Full Length Article

Sooting propensity of dimethyl carbonate, soot reactivity and characterization

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A B S T R A C T

Oxygenated compounds have gained interest in the last few years because they represent an attractive alternative as additive to diesel fuel for reducing soot emissions. Although dimethyl carbonate (DMC) seems to be a good option, studies about its propensity to form soot, as well as the knowledge of the characteristics of this soot are still missing. For that reason, this paper focuses on the potential of DMC to form soot, as well as on the reactivity and characterization of this soot. Results from pyrolysis experiments performed in an atmospheric pressure flow reactor at different temperatures (1075–1475 K) and inlet DMC concentrations (approximately 33,333 and 50,000 ppm) show that both soot and gas yields are affected by the pyrolysis temperature, while an increase in the inlet DMC concentration only affects slightly the soot yield, without notable influence on the gas yield. DMC shows a very low tendency to produce soot because the CO/CO_2 formation is favoured and thus few carbon atoms are available for soot formation. A chemical kinetic model developed, without incorporating soot particles dynamics, can predict well the gas-phase trends. The comparison of the soot amount profile obtained with the PAH amount profile determined by the model suggests a good first approach toward a model including soot formation. The soot reactivity study toward O_2 (500 ppm) and NO (2000 ppm) at 1475 K, as well as its characterization, show that the higher the temperature and the inlet DMC concentration of soot formation, the lower the reactivity of the soot.

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1. Introduction

Dimethyl carbonate (DMC, $CH_3OCOOCH_3$), a carbonate ester, is an attractive oxygenate compound for using as diesel fuel component for reducing soot emissions due to its good characteristics, such as: (1) 100% miscibility in diesel; (2) 53 wt% in oxygen content; (3) no carbon–carbon atomic bonds; and (4) relatively high H/C ratio [1,2].

Diesel-DMC blends have been tested in diesel engines showing potential to reduce smoke and soot emissions (e.g. [1]). Furthermore, when comparing with diesel and biodiesel emissions, adding DMC to diesel showed the capacity to reduce unregulated carcinogenic emissions, such as benzene and 1,3-butadiene [2].

Previous studies have contributed to the knowledge of the DMC decomposition and the DMC combustion (e.g. [3–5]). Kinetic studies on DMC conversion are also reported in literature [5–7]. However, experimental data on sooting tendency of DMC complemented with computations based on detailed chemical kinetic mechanisms, and furthermore reactivity and characterization

studies of the soot obtained from the DMC conversion, are still missing. The determination of the potential of DMC to form soot is important to establish practical conclusions on how the addition of DMC to diesel fuel affects the sooting tendency of fuel mixtures. Furthermore, knowledge of the soot reactivity is important to develop soot reduction strategies. Therefore, the main goals of the present work are to perform the DMC pyrolysis in a wide range of temperature (1075–1475 K) and with different inlet DMC concentrations (33,333 and 50,000 ppm, corresponding to 100,000 and 150,000 ppm of inlet total carbon amount, respectively) in order to study the ability of DMC to form soot under different pyrolytic conditions, and to compare the experimental data with the results of a detailed gas-phase chemical kinetic model, which involves the formation of species known to be involved in the soot formation process. Additionally, the reactivity study of soot samples toward different gases present in the combustion chamber of a diesel engine, such as O_2 and NO, is carried out, as well as the characterization of soot samples using several instrumental techniques (elemental analysis, determination of the BET surface area with N_2 at 77 K, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and Raman spectroscopy), in order

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to evaluate their composition and structural properties, and relate them to their reactivity.

2. Experimental procedure and set-up

The atmospheric thermal decomposition of DMC was carried out varying the reaction temperature (1075, 1175, 1275, 1325, 1375, 1425, and 1475 K) for each inlet DMC concentration studied (approximately 33,333 and 50,000 ppm). The experimental facility used was described elsewhere (e.g. [8]) and is briefly reiterated here. Reaction takes place within a quartz tube reactor of 45 mm internal diameter and 800 mm length situated inside an electric furnace. The reactor inlet and outlet are air-cooled without direct contact with the reaction mixture, and resulting in an isothermal reaction zone length of 160 mm, with a flat temperature profile ±25 K. The longitudinal temperature profile inside the reactor is measured with an S-type thermocouple at a total N_2 flow rate of 1000 mL (STP)/min with an estimated uncertainty of ±5. Example of temperature profiles for 1475, 1375, and 1275 K are provided in the supplementary material (Fig. S1). DMC is fed into the reactor in gas-phase using an isocratic HPLC pump, a thermally isolated line, and N_2 as carrier gas. N_2 is added into the reactor to obtain a total gas flow rate of 1000 mL (STP)/min, resulting in a gas residence time in the reaction zone dependent on temperature, $t_r = 4168/T(K)$ (s) ($t_r = 2.83–3.88$ s, in the temperature range studied).

The reactor outlet is linked to a soot collection system consisting of a quartz fiber filter with a pore diameter lower than 1 μm, and a light gases measurement system consisting of a gas chromatograph (GC) (Agilent 6890A) (accuracy of ±10 ppm), which is calibrated to quantify: methane, methanol, ethylene, acetylene, ethane, dimethyl ether, propadiene, propylene, propane, 1,3-butadiene, benzene, ethylbenzene, toluene, CO, CO_2, and H_2. The total time for each experiment was fixed in 3 h, not exceeding an overpressure limit of 1.3 bar inside the reactor in order to avoid perturbations in the experimental set-up.

Reactivity experiments were carried out using the facility and following the steps described in previous works [8,9]. Briefly, the reaction takes place within a quartz tubular reactor which has a bottleneck in the middle in which a quartz wool plug is introduced to locate the soot/silica sand mixture (i.e., 10 mg of soot mixed with 300 mg of silica sand (150–300 μm) to prevent soot particle agglomeration and to be able to consider isolated particles), resulting in a thin layer. The reactor is located in an electrical furnace which is heated to the reaction temperature (1275 K) at 10 K/min in a N_2 atmosphere (1000 mL (STP)/min). Once the reaction temperature desired is reached, part of the N_2 flow is replaced by the flow of the reactant gas, O_2 or NO, to attain a concentration of 500 ppm of O_2 or 2000 ppm of NO in the total flow rate of 1000 mL (STP)/min. These O_2 and NO concentrations were selected to be consistent with previous experiments [8,9]. The gas products are air-cooled down to room temperature and measured by continuous CO/CO_2 and NO ABB infrared analyzers, which provide uncertainty measurements below 5%.

Selected soot samples were characterized by different instrumental techniques, namely: elemental analysis, determination of the BET surface area with N_2 at 77 K, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and Raman spectroscopy.

Before performing both soot reactivity experiments and soot characterization, the soot samples were undergone to a thermal annealing during 1 h in a N_2 atmosphere at their formation temperature in order to eliminate the adsorbed compounds [8].

3. Kinetic model

The chemical reaction mechanism used for the simulations of the experimental results was built based on Alzueta et al. [7] mechanism, which implements the DMC conversion sub-mechanism by Glaude et al. [6]. With the aim of improving model predictions under sooting conditions, reactions involving benzene, toluene, and other intermediates such as phenyl radicals [10] were added to the base mechanism [7]. Also, the mechanism was extended to include different pathways for the polycyclic aromatic hydrocarbon (PAH) formation, which are generally accepted to be the responsible molecules for the soot particle inception stage [11,12], specifically: (1) H-abstraction/C_2H_2-addition (HACA) (starting with the C_2H_2 addition to phenyl radical); (2) the combination of phenyl radicals with benzene; (3) the cyclopentadienyl radicals recombination; and (4) the combination of benzyl and propargyl radicals. The HACA mechanism occurs through a two-step repeating sequence involving hydrogen abstraction to activate aromatics, followed by subsequent acetylene addition. This process continues leading to the sequential formation of multi-ring structures [13]. The rate constants proposed by Appel et al. [11] for PAH growth up to pyrene and the rate constants for the PAH growth from pyrene up to coronene proposed by Richter et al. [12] were used. Mechanism for the PAH oxidation by Appel et al. [11] was also added. In this way, the kinetic model only includes gas-phase chemistry and does not include soot particle dynamics. However, this gas-phase model could be a first approach toward a complete model including soot formation.

The modified gas-phase reaction mechanism consists of 262 chemical species and 1182 reactions (It can be found in the supplementary material). All model computations were conducted with the SENKIN code of the Chemkin software package [14].

4. Results and discussion

Fig. 1 presents the soot and gas yields (in percentage), as a function of temperature, obtained during the pyrolysis of different inlet DMC concentrations. Both soot and gas yields are defined as the carbon amount in soot and gases, respectively, related to the total carbon amount at the reactor inlet [9]. It is worth to clarify that the gas yield includes the DMC amount that did not react and was found at the reactor outlet. It can be observed that, for both inlet DMC concentrations, soot appears to be formed from 1375 K, reaching a maximum soot yield value of approximately 9 and 12% at 1475 K, for $[DMC]_{inlet} = 33,333$ and 50,000 ppm, respectively. The rise of temperature causes both an increase in soot yield and a decrease in gas yield for the two inlet DMC concentrations evaluated. This is consistent with previous findings [8,9]. An increase in the DMC concentration only affects slightly the soot yield, without notable influence on the gas yield.

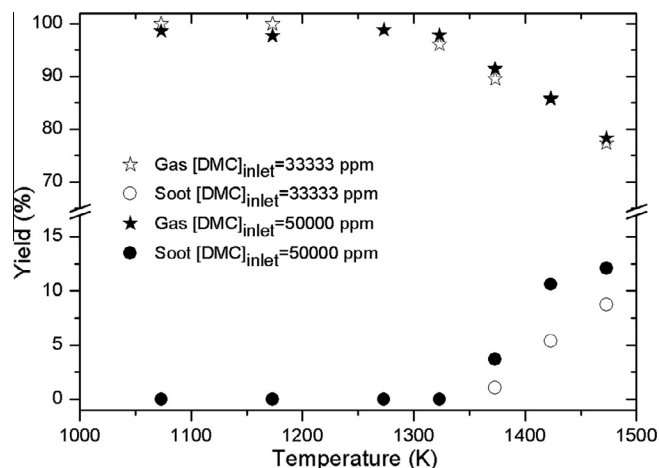**Fig. 1.** Soot and gas yields, as a function of temperature, obtained in the DMC pyrolysis of 33,333 and 50,000 ppm from 1075 to 1475 K.