will result in a surface enrichment of the catalyst. This enrichment of the catalyst in the washcoat layer of ceramic monoliths during drying has also been observed using MRI [6]. In addition, drying is an extremely energy intensive process therefore a better understanding of the

---

[*] Corresponding author. Tel.: +44 1223 761628.
E-mail address: npr24@cam.ac.uk (N.P. Ramskill).

0920-5861/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cattod.2013.06.023

drying mechanism is required to allow for optimal drying cycles to be designed to improve the overall efficiency of the process.

Traditionally drying is studied using gravimetric methods, humidity and temperature measurements from which the drying and rates of drying curves can be determined [7]. Although these techniques are well established in both industry and research, they are somewhat limited in that they are only able to provide bulk measurements and the process itself must be treated as a black box. The application of MRI to study the drying process enables spatially resolved measurements of moisture content to be made non-invasively thus offering insight to the process that was not previously possible. From the spatially resolved measurements of moisture content, local mass transfer phenomena can be investigated and used to determine how they are manifested in the overall drying mechanism. These techniques can therefore be used to elucidate upon how the structure of the DPF substrate influences the kinetics of the drying process. Whilst, superficially, DPF are similar to the flow-through monolith systems studied in [8–11]; due to the porous, and hence permeable, walls separating the channels, DPFs are characterized by fundamentally different liquid and gas mass transfer characteristics. In the present work, MR techniques are used to demonstrate how the drying characteristics of the more porous DPF structure differ from those of a simple flow-through monolith.

The second part of the work uses magnetic resonance imaging (MRI) velocimetry [12,13] to non-invasively investigate the transport of the exhaust gas in DPFs. MRI velocimetry has previously been demonstrated to be an extremely useful tool in the study of dynamic systems with applications such as investigating structure–hydrodynamic relationships, and the validation of computational modelling with experimental evidence [14]. To date, the majority of the work on the hydrodynamics of gas flow in DPFs has been computational modelling [15–20]; gas flow through the DPF will influence soot deposition within it. In turn, the soot deposition profile within the DPF channels has been shown to have a significant effect on the filter performance in terms of filtration efficiency, pressure drop and regeneration [18–20]. It has been shown that the initial deposition of particles occurs preferentially at the end of the inlet channel; deposition at the beginning of the inlet channel is prevented due to the inertial forces of the gas flow created by the *vena contracta* at this point. However inertial effects appear to have a lesser effect on the deposition of the smaller soot particles and the soot deposition profile closely matches the through-wall velocity profile [18,19]. Therefore a good understanding of how the flow field of the exhaust gas influences the deposition and dispersion of the soot particles along the length of the filter channels is necessary. The aim of this work is therefore to demonstrate the nature of MRI velocimetry data that can be acquired in a DPF and which will be used for comparison with the outputs of numerical simulations in later work. In this work we report velocimetry experiments of a liquid flow; ongoing experiments are addressing gas flow.

The structure of the paper is as follows. First, a brief introduction to the principles of MRI and motion encoding of an image will be given providing the reader with a conceptual framework for the results and their interpretation. Second, MRI has been used to compare the drying processes occurring within a DPF and flow through monolith. Finally, the application of MRI velocimetry to acquire spatially resolved measurements of the flow field in a DPF is demonstrated.

2. Principles of magnetic resonance imaging

In this research, magnetic resonance (MR) techniques are employed to address two aspects of DPFs associated with their preparation and operation. MR techniques have gained prominence in the field of chemical engineering research as they can be used to non-invasively provide a wealth of information pertaining to the chemical and dynamic nature of a range of opaque systems of interest [14]. MR techniques have found a particularly strong application in the study of porous media such as catalysts [21–23], construction materials [24–26] and pharmaceuticals [27,28]. MRI can also be used as a motion sensitive technique to acquire spatially resolved measurements of transport characteristics such as velocity, dispersion and molecular diffusion [12,13]. MRI velocimetry is therefore an extremely useful tool in the study of dynamic systems with applications such as investigating structure-hydrodynamic relationships, and validation of computational modelling with experimental evidence [14].

This section provides the reader with a brief introduction to the principles of magnetic resonance imaging and velocimetry. The interested reader is directed to the texts by Callaghan [29] and Haacke [30] and review articles by Mantle and Sederman [12] and Caprihan and Fukushima [13] for further detail.

When NMR active nuclei (e.g. ^{1}H or ^{13}C) are placed in an external magnetic field (B_0), the nuclei will precess at a characteristic frequency known as the Larmor frequency (ω_0) as given by:

$$\omega_0 = \gamma B_0 \tag{1}$$

where γ is the gyromagnetic ratio which is characteristic of the nuclei under observation. Considering the system in the rotating frame at reference frequency, ω_0, spatial dependence of the precession frequency is achieved by applying a spatially dependent magnetic field gradient, **G**, and can be expressed as follows:

$$\omega(\mathbf{r}) = \gamma \mathbf{G} \cdot \mathbf{r} \tag{2}$$

where $\omega(\mathbf{r})$ is the precession frequency at the **r** which is the position vector $[x\,y\,z]$. The precessing nuclei in a volume element induce a voltage in the receiver coil and the complex NMR signal, $S(t)$, is detected in the time domain. The time-dependent signal is then Fourier transformed into the frequency domain where it is represented by the spin-density function, $\rho(\mathbf{r})$. The Fourier conjugate relationship between the time and frequency domain of the NMR signal is shown below:

$$\begin{aligned} S(t) &= \iiint \rho(\mathbf{r}) \exp[i\gamma \mathbf{G} \cdot \mathbf{r}t]\mathrm{d}\mathbf{r} \\ \rho(r) &= \iiint S(t) \exp[-i\gamma \mathbf{G} \cdot \mathbf{r}t]\mathrm{d}t \end{aligned} \tag{3}$$

From this a spin-density map, i.e. an image, is obtained by taking the modulus of the complex function, $\rho(\mathbf{r})$. In the case of the drying experiments, it therefore follows that the spin-density map provides spatially resolved measurements of the water content within the monolith sample.

In the case of MRI velocimetry, one is interested in the phase of the complex signal as this provides information pertaining to the motion of the spins. Describing the position of the spins following the path, $\mathbf{r}(t)$, in terms of Newtonian kinematics neglecting acceleration and higher order terms, the phase, $\phi(\mathbf{r}, t)$,, of the signal in the presence of the magnetic field gradient, $\mathbf{G}(t)$, is given by the following expression:

$$\phi(\mathbf{r}, t) = \gamma \mathbf{r} \cdot \int \mathbf{G}(t)\mathrm{d}t + \gamma \frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t} \cdot \int t\mathbf{G}(t)\mathrm{d}t + \cdots \tag{4}$$

The total phase of the NMR signal is determined by the relative contributions of the zeroth (position) and first (velocity) moments of the gradient waveform which are represented by the first and second terms on the right hand side of Eq. (4) respectively. Considering an NMR experiment whereby the spins are subjected to bipolar