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Comparison of the morphological and chemical composition of particulate matter in the vehicles using gasoline and lpg at idle mode

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Abstract
In this paper we present the results of the measurements and analysis of particulate emissions of vehicles using the conversion system to use both LPG and gasoline fuels. The vehicles (n = 10) were measured using two different methods at the idle mode. The results show that the total number of particles from LPG-fueled vehicles is 1-1.35 times higher than gasoline-fueled vehicles for both $PM_{2.5}$ and PM_{10} in most cases. An increase of the metal components in PM of LPG-fueled vehicles compared to gasoline-fueled vehicles, which might be related to lubricant was observed.

Keywords: PM; Microparticles; Exhaust; LPG; Gasoline; Idle mode

1. Introduction

Currently, under the impact of strict regulations on limiting the emission of hazardous components in the exhaust of internal combustion engines, the trend to gradually switch to new fuels to replace traditional liquid fuels is considered as a potential direction [1]. Especially among the alternative fuels, liquefied petroleum gas (LPG) stands out as a fuel with many advantages such as higher potential energy, easier maintenance, and storage, etc [2], [3].

LPG is a mixture containing mostly propane, butane and a small proportion of propylene and butylene. The change in LPG content mainly depends on the ambient temperature condition. At low temperatures, a mixture with a high propane content is used, at a rate of 40-60%, while at higher temperatures, the content of butane is higher (up to 60%), due to the evaporation point of butane is low [4].

Compared with gasoline, LPG also has many advantages such as low cost, low reported carbon dioxide emissions, reduce PM emissions [3], [4], etc. The characteristics of the components, as well as the physicochemical properties of LPG (Table 1), allow it to possess favorable conditions for the formation of the mixture as well as improve the thermal efficiency and emission characteristics [4], [5].

The use of LPG has many advantages compared to other types of fuels, which are shown in several outstanding features such as the ability to store under room temperature conditions; availability and wide range of applications, from light to heavy vehicles, onshore as well as in the maritime industry [4].

Over the past decades, many studies have been conducted to perfect the combustion process of LPG fuel in internal combustion engines to improve thermal efficiency [6], [7], [8], [9], [10] as well as minimize the emission of toxic substances into the environment [10], [11], [12]. And they show that not only low PM emissions but the total THC and NO_x emissions of LPG direct injection engines are also significantly lower than direct injection gasoline engines [11], [12]. Simple chemical composition, LPG is burned with almost no particle emissions. And the reported emissions of hydrocarbons, carbon monoxide and NO_x are relatively less than gasoline and much less than diesel [4].

In the Vladivostok area, the large number of vehicles fitted with a converter (bi-fuel LPG system) allowed to use two types of fuel, LPG and gasoline. These vehicles have received good feedback from users, especially in terms of cost. However, the lack of studies to compare the emission of particulate matter in specific working modes under real conditions [2], [13], [14] in this region motivates us to study this issue. In this study, we conducted a comparison of particulate emissions at idle mode for operating vehicles using a bi-fuel LPG system, so that the engine can run with LPG or gasoline. Because the idle mode not only adversely affects the health, environment, and performance of the vehicles, it is also a source of air pollution by pollutants such as PM, NO_x, CO_2, and volatile organic compounds (VOC) [15]. Recent studies indicate that idling mode of a vehicle can take up to 6 to 16 hours per day [16], [17]. Especially in topographical conditions as well as the situation of the roads in the Vladivostok region, the idle mode occupies a relatively large part in the actual operation of the vehicles on curvy and narrow roads and/or places where traffic congestion often occurs.

Table1: Octane numbers of LPG components and gasoline [5]

Component	Formula	Heat capacity ($J{\cdot}K^{-1}{\cdot}mol^{-1}$)	Research Octane Number	Motor Octane Number
propane	C_3H_8	73.60	111.5	100
n-butane	C_4H_{10}	98.49	95	92
Isobutene	C_4H_8	118-128.6	100.4	99
Propylene	C_3H_6	90-100	100.2	85
n-butane-1	C_4H_{10}	98.49	100	80
n-butane-2	C_4H_{10}	98.49	101	83
gasoline	C_8H_{18}	240-256	92-95	83-86

2. Materials and methods

In order to reduce the exhaust temperature as well as to avoid water condensation in the Aerotrack 9306 V2 instrument, we designed a special dilution system for sampling (Figure 1).

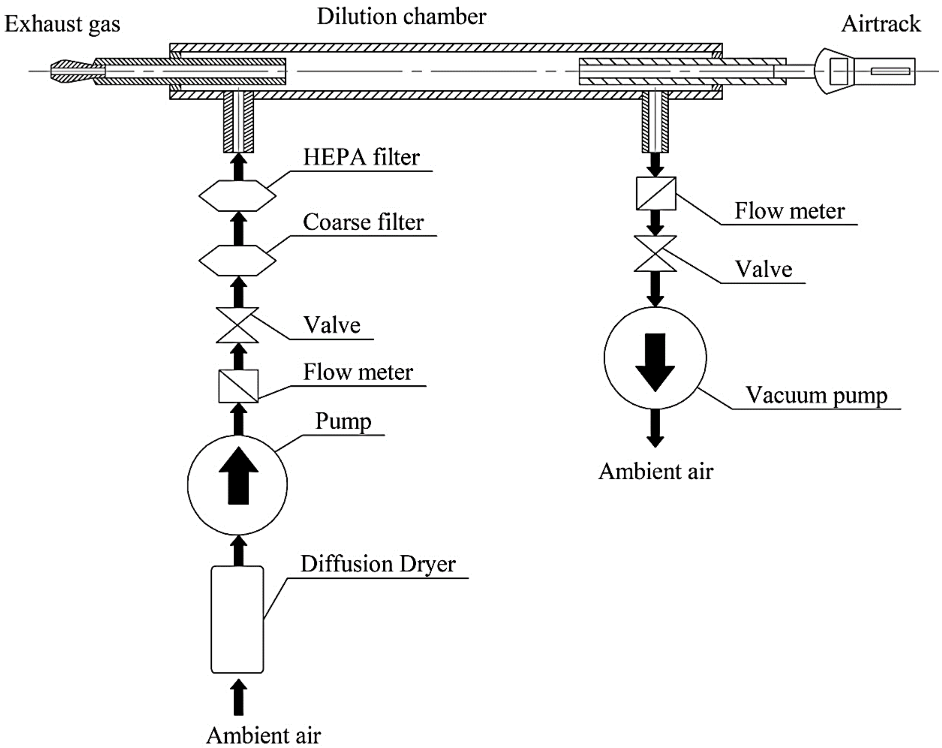

Figure 1. The dilution system use a through a high-efficiency particulate air (HEPA) filter

Measurements were taken every 3 times for each vehicle with an Aerotrack 9306 V2 instrument (TSI, USA). Each measurement sampling time was 1 minute. The total air volume analyzed was 2.83 liters. The device for counting the aerosol particles has 6 measurement channels in the range of 0.3, 0.5, 1.0, 3.0, 5.0, 10.0 μm. It was installed through a dilution system with a dilution factor equal to 10. The dilution system use a through a high-efficiency particulate air (HEPA) filter to avoid the particle effects on the background level of the emission facility.

For the study, 20 samples of the exhaust gases of passenger cars operating on gasoline and LPG fuel for total particles were selected (Table 2).

Next, samples of particulate matter were collected from the exhaust gases of automobiles into pure water using an aspirator. The elemental analysis of additional components was carried out using an atomic emission spectrometer with an inductively-coupled plasma ICE-9000 (Shimadzu, Japan). The results of the analysis of the content of metals are presented in Figure 2.

In order to granulometric analysis, the sample was analyzed on an Analysette 22 NanoTec laser particle analyzer (Fritsch, Germany). The measurements will be carried out in "nanotec" mode with carbon/water 20°C settings in three repetitions. The method collect experimental samples were described earlier for the car particle exhaust [18].

Table2: Characteristics of vehicles and ambient conditions

No.	Band	Year mode	Volume	Mileage, km	Temperature, °F	Humidity, %
1	Suzuki Escudo	2002	2.0	280000	63	27
2	Toyota Corolla	1997	1.6	500000	61	39
3	Toyota Ipsum	2003	2.4	270000	41	24
4	Toyota Premio	2001	1.8	220000	28	40
5	Nissan Serena	2002	2.0	238000	32	30
6	Toyota Corolla Fielder	2013	1.5	118859	39	33
7	Toyota Noan	2013	2.0	137296	41	31
8	Range Rover Vogue	2003	4.4	250000	41	31
9	Toyota Surf	2002	2.7	208000	43	23
10	Nissan Lafesta	2008	2.0	107178	18	73

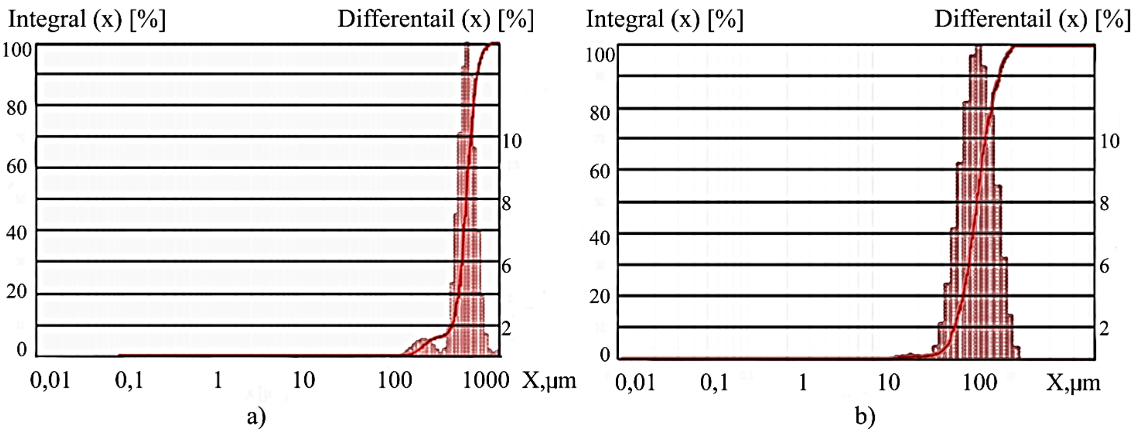

Figure 2. Granulometric data of particles at idle mode: a) gasoline, b) LPG

3. Results and discussion

According to the results obtained by Aerotrack for the first 20 samples, it was found that the total number particles of LPG-fueled vehicles exhibit an increase in the number of $PM_{2.5}$ (9/10 vehicles) and PM_{10} (8/10 vehicles) comparing with that used gasoline (Table 3). The increasing observed for $PM_{2.5}$ and PM_{10} is 1.15-1.5 times.

According to the results of the elemental analysis of additional components from the ICE-9000 device, it was observed that, in terms of mass, the metal components Pb, Cd, Mn in the PM in the exhaust of LPG-fueled vehicles 7, 8, 9 and 10 are 1.3 -2 times higher than gasoline-fueled vehicles (Figure 3).

Whereas, in vehicles 3, 5, and 6, the results showed the opposite, except for Mn. The cause of this phenomenon may be related to the lubricant quality as well as the technical condition of the vehicles, which we will discuss below.

According to the obtained results by the Analysette 22 NanoTec laser particle analyzer (Fritsch) for particle granulometry, a clear difference in the particle size distribution observed between LPG and gasoline mode. The dominant sizes are in the range of 3 to 10 µm, corresponding to 95-96%, from LPG-fueled vehicles. Meanwhile, in gasoline-fueled vehicles, the range of particle size is in the range of 100-1300 µm, accounting for up to 98% (Figure 2). This can be explained by the design features of the direct injection internal combustion engine. In idle mode, engines often work with a highly rich fuel-air mixture and do not operate at the highest temperatures as well as smaller engine speeds resulting in poorer mixture formation. The higher the viscosity fuel, the harder it is to form a mixture. This results in incomplete combustion of fuel and leads to high fuel residue in the exhaust gas [15], [19]. And, the particles in the exhaust contain unburnt fuel that makes them more hydrophobic. As a result, particles tend to aggregate to become larger particles, and these particles may not even decay even during the ultrasound [20]. For LPG fuel, this phenomenon is less common because before entering the cylinder, it is reduced pressure and heated to form a gas. Therefore, LPG fuel burns more thoroughly and particles are smaller (there are fewer particle agglomerations). This shows a trend of emission of smaller sized particles when running on LPG. This trend can be seen in the studies of Myung et. al, 2012 [1]. This result is also consistent with the result obtained from Aerotrack 9306 V2 because the Aerotrack 9306 V2 device only counted particles within the range of 0.3-10 µm. In this range, $PM_{2.5}$ and PM_{10} particles in LPG fuel mode might be more than gasoline.

With the ability to penetrate through the inhalation route, particles, smaller than 10 µm in size, are of great interest to researchers. Due to their smaller size and lighter, they are suspended in the air longer and are likely to disperse further from the source [21]. The larger particles, meanwhile, are thought to have less direct health effects, mainly causing harm to the environment. Due to their large size and mass, their dispersion ability is less and more likely to accumulate on the ground. And if they contain many toxic ingredients, they can directly affect groundwater as well as plants. This shows that the particles from the exhaust gas of Gasoline-fueled vehicles have a wide range of influence, both in health and the environment. Whereas, the particles when running LPG primarily impact on health.

Table3: Listed results of $PM_{2.5}$ and PM_{10} in term of particle number and mass

Accumulative: Average number of particles in 1 litre exhaust gas							
No.	Characteristics			$PM_{2.5}$ (#/l)	PM_{10} (#/l)	$PM_{2.5}$ (µg/l)	PM_{10} (µg/l)
1	Suzuki Escudo	2002	LPG	909713	6810	202	129
			Gasoline	786028	4627	154	86
2	Toyota Corolla	1997	LPG	51089	313	8	16
			Gasoline	62868	301	9	16
3	Toyota Ipsum	2003	LPG	69560	4430	38	393
			Gasoline	57591	2559	23	225
4	Toyota Premio	2001	LPG	76377	1283	16	106
			Gasoline	69953	1355	16	110
5	Nissan Serena	2002	LPG	39895	297	7	15
			Gasoline	31855	213	5	11
6	Toyota Corolla Fielder	2013	LPG	58958	1992	20	156
			Gasoline	50588	1253	14	95
7	Toyota Noan	2013	LPG	94124	734	15	47
			Gasoline	69791	716	12	57
8	Range Rover Vogue	2003	LPG	170244	577	17	37
			Gasoline	153881	477	15	32
9	Toyota Hilux Surf	2002	LPG	302913	855	38	41
			Gasoline	201123	650	26	33
10	Nissan Lafesta	2008	LPG	73225	758	13	52
			Gasoline	60576	899	13	67

Metal components, when vehicles run on LPG fuel, indicate the fact that they are derived primarily from lubricating oil [22]. Because the composition of LPG is said to contain no metals. Cadmium is present in lubricating oils as an anti-wear additive of cadmium dialkyl dithiophosphates [22]. Cadmium is accepted to not essential for plants, animals, and humans. Higher doses of cadmium from ingestion and inhalation can cause toxic effects for humans [23]. While Mn is thought to be non-toxic to humans, lead is a very toxic metal. The element Pb causes damage to the nervous system and causes brain disorders when exposed for a long time. The appearance of these three metals in exhaust gases supports the hypothesis of burnt lubricating oil as analyzed above.

The effect of lubricant composition on vehicle exhaust was studied [24], [25] has shown that lubricant has little effect on the vehicle's gaseous emissions. It mainly affects the particle distribution, especially the particles in the nucleation mode when vehicles running at idle or low load. Lubricants in gasoline-fueled engines are deteriorated much faster than LPG-fueled vehicles because of the higher rate of nitrification and oxidation [26]. On the other hand, gasoline can be dissolved with lubricating oil not only to reduce the viscosity index of the oil but also to reduce the temperature of the lubricant flash point, ie to reduce the temperature at which the lubricant can ignite [26].

Recent studies have shown that a reduction in maximum speed, power, torque as well as increase the ash content in lubricant when using LPG fuel [26], [27]. The greater the degree of decline as the oil gets more deteriorated. Therefore, to balance the power as well as torque in bi-fueled vehicles, LPG fueled mode is usually calibrated in the direction of increasing power and torque, that is, increasing the amount of LPG fuel enters the cylinder or increasing the fueling time. This happens even under low-speed conditions, such as idle mode. In this case, the burning process of fuel in the cylinder is prolonged making the possibility of burning lubricant is very high. This explains the increase ash content in lubricating oil as shown in the study [26]. The flammability of oil is even more serious for gasoline and LPG-fueled vehicles since gasoline plays a major role in reducing the temperature of the lubricant flash point. The more deteriorated the oil, the greater the amount of gasoline dissolved in the oil. And, when switching to LPG fuel mode, lubricating oil is even more prone to fire. As a result, the amount of metal in the exhaust will increase according to the level of oil deteriorate. Not only that, but the amount of burnt oil will also contribute to creating more particles. This phenomenon can be observed in vehicles number 6 to 10.

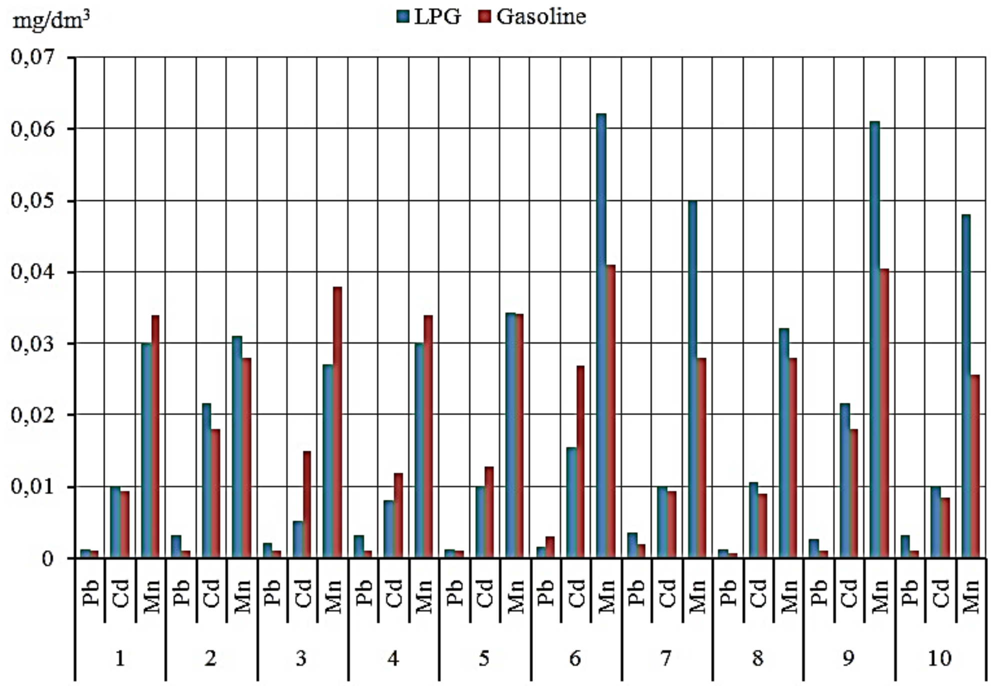

Figure 3. Metal compositions in exhaust gas LPG and gasoline fueled vehicles

4. Conclusion

Measurements of the vehicle's particulate emissions in real-work conditions allowed us to accurately assess the contribution to the total emissions of the two common fuels used in the Vladivostok region.

The combination of two different measurement methods provides an overview of the particle distribution of the vehicles. This provided a more comprehensive comparison of contributions to total particle emissions as well as health and environmental impacts.

From the standpoint of human health, the most harmful particles are particles smaller than 10 micrometers in size, because of their ability to penetrate through the breath. However, from an environmental standpoint, this limit is not limited, and larger particles can also cause negative effects on the environment.

Since the particle counting range of the Aerotrack 9306 V2 particle counting device is limited by the particle size of less than 10 μm. Therefore, from the standpoint of human health, the particle counting method using the Aerotrack 9306 V2 device gives more detailed results. However, results from laser light scattering methods allow for a more comprehensive assessment.

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