Pak. J. Engg. & Appl. Sci. Vol. 10, Jan., 2012 (*p.* 29-35)

A Comparative Study on VOCs and Aldehyde-Ketone Emissions from a Spark Ignition Vehicle Fuelled on Compressed Natural Gas and Gasoline

Asad Naeem Shah[1], Ge Yun-shan[2], Tan Jian-wei[2] and Wang Jun-fang[2]

1. Department of Mechanical Engineering, University of Engineering and Technology, Lahore 54000, Pakistan
2. School of Mechanical and Vehicular Engineering, Beijing Institute of Technology, Beijing 100081, P. R. China
* Corresponding author; E-mail address: anaeems@uet.edu.pk or naeem_138@hotmail.com

Abstract

In this work, an experimental study was conducted on a spark ignition (SI) vehicle fuelled on compressed natural gas (CNG), and gasoline to compare the unregulated emissions such as volatile organic compounds (VOCs) and aldehyde-ketones or carbonyls. In the meantime, ozone forming potential (OFP) of pollutants was also calculated on the basis of their specific reactivity (SR). The vehicle was run on a chassis dynamometer following the Chinese National Standards test scheduled for light duty vehicle (LDV) emissions. According to the results, total aldehyde-ketones were increased by 39.4% due to the substantial increase in formaldehyde and acrolein+acetone emissions, while VOCs and BTEX (benzene, toluene, ethyl benzene, and xylene) reduced by 85.2 and 86% respectively, in case of CNG fuelled vehicle as compared to gasoline vehicle. Although total aldehyde-ketones were higher with CNG relative to gasoline, their SR was lower due decrease in acetaldehyde, propionaldehyde, crotonaldehyde, and methacrolein species having higher maximum incremental reactivity (MIR) values. The SR of VOCs and aldehyde-ketones emitted from CNG fuelled vehicle was decreased by above 10% and 32% respectively, owing to better physicochemical properties and more complete burning of CNG as compared to gasoline.

Key Words: *Compressed natural gas, unregulated emissions, carbonyls, volatile organic compounds, spark ignition vehicle.*

1. Introduction

Increasing concerns on global warming and exhausting fossil fuel deposits are the main stimuli for researchers endeavoring to find alternative means of energy for transportation sector over the past few years. Vehicular exhaust is one of the major anthropogenic sources of air pollution and affects badly to the quality of the urban air [1]. Use of alternative fuels, especially CNG is not only beneficial to overcome the issue of fuel shortage but also to reduce the global warming owing to the decrease in photochemical smog or ozone. CNG improves air quality by creating less ozone and CO emissions, thus vehicles running on CNG produce the lowest levels of reactive compounds as compared to any alternatively fuelled vehicles [2].

CNG is a promising alternative fuel which is easily available in many developed and developing countries at relatively low prices. Owing to tax rebates, the prices of CNG are less than fossil fuel in most of the European countries, especially in Italy, it costs almost half as compared to diesel (0.66 compared to 1.1 euro/kg) [3]. In order to encourage the use of CNG as a substitute fuel in Mexico City, authorities are evaluating the viability of CNG to be used in private and commercial vehicles, police patrols, and microbuses to decrease air pollution [4].

CNG is a non-toxic fuel having the highest hydrogen-to-carbon ratio among the other hydrocarbons, and hence leading to the diminution of carbon dioxide (CO_2) [3]. Extremely low photochemical reactivity, zero evaporative emissions, very good antiknocking properties, decreased cold start and low-temperature emissions with increased cold start capability, low emission lean-burning, higher ignition temperature, and reduced emissions of CO_2 are the key factors which are responsible for making CNG as one of the most attractive alternative fuels for fossil fuels in the sector of transportation [2].

Current work is aimed at the experimental investigation of unregulated emissions like VOCs and aldehyde-ketones emanated from SI car fuelled on CNG and gasoline fuels. Furthermore, these pollutants have been compared in terms of their emission factors (EF) and SR to investigate their photochemical smog or OFP. Although some researchers have worked on regulated emissions from CNG-fuelled SI vehicles, a limited data is available on unregulated emissions, particularly on carbonyls and VOCs emissions from vehicles fitted with three-way catalytic converter. To best of author's knowledge, these pollutants have not yet been discussed in terms of their OFP or SR under the Chinese National Standards.

VOCs are thought to be major precursors of photochemical smog, which actively participate in many health hazards and toxic activities. They play a key role in the elevation of terrestrial ozone during the sunny periods and in the formation of aerosols, and are also actively involved in the depletion of stratospheric ozone [5]. A group of VOCs comprising benzene, toluene, ethyl benzene, and xylene is known as BTEX which has the great potentials for both peroxyacetyl nitrate (PAN) and ozone [6]. Benzene, an important component of VOCs, is believed to be responsible for increasing the risk of leukemia [7].

Aldehyde-ketones play a predominant role on the tropospheric chemistry and are important precursors to ozone, PAN and free radicals [8]. Some aldehyde-ketones like acetaldehyde, acrolein and formaldehyde are not only mutagenic and toxic, but also carcinogenic to human body [9]. Acetaldehyde and acetone have been reported to be actively involved in the photochemical smog generation cycle [10].

2. Experimental Setup

2.1 Test Vehicle, Fuels, and Driving Cycle

A dual-fuel 4 cylinder SI vehicle was used in this study. It is a recent model, multi port fuel injected (MPFI) and Euro 3 compliant passenger vehicle having maximum power of 62 kW and a displacement volume of 1.3 L. It was run on a 1.0 m single-roll DC electric chassis dynamometer (ONO SOKKI Inc.). Prior to the starting of experiments, vehicle was soaked overnight in the laboratory and the Chinese type I test GB 18352.3-2005 [11] standard protocol was followed while performing the experiments. Thus, a cooling fan was used in front of the car to avoid it from heating up during the study. The experimental setup is shown in Fig. 1 as the schematic diagram. Two test fuels were used in this study, which are unleaded gasoline having research octane number (RON) 93 and CNG, with gasoline as a reference or base-line fuel. The fuels were purchased from the gasoline and CNG stations, and hence are the representatives of the fuels which are used in Beijing, P. R. China. The properties of both fuels are given in Table 1 [12].

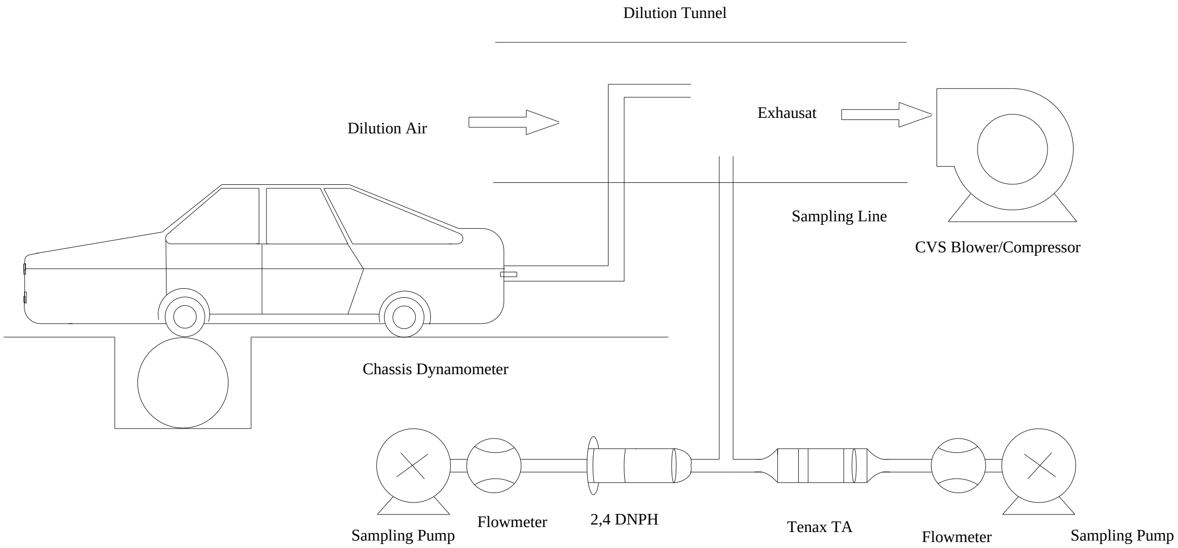

Fig. 1: Experimental Setup

Table 1: Properties of test fuels [12]

PROPERTIES	CNG	GASOLINE
Density (kg·L^{-1}) at 20˚C	0.445	0.74
Boiling point (˚C)	-162	30~200
Auto-ignition temperature (˚C)	650	450
Lower calorific value (MJ•kg^{-1})	49	46
Latent heat of vaporization (kJ•kg^{-1})	510	310
Octane number (RON)	127	93
Stoichiometric air-fuel ratio	17.3	14.7
Compression ratio	14:1	10:1

The experiments were conducted following the Chinese National Standards for Emissions of the Light Duty Vehicles, similar to the European Emission Cycle (70/220/EEC). Part 1 of the cycle consists of four sub-cycles each of which takes 195 sec, so total 780 sec are required for part 1 to be completed. This part is also called as urban driving cycle because it simulates the urban area. Part 2 of the cycle is named as the extra urban driving cycle, and takes 400 sec in its completion. This part simulates the main motor-way, out of the urban zone with more aggressive speed conditions. The total time of operation of this cycle is 1180 seconds with an average speed of the vehicle 33.58 km/hr [11]. The cycle is shown in Fig. 2.

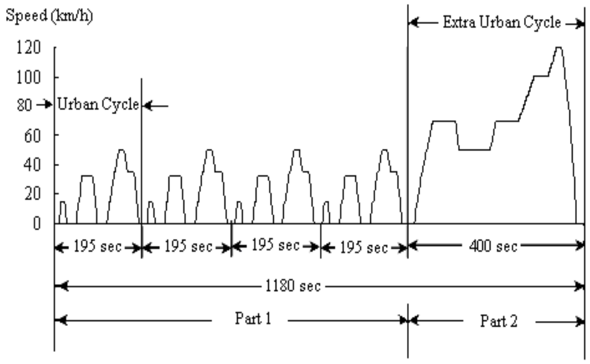

Fig. 2 Operating cycle of the test car according to the Chinese type I test standard [11]

2.2 Sampling Methodology and Analysis

The vehicle exhaust was introduced into a dilution tunnel based on standard critical flow venture-constant volume sampler (CFV-CVS). In order to dilute and cool the exhaust from the tailpipe, and hence eliminate the problem of water condensation during the sampling, the exhaust was mixed with the fresh and filtered atmospheric air. During the tests, the ambient pressure and temperature were about 100 kpa and 25°C, respectively. The diluted mixture was constantly monitored for its temperature and pressure during the flow through the CFV. The flow rate of the mixture was 10 m^3/min and dilution ratio was about 15 to keep the maximum tunnel temperature less than 52˚C. The dilution ratio was measured with the help of two concentrations of carbon dioxide (CO_2) by using two gas analyzers SEMTECH-DS and HORIBA (MEXA 7400 H) at the entrance and exit of the dilution tunnel. The sampling was accomplished as per sampling scheme shown in the Fig. 1.

The Tenax TA® tube and 2, 4-dinitrophenyl-hydrazine (DNPH) coated silica gel cartridge (Accustandard® Inc.) were used to trap the VOCs and aldehyde-ketone pollutants respectively, as discussed elsewhere [13-17]. For the suction of pollutants, constant volume sampling pump was used which enabled the exhaust material to be drawn in sampling cartridge. The sampling volume was kept 220 mL which took 10 min to sample the material at every mode. Each tube or cartridge was used to trap the exhaust material for each transient cycle. Total two tubes/cartridges were used for VOCs as well as Aldehyde-ketones emissions during the complete cycle. One cartridge was used for the urban (part 1), while the other used for the extra urban (part 2) of the cycle. The sampling process was accomplished two times on the same cycle, thus, pollutants analyzed and discussed on the basis of their average values. After sealing with aluminum foil, the sampling cartridges were refrigerated at about -10˚C

2.2.1 Qualitative and Quantitative Analysis of VOCs

The species trapped in Tenax TA® were extracted using automatic thermal desorber in which Tenax tubes were first blown by the dry inert gases.

The desorbed compounds were cryogenically concentrated during a cold trap at -10°C. After focusing, the trapped pollutants were heated from -10˚C to 280°C at 40˚C/sec for 160 sec to volatilize the species into gas chromatograph through a fused silica capillary column (HP-5MS, 30 m × 0.25 mm × 0.25 µm) as discussed elsewhere [15-18]. The column flux was 1 mL/min, while the carrier gas was helium (99.999%), and the oven temperature was programmed from 35˚C to 280˚C for 10 min at the rate of 5˚C/min. The US environment protection agency (US EPA, 1999) standard method TO-17 [19] was used for the analysis of VOC species.

The VOCs were identified by comparing their retention times of chromatographic peaks with those of standard solutions purchased from Sino-Japan Friendship Center for Environment Protection. This was accomplished with the comparison of their mass spectra with those available in the US National Institute of Standards and Technology (NIST05) library as discussed elsewhere [15, 17-18]. After the identification, VOCs were quantified with the help of external standard method by making their linear standard curves. The purchased standard liquids were taken in 1µL, 2 µL, 4 µL, 10 µL, 20 µL and 40 µL respectively using micro- sampler. The compounds were then analyzed using certain chromatographic conditions. According to these standard curves, the target compounds were quantified by the regression method of their peak areas. In this case, relative standard deviation (RSD) of each compound peak area was taken [15, 17]. The characteristics of mass spectrometer (MS) are listed in Table 2

Table 2: MS characteristics

PARAMETER	SPECIFICATION
Acquisition mode with range	SCAN with a range of 35-450 amu
Electron voltage	1.0 kV
Temperature of transfer line to MS	250ºC
Ion source with temperature	Electron impact (EI) 70 eV, 200ºC
Solvent cut time	2.5 min

2.2.2 Qualitative and Quantitative Analysis of Aldehydes-ketones

In order to extract the species trapped in 2, 4-dinitrophenylhydrazine (DNPH) coated silica gel cartridges (Accustandard® Inc.), solid phase extraction (SPE) process was used as discussed elsewhere [13-14, 18]; however, given here briefly for the interest of the readers. In this case, the sampled material taken in cartridge was placed on an extractor in the solid phase, and sampled material was eluted from the cartridges with the help of washing with 3 mL acetonitrile. The elute material was collected, filtered, and then poured into a flask of 5 mL volume to obtain a solution of acetonitrile with constant volume. In order to elute the formed aldehydes and ketone-DNPH derivatives, a C18 column (XDB-C18 Agilent Eclipse with a size of 4.6 mm x 150 mm, 5µm) was used. Acetonitrile and distilled water were used as mobile phases in accordance with a volume ratio of 60% acetonitrile/40% water (v/v). The injected volume, flow rate and temperature gradient were 25µL, 1.0 mL/min and 25˚C respectively. Compounds were analyzed using high performance liquid chromatographic (HPLC) system using an automatic injector and an ultraviolet detector which detected the compounds at 360 nm.

After extraction, aldehyde-ketones were identified by matching their HPLC retention time with those of authentic standards. For the quantification of the species, the method of external standard was used as discussed earlier.

3. Results and Discussion

3.1 VOCs Emissions

Fig. 3 shows a substantial abatement in VOCs emissions for CNG fuelled vehicle as compared to gasoline vehicle. Components such as benzene, toluene, butyl acetate, ethyl benzene, p,m-xylene, styrene, o-xylene, and n-undecane were decreased by 86.2, 83.4, 82.2, 89.6, 85.7, 96%, 88.4, and 30.1% respectively. Consequently, an overall decrease was 85.2% and about 86% in VOCs and BTEX emissions, respectively.

This reduction in VOCs, especially in BTEX emissions is attributed to the better mixing of CNG with air, and to its more even distribution to the cylinder. This leads to the more complete combustion, and hence to higher combustion temperature in case of CNG fuel, relative to gasoline. Higher temperature is prone for the decomposition of VOCs; particularly, benzene, toluene and xylene isomers have been reported to be decreased significantly at higher temperature [20-21]. Similar finding was also given by Gaffney and Marley [22] that total VOC-components reduce in case of CNG and LPG as compared to alcohol or gasoline fuels. Moreover, CNG contains less aromatic content and has a higher hydrogen/carbon ratio, both of which are responsible for the reduction of VOC species in case of CNG fuelled vehicle. Yang, et al. [23] have reported that low content of aromatics and a higher H/C ratio allow better reduction of aromatic hydrocarbons (VOCs).

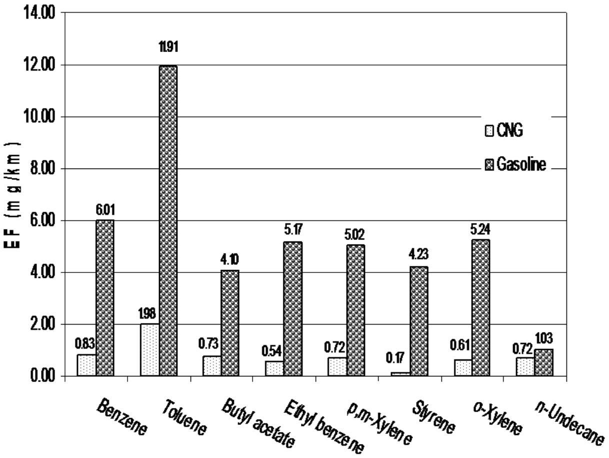

Fig. 3 VOCs emissions comparison of CNG and gasoline fuels

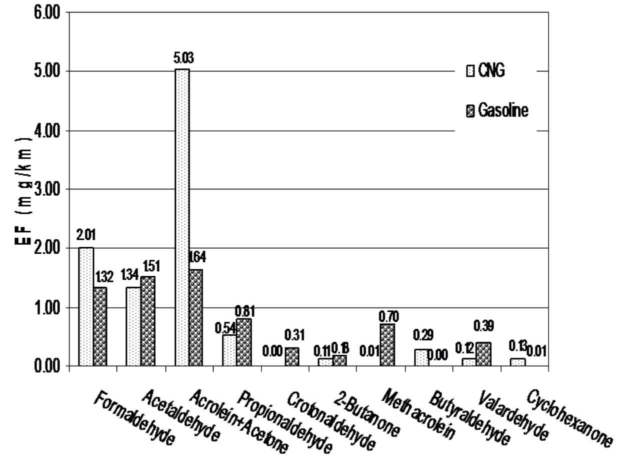

Fig. 4 Aldehyde-ketones emissions comparison of CNG and gasoline fuels

3.2 Aldehyde-ketones Emissions

As presented in Fig. 4, acrolein and acetone are discussed together in this study because of their same retention time (almost same). As per experimental findings, acetaldehyde, propionaldehyde, 2-butanone, methacrolein, and valardehyde were decreased by 11.3, 33.3, 35.2, 98.6, and 69.2% respectively, in case of CNG fuelled vehicle relative to gasoline vehicle. However, formaldehyde and acrolein+acetone were increased by 1.5 and 3 times, respectively. Consequently, there was an over all increase of 39.4% in aldehyde-ketone pollutants due to significant increase in formaldehyde and acrolein+acetone emissions.

The abatement in acetaldehyde, propionaldehyde, 2-butanone, methacrolein, and valardehyde emissions from CNG fuelled vehicle relative to gasoline vehicle is due to the difference in physicochemical properties of the two fuels. Properties like higher octane number, higher flame temperature, negligible sulfur content, higher compression ratio, higher hydrogen/carbon ratio, comparable flame speed, and higher air/fuel ratio leading to lean-burning, advance the combustion process of CNG fuelled vehicle. On the other hand, rise in formaldehyde with CNG may be attributed to relatively more lean-burning of CNG in the combustion chamber, which might not be suitable for the oxidation of formaldehyde. Further, the increase in acrolein+acetone emissions with CNG compared with gasoline is ascribed to the restraint in the oxidation of their precursors in case of CNG fuel.

The contribution of formaldehyde, acetaldehyde, acrolein+acetone, and propionaldehyde to total aldehyde-ketones emissions is 93 and 77% with CNG and gasoline, respectively. This finding is similar to that of previous study that 90% of aldehyde-ketones come from acetaldehyde, acrolein+acetone, formaldehyde, and propionaldehyde [24]. Grosjean, et al [25] have reported that acetaldehyde, acetone, formaldehyde, and propionaldehyde are the four largest contributors to aldehyde-ketone emissions from vehicles.

3.3 Specific Reactivity of the Pollutants

The OFP of the VOCs and aldehyde-ketones may be calculated on the basis of their SR which is defined as the mass of ozone (O_3) potential (in mg) per milligram mass of the non- methane organic gases (NMOG) for the emissions, and can be evaluated as under [26]:

$$SR = \frac{\sum (NMOG_j \bullet MIR_j)}{\sum NMOG_j} \tag{1}$$

The subscript j stands for a certain compound other than methane or a non-methane organic gas (NMOG) like VOCs and aldehyde-ketones, and MIR stands for maximum incremental reactivity. Carter and Lowi [26], examined air modeling based on ozone forming reactivates of species and proposed the MIR factor as an index for ozone formation, which was issued by the California Air Resource Board (CARB) in 1992, and is given as APPENDIX.

As presented in Fig. 5, the SR of VOCs emanated from CNG was 10.4% lower, relative to gasoline. Moreover, the SR of aldehyde-ketones pollutants was decreased by 32.7% in case of CNG, compared with gasoline. This reduction in SR of VOCs with CNG as compared to gasoline is due the reduction in VOCs emissions, particularly in toluene and xylene isomers carrying the highest MIR values among the other VOC-components. It is of great concern to note that even though the total aldehyde-ketones emissions increased in case of CNG, their SR calculated on the basis of equation (1) was lower as compared to gasoline. This enigma comes to end very soon when individual components and their corresponding MIR values are observed from APPENDIX. Acetaldehyde, propionaldehyde, crotonaldehyde, and methacrolein showing higher MIR values were decreased appreciably in case of CNG, relative to gasoline fuel. Even crotonaldehyde and methacrolein, important species of aldehyde-ketone, were totally absent in case of CNG fuel. Consequently, the SR of aldehyde-ketones emitted from CNG fuelled car decreased as compared to gasoline fuelled car. This is an important finding showing the advantage of CNG over gasoline fuel.

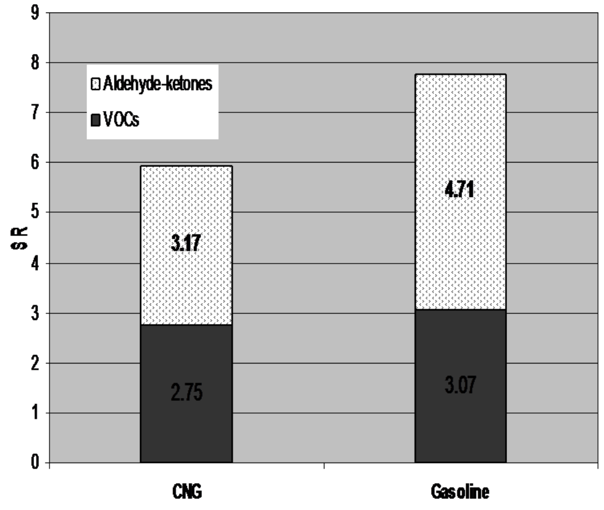

Fig. 5: Specific reactivity of unregulated emissions from CNG and gasoline fuels.

4. Conclusions

An experimental study was conducted on an SI vehicle fuelled on CNG and gasoline separately for the comparison of unregulated pollutants and their SR. It was revealed that all the individual VOC-components were decreased, resulting in an over all decrease of 85.2% with CNG as compared to gasoline. Further, the BTEX components were reduced by around 86% in case of CNG fuelled vehicle, relative to gasoline vehicle. Moreover, acetaldehyde, propionaldehyde, 2-butanone, methacrolein, and valeraldehyde were decreased, where as formaldehyde and acrolein+acetone increased, resulting in an over all increase of 39.4% in case of CNG, compared with gasoline fuel. Furthermore, the specific reactivity, and hence ozone forming potential of VOCs was decreased by 10.4% with CNG, relative to gasoline. Also, the SR of aldehyde-ketones was reduced by 32.7% in case of CNG fuelled vehicle as compared to gasoline vehicle.

5. Acknowledgements

The authors are thankful to the laboratory staff for their technical guidance during the experiments. Current study was financially supported by the National Natural Science Foundation (NNSF) of China under the grant # 50576063.

6 References

[1] Correa, S. M., Arbilla, G; Atmos. Environ. 42(2008) 769-775.

[2] Gandhidasan, P., Ertas, A., Anderson, E. E; Journal of Engg for Gas turbine and Power (ASME), 113(1991) 101-107.

[3] Turrio-Baldassarri, L., Battistelli, C. L., Conti, L., Crebelli, R., De Berardis, B., Iamiceli, A. L., Gambino, M., Iannaccone, S; Sci. Total Environ., 355(2006) 64-77.

[4] Schifter, I., Diaz, L., Lopez-Salinas, E., Avalos, S; Environ. Sci. Technol., 34(2000) 2100–2104.

[5] Theloke, J., Friedrich, R; Atmos. Environ., 41(2007) 4148-4160.

[6] Derwent, R. G., Jenkin, M. E; Atmos. Environ., 25(1991) 1661-1678.

[7] U. S. EPA, 1, 450 (1990).

[8] Pang, X., Mu, Y., Yuan, J., He, H; Atmos. Environ., 42(2008) 1349-1358.

[9] Carlier, P., Hannachi, H., Mouvier, G; Atmos. Environ., 20(1986) 2079-2099.

[10] Poulopoulos, S. G., Samaras, D. P., Philippopoulos, C. J; Atmos. Environ., 35(2001) 4399-4406.

[11] Yan, D., Yun-shan, G., Jun-fang, W., Jian-wei, T., Ke-wei, Y; J. of Beijing Institute of Tech., 19(2010) 31-36

[12] Guan-jing, W; Clear Fuel for Vehicle, Petroleum Industry Publishing House, Peoples Republic of China (in Chinese language).

[13] Shah, A. N., Ge, Y., Tan, J; Jordan Journal of Mech. & Indus. Engg., 3(2009) 111-118.

[14] Shah, A. N., Ge, Y., Jiang, L., Liu, Z; Turkish J. Emg. Env. Sci. 33(2009) 259-271.

[15] Shah, A. N., Ge, Y., Jiang, L; The Arabian Journal for Science and Engineering, AJSE B-Engineering (accepted for Publication).

[16] Shah, A. N, Ge, Y., Zhao, H; Jordan Journal of Mech. & Indus. Engg., 4(2010) 340-345.

[17] Shah, A. N., Ge, Y., Tan, J., Liu, Z; Pak. J. Sci. Ind. Res., 52(2009) 158-166.

[18] Shah, A.N., Ge, Y., Shaikh, M.A; Mehran University Research Journal of Engineering & Technology (MURJET), 28(2009) 581-590.

[19] US. Environment Protection Agency (US EPA), "Determination of volatile organic compounds in ambient air using active sampling onto sorbent tubes". Compendium method TO-17, 1999.

[20] Di, Y., Cheung, C. S., Huang, Z; Sci. Total Environ., 407(2009) 835-846.

[21] Cheung, C. S., Di, Y., Huang, Z; Atmos. Environ., 42(2008) 8843-8851.

[22] Gaffney, J. S., Marley, N. A; Atmos. Environ., 43(2009) 23-36.

[23] Yang, H., Chien, S., Cheng, M., Peng, C; Environ. Sci. Technol., 41(2007) 8471-8476.

[24] Turrio-Baldassarri, L., Battistelli, C. L., Conti, L., Crebelli, R., De Berardis, B., Iamiceli, A. L., Gambino, M., Iannaccone, S; Sci. Total Environ., 327(2004) 147-162.

[25] Grosjean, D., Grosjean, E., Gertler, A. W; Environ. Sci. Technol., 35(2001) 45-53.

[26] Carter, W. P. L., Lowi, A; Society of Automotive Engineering (SAE) Tech. Paper Ser., No. 900710(1990).

APPENDIX [24]

MIR values for VOCs and aldehyde-ketones emissions

VOCs	**MIR**	**Aldehyde-ketones**	**MIR**
Benzene	0.42	Formaldehyde	7.15
Toluene	2.73	Acetaldehyde	5.52
Butyl acetate	n/a	Acrolein+Acetone	6.77*,0.56**
Ethyl benzene	2.70	Propionaldehyde	6.53
p,m-Xylene	7.64	Crotonaldehyde	5.42
Styrene	2.22	2-Butanone	1.18
o-Xylene	6.46	Methacrolein	6.77
n-Undecane	0.42	Butyraldehyde	5.26
		Valeraldehyde	4.41
		Cyclohexanone	n/a

6.77* is for acrolein and 0.56** is for acetone