A combined modeling and experimental study on low- and high-temperature oxidation chemistry of OME3 as novel fuel additive

Kevin De Ras*[1], Ruben Van De Vijver[1], Hwasup Song[2], Luc-Sy Tran[2], Marvin Kusenberg[1], Thomas Panaget[2], Joris Thybaut[1], Guillaume Vanhove[2], and Kevin Van Geem†[1]

[1]Laboratory for Chemical Technology, Ghent University, Technologiepark 125, B-9052 Gent, Belgium – Belgium

[2]Physicochimie des Processus de Combustion et de l'Atmosphère - UMR 8522 – Université de Lille, Centre National de la Recherche Scientifique : UMR8522, Centre National de la Recherche Scientifique : UMR8522 – France

Abstract

The present research focuses on combined modeling and experimental work on the combustion of oxymethylene ethers (OMEs). OMEs are promising synthetic fuels which can be produced in a carbon-neutral manner starting from captured CO2 and renewable energy. Moreover, blending them with conventional diesel reduces soot emissions because of the absence of carbon-carbon bonds. This results in less harmful emissions and contributes to a more sustainable transport sector as aimed by the Paris climate agreement objectives. To promote the use of these kind of molecules as fuel additive, it is important to understand their low- and high-temperature combustion kinetics. The development of detailed microkinetic models provides this fundamental insight and enables predictive simulations for combustion applications.
During the last decade, great progress has been made in the construction of reliable kinetic models for numerous technologically important radical chemistry processes. The resulting models typically contain hundreds of species, and several thousands of associated reactions. The manual generation of microkinetic models would be a tedious, error prone and often incomplete process. To prevent this, automatic kinetic model generation routines have been developed to systematically develop models, such as Genesys at the Laboratory for Chemical Technology (Ghent University) [1]. A kinetic model for both oxidation and pyrolysis has been developed for OME3 based on first principles using Genesys.

A prerequisite for the generation of detailed kinetic models is the availability of accurate thermodynamic and kinetic data for species and reactions respectively. Ideally, these parameters are available from experiments or high-level quantum chemical calculations. Since these methods are expensive and time-consuming, Genesys instead often relies on approximation methods such as group additivity and rate rules. In this work, thermodynamic and kinetic parameters are obtained from quantum chemical calculations at the CBS-QB3 level of theory for important reaction pathways for both low- and high- temperature oxidation of

*Speaker
†Corresponding author: Kevin.VanGeem@UGent.be

OME3. The results of these calculations are extrapolated to be valid for long-chain OMEs by regression of new group additive values and rate rules.

Within Genesys, the possible reactions are generally defined in terms of reaction families, e.g. hydrogen abstraction by molecular oxygen from a secondary carbon atom. Reaction families from earlier studies on smaller oxymethylene ethers such as dimethoxy methane [2] are taken over and applied for the OME3 model. The outcome is a model containing the chemistry for OME3. To include the chemistry of smaller (oxygenated) hydrocarbons in the final model, the Genesys model is merged with the AramcoMech 1.3 base model [3].

Both flat flame burner and rapid compression machine experiments have been performed with OME3 for validation of the combustion model. The flame experiments are performed at 0.053 bara and with a fuel composition of 20 mol% OME3 and 80 mol% CH4. Some measured concentration profiles in function of the height above burner (HAB) of small species (i.e. OME3, CH2O, CH3OH, H2, CO2 and CO) are shown in Figure 1. Other important species which are observed include ethane, ethylene, dimethyl ether, methyl formate, dimethoxy methane and methoxymethyl formate.

Ignition delay times have been measured via rapid compression at 5 bara for and to additionally validate the low-temperature section of the model. Samples were taken to identify the reactants and products, including OME3, methyl formate, methoxymethyl formate and methoxymethoxymethyl formate. Similarly, pyrolysis experiments are performed for OME3 in a bench-scale steam cracker setup over a broad range of temperatures (723 K – 1073 K) to validate both the primary and secondary chemistry of the pyrolysis model.

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