



Gas phase carbonyl compounds in ship emissions: Differences between diesel fuel and heavy fuel oil operation



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HIGHLIGHTS

- We investigate carbonyl compounds emission in the gas phase of a ship diesel engine.
- Two fuel types tested heavy fuel oil (HFO) and diesel fuel (DF).
- Carbonyl emission factor and emission contribution are different in HFO than in DF.
- Carbonyl compounds emissions factor in HFO are higher than in DF with 3 folds.
- Formaldehyde is predominate carbonyl in both fuel operations.

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ABSTRACT

Gas phase emission samples of carbonyl compounds (CCs) were collected from a research ship diesel engine at Rostock University, Germany. The ship engine was operated using two different types of fuels, heavy fuel oil (HFO) and diesel fuel (DF). Sampling of CCs was performed from diluted exhaust using cartridges and impingers. Both sampling methods involved the derivatization of CCs with 2,4-Dinitrophenylhydrazine (DNPH). The CCs-hydrazone derivatives were analyzed by two analytical techniques: High Performance Liquid Chromatography–Diode Array Detector (HPLC–DAD) and Gas Chromatography–Selective Ion Monitoring–Mass Spectrometry (GC–SIM–MS). Analysis of DNPH cartridges by GC–SIM–MS method has resulted in the identification of 19 CCs in both fuel operations. These CCs include ten aliphatic aldehydes (formaldehyde, acetaldehyde, propanal, isobutanal, butanal, isopentanal, pentanal, hexanal, octanal, nonanal), three unsaturated aldehydes (acrolein, methacrolein, crotonaldehyde), three aromatic aldehyde (benzaldehyde, *p*-tolualdehyde, *m,o*-molualdehyde), two ketones (acetone, butanone) and one heterocyclic aldehyde (furfural). In general, all CCs under investigation were detected with higher emission factors in HFO than DF. The total carbonyl emission factor was determined and found to be 6050 and 2300 $\mu\text{g MJ}^{-1}$ for the operation with HFO and DF respectively. Formaldehyde and acetaldehyde were found to be the dominant carbonyls in the gas phase of ship engine emission. Formaldehyde emissions factor varied from 3500 $\mu\text{g MJ}^{-1}$ in HFO operation to 1540 $\mu\text{g MJ}^{-1}$ in DF operation, which is 4–30 times higher than those of other carbonyls. Emission profile contribution of CCs showed also a different pattern between HFO and DF operation. The contribution of formaldehyde was found to be 58% of the emission profile of HFO and about 67% of the emission profile of DF. Acetaldehyde showed opposite behavior with higher contribution of 16% in HFO compared to 11% for DF. Heavier carbonyls (more than two carbon atoms) showed also more contribution in the emission profile of the HFO fuel (26%) than in DF (22%).

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1. Introduction

Ships and marines emissions make a considerable contribution to both gaseous and particulate air pollutants in the atmosphere, particularly on the ports and coastal regions (Miola and Ciuffo, 2011). These toxic pollutants have been associated with serious adverse health effects, including premature death and respiratory symptoms (Corbett et al., 2007; Song, 2014). Carbonyl compounds (CCs) are well known to be critically important in atmospheric chemistry (Sawant et al., 2007) and they attract immense attention due to their adverse health effects on humans (Weng et al., 2010). Certain CCs such as formaldehyde, acetaldehyde and acrolein are known to be toxic, mutagenic or carcinogenic and thus have been identified as hazardous air pollutants. (Bhattacharya and Tulsawani, 2008; IARC, 2006). A summary of health hazards associated with carbonyl compounds are listed Table 1 (Karavalakis et al., 2010). The primary emission sources of CCs are diverse and include: motor vehicles (Pang and Mu, 2007), incomplete combustion of hydrocarbon fuels in industrial processes (Liu et al., 2006), cigarette smoke (Pang and Lewis, 2011), biomass burning (Seco et al., 2007), the frying process as a by-product of vegetable oil degradation (Katragadda et al., 2010), wine production (Culleré et al., 2009) and urban incineration (Dai et al., 2012). CCs can also be produced as secondary airborne pollutants via the photochemical oxidation of atmospheric hydrocarbons (Moussa et al., 2006).

Sampling and analysis of CCs started in the middle of the fifties during the last century. Earliest measurements were performed for CCs in cigarette smoke by Touey (1955), who used a precipitation method to assess the total aldehyde content by their reaction with (5,5-dimethyl-1,3-cyclohexanedione) in gas-absorption flasks to form dimedon. Later techniques resolved CCs in tobacco smoke using liquid chromatography based on their 2,4-dinitrophenylhydrazine derivatives (Houlgate et al., 1989). Recently, different methods were used to analyze CCs in different sources. High performance liquid chromatography (HPLC) represents the most convenient method for the analysis with conventional UV–VIS detectors (Feng et al., 2011; Karavalakis et al., 2011). Moreover, on-line capillary liquid chromatography (Prieto-Blanco et al., 2011) and gas chromatography mass spectrometry (GC–MS) (Pang and Lewis, 2011) were employed in the investigation of the CCs. Most of these analytical methods depend on the same principle of sampling, which involves the derivatization of CCs with 2,4-dinitrophenylhydrazine (DNPH) to produce stable CCs-hydrazone derivatives.

Carbonyl compounds emission from heavy-duty diesel engines have been intensively investigated recently using different fuel blends such as ethanol–diesel blends (Song et al., 2010) or biodiesel blends (Karavalakis et al., 2011). These studies revealed that the use of biodiesel or ethanol–diesel fuels led to significant increases in the emission of most carbonyl compounds due to the high oxygen containing additives. To our knowledge there is no any study discussing the carbonyl compounds in the emissions of ship engines operated with heavy fuel oil or distillate oils. In this study we investigated carbonyl compounds emission in the gas phase of a ship diesel engine fueled with heavy fuel oil (HFO) and standard diesel fuel (DF, contained 3.2% biodiesel) respectively. The study was carried out as part of a project of the Helmholtz Virtual Institute for Complex Molecular System in Environmental Health (HICE). CCs were collected using 2,4-dinitrophenylhydrazine (DNPH) cartridges and impingers. The CCs were analyzed using a sensitive and versatile analytical GC–SIM–MS method. Multiple repetitions were performed for each fuel type according to the ISO 8178-4 E2 method. The differences in the emission factor and emission profile for each fuel type were investigated and evaluated. The results were

compared to recent studies concerning the emission profile of CCs in DF operation in diesel engine.

2. Experimental part

2.1. Engine description, fuel properties and test cycle

Experiments were carried out at the Institute of Piston Machines and Internal Combustion Engines in the University of Rostock, Germany during a sampling campaign between November 12th and November 30th 2012. A single-cylinder diesel research engine (Bank et al., 2013; Etzien et al., 2013) was used to perform these experiments. The engine was able to operate with both standard DF and HFO, mimicking the common dual fuel use HFO for open sea cruising and DF for harbor times or cruising in sulfur emission control areas (SECA's) such as in the Baltic sea, and has a common rail injection system with system pressures up to 1300 bar. Further details regarding the engine are listed in Table 2. Almost all of the operating parameters – including the injection parameters – could be adjusted within the physical ranges of the engine.

Two different fuels were used for the operation. Heavy fuel oil HFO 180 was used as a representative fuel for ship operation in SECAs. On the other hand, a distillate Diesel Fuel DF according to DIN EN 590 was used as a light fuel operation standard. The used DF contained 3.2% rapeseed oil-methyl ester as biodiesel component. The properties of both fuels are listed in Table 3.

The emission testing was performed in these experiments with the engine operating on a test bench. In order to obtain the representative pattern under operating conditions, the engine was run at four different operating load points of 100%, 75%, 50%, 25% loads at nominal speed of 1500 min⁻¹. The duration of each operation point was set according to the weighting factors in ISO 8178-4 E2, starting with 100% engine load for 20 min then reduced to 75% load for 60 min and reduced again to 50% and 25% load for 10 min each respectively. The total cycle duration was 2 h with two cycles run per experiment and two experiments per day. Furthermore, 8 and 7 repetitions were performed for DF and for HFO operation respectively. Some of the repetitions were discarded either due to changes in sampling conditions or due to sampling problems. Therefore, the results shown in this study were derived from 6 to 5 replicate samplings for DF and HFO operation respectively.

2.2. Sample collection and preparation

Emission samples were collected with a different dilution ratio (DR) from the main engine stack depending on the fuel type. A gas phase sampling line was assembled directly after aerosol sampling system consisting of a porous tube and ejector diluter (Venacontra, DAS, Finland) as shown in Fig. 1A. The final applied dilution ratios were approximately 40 for the DF repetitions and 12 for HFO repetitions. To collect the gas phase, quartz fiber filters were used to remove the particles from the gas phase sampling line. To achieve a stable sampling flow rate during the experiments, critical nozzles were used with a fixed flow rate of 0.2 L min⁻¹. The total sample volume collected was around 48 L per repetition. Two sampling techniques of DNPH cartridges and impingers were used to collect CCs in the gas phase. Both sampling techniques depend on the derivatization of the carbonyl group in CCs with DNPH in acidic media which is known as Brady's test (Kadam et al., 2012). Samplings of CCs were obtained using both sampling techniques in parallel as shown in Fig. 1B.

The first sampling technique was the acidified impingers of DNPH, similarly as described in (Parmar et al., 2004). Three impingers were connected in series using 6 mm glass tube

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