



Pyrolysis of dimethyl carbonate: PAH formation



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ABSTRACT

The formation of the 16 polycyclic aromatic hydrocarbons (PAH), classified as priority pollutants by the Environmental Protection Agency (EPA), has been studied in the pyrolysis of dimethyl carbonate (DMC) at different reaction temperatures (1075–1475 K). PAH have been quantified by gas chromatography–mass spectrometry (GC–MS). The PAH speciation showed that C₁₀–C₁₆ PAH: NAPH, ACNY, PHEN, FANTH PYR, FLUO, ANTH, and some C₂₀–C₂₂ PAH: B[a]P, I[123-cd]P, and B[ghi]P, were present in high concentrations. The predominant PAH were NAPH and ACNY, and were found in significant concentrations in all phases analysed (gas phase, adsorbed on soot, and stuck on reactor walls). PAH were predominantly present in the gas phase, except at higher temperatures where most of the PAH were adsorbed on soot. The toxic potential, B[a]P-eq concentration, was determined according to the amount of PAH present in the different phases. The results showed that the highest B[a]P-eq concentration was found for the PAH adsorbed on soot corresponding to the experiment performed at 1375 K.

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1. Introduction

Global warming and other environmental problems have increased investigations to reduce and prevent the pollution in different ways. In the last years, new diesel additives are being considered in order to reduce some atmospheric pollutant emissions from diesel engines. Nowadays, different countries use biofuels because of their renewable character, and also because these fuels can contribute to greenhouse gases mitigation produced by the transport sector [1]. Oxygenated compounds, which are able to be blended with diesel fuel, have been proposed to achieve this objective [2], mainly by reducing the formation of soot in the combustion chamber. Pepiot-Desjardins et al. [3] performed a structural group analysis according to their soot reduction tendency, using oxygenated fuels, such as alcohols, ethers, esters, ketones and aldehydes, and found that all these oxygenated chemical groups reduced the sooting tendency of the base fuel.

In recent years, the use of dimethyl carbonate C₃H₆O₃ (DMC) has increased in interest because it can be produced, through a sustainable process, by catalytic oxidative carbonylation of methanol with oxygen [4]. Although DMC is not suitable for using alone in diesel engines because of its low cetane number, low calorific value and high latent heat of evaporation [5], DCM can be part of blended

diesel fuels and therefore used in diesel engines. Besides, DMC has been taken into account for its features: high oxygen content, 53.29 wt.%, high solubility in diesel fuel, low boiling point (which favours spray atomization and mixing), and no C–C bonds (which contributes to the reduction of particulate matter emissions) [6]. Furthermore, DMC decomposition leads to the formation of the methoxy formyl radical (CH₃OC•=O), a key intermediate in oxygenate chemistry, which can decompose by two paths giving either CO or CO₂ [7]. In this way, these pathways act to remove carbon from the typical reaction pathways leading to soot formation, being a desired characteristic of the oxygenated additives. Thus, these features make DMC to be a good candidate as fuel additive to reduce soot particles if used as diesel engine fuel.

Some studies have been done in order to analyse the effect of the presence of DMC on the combustion emissions. In this context, Rounce et al. [8] carried out a study in a single cylinder, pump-line-nozzle, direct-injection diesel engine, and made some observations about the emissions of DMC blended with diesel, such as the increase of the values of NO_x and unburnt total hydrocarbons (THCs), while CO and particulate matter were reduced by up to 50%. Cheung et al. [9] studied the emissions of diesel-dimethyl carbonate blends in a 4-cylinder direct injection diesel engine, and also found that particulate matter emissions were significantly reduced. Fabbri et al. [10] performed their experimental study in a jacketed glass plug flow reactor and studied the emissions in the pyrolysis of a biodiesel-like blended material with dimethyl carbonate, where

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naphthalene was the principal polycyclic aromatic hydrocarbon (PAH) emitted from this blend.

The formation of PAH is related to soot formation under pyrolytic conditions through the well-known HACA mechanism. The HACA route involves the abstraction of hydrogen and the consecutive addition of acetylene, forming aromatic compounds followed by subsequent growth up to the inception and nucleation of the soot particles. Other mechanisms have been proposed in order to understand the complex formation of PAH and the consecutive formation of nascent soot particles [11], such as: the combinative growth mechanism, which explains a PAH growth with condensations of rings, and the cyclopentadienyl recombination, which shows that naphthalene can be formed through the cyclopentadienyl radical dimerization. In conclusion, PAH and soot formation are closely related within the combustion process, and most notably under pyrolytic conditions.

The study of PAH formation is also important because of their carcinogenic and mutagenic character. Sixteen PAH, shown in Table 1, have been classified by the US Environmental Protection Agency (EPA) as priority pollutants because of their carcinogenic potential [12].

To our knowledge, there is not any study in the literature that addresses the formation of the 16 priority PAH, formed during the DMC conversion under pyrolytic conditions. However, it is important to point the work performed by our research group [13], which analyses the conversion of DMC, covering a detailed analysis of light gases, with a chemical kinetic model, soot propensity, soot reactivity and characterization.

In this context, the present work reports data on the formation and the distribution of the 16 priority PAH between the gas phase and soot surface during the pyrolysis of DMC in a tubular flow reactor, using different reactions temperatures (1075–1475 K), and also shows the toxicity of the effluent obtained.

2. Methodology

2.1. Experimental setup

The experiments were carried out under well controlled laboratory conditions. A detailed description is found elsewhere [14]. A scheme of the installation is shown in Fig. 1. The installation consists of four systems clearly defined: 1) gas feeding system, 2) reaction system, 3) soot and EPA-PAH collecting system and 4) gas analysis system.

The concentration of DMC was kept constant (50000 ppm), and it was obtained by pumping liquid DMC with an isocratic HPLC pump and vaporizing it by means of an electric resistance. Nitrogen (N_2) was added in order to obtain the desired total flow rate.

A vertical quartz flow reactor of 45 mm inside diameter, and 800 mm in length was used to perform the reactions. A reaction zone of 160 mm was identified, taking into account the zone where an isothermal profile is achieved. The reactor inlet and outlet were cooled, by external compressed air, allowing a good control of the temperature profile inside the reactor. The temperatures in this study are in the range of 1075–1475 K. The total flow rate in all experiments is 1000 mL (STP)/min. With a constant STP flow rate and considering the volume of the reaction zone, the temperature-dependent gas residence time is given by: t_r (s) = 4168/T (K). Each experiment lasted 3 h, in order to get representative amounts of soot and PAH to further analysis.

2.2. Sample treatment and gas analysis

The outlet gases from the reaction system were analysed by a gas chromatograph, Agilent Technologies 6890N, equipped with a HP-

PLOT Q column linked to a thermal conductivity detector (TCD), and an HP-PLOT Molesieve column coupled to a flame ionization detector (FID). This equipment was used to measure light gases and some small hydrocarbon species. The calibration of this device was done with a standard mixture of C_2H_2 , H_2 , CH_4 , C_2H_4 , C_2H_6 , C_3H_8 , C_3H_6 , 1,3-butadiene, *i*- C_4H_{10} , *n*- C_4H_{10} , C_6H_6 , C_7H_8 and C_8H_{10} . DMC was calibrated with a standard gas cylinder. The measurement uncertainties were estimated as $\pm 5\%$ for the gas chromatograph, but not less than 10 ppm.

Soot was collected at the end of the reactor by using a quartz fiber cartridge with a pore diameter lower than 1 μ m. The amount of soot was calculated by weight difference of the cartridge, before and after each experiment. PAH were collected using a XAD-2 resin, which was placed into a thin glass tube after the cartridge used to collect soot. The resin used, with a total weight of 5 g, was divided in two parts: 3 g was used to collect PAH and 2 g was used as blank to ensure that all PAH were previously adsorbed on the first tube part. These two resin fractions were subsequently analysed separately. Some PAH could be stuck on the reactor walls, and 100 mL of dichloromethane were used to wash the reactor walls in order to collect these PAH. Thereby, the samples obtained from the gas phase (resin), soot and reactor walls, were analysed immediately after each experiment to avoid losses of the target compounds. The methodology developed by Sánchez et al. [15] was followed. Each sample obtained was subjected to Soxhlet extraction, following the EPA 3540C method [16], using dichloromethane as solvent, then the samples obtained were concentrated using a rotary evaporator. Deuterated aromatic compounds (1,4-dichlorobenzene- d_4 , naphthalene- d_8 , acenaphthene- d_{10} , chrysene- d_{12} , perylene- d_{12} and phenanthrene- d_{10}) were used as internal standards. The 16 selected PAH were quantified using a 7890A gas chromatograph coupled to a MSD 5975C mass selective detector (GC–MS) of Agilent Technologies equipped with a capillary column DB-17Ms Agilent Technologies (60 m \times 0.25 mm ID \times 0.25 μ m), virtually equivalent to (50% phenyl)-methylpolysiloxane column. This analysis was performed with selected ion monitoring (SIM), in order to improve the selectivity and sensitivity. The chromatographic conditions were: 1 μ L injection volume in splitless mode; helium was used as the carrier gas (flow rate of 1 mL(STP)/min); injector temperature: 575 K; temperature program: 355 K (15 min), 355–385 K at 5 K/min, 385 K (5 min), 385–565 K at 5 K/min, 565 K (35 min), 565–595 K at 1.5 K/min, 595 K (5 min); transfer line temperature, 555 K; ion source temperature, 505 K; analyser temperature, 425 K; detector temperature, 525 K. The method was calibrated by using standard solution of the selected PAH. Both, the deuterated mix and standard solution of PAH, were purchased from Dr. Ehrenstorfer GmbH (Germany). The recommended steps of the EPA 8270D method were followed for PAH quantification [17]. This PAH quantification methodology has demonstrated recoveries higher than 80% in most cases [18]. Further and more detailed information of the whole method used, including the calibration and repeatability, can be found elsewhere [15].

3. Results

3.1. Yield to products

The formation of PAH was evaluated in the pyrolysis of DMC by analysing the influence of the reaction temperature. The yield to soot, gases and PAH obtained from the products found at the reactor outlet are shown in Fig. 2a. These yields are defined as the relationship, in percentage, between the carbon amounts found in soot, outlet gases or PAH, related to the carbon amount fed at the inlet of the reactor. The DMC conversion and CO and CO_2 concentrations are shown in Fig. 2b.

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