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A study of dimethyl carbonate conversion and its impact to minimize soot and NO emissions

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Abstract

Fuel reformulation through the use of oxygenated compounds has been considered as an interesting option both, to reduce the harmful soot emissions and to overcome the dependence on fossil fuels, since many of them are bio-derived fuels. Dimethyl carbonate (DMC) is of interest as oxygenated fuel additive since it presents a relative high oxygen content as compared with other additives and suitable characteristics to be used in combustion systems. The present work includes the analysis of different fundamental aspects of the DMC combustion process: its oxidation behavior (through experimental and computational analysis), its tendency to produce soot and the role of the NO presence in the reaction system. Experiments are performed under well controlled conditions using specifically designed flow reactor systems. Results obtained contribute to extend the available experimental database on DMC, and show the low tendency of DMC to form soot compared to other oxygenates and its capacity to contribute to NO reduction under specific fuel-rich conditions. Modeling calculations are able to reproduce reasonably well the experimental trends observed, and highlight the sensitivity of the results to the thermodynamic data of DMC and DMC derived species.

Keywords: DMC; Soot; NO; Oxygenated additives; Combustion

1. Introduction

In the line of replacing or minimizing the use of fossil fuels, different alternative fuels such as biofuels are of increasing interest in the research community. Particularly, oxygenated compounds, that can be obtained in biorefinery processes, either used directly as fuel or as additives to diesel fuels, can be appropriate to reduce the emissions of soot in diesel engines.

Ren et al. [1] analyzed the influence of blending different oxygenated compounds (esters, ethers and alcohols) with diesel on the combustion and emissions of a diesel engine. The authors observed that,

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regardless of the kind of oxygenate additive, soot emissions were decreased, in particular, with the increase of the oxygen mass fraction in the blends, without increasing the NO_x emissions and without reducing engine thermal efficiency. Hydrocarbons (HC) concentrations also decreased with the increase of oxygen mass fraction in the blends. Westbrook et al. [2] conducted a chemical kinetic modeling study of the effects of oxygenated compounds with different functional group on soot emissions from diesel engines, and observed that for the same mass fraction of oxygen, esters were less effective than ethers or alcohols. In this research line, Pepiot-Desjardins et al. [3] analyzed the influence of the functional group for soot reduction tendency of oxygenated fuels. They highlighted two main factors that can decrease the tendency to form soot precursors: the oxygen content in the molecule and the dilution effect due to the replacement of part of the fuel by less sooting precursor compounds. Other important properties of fuel additives listed by McEnally and Pfefferle [4] to reduce soot are: a small number of carbon atoms in their structure, the presence of interspersed oxygen atoms within the carbon chain and the absence of ramifications. In addition, to obtain a good performance of the fuel-oxygenated additive blend, the cetane number should be around 50–60 and the oxygen weight content in the blend between 10% and 20% [5].

Considering these characteristics, dimethyl carbonate (DMC), $CH_3OCOOCH_3$, has been suggested as a promising oxygenated additive to diesel fuels due to its high oxygen content [6,7], the absence of carbon–carbon atomic bonds, suitable boiling point and solubility in diesel fuel [7]. DMC has been also considered as an option for replacing methyl tertiary butyl ether (MTBE) in commercial gasoline to meet with Clean Air Act specification for oxygen in gasoline [8]. In addition to its good properties as an additive to diesel fuels, DMC can be synthesized by transesterification of cyclic carbonates with methanol; and these two components can be obtained from biorefinery processes [9,10]. Preliminary results on the use of DMC as a fuel additive in a diesel engine, equipped with exhaust gas recirculation, suggest that both lower soot and NO_x emissions can occur [e.g. 11]; however, the relative importance of using DMC as an additive on these emissions is unknown. Under laboratory scale conditions, Chen et al. [12] investigated the effect of different oxygenated compounds, including DMC, on laminar premixed low pressure (30 Torr) n-heptane flames. The authors observed an early formation of CO_2 in the DMC-doped flame, which was attributed to the decomposition of DMC and its subsequent intermediates. They also concluded that the C_1–C_5 hydrocarbon intermediates and benzene concentrations decreased when any of the oxygenated compounds were added to the n-heptane flame.

Although there is evidence that it is possible to add fractions of DMC to both gasoline and diesel fuels maintaining a good engine performance [8], laboratory scale studies regarding this compound are very limited despite the importance of these studies to characterize the reaction scheme involving its conversion process. Therefore, there is a clear need to develop further studies to understand how the oxidation of this compound occurs and to investigate its contribution to the minimization of pollutant emissions.

In 1997, Bilde et al. [13] investigated the atmospheric chemistry of DMC in the 252–370 K temperature range by using flash photolysis-resonance fluorescence techniques, to address the environmental impact of DMC in the case that it is released into the atmosphere. The authors concluded that, under these conditions, the reactivity of DMC toward OH radicals is low and is comparable to that of ethane. Subsequently, Sinha and Thomson [14] performed an experimental study of the oxidation of DMC in a diffusion flame, at atmospheric pressure and in the 200–2000 K temperature range. They outlined that the conversion of DMC produces very low levels of methane, ethane, ethylene, and acetylene, due to the presence of oxygen on the central carbon in DMC that favors the breakage of the O–CO bond, forming methoxy radical. The experimental results from this study were further used to develop a chemical kinetic mechanism for DMC oxidation [6]. In this way, Glaude et al. [6] proposed a reaction mechanism for the oxidation of DMC and used it to kinetically analyze its combustion in an opposed flow diffusion flame. They identified the reactions with H and OH radicals as the main consumption paths of DMC.

Recently, Hu et al. [15] have published an experimental and kinetic modeling study on ignition delay times, in the 1100–1600 K temperature range, for equivalence ratios in the range ϕ=0.5–2.0. Their results indicate that the DMC is mainly consumed through H abstraction and that unimolecular decomposition is not relevant under their conditions.

To our knowledge, up to date, these are the only studies that address the conversion process of DMC under well-characterized laboratory conditions. All of them have been focused on the conversion of DMC, both experimental and kinetic modeling points of view, but so far the studies have not concentrated on the formation of pollutant emissions. Therefore, the present study on the conversion of DMC over a wide range of operating conditions, and in the presence of NO, provides necessary experimental data, both to get insight into the phenomena controlling the process and to improve and update a gas-phase combustion scheme applicable in different reaction environments. In particular, emphasizing the impact of DMC addition on the emissions of pollutants, specifically on soot formation and NO reduction.

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