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Influence of Fuel Types and Combustion Environment on Emission of VOCs from Combustion Sources: A Review

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ABSTRACT

Volatile Organic Compounds (VOCs) are toxic or or carcinogenic, as well as creating photochemical fumes in the presence of sunlight, damaging the environment. In this study, the damages of VOCs to the environment and human health are discussed first. In addition, the definition and classification of the VOC of important international bodies are given in detail and the VOCs that are considered the most harmful and subject to legislative purposes in the context of this definition and classification are examined. Then, the harmful and abundant of VOC species emitted by the power plants and internal combustion engines, which are the main subject of the study, were examined and the parameters affecting the emission of these emitted gases are discussed under separate titles. The parameters affecting the VOCs release in the combustion event vary depending on the fuel and combustion system. By determining the effects of these parameters on VOCs emission, necessary conditions were determined to reduce the emission of these harmful components. Thus, some insights were tried to be given about the reduction of VOC emissions that may occur by burning fossil fuels in thermal power plants and internal combustion engines.

Keywords: Combustion parameters, PAHs, Power stations, Toxic and carcinogens, Vehicles exhaust, VOCs

Yakıt Türleri ve Yanma Ortamının Yanma Kaynaklarında Uçucu Organik Bileşiklerin (VOCs) Oluşumuna Etkisi: Derleme Bir Çalışma

ÖZ

Uçucu Organik Bileşikler (VOCs) zehirleyici veya kanser yapıcı maddeler olmaları yanı sıra güneş ışığının varlığında fotokimyasal duman oluşturarak çevreye zarar verirler. Bu çalışmada ilk önce VOC’lerin çevreye ve insan sağlığına zararları tartışılmıştır. Peşi sıra önemli uluslararası kuruluşların VOC'i tanımı ve sınıflandırılması ayrıntılı bir şekilde verilmiş ve bu tanımlama ve sınıflandırma bağlamında yasama denetiminin tabi tuttukları en zararlı VOC’ler irdelenmiştir. Ardından çalışmanın ana konusu olan termik güç santralleri ile içten yanmalı motorlar tarafından çevreye salınan zararlı ve emisyonu yüksek VOC bileşenleri incelenmiş ve salınan bu zararlı gazların emisyonuna etki eden parametreler ayrı başlıklar altında ele alınmıştır. Yanma olayında VOC'lerin salınımını etkileyen parametreler, yakıt ve yanma sistemine göre değişkenlik göstermektedir. Bu parametrelerin VOC'lerin salınımına etkilerinin tespitiyle bu zararlı bileşenlerin emisyonunun azaltılabilmesi için gerekli şartlar belirlenmeye çalışılmıştır. Böylece termik güç santralleri ile içten yanmalı motorlarda fosil yakıtların yanmasıyla oluşabilecek VOC emisyonlarının azaltılması konusunda bir fikir oluşturulmaya çalışılmıştır.

Anahtar Kelimeler: Enerji santralleri, PAHs, Taşıt egzozu, Toksik ve kanserojenler, VOCs, Yanma parametreleri

INTRODUCTION

Volatile organic compounds (VOCs) are attracting considerable attention from scientific and governmental organisations because of their known impact on human health and environment. Therefore an increasing number of VOCs are already the subject of legislative control. These pollutants are emitted via two sources: one natural, the other anthropogenic. VOCs are very important precursors of tropospheric ozone and have the potential to affect quality of life and global climate change. Many of the primary VOCs and their oxidized products constitute a significant part of the secondary pollutants in urbanized areas. VOCs control the oxidation capacity of the troposphere, due to the rapid reaction rates with the hydroxyl radical (OH). VOCs pollution caused by anthropogenic emission poses an increasingly serious concern for human health, environment and global climate. Among the main anthropogenic sources are motor vehicle exhaust emissions, industries, biomass and biofuel combustion, use of chemical solvents, etc. VOCs have a direct impact on the environment. However, they contribute indirectly through the formation of secondary organic aerosols in climate change. Even a very small amount of some of the VOCs can adversely affect human health. Therefore, it is necessary to determine the parameters affecting the emission by analysing the emission sources well. Emission of these harmful gases emitted to the environment can be minimized through these parameters [1–3]. The main concern of this work is with stationary combustion units and vehicles. Since these two important sources comprise most of anthropogenic related emissions [2]. Especially the most abundant source of VOCs in cities is released from internal combustion engines to the environment. Combustion engines used in cars, ships, airplanes, power stations, etc. emit many air pollutants that have many different negative effects on public health and natural environment. One of the most important of these harmful gases is VOCs. Gasoline and diesel cars cause VOC emissions through the evaporation of fuel from gasoline vehicles in addition to emission of VOC from exhaust when operating [4–10].

According to Elsom, 32% of the volatile organic compounds in the urban areas of Australia are released into the environment by motor vehicles [11]. Wang et al. report that 46% volatile organic compounds in Beijing are caused by vehicle emissions [3]. Cai et al. also inform that VOCs emissions in Shanghai are caused by 25% emissions from vehicle exhausts [2]. Gaur et al. state that vehicular emissions are one of main sources of VOCs in urban areas in India [12]. The majority of VOCs emissions in Bursa (one of the largest industrial cities in Turkey) are released by traffic and industrial facilities [13]. Work of Yurdakul et al. showed that gasoline and diesel exhaust emissions main contribution to VOC concentrations in Ankara, Capital of Turkey [14]. From all these studies conducted in different countries of the world, it shows that the vast majority of human-induced VOCs emissions are caused by vehicles.

There are hundreds of compounds that can fall into the VOCs category. Therefore VOC definitions, limits and calculations are different all over the world according to different international bodies [15–17]. In this study, first of all different opinions of all these international organizations about VOCs are presented. The definition, classification and impact of most dangerous and abundant VOCs in the environment produced from anthropogenic sources will be explored. Their effects on human and environment will also be examined in detail. Afterwards on effect of parameters on VOCs release in power plants and internal combustion engines will be investigated thoroughly. Finally discussion and conclusion section will be introduced.

Definition and Classification of VOCs

The literature survey revealed that there are many hundreds of compounds, which can come within the category of VOCs. VOC definitions, limits and calculations are different all over the world. The definition of VOCs from according to different international bodies as follows. For the United States Environmental Protection Agency (USEPA) the term VOC has a special regulatory meaning. This revised definition dated on 31 03 2009. It is defined in 40 CFR 51.100(s) as follows: "Volatile organic compounds (VOC) means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions." After definition organic compounds which have negligible photochemical reactivity excluded from VOCs extensive possible species. This list includes mostly chlorofluorocarbons. The two most important organic compounds that are not classified as VOC are methane and ethane [15]. We can see similar definition of the Environment Canada. Here VOCs are defined under Schedule 1 (item 65) of the Canadian Environmental Protection Act. According to this definition "VOCs are organic compounds containing one or more carbon atoms that have high vapour pressures and therefore evaporate readily to the atmosphere" According to the Environment Canada "this definition excludes photochemically low-reactive compounds such as methane, ethane and the chlorofluorocarbons (CFCs)" [16]. Immediately following definition in the document it is mentioned that the most of programs in Canada pay attention to the 50 to 150 most abundant compounds containing 2 to 12 carbon atoms. Above two important definitions differs fundamentally from the EU description defined in the Solvents Directive (2004/42/EC) where "a VOC is any organic chemical with boiling point below 250°C at a standard atmospheric pressure of 101.3 kPa" [17]. To be given as grams VOC per litre product. From this definition it can be seen that reactivity is not taken for consideration.

One of the most prominent sources of VOCs is the polycyclic aromatic hydrocarbon species. PAHs may be divided two subclasses; volatile PAHs and non-volatile PAHs. Non-volatile PAHs, which are known collectively as Toxic Organic Micro-pollutants (TOMPS), will not be examined in this study, while volatile PAHs are dealt with under the VOCs title. Therefore, in this work the use of the PAH terminology refers to the volatile group, although such terminology has been applied in the literature to non-volatile matters as well.

Current interest in PAHs and soot has arisen from health concerns that some PAHs are carcinogenic agent and others may be mutagenic carcinogenic agent [18]. Considerable effort has been expended in recent years to identify reactions leading to ring formation in flames of aliphatic fuels [19, 20].

Environmental Considerations and Health Effect Concerning VOCs

Natural biogenic VOCs emissions come from vegetation, trees, animals, forest fires and anaerobic processes in marshes and bogs. Human-made VOCs arise mainly from industrial process, oil refining, petrol storage and distribution, solvent usage, land-filled wastes, food manufacture, agriculture activities and combustion systems, especially motor vehicle exhausts and stationary industry combustion systems [21].

VOCs are both primary and secondary pollutants. Their anthropogenic emission cause concern in three main areas, ground level ozone formation, toxic or carcinogenic health effects and the ozone layer depletion and VOCs play a minor part in the global climate change [22]. However, the importance of the emissions of VOCs from anthropogenic activity in the global tropospheric ozone is still being evaluated and their emissions are not considered significant when compared to the main ‘greenhouse’ gases, such as CO_2, H_2O and CH_4 [23].

The ozone layer depletion

The stratospheric ozone layer protects the earth from the Sun’s harmful ultraviolet radiation. Destruction of this ozone layer is feared to cause skin cancer and eye damage. Many VOCs are stable enough to persevere in the atmosphere and to resist the tropospheric removal processes and to reach the stratosphere [24].

Ground level ozone formation

The formation of tropospheric ozone is the most significant environmental problem associated with VOCs. It is formed in a series of complex chemical reactions occurring between atmospheric oxygen, oxides of nitrogen (NOx) and VOC species in the presence of sunlight, generally in warm, still weather conditions. It can occur in greatly differing scales. The more reactive volatile organic species react fast, within a few hours, and therefore their affect can be observed close to the point of emission. The less reactive volatile organic compounds will disperse before reactions occur and they increase ozone concentrations beyond the borders of the source of the emissions. This ozone can be transported considerable distances in the air [25]. Low-level ozone is a hazard to human health, being an irritant to the respiratory system, which can produce asthma-like symptoms, particularly in children. At the same time it affects crops, and plants [22].

Not all VOCs emitted into the atmosphere contribute equally to ozone formation. Although all take part in the ozone-forming reactions, some substances are more reactive than others. Therefore it is crucial to find the role of each individual VOC with respect to ozone formation. The Photochemical Ozone Creation Potential (POCP) factor is a measure of how quickly a substance will react with nitrogen oxides to form ozone [26]. POCP used by the United States Environmental Protection Agency (USEPA) as a basic measure to compare reactivities of volatile compounds and according this measurement more reactive volatile organic compounds are subjective primarily legislative purpose. However current “mass-based” legislation in Europe does not distinguish between the reactivities of different VOCs in terms of ozone creation potential. If further VOC reduction measures are to be considered, then replacing highly reactive VOCs with less reactive VOCs could be a more focused, cost and time effective approach.

Toxic or carcinogenic human health effects of VOCs

VOCs can have important effects on human health through direct mechanisms and their indirect effects owing to photochemical ozone formation [18, 27–32]. Some VOCs affect the human senses through their odour, some employ a narcotic effect while certain species are toxic and some of them even have bad effect development of brain of newborn and young infants [27]. Here, the main concern focuses on long-term (chronic) exposure to low levels of VOCs, particularly those that are known or suspected carcinogens (cancer-causing agents). Two basic classes of carcinogens are recognised as genotoxic and non-genotoxic. Genotoxic agents cause cancer by reacting directly with the hereditary material (DNA) within the cells, whereas non-genotoxic agents do not act directly on DNA, but exert their effects through other mechanisms. It appears that non-genotoxic agents only cause cancer once a certain threshold of exposure has been exceeded. In other words, it is possible to determine exposure levels, below which there is 'zero' risk. Genotoxic agents on the other hand are not thought to show such a ‘threshold’ effect, so it is theoretically impossible to define levels of exposure below which the risks are so low as to be undetectable by any feasible study. One of the best-studied VOCs with respect to cancer is benzene, which is a genotoxic carcinogen, associated with some cancers of the leukaemia variety [33]. Furthermore, the review of Stafford et al. on environmental exposures to organic compounds showed that chemical exposure to benzene during pregnancy may put mothers at a higher risk of giving birth to children with leukaemia [34]. Another VOC known or suspected as a carcinogen is 1,3-butadiene [22], potentially the most significant genotoxic carcinogen and widely distributed in the air (from combustion, specially exhaust fumes), being associated with certain types of leukaemia and lymphomas (cancer of the lymph system). Formaldehyde is another potential leukaemia generating carcinogen [34].

Many of the VOCs above are shown to possess carcinogenic agents. However, quantification of the risk due to environmental exposure to suspected agents is limited since it is difficult to reliably assess exposure levels [34].

Health Hazardous VOCs in Power Plants and Internal Combustion Engines

It is noteworthy to determine environmentally most harmful VOCs in combustion processes. Literature review has been completed to be able to identify more harmful and abundant species in power plants and internal combustion engines. The important VOCs that emerge from these two sources will be discussed below under two semi-titles.

Health hazardous VOCs in power plants

It is necessary to identify the most abundant and hazardous VOCs in coal fired power stations. To this end an extensive literature survey has been completed to be able to tackle this issue more efficiently. However, the main problem faced in this area is a considerable lack of information [35–37]. This can be related to the majority of VOCs species are intermediate species of combustion products and therefore the difficulties in sampling and accurately determining volatile organics in real emissions [38].

The most abundant compounds are formaldehyde and acetaldehyde, aromatic and aliphatic hydrocarbons species especially toluene, benzene, ethyl-benzene, xylenes, and chlorinated hydrocarbons, but available data concerning the emissions of VOCs from power stations is incomplete and the most abundant product is found not to be the same in every power station [36].

Some of these compounds form during combustion and some of them are present in the fuel. For example, according to Garcia et al. the emission of aldehydes depends on the type of coal, but hydrocarbon emissions will increase with the load [36]. The implementation of the efforts to reduce the emissions of VOCs requires a fundamental knowledge of species emitted into the atmosphere in order to evaluate their local and global impact and the consequential development of suitable abatement technologies. On the other hand, the behaviour of VOCs depends on the option chosen for SOx and NOx control in an integrated pollution control system. It is therefore necessary to establish procedures for the optimal utilisation of coal with respect to the emissions of VOCs in plant using state-of-the-art SOx and NOx control points.

It is essential to emphasise that the main target should be defining important harmful VOC on the environment and health. Therefore, we need to compare effect of some operating conditions and other parameters to obtain the entire picture of the emissions level first. Later it should be looked at the perspective of the more dangerous species such as benzene, formaldehyde, acetaldehyde and 1,3-butadiene, rather than the abundant aliphatic hydrocarbon species (e.g. in oil), which are less harmful when compared with the above mentioned species [39].

Health hazardous VOCs in internal combustion engines

The six main aromatic hydrocarbon groups detected in vehicle exhaust emissions are benzene, toluene and their derivatives [40, 41]. According to Winebrake et al. vehicles are the biggest contributors of four important hazardous pollutants namely, benzene, 1,3 butadiene, acetaldehyde and formaldehyde [42]. Muezzinoglu et al. determined the daily pattern of VOC levels in İzmir (Turkey) city centre and discovered that toluene was the most abundant VOC and that xylenes, benzene and alkyl benzene were followed [43]. In addition, they determined that most of these emissions were caused by motor vehicle emissions. This is expected since benzene was highly correlated with other aromatic VOCs, toluene, xylene, and ethyl benzene, suggesting vehicles as primary contributors [44]. The above discussed studies and similar researches form an agreement on the most abundant VOCs that are released to the environment and at the same time scientists ally that these species dangerous to both human health and environment.

Effect of Relevant Factors on Vocs Release in Power Plants

The type of toxic organic substances emitted depends upon the fuel characteristics, boiler type and operating parameters. PAHs are formed more in the fuel-rich combustion regions than the lean flame zones. They can be spread as contaminants depending the operating conditions and design of the burner. Therefore, it is essential to determine the chemical and fluid dynamical mechanisms that lead to PAHs formation and destruction in power stations. However, it is quite difficult to examine the chemistry of PAHs formation and reduction in the highly turbulent environment of a power plant [45].

Experimental studies on the observation of polycyclic aromatic ring formation in flames are inadequate since the presence of soot can make measurement difficult. Few modelling works has been developed as the complex chemistry and thermodynamics are not satisfactorily understood for flame modelling of PAHs and soot [46].

According to Bonfanti et al there are qualitative differences in the VOCs profiles only when there are strong variations in process parameters or in fuel characteristics [47]. Pisupati et al. used three different conditions to provide some foundation as to the effect of different parameters on the formation of incomplete hydrocarbon species for different fuels (such as natural gas, coal, coal-blend fuels), different operating conditions and different combustors [48]. They found that the most common VOCs in the flue gas of coal-fired power burners were PAHs.

In power combustion different kinds of mechanism can lead to different levels of VOC formation. Here we thoroughly examine the effect of parameter change on the formation of VOCs. Hence, we will analyse each of these parameters as a separate issue. These mechanisms are classified briefly below:

- Operating Conditions
- Effect of Fuel Type
- The Type of Combustor

Effect of operating conditions on VOCs emission

Harrison and Bonfanti et al. remarked that when combustion parameters are optimised for high combustion efficiency, VOC emissions decreased dramatically in the combustion chamber [38 and 47]. Furthermore, they revealed that when combustion efficiency was low more VOCs (especially PAH compounds) were observed. Moreover, they pointed out that when the firing rate was increased the concentration of VOC emissions decreased slightly and that when the swirl number was increased the VOCs emissions were sharply decreased. Essentially, they are observing the effects of turbulence with respect to decreasing VOCs emissions.

Important operating parameters on the efficiency of combustion are temperature, residence time and fuel particle size and the rate of air and fuel mixing. These parameters are influencing the formation and destruction of VOCs species [39].

Temperature

Concentrations of VOCs reduce very fast with increasing temperature and, theoretically, with efficient fuel mixing and adequate residence times. The temperature of most utility boilers (800-1500^{o}C) would cause complete destruction of most PAH compounds [49]. Even single ring aromatic compounds tend to break up at temperatures above 1500^{o}C, releasing small non-aromatic species [50]. However, according to [51], peak formation of the different PAHs in a flame is not only a function of temperature but it is also sensitive to fuel. The relationship between fuel content and temperature is somehow interrelated for the determination of the peak formation of PAHs.

Pisupati et al. investigated the influence of combustor temperature in a bench-scale drop-tube reactor [48]. The results unveiled almost constant amounts of PAH in the solid phase, while the PAH concentrations in the vapour phase increased as a function of temperature. The PAH formation rate at around 1300^{o}C was exceeded by the PAH oxidation rate and PAH yielding in the vapour phase began to reduce.

Residence time and fuel particle size

The particle size affects the combustion rate. Therefore, the residence time becomes a vital factor for unburned hydrocarbon destruction in the combustion zone. Burning of solid particles takes places in a series of repeated steps: combustion of volatile species close the surface of the particles accompanied by combustion of the residual solid composition. The bigger the particle, the more cycles required for complete burning and hence residence time becomes very vital. Therefore non-pulverised coal combustion boilers have higher unburned hydrocarbon emissions than pulverised coal combustors [39].

The rate of air and fuel mixing

There are two types of fuel combustion with regard to mixing; one is premixed fuel combustion and the other non-premixed (diffusion) flame. In coal combustion, unburned hydrocarbons can be yielded directly from the nature of the diffusion combustion. This can be related to the nature of very lean and very rich regions formed within the combustion chamber that do not back up fast burning [51]. Therefore, the air/fuel ratio and the turbulence, which causes the efficient mixing between air (oxygen) and fuel, affect the chemical nature of the fuel combustion. The mixing of the fuel and air is the most crucial element with regard to the efficiency of combustion and destruction of unburned hydrocarbons. Systems with frequent start-up and shut-down or non optimal operation due to variations in the supply of fuel or air will be afflicted by poor air/fuel ratios. A poor air supply can also result in a lowering of the combustion temperature. This results in incomplete combustion, which means more emissions going to the atmosphere [39]. Moreover, Pisupati et al. claimed that the PAHs emissions is reduced with an increase in the excess air rate, but they did not provide relevant information on optimisation of this rate in their work [48].

Effect of the nature of the fuel on VOCs emission

Coal is made up of a wide range of organic compounds. The molecular structure of coal is still not fully understood. Organic matter is released during the heating of coal to 300^{o}C. It is assumed that pyrolysis does not occur at this temperature. The amount of volatile matter decreases as the carbon constituents of the coal increases with the ageing process that starts with peat, lignite or brown coals, ranging through sub-bituminous and bituminous to anthractitic coals that are primarily used for metallurgical processes. This evidence, along with evidence that there is an increase in the average PAH ring size with increasing coal rank and hydrocarbons in coal, becomes increasingly aromatic by the coalification process.

Since coal is a hydrocarbon mineral, inefficient combustion or utilisation of coal leads to the emissions of organic compounds to the environment. Hundreds of organic compounds have been identified. For ease of study, groups of compounds such as VOCs and PAHs have been classified based on chemical or physical properties. However, such groups are often poorly defined. It is easier to study emissions from activities such as coal combustion in terms of a group of organic compounds rather than trying to identify and quantify many individual compounds.

Garcia et al. concluded from a study on several coal-fired power stations that the fuel type had less impact on hydrocarbon emissions than the load or the burner type and emphasised that no significant trend between emissions and coal type could be established [36]. Later on Pisupati et al. supported this observation [48]. Furthermore, according to Brooks PAHs formation depends upon the carbon to the hydrogen ratio of the fuel and its molecular structure [52]. The more aromatic PAH type compounds already present in the fuel the more likely that such compounds and the derivatives of such compounds will be released. However, Chagger et al. supported the idea of fuel having less effect on exit emissions when compared to the operating conditions, but they also suggested the formation of different peak VOCs in the flame may be the result of the combined effects of the nature of the fuel and temperature [51].

In inefficient combustion systems some compounds present in the fuel may be released in the same form as in the fuel. Simple pyrolysis may also release single or multiple ring compounds, which were originally present as larger molecules in the fuel or as part of the complex fuel matrix. The addition of small ring systems, either from small precursors present in the original fuel or from pyrolysis products, may occur. Although combustion degrades the large aromatic structures, these structures may reform in the combustion zone or elsewhere in combustion system. The formation of organic compounds from elemental sources is also possible in rich flames or at lower temperatures [50].

Pisupati et al. revealed that there are no significant emissions differences with regard to the fuel type or form found in the PAHs compounds [48]. However, Bonfanti et al. show when coal has different values of volatile matter for a fixed carbon ratio, it exhibits significant differences in behaviour with respect to the formation of incomplete combustion products [47].

Bonfanti et al. compared pulverised coal with oil for PAHs emissions and they observed that the average emissions from coal combustion were around 10% of those from oil combustion [47]. During the combustion of pulverised coal, as long as the process conditions are well-optimised, the total levels of VOCs are much smaller compared to oil combustion (an averaged reduction of around two times). This reduction is mainly due to a decrease in aliphatic hydrocarbons, which are of smaller environmental concern than aromatics. On the other hand, the influence of the process parameters on VOC emissions is much more important in coal combustion than that of oil [47]. However, Garcia et al.

suggest that the effluent emissions seem to be of the same order of magnitude for oil-fired and coal-fired power stations, although there are incompatible results for a number of compounds [36]. For certain compounds, the effluent is more abundant with coal, for some others it is the opposite. From this point of view the only one agreement that can be drawn from the work of Garcia et al. and Bonfanti et al. is that there are different VOCs species emitted from coal and oil combustion [36, 47]. Garcia et al. mainly concentrated on the identification of specific species in both fuels [36] while Bonfanti et al. emphasised on the amount of the overall emission [47]. Optimal integration between different pollutants mechanism is vital in order to prevent adverse effect on the formation of the other types of pollutant. Masclet et al. suggest that combustion modifications to reduce NOx emissions from coal-fired power stations can sometimes lead to an increase in the PAHs emissions but a decrease in the nitro-PAH derivatives [35]. That is why the overall optimisation of parameters is essential for minimising the emission of VOCs, SOx, and NOx, respectively.

Effect of the type of combustor on VOCs emission

Temperatures in fluidised bed combustion (FBC) systems are predominantly lower (between 800-900^{o}C) than pulverised coal fired boilers. These lower temperature values and other combinations of combustion characteristics of the FBC may result in more unburned hydrocarbon being released. According to Citiroglu et al. the average emissions of unburned hydrocarbons from fluidised beds (<200ppb) are higher than those from other types of coal combustion (<30ppb) [53]. Chadwick et al. found that emissions of PAHs from fluidised beds are significantly higher than even industrial systems [54]. Furthermore, Chagger et al. examined the affect of coal volatile composition, air /fuel ratio, temperature-time history on pollutant formation [49]. They used the above parameters for both pulverised coal and fluidised bed combustion. They suggested that in coal combustion significant products of VOCs may be released into the atmosphere in the case of incomplete combustion from coal fired combustors. They observed an important difference between pulverised coal and fluidised bed combustion even though they do not give any comparison values with respect to the emission of VOCs between these two combustor types. In fluidised bed combustion there is weak relation between the coal rank and the nature of PAH emissions, but in pulverised combustion it was difficult to establish this kind of claim. Moreover, Masclet et al. claimed that liquid fuel fired power stations emit more pollution in the form of significant amounts of pyrene, which is reputed to be particularly carcinogenic in the form of its derivatives [35]. Moreover, Masclet et al. suggest that it should not be generalised any specific emission only with respect to the type of power stations since a combination of combustion conditions, the characteristics of the fuel and type of furnace give a more realistic picture on emissions [35].

Effect of Parameters on VOCs Release from Vehicular Sources

There are many sources of important pollution such as NOx, SOx, unburned hydrocarbons (VOCs and PAHs) and particulate matter in our breathing atmosphere that is caused by the technology people use. One of these sources, perhaps the most, is caused by harmful unburned hydrocarbons. The results of many scientific researchers have shown that vehicle emissions are one of the most important factors underlying this source [2, 12, 55]. The fuels used by vehicles are complex blends containing very large number of chemical species, and the composition of these fuels has been improved significantly over the past century with the development of internal combustion engines. In this way, harmful emissions are minimized and energy efficiency is tried to be maximized. Vehicle emissions consist of VOCs, CO, NOx and PM. Emissions are dependent on both internal combustion engine operating parameters such as engine temperature, speed, load, air/fuel ratio and spark timing as well as fuel type. These emissions arise from complex interaction mechanisms between fuel and internal combustion engine parameters. The amount and constitution of emissions from the vehicle exhaust pipe depends on engine equipment, operating conditions, after-treatment catalysts and fuel types. Engine and after-treatment factors are generally bigger than fuel types. But it should be remembered that engine and after-treatment equipment may need certain fuel characteristics [56]. As a result, the best expectations to achieve the highest efficiency and lowest emissions are to optimize the entire engine, fuel and after-treatment system.

Mobile motor vehicles are the biggest source of direct VOCs emission discharged into the environment. Although some VOCs are not included in the content of gasoline or diesel fuels, they can be released into the environment as intermediate compounds as a result of incomplete combustion. Incomplete combustion occurs if there is not enough air or time or the adequate high temperature to burn all the fuel in an engine cylinder [57]. Due to the high power and high acceleration rates, full combustion does not occur in car engines. Pyrolysis may be activated if there is a lack of air in the combustion process. This thermal decomposition process initiates the formation of intermediate hydrocarbons species that do not initially exist in fuel [58]. This also shows how many aromatic hydrocarbons, such as benzene, toluene, xylene, are yielded. Aromatic hydrocarbons are an important species of motor vehicle exhaust emissions. The six main aromatic hydrocarbon groups observed in vehicle exhaust emissions are benzene, toluene, xylene, ethyl-toluene, ethyl-benzenes and tri-methyl benzenes [40, 41]. All of these chemical species are dangerous to environment and human health. All mobile vehicles have the potential to generate these compounds due to incomplete combustion. In other words, the amount of emission of VOCs relies on the constituent of the fuel, the engine type, the operating temperature, the emission control technique used and the age and state of the vehicle. It may be expected that some VOC types emissions from automotive sources will continue to change; Automotive emission control technology and efforts to improve gasoline or diesel fuel quality will lead to a reduction in the release of volatile organic compounds (VOC) into the environment [55]. Determining which parameters affect VOCs emissions in motor vehicles is necessary to reduce emissions further. The formation of VOCs with changing operational parameters, nature of fuel and fuel composition, which are believed to affect the formation or reduction processes, will be examined thoroughly below.

Effect of operating conditions on VOCs emission

The working conditions of the vehicles may change depending on the seasons, geographical conditions of the roads, their load and driving style and duration. For example, a loaded vehicle needs to reach the ideal operating temperature in order to gain acceleration on an uphill slope, and this can only be achieved with a rich mixture. Since the combustion speed of the rich mixture is higher, it is more suitable for the increasing speed of the engine. With the rich mixture, the efficiency (power) of the combustion per unit time increases while the efficiency (torque) of the combustion in a cycle decreases, so that the unburned harmful emission, such as VOCs, discarded in the atmosphere increases. Using internal combustion engines at maximum torque speeds can limit VOCs emissions from vehicles to the atmosphere [59, 60].

Effect of the temperature on VOCs emission

Cooling systems are used to keep the temperature of the engine within the safe range specified in the factory while keeping ideal operating temperature conditions. However, increasing compression ratios and engine torques increase the temperature of combustion in the combustion chambers (> 1600℃) while is reducing emissions of VOC species. However this is increasing the formation of NOx compounds, an important harmful combustion product. NOx is especially seen in the emissions of diesel engines. To avoid NOx emissions, the number of diesel engines with low compression ratios and revolutions needs to be increased. Therefore integrated approach should be used for different class of harmful gas emission (such as VOCs, NOx and SOx) in internal combustion engines [61, 62].

Effect of the fuel type on VOCs emission

Incomplete combustion is main sources of VOCs, PAHs and other unburned hydrocarbon species in internal combustion engines. Fuel properties itself is one of an important factor for efficient combustion. Nowadays, fuel refineries add many additives to the fuel in order to develop fuel that less damages the environment as much as possible and can burn fully. Fuels used in internal combustion engines are being improved day by day with Octane and Cetane numbers, lower heat values, densities, evaporation properties as well as some added substances [63]. Increasing the properties of the fuels and the changes made in the fuel equipment, efforts are made to establish a homogeneous mixture that will ensure complete combustion. New systems are being developed, both in terms of the amount and proportion of fuel/air introduced into the combustion chamber, as well as to achieve the desired combustion speed at every corner of the combustion chamber simultaneously. However, diesel engines always work with poor mix. Although partially rich concentrations occur in the areas where the fuel is sprayed within the combustion chambers, the delay in the evaporation of the fuel does not allow full combustion by prolonging the combustion time. Although some VOCs are not included in the content of gasoline or diesel fuels, they can be released into the environment as intermediate compounds as a result of incomplete combustion. Winebrake et al. compared VOC and carbonyl emissions for conventional gasoline powered vehicles against alternative fuels, such as rearranged gasoline, natural gas, ethanol and liquid petroleum gas [42]. They found that newer fuels produce generally less benzene and other aromatic VOCs emissions. However, they found that ethanol and compressed natural gas cause greater emissions of formaldehyde and acetaldehyde.

Effect of the type of internal combustion engines on VOCs emission

Type of the engines and shape of the combustion chambers affect the combustion of the fuel. Homogeneously mixed stoichiometric fuels contribute to reduce unburned hydrocarbon species such as VOCs and PAHs as the combustion efficiency is high. For this reason before the air/fuel mixture goes into the combustion chambers, turbulence must be produced inside the intake manifold. Proportional turbo systems with different cross-sections and turbulence-forming intake manifold designs, variable compression ratios and variable valve system timing and all changes made in the shape of the combustion chamber are designed to increase the efficiency of combustion by forming a homogeneous mixture. Optimization studies are carried out to increase the speed of the engine. Thus, the power produced by engines per unit mass increases day by day [64, 65].

Effect of the after combustion systems on VOCs emission

Technological improvements in internal combustion engines bring to various control systems before and after the combustions. In gasoline engines, the stoichiometric air / fuel ratio can be controlled momentarily according to the need, while in diesel engines, combustion occurs by the amount of fuel injected into the excess air. In diesel engines, rich mixture can occur in areas where the fuel injected into the combustion chamber can be homogenized by evaporation and turbulence. In the combustion chamber there is always a poor mixture in the volume outside the place where the fuel is sprayed and the combustion time is prolonged. The main aim is the stoichiometric rate of air/fuel mixture to be getting into the combustion chambers to burn completely. Homogeneously mixed necessary amount of air/fuel mixture can be totally burn fast enough to not produced chemically undesired gases such as VOCs [66]. While the gases coming out of the combustion chamber discharge their energy onto the turbo system; it is also possible to burn the gases which have not been fully reacted by the catalytic converter and ad-blue systems following the exhaust manifold. Thus, efforts are made to limit the emission of VOCs, PAHs, PM and NOx derivatives that accumulate in the atmosphere. Although measures are taken before, during and after combustion and emission controls are increased, the amount of gases discharged from these vehicles to our atmosphere cannot be reduced due to the increase in the number of vehicles day by day [67].

CONCLUSIONS and DISCUSSION

The combustion of fuel in power stations and internal combustion engines especially vehicles lead to the emission of important hazardous of VOCs into the environment. These products of incomplete combustion pose a risk to both environment and human health. There are extensive possible VOCs species exist in combustion phenomena. Therefore, it is necessary to identify the most abundant and hazardous VOCs in these sources. Organic compounds may be released from combustion systems as intact fuel, as decomposition products of larger molecules, or as products of the interaction of precursor molecules. The final products are determined by the fuel type, operating parameters and combustion conditions. High temperatures with lean burn result in the destruction of organic molecules, while low temperatures and excess air levels allow PAHs to form. Long residence times in the combustion zone allow efficient organic destruction, while long residence times in cooler areas enhance reformation. Furthermore fuel properties affect the emission of pollutants. For example, the more aromatic compounds present in the fuel, the more likely that derivatives of such compounds, may be released into environment. Optimal integration between VOCs and other pollutants is vital in order to prevent adverse effect on the formation of the other types of pollutant. Sometimes combustion modifications to reduce some pollutants such as NOx emissions can lead to an increase in the PAHs emissions but a decrease in the nitro-PAH derivatives. That is why the overall optimisation of parameters is essential for minimising the emission of VOCs, PM, SOx, and NOx, respectively.

In this study, general principles were tried to be established on VOC emission arising from vehicles. Since operating and experimental sampling conditions have a major impact on the exhaust gas composition of internal combustion engines. The studies must meet the same conditions, so it is possible to make comparisons. Therefore, caution should be exercised when comparing the literature results [68]. It is attempted to minimize the damages of emissions from vehicles to the atmosphere with the improvements in the fuel characteristics used in internal combustion engines, enhancements in the physical characteristics of the engine and the advances in its side systems. Increasing technological developments are insufficient to reduce the lasting effect of the emissions. In the near future, countries with very large and populated cities will have to impose increasingly stringent rules to limit or prohibit the use of diesel engines as a precaution against pollution in their atmosphere. Recently many countries are restricted to use of passenger vehicles operated with diesel engines.

It can be concluded that investigation of emissions of hazardous VOCs is very important since they are carcinogenic and the same time very harmful to environment, especially VOCs play a key role ground level ozone formation. In this study, VOC emissions from power stations and vehicles are examined thoroughly, as they are responsible about half of the VOC emissions generated by anthropogenic sources. In this paper the effect of parameters, fuel types and combustion environment on VOCs emissions are investigated. This work may help to have over all ideas of how each of these parameters affects emissions of VOCs on combustion sources. Therefore this could be a helpful review for researchers working on reducing VOC emissions from combustion sources and it may be a helpful guidance for some government employees working on preventive measurements on VOCs.

NOTE: A part of this paper was previously presented at the "13th International Combustion Symposium" in Bursa on September 9-11, 2015 [69].

DEDICATION

This paper is dedicated to the memory of the co-author, Prof. Dr. Bülent Özdalyan, who recently passed away.

REFERENCES

[1] Sahu L.K. Volatile Organic Compounds and their Measurements in the Troposphere, Curr Sci., 102:12 1645-1649, 2012.

[2] Cai C., Geng F., Tie X., Yu Q., An J. Characteristics and Source Apportionment of VOCs Measured in Shanghai, China, Atmos Environ, 44:38 5005-5014, 2010.

[3] Wang M., Shao M., Chen W., Yuan B., Lu S., Zhang Q. Validation of Emission Inventories by Measurements of Ambient Volatile Organic Compounds in Beijing, China, Atmos Chem Phys Discuss, 13:10 26933-26979, 2013.

[4] Schauer J.J., Kleeman M.J., Cass G.R., Simoneit B.R.T. Measurement of Emissions from Aair Pollution Sources. 2. C1 through C30 Organic Compounds from Medium Duty Diesel Trucks, Environ Sci Technol, 33:10 1578-1587, 1999.

[5] Siegl W.O., Hammerle R.H., Herrmann H.M., Wenclawiak B.W., Luers-Jongen B. Organic Emissions Profile for a Light-Duty Diesel Vehicle, Atmos Environ, 33 797-805, 1999.

[6] Lloyd A.C., Cackette T.A. Diesel Engines: Environmental Impact and Control, J Air Waste Manage Assoc, 51 809-847, 2001.

[7] Maricq M.M. Chemical Characterization of Particulate Emissions from Diesel Engines: A Review, J Aerosol Sci, 38:11 1079-1118, 2007.

[8] Yamada H. Contribution of Evaporative Emissions from Gasoline Vehicles toward Total VOC Emissions in Japan, Sci Total Environ, 449 143-149, 2013.

[9] Inomata S., Yamada H., Tanimoto H. Investigation on VOC Emissions from Automobile Sources by Means of Online Mass Spectrometry, Curr Pollut Reports, 2:3 188-199, 2016.

[10] European Environment Agency (EEA). Air Quality in Europe 2019, Copenhagen, 2019.

[11] Elsom D.M. Air Quality Management-Highlighting Good Practice, Clean Air Environ Qual, 38:1 36-43, 2004.

[12] Gaur M., Singh R., Shukla A. Volatile Organic Compounds in India: Concentration and Sources, J Civ Environ Eng., 6:5 1-7, 2016.

[13] Civan M.Y., Kuntasal Ö.O., Tuncel G. Source Apportionment of Ambient Volatile Organic Compounds in Bursa, a Heavily Industrialized City in Turkey, Environ Forensics, 12:4 357-370, 2011.

[14] Yurdakul S., Civan M.Y., Tuncel G. Volatile Organic Compounds in Suburban Ankara Atmosphere, Turkey: Sources and Variability, Atmos Res., 120:121 298-311, 2013.

[15] USEPA. Technical Overview of Volatile Organic Compounds, Available from: https://www.epa.gov/indoor-air-quality-iaq/technical-overview-volatile-organic-compounds, Retrieved August 30, 2018.

[16] Environment Canada. Volatile Organic Compounds Overview, Available from: https://www.canada.ca/en/environment-climate-change/services/managing-pollution/sources-industry/volatile-organic-compounds-consumer-commercial/overview.html, Retrieved August 30, 2018.

[17] EUR-Lex. Directive. EUR-Lex. Directive 2004/42/CE of the European Parliament and of the Council of 21 April 2004, Available from: http://eur-lex.europa.eu/legal-content/EN/TXT/?qid=1435853829678&uri=CELEX:32004L0042, Retrieved August 30, 2018.

[18] Yang M. A Current Global View of Environmental and Occupational Cancers, J Environ Sci Heal Part C, 29 223-249, 2011.

[19] Frenklach M., Wang H. Detailed modelling of PAH Profiles in a Sooting Low-pressure Acetylene Flame, In (Ed: Bockhorn H.). Soot Formation in Combustion. Springer: Heidelberg, p. 165-192, 1994.

[20] Miller J., Melius C. Kinetic and Thermodynamic Issues in the Formation of Aromatic-Compounds in Flames of Aliphatic Fuels, Combust Flame. 91 21-39, 1992.

[21] Derwent R. Hydrocarbons in the Atmosphere: Their Sources, Distributions and Fates, In (Eds: Leslie G., Perry R.), VOCs in the Environment, Proceedings of the International Conference, Lonsdale Press Ltd: London, 1993.

[22] Murlis J. Volatile Organic Compounds: UK Policy, In (Eds: Leslie G., Perry R.), VOCs in the Environment, Proceedings of the International Conference, Lonsdale Press Ltd: London, 1993.

[23] Sandroni S., Anfossi D. Historical Data of Surface Ozone at Tropical Latitudes, Sci Total Environ., 148 23-29, 1994.

[24] Tsani-Bazaca E, De Saeger E. Comparative Evaluation of VOC Measurements in Some EEC Laboratories, In (Eds: Leslie G., Perry R), VOCs in the Environment, Proceedings of the International Conference. Lonsdale Press Ltd: London, 1993.

[25] Derwent R., Jenkin M. Hydrocarbons and Long-Range Transport of Ozone and PAN Across Europe, Atmos Environ, 25A 1661-1678, 1991.

[26] Derwent R., Jenkin M., Saunders S. Photochemical Ozone Creation Potentials for a Large Number of Reactive Hydrocarbons under European Conditions, Atmos Environ, 30 181-199, 1996.

[27] Schroeder H. Developmental Brain and Behavior Toxicity of Air Pollutants: A Focus on the Effects of Polycyclic Aromatic Hydrocarbons (PAHs), Crit Rev Environ Sci Technol, 41 2026-2047, 2011

[28] Claxton L. The History, Genotoxicity and Carcinogenicity of Carbon-Based Fuels and their Emissions: Part 2: Solid Fuels, Mutat Res, 762 108-122, 2014.

[29] Claxton L. The History, Genotoxicity and Carcinogenicity of Carbon-Based Fuels and their Emissions: Part 1. Principles and Background, Mutat Res., 762 76-107, 2014.

[30] Claxton L. The History, Genotoxicity and Carcinogenicity of Carbon-Based Fuels and their Emissions: Part 3: Diesel and Gasoline, Mutat Res. 763 30-85, 2015.

[31] Claxton L. The History, Genotoxicity and Carcinogenicity of Carbon-Based Fuels and their Emissions: Part 5. Summary, Comparisons, and Conclusions, Mutat Res, 763 103-147, 2015.

[32] Claxton L. The History, Genotoxicity and Carcinogenicity of Carbon-Based Fuels and their Emissions: Part 4- Alternative Fuels, Mutat Res. 763 86-102, 2015.

[33] Zhou J., You Y., Bai Z., Hu Y., Zhang J., Zhang N. Health Risk Assessment of Personal Inhalation Exposure to Volatile Organic Compounds in Tianjin, China Sci Total Environ, 409 452-459, 2011.

[34] Stafford D., West R., White A. Review of Occupational and Environmental Exposures to Organics and Associations with Leukaemia and Preleukaemia. In (Eds: Leslie G., Perry R.), VOCs in the Environment, Proceedings of the International Conference, Lonsdale Press Ltd: London, 1993.

[35] Masclet P., Bresson M., Mouvier G. PAHs Emitted by Power Stations, and Influence of Combustion Conditions, Fuel, 66 556-562, 1987.

[36] Garcia J., Beyne-Masclet S., Mouvier G., Masclet P. Emissions of Volatile Organic Compounds by Coal-Fired Power Stations, Atmos Environ, 26A: 1589-1597, 1992.

[37] Miller C., Srivastava R., Ryan J. Emissions of Organic Hazardous Air-Pollutants from the Combustion of Pulverized Coal in a Small-Scale Combustor, Environ Sci Technol, 28 1150-1158, 1994.

[38] Harrison P. In Flame Measurement of Specific VOCs from Combustion of Pulverised Fossil and Renewable Fuels, Imperial College London, 2002.

[39] Arslan O. Modelling Emissions of Volatile Organic Compounds (VOCs) in Modern Power Plants, Imperial College London, 2002.

[40] Jenkin M.E., Saunders S.M., Wagner V., Pilling M.J. Protocol for the Development of the Master Chemical Mechanism, MCM v3 (Part B): Tropospheric Degradation of Aromatic Volatile Organic Compounds, Atmos Chem Phys., 3:1 181-193, 2003.

[41] Saunders S.M., Jenkin M.E., Derwent R.G., Pilling M.J. Protocol for the Development of the Master Chemical Mechanism, MCM v3 (Part A): Tropospheric Degradation of Non-Aromatic Volatile Organic Compounds, Atmos Chem Phys., 3:1 161-180, 2003.

[42] Winebrake J.J., Wang M.Q., He D.Q. Toxic Emissions from Mobile Sources: a Total Fuel-Cycle Analysis for Conventional and Alternative Fuel Vehicles, J Air Waste Manage Assoc., 51 1073-1086, 2001.

[43] Muezzinoglu A., Odabasi M., Onat L. Volatile Organic Compounds in the Air of Izmir, Turkey, Atmos Environ., 35:4 753-760, 2001.

[44] Caudill M. Multivariate Receptor Modeling Applied to PM2.5 and Air Toxics Monitoring Sites in the Midwest, 2010.

[45] Melius C., Colvin M., Marinov N., Pitz W., Senkan S. Reaction Mechanisms in Aromatic Hydrocarbon Formation Involving the C_5H_5 Cyclopentadienyl Moiety, In 26th Symposium (International) on Combustion, 685-692, 1996.

[46] Castaldi M., Marinov N., Melius C., Huang J, Senkan S., Pitz W. Experimental and Modeling Investigation of Aromatic and Polycyclic Aromatic Hydrocarbon Formation in a Premixed Ethylene Fame, In 26th

Symposium (International) on Combustion, 693-702, 1996.

[47] Bonfanti L., Demichele G., Riccardi J., Lopezdoriga E. Influence of Coal Type and Operating Conditions on the Formation of Incomplete Combustion Products. Pilot Plant Experiments, Combust Sci Technol., 101 505-525, 1994.

[48] Pisupati S., Wasco R., Scaroni A. An Investigation on Polycyclic Aromatic Hydrocarbon Emissions from Pulverized Coal Combustion Systems. J Hazard Mater, 74:1 91-107, 2000.

[49] Chagger H., Jones J., Pourkashanian M., Williams A., Owen A., Fynes G. Emission of Volatile Organic Compounds from Coal Combustion, Fuel, 78 1527-1538, 1999.

[50] Sloss L., Smith I. Organic Compounds from Coal Utilisation. London, 1993.

[51] Chagger H., Jones J., Pourkashanian M., Williams A. The Nature of Hydrocarbon Emissions Formed During the Cooling of Combustion Products, Fuel, 76:9 861-864, 1997.

[52] Brooks G. Air Toxic Emissions from Coal and Oil Combustion Sources, Research Triangle Park, NC, 1989.

[53] Citiroglu M., Yardim M., Ekinci E. Determination of Polycyclic Aromatic Hydrocarbons (PAH) in Cyclone and Bottom Ashes in a Fluidised Bed Combustor. In: FBC Technology and the Environmental Challenge. In Proceedings of the Institute of Energy’s 5th International Fluidised Combustion Conference, Adam Hilger, 311-318, 1991.

[54] Chadwick M., Highton N., Lindman N.(Eds). The Environmental Significance of Coal-derived Carbon Compounds. In Environmental Impacts of Coal Mining Utilization. Pergamon: Oxford, UK, p. 218-244, 1987.

[55] Robert C. An Ecological Risk Assessment of Formaldehyde, Hum Ecol Risk Assess An Int J, 9:2 483-509, 2003.

[56] Wallington T.J., Kaiser E.W., Farrell J.T. Automotive Fuels and Internal Combustion Engines: A Chemical Perspective, Chem Soc Rev., 35-4 335-347, 2006.

[57] Rubin E.S. Introduction to Engineering the Environment. McGraw-Hill: Boston, 2001.

[58] Baumbach G. Air Quality Control. Springer Verlag: Berlin, 1996.

[59] Lapuerta M., Martos F., Herreros J. Effect of Engine Operating Conditions on the Size of Primary Particles Composing Diesel Soot Agglomerates, J Aerosol Sci., 38:4 455-466, 2007.

[60] Rakopoulos C., Giakoumis E. Review of Thermodynamic Diesel Engine Simulations under Transient Operating Conditions, 2006.

[61] Nam E., Kishan S., Baldauf R., Fulper C., Sabisch M., Warila J. Temperature Effects on Particulate Matter Emissions from Light-Duty, Gasoline-Powered Motor Vehicles, Environ Sci Technol. 44:12 4672-4677, 2010.

[62] Takeyuki K., Bae M. High Combustion Temperature for the Reduction of Particulate in Diesel Engines, SAE Trans., 97 692-701, 1988.

[63] Vander Wal R., Mueller C. Initial Investigation of Effects of Fuel Oxygenation on Nanostructure of Soot from a Direct-Injection Diesel Engine, Energy Fuels, 20:6 2364-2369, 2006.

[64] Germane G.J., Wood C.G., Hess C.C. Lean Combustion in Spark-Ignited Internal Combustion Engines-A Review, Presented at the October 31, 1983.

[65] Soid S., Zainal Z. Spray and Combustion Characterization for Internal Combustion Engines Using Optical Measuring Techniques-A Review, Energy, 36:2 724-741, 2011.

[66] Abu-Jrai A., Tsolakis A., Megaritis A. The influence of H_2 and CO on Diesel Engine Combustion Characteristics, Exhaust Gas Emissions, and after Treatment Selective Catalytic NOx Reduction, Int J Hydrogen Energy, 32:15: 3565-3571, 2007.

[67] Reşitoğlu İ., Altinişik K., Keskin A. The Pollutant Emissions from Diesel-Engine Vehicles and Exhaust Aftertreatment Systems, Clean Technol Environ Policy, 17:1 15-27, 2015.

[68] Pereira K.L., Dunmore R., Whitehead J., Alfarra M.R., Allan J.D., Alam M.S., Technical Note: Use of an Atmospheric Simulation Chamber to Investigate the Effect of Different Engine Conditions on Unregulated VOC-IVOC Diesel Exhaust Emissions, Atmos Chem Phys., 18:15 11073-11096, 2018.

[69] Arslan Ö. The Impact of the Release of VOCs and PAHs from Power Stations on the Environment and Human, 13th International Combustion Symposium, 9-11 September, Bursa-Türkiye, 2015.