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Abstract

The speciated exhaust emissions of VOCs in the C_2-C_{19} range were measured on 4 Euro-4 certified vehicles (3 diesel and 1 gasoline) equipped with a catalytic converter, according to 5 real-world driving cycles. To determine the effects of blended fuels on the emission factors, several test fuels were used: gasoline, E10 (10% of ethanol, by volume), diesel, B5, B30 (5% and 30% of biodiesel or FAME) and HVO (pure Hydrotreated or Hydrogenated Vegetable Oil). These tests were performed on a chassis dynamometer with constant volume sampling (CVS). The sampling of compounds was made using dedicated Carbotrap and Tenax cartridges, analysed by GC-FID and GC-MS respectively. Carbonyl compounds were sampled on DNPH-coated cartridges and analysed by UV-HPLC. The emission factors of individual pollutants were determined, especially of 1,3-butadiene, benzene, and formaldehyde, which are recognized as genotoxic carcinogens. Detailed speciation of the emissions shows changes with the composition of the biofuel in the levels of hydrocarbons, aromatic compounds and carbonyls present in diesel and gasoline engine exhaust gases. This evolution of the emission factors for the different compound families is compared to the results obtained in previous studies, where the influence of driving cycles, technology and type of fuels were evaluated (Caplain et al., 2006). In the framework of this study, the first results show that an addition of ethanol in the unleaded gasoline leads to a decrease of the emissions of aromatics especially of benzene and an increase of the 1,3-butadiene emission. An increase of aromatics emissions but no specific trend for carbonyl compounds emission factors was observed when partially substituting biodiesel to diesel. Pure HVO leads to higher carbonyl emissions than pure or substituted diesel fuel.

Introduction

Volatile organic compounds (VOCs) play a major role in urban atmospheric chemistry. They are important precursors of photochemically formed secondary pollutants, such as ozone, which poses a serious air pollution problem. They are also compounds that adversely affect the human health due to their high toxicity (e.g. benzene, 1,3-butadiene). Vehicular traffic highly contributes to these VOCs emissions and, to reduce these emissions, biofuels are introduced in EU, partially substituting petroleum diesel by fatty acid methyl esters (FAMEs), commonly known as biodiesel, and gasoline by ethanol. Biodiesel blends up to 30% by volume can be used for diesel engine without modification because of their properties similar to those of diesel. It is recognized that there is a substantial reduction in regulated emissions such as HC, CO, PM with the exception of NOx emissions when diesel vehicles are fuelled with biodiesel. With the increasing percentage of biofuels in the petroleum based fuels supplied at gas stations and the development of the synthetic biofuels, it is relevant to assess the pollutants in car exhaust with these alternative fuels, under various traffic conditions. In this work, we report the emission factors (EF) of the speciated gas phase hydrocarbons and carbonyls collected from recent technology (Euro 4) light vehicles fuelled with conventional fuel or biofuel, to determine the effect of biofuel on the unregulated exhaust emissions, with a special interest in toxic and carcinogenic compounds. The blends selected in this study were a blend of 10% ethanol in gasoline (E10) and blend of 5 % and 30 % of biodiesel (FAMEs) in the diesel fuel (called B5 and B30). A 100% pure HVO was also tested. The emission factors of unregulated pollutants emission were measured using real-world test driving cycles performed on a chassis dynamometer with constant volume sampling (CVS) at INRETS facility. The tailpipe emissions were sampled for light hydrocarbons (C_2-C_6), semi-volatile hydrocarbons (C_7-C_{19}) and carbonyl compounds. The results obtained in this work are compared to the data obtained in the previous Artemis Project study (Caplain et al., 2006), which investigated the emissions of cars complying to less restrictive standards (Euro 3 and before).

1. Materials and methods

1.1 Vehicles, fuels and driving cycles

The unregulated pollutants (VOCs) were sampled and analysed for gasoline (GDI) and diesel (D1, DPF, LDD) vehicles, all Euro-4 certified, using real-world test driving cycles. The gasoline car is equipped with a direct injection and turbocharged engine. This type of spark ignition engine is an emergent and promising technology to reach better performances and decrease pollutant emissions. For diesel engines, the first one (D1) has direct and common rail injection. The second one (DPF) is equipped with a fuel-borne catalyst (FBC) type particulate filter on the exhaust. The third vehicle (LDD) is a 3.5 t gross weight light-duty diesel van. All three Diesel vehicles have turbocharged engines.
The GDI car was fuelled with the reference gasoline and with E10. The three diesel vehicles were run successively on the 4 following fuels: reference diesel fuel, B5, B30 and HVO. When shifting fuels, the vehicle was run dry and the fuel pipes "rinsed" with the new fuel. The vehicle was then driven along dozens of kilometres till the tank was empty again. The gasoline and diesel reference fuels are used as bases for comparisons. They are both neat petroleum based fuels, and are used currently in Europe for vehicle certification. The driving cycles were the Artemis cycles (urban, rural and motorway) analysed separately and an INRETS specific short urban cycle (IRSUC) (André et al., 2006) whose aim is to assess the effect of "cold start" and "hot start" in urban traffic.

1.2 Sampling and analysis

The vehicle exhaust gas is diluted with filtered ambient air using a constant volume sampler (CVS). This method of sampling reflects the natural dilution and cooling of the exhaust gas as it leaves the tailpipe and eliminates the problem of water condensation during the sampling. VOCs are sampled in the dilution tunnel using sorbent tubes: Carbotrap B and C, Carbosieve III for "light" hydrocarbons (C_2-C_6), Tenax for semi-volatile hydrocarbons (C_7-C_{19}), and DNPH-coated silica cartridges for carbonyl compounds. Before each set of sampling of exhaust gas the background contribution of the dilution air was measured. The procedure for the sampling and the analytical methods used for the analysis of the light and semi-volatile hydrocarbons were already applied for the Primequal – Predit Research Programs (Caplain et al., 2006) and improved in this work the Carbotrap and Tenax samples were analysed by a thermal desorption preconcentration method, followed by quantification by high resolution gas chromatography with a flame ionisation detector (GC/FID) for compounds from C_2 to C_6 and with a mass spectrometer detector (GC/MS) for the compounds from C_7 to C_{19}. DNPH cartridges were analysed by the standard UV-HPLC method.

2. Results and Discussion

2.1 Compound families characterised in the exhaust gas

The different compound families characterised by GC are alkanes (C_2 to C_{19}), alkenes (C_2 to C_6) and aromatics compounds (BTEX, propylbenzene and butylbenzene (linear or branched – chain alkyl). For the GDI vehicle fueled with E10, depending on the driving cycle, the aromatics mass proportion in the total hydrocarbon species (except carbonyls) varies from 31 to 66%, the alkanes proportion from 33 to 59%, and the alkenes proportion from 1 to 11%. The same car fuelled with the reference gasoline emits from 19 to 78% aromatics species, 2 to 72% alkanes and 2 to 10% alkenes. The fraction of alkanes and olefins decreases from Artemis- urban to Artemis-motorway while the proportion of aromatics increases when the GDI vehicle is fuelled with the reference gasoline. The trend is reversed with E10.

For the emission factors of the different compound families emitted by diesel engines, no trends were observed with respect to the four fuels under test. As for gasoline engine, the major VOC groups emitted by the diesel vehicles fuelled with different biodiesel blends are alkanes and aromatic compounds. For example with the LDD vehicle, the emission of aromatics decreases from B5 to HVO (e.g. cold cycle 65% - 19% - 16%) and the emission of alkanes increases from B5 to HVO (e.g. cold cycle 18 - 82%).

The carbonyl emissions are dominated by formaldehyde, acetaldehyde, butyraldehyde and acroleine, as previously observed (Corrêa and Arbilla, 2008). Propionaldehyde, crotonaldehyde and methacroleine were also present in the exhaust gases. The other carbonyl compounds (benzaldehyde, valeraldehyde, tolualdehyde, hexaldehyde) are negligible. The emission factors of all the aldehydes are strongly correlated.

2.2 Influence of cold and hot starts on the emissions

The influence of cold or hot starts on the VOCs composition was determined by the difference of the emissions obtained during the IRSUC cold and IRSUC hot cycles. The measured emission factors of the VOCs grouped in different substance classes are given in Table 1. The total VOCs emission factor is larger for the hot IRSUC whatever the technology of diesel vehicle and the type of blended diesel fuel, but for carbonyls the situation is reversed with an overproduction in the cold cycle. For the diesel vehicle D1 fuelled with blended fuels B5 and B30, the amount of total emitted VOCs is twice more important in a hot start than a cold one while for the DPF diesel car fuelled with blended fuel B5, the amount of emitted VOCs is 11 times more important. A six-fold increase of VOCs emission is also observed with the LDD diesel vehicle when it is fuelled with blended biodiesel B5. For these two latter vehicles and the two other blended fuels, the variation of the emission factor is not marked. We can also notice that for the two IRSUC cycles the emission factors of the diesel vehicles fuelled with biodiesel blends are higher than those obtained with regular diesel fuel, except in the case of B5 tested in cold start condition, where the use of biofuel decreases the emissions. The emission factor obtained with the IRSUC cold driving cycle also increases from the diesel vehicle D1 to LDD with B30 and HVO fuel, showing an influence of the vehicle technology (engine, particulate filter) on the emissions. In the case of LDD the emission of aromatics compounds decreases from cold to hot driving cycle (e.g. B5: 65 % - 15%) and the emission of alkanes increases from cold to hot driving cycle (e.g. B5: 18% - 79%). For carbonyl compounds, the emission factor decreases when increasing the content of biofuel in the blends, though the use of pure HVO leads to higher emissions.

The gasoline engine VOCs emissions (Table 2) are not influenced by fuel blend (E10) in the case of cold and hot IRSUC cycles (EF ≈ 110 $mg.km^{-1}$). Nevertheless, an addition of ethanol increases the emission of alkanes (3 to 74 $mg.km^{-1}$) and reduces the emission of aromatics (86 to 39 $mg.km^{-1}$), especially for the IRSUC cold cycle, and of carbonyl compounds. For the IRSUC hot cycle, the difference between E10 and gasoline is reversed (alkanes decrease from 66 to 35 $mg.km^{-1}$, while aromatics increase from 50 to 69 $mg.km^{-1}$. A higher emission of aromatics is observed with the reference gasoline fuel in cold start conditions, and in hot start conditions with E10. Whatever the fuel used, alkenes emissions are 10 to 20 times larger for IRSUC cold than for IRSUC hot.

2.3 Influence of driving cycle on the emissions

The use of B5 and B30 blends leads to a reduction of total VOCs emission factor for Artemis-urban driving cycle (DPF B5 21.48 $mg.km^{-1}$, B30 5.85 $mg.km^{-1}$) while the use of HVO increases the emissions (D1 76.27 $mg.km^{-1}$, DPF 53.7 $mg.km^{-1}$) compared to reference diesel (D1 16.1 $mg.km^{-1}$, DPF 36.72 $mg.km^{-1}$) (Table 3). For all the vehicles under test, the highest emissions of every pollutant analysed in this study are observed during the Artemis urban driving cycle. The pollutants with the highest emission factors are ethane, propane, toluene, ethylbenzene, C_3 benzene and saturated alkanes C_{10} to C_{14}. The reduction observed with B5 and B30 may be due to the intrinsic oxygen contained in the methyl ester (Sureshkumaret al., 2008).

Table 1*: IRSUC cold and IRSUC hot Diesel vehicles emission factors (mg.km-1)*

	IRSUC cold				IRSUC hot			
	Ref.	B5	B30	HVO	Ref.	B5	B30	HVO
Vehicle D1								
Alkenes	1.77	4.55	2.07	0.54	13.19	10.19	0.65	2.25
Alkanes	1.61	5.54	5.40	17.95	8.86	9.07	18.61	33.79
Aromatics	3.81	4.82	8.81	22.29	5.87	8.85	20.24	13.58
Carbonyls	4.87	3.29	3.17	1.29	3.67	1.40	1.08	3.29
1,3-butadiene*	26.8	378.5	126.6	N.D.	155.7	765.9	362.9	1098.3
Benzene*	13.5	130.6	54.1	11.9	14.4	16.0	34.9	43.9
Formaldehyde*	836.1	698.9	482.2	296.4	710.9	335.1	283.3	591.0
Vehicle DPF								
Alkenes	2.21	3.02	0.73	1.68	0.73	2.38	1.75	0.47
Alkanes	26.36	1.59	26.55	25.19	8.13	61.78	21.21	14.68
Aromatics	35.73	2.88	10.35	23.71	8.98	22.44	22.95	17.33
Carbonyls	1.97	No data	1.40	3.98	8.74	1.41	2.17	7.72
1,3-butadiene*	9.6	16.6	103.4	N.D.	5.5	N.D.	N.D.	17.3
Benzene*	15.8	41.1	12.3	7.6	18.2	7.2	11.9	9.7
Formaldehyde*	613.3	No data	347.4	723.6	298.3	337.3	579.3	1015.0
Vehicle LDD								
Alkenes	1.27	2.10	1.92	0.76	0.73	3.89	0.74	1.20
Alkanes	19.95	2.36	37.44	56.09	19.47	60.82	29.86	57.29
Aromatics	12.69	8.55	9.27	11.02	15.63	11.83	6.94	5.11
Carbonyls	7.81	7.10	3.29	3.74	1.52	3.91	1.24	4.40
1,3-butadiene *	5.8	N.D.	N.D.	0.4	N.D.	N.D.	N.D.	2.4
Benzene*	68.8	29.8	71.0	42.1	26.9	60.6	38.4	37.8
Formaldehyde*	898.4	934.5	428.2	338.9	283.0	1050.8	333.9	366.7

*except benzene, formaldehyde and 1,3- butadiene in µg.km^{-1}.

The results obtained with the reference diesel (16, 37, 41 mg.km^{-1} respectively for D1, DPF and LDD) may be compared with the data on Euro-3 diesel vehicles (Caplain et al., 2006). Compared to Euro-3 vehicles the emission factors of Euro-4 vehicles are divided by a factor 10 to 100 for IRSUC cold, 15 to 30 for IRSUC hot, 30 to 100 for the Artemis-urban and motorway driving cycles. Whatever the Artemis cycle and type of fuel, for gasoline vehicle the total VOCs emissions decrease in the following order: Artemis-urban > Artemis-rural > Artemis-motorway, and especially the light saturated and unsaturated COV ($C_2 - C_6$) (Table 2). Compared to diesel car real-world test driving cycles, VOCs emission levels are higher (e.g. IRSUC cold GDI E10 126 mg.km^{-1}, D1 B5 14.9 mg.km^{-1}). The same observation holds for the carbonyl compounds.

For all the vehicles, driving cycles and fuels used in this study, the emission factor observed for 1,3-butadiene, benzene and formaldehyde is quite low compared to emission factors obtained in previous studies (Aakko et al., 2006).

*Table 2: Artemis and IRSUC driving cycles gasoline vehicle emission factors (mg.km^{-1}) **

	IRSUC cold		IRSUC hot		ARTEMIS-urban		ARTEMIS-rural		ARTEMIS-motorway	
	Ref.	E10	Ref.	E10	Ref.	E10	Ref.	E10	Ref.	E10
Vehicle GDI										
Alkenes	21.29	12.93	N.D.	0.24	18.07	0.52	1.00	0.47	0.20	0.91
Alkanes	3.07	73.73	66.91	35.19	138.16	20.38	9.15	15.62	5.75	3.62
Aromatics	86.30	39.38	50.19	68.74	36.51	26.64	6.23	15.46	4.71	3.68
Total VOC	110.66	126.03	117.10	104.16	192.74	47.55	16.39	31.55	10.66	8.22
1,3-butadiene *	N.D.	483.05	N.D.	N.D.	N.D.	27.48	14.87	35.39	N.D.	N.D.
Benzene*	N.D.	37.5	N.D.	16.0	118.8	N.D.	7.4	N.D.	182.7	N.D.
Formaldehyde*[a]	990	850	570	350	2790	1320	430	220	170	210

[a] only formaldehyde has been quantified for the GDI vehicle

*Table 3: Artemis driving cycle Diesel vehicle emission factors (mg.km^{-1}) **

	ARTEMIS-urban				ARTEMIS-rural				ARTEMIS-motorway			
	Ref.	B5	B30	HVO	Ref.	B5	B30	HVO	Ref.	B5	B30	HVO
Vehicle D1												
Alkenes	0.36	2.82	0.46	2.05	0.35	0.98	0.24	0.31	0.72	0.08	0.21	0.16
Alkanes	6.22	4.98	2.31	53.88	0.88	3.81	3.97	11.61	5.76	0.85	1.83	5.91
Aromatics	9.48	7.51	3.70	20.34	2.10	0.52	6.01	3.48	3.73	1.09	4.66	2.91
Carbonyls	11.09	9.95	3.03	9.73	1.62	3.28	1.24	1.39	2.06	1.11	2.40	0.92
1,3-butadiene*	N.D.	N.D.	N.D.	343.3	20.6	71.9	N.D.	28.9	41.4	N.D.	N.D.	N.D.
Benzene*	N.D.	N.D.	N.D.	31.2	1.4	0.4	11.2	12.1	1.2	N.D.	9.4	7.5
Formaldehyde*	1463.2	1423.5	659.6	1248.6	352.7	499.5	288.1	115.1	551.6	168.1	331.4	123.7
Vehicle DPF												
Alkenes	0.50	0.24	N.D.	0.05	0.20	0.18	0.18	N.D.	0.33	0.01	0.03	0.44
Alkanes	25.27	8.32	2.19	39.73	0.74	1.80	2.00	3.46	1.45	2.45	1.90	1.00
Aromatics	10.96	12.93	3.66	13.93	1.87	3.15	0.01	4.83	1.90	3.51	1.11	2.14
Carbonyls	6.61	12.62	Nodata	15.23	0.89	0.96	1.97	3.76	1.46	0.83	1.31	3.59

1,3-butadiene*	N.D.	N.D.	N.D.	4.7	N.D.	N.D.	N.D.	4.9	5.8	9.5	N.D.	0.1
Benzene*	22.2	19.8	15.5	20.5	N.D.	9.5	5.1	3.7	N.D.	2.4	5.5	0.2
Formaldehyde*	1965.6	1687.1	Nodata	3532.9	226.7	267.9	362.6	656.2	377.4	214.7	228.9	357.7
Vehicle LDD												
Alkenes	0.63	1.61	N.D.	0.75	0.77	0.14	0.23	0.19	0.73			
Alkanes	30.47	39.26	6.26	21.33	3.04	0.15	4.05	0.06	0.38			
Aromatics	9.93	9.40	N.D.	4.21	1.25	2.44	1.27	N.D.	5.94	No data		
Carbonyls	4.20	7.82	7.69	13.89	0.92	1.91	0.81	3.22	1.07			
1,3-butadiene*	N.D.	2.9	N.D.	1.5	N.D.	N.D.	N.D.	N.D.	N.D.			
Benzene*	N.D.	20.1	N.D.	30.7	N.D.	7.2	15.1	N.D.	4.9			
Formaldehyde*	930.1	2301.5	1624.6	3445.7	163.7	485.3	161.8	826.0	164.8			

2.4 Influence of biofuels

An addition of ethanol to the reference fuel seems to reduce the emissions of volatile organic compounds in the exhaust gas, especially for the Artemis-urban driving cycle (from 192 to 47 mg.km^{-1}). Formaldehyde and acetaldehyde emissions also decrease when switching from reference gasoline to E10.

Changes are observed in the aromatics and alkanes emissions when fuelling diesel engines with biodiesel blends instead of reference diesel. For D1 under IRSUC cold and hot cycles, the amount of aromatics and alkanes emitted increases significantly when the percentage of biodiesel increases in the fuel (Ref < B5 < B30 < HVO). The trend is less pronounced for the other driving cycles. For this vehicle, the biodiesel content seems to have a positive influence on the emission factors. The results obtained for the two others diesel vehicles (DPF, LDD) are not so clear, and a weak increase of the emission factors from reference diesel to HVO is noted. The use of biofuel decreases slightly the production of carbonyls compared to reference gasoil, except for the Artemis urban cycle, but pure HVO leads also to high emissions of carbonyls.

Conclusions

The analysis presented in this study shows that the use of biofuel pure or in blends at different concentration (E10, B5, B30, HVO) in gasoline or diesel engines and under different driving cycle conditions, has an impact on the tailpipe emissions. Non-regulated pollutants mainly emitted are alkanes and aromatics compounds whatever the type of engine. On the whole, the addition of ethanol to gasoline reduces the aromatics emissions but does not affect the total VOCs emissions as regards IRSUC cold and IRSUC hot cycles, where the emissions levels stay almost similar. With biodiesel blends, the emission factors are higher with the hot start driving cycle than with the cold start one. For the Artemis driving cycles, the emission factors of the gasoline vehicle are reduced when going from urban to rural to motorway driving cycle, but no clear trend is noted with the diesel vehicles. The emission factors obtained during this study are significantly reduced compared to the ones obtained with Euro-3 compliant diesel and gasoline vehicles.

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