Emissions of Gasoline Combustion by Products in Automotive Exhausts

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Abstract- Increased gasoline consumption in automotive engines have triggered the emissions of greenhouse gases (GHG) especially carbon dioxide (CO_2) from automotive exhausts. These exhaust emissions depend on factors like the engine combustion design and operating conditions, fuel grade and lubricant, the state of maintenance and local road conditions and continue to affect the concentration of pollutants emitted by automotives like CO_2 and unburnt hydrocarbons which are very toxic to humans, leading to environmental pollution. In pursuant of improved efficient engine and less toxic emissions, the use of gasoline blends and biofuels are not the panacea since the exhaust-gas concentration and its constituent are not indicative of the contribution of the constituent to the overall emission due to variations in exhaust-gas flow rate with different engine types and automotive sources. Moreover real-time monitoring, turbo-charging technologies, fuel injection strategies and catalytic exhaust aftertreatment may reduce emissions if compared to base engines but significant risk of CO_2 induced climate change continue to persist, while CO_2 capture technologies such as adsorption and absorption are limited in contrast to new developments in engine and exhaust technologies that are cheaper and locally sourced and could become the next trajectory.

Index Terms- carbon dioxide, combustion, emission, engine, gasoline

I. INTRODUCTION

Research and development has elucidated the relationships between vehicular operating conditions and vehicle emissions, but questions arise regarding the relationship between on-road vehicle emissions and stationary emissions as well as changes in vehicle speed and engine load that occur as driving conditions change relative to type of fuel and combustion engine [1]. Studies have shown that transport is a major contributor to the emission of greenhouse gases (GHG) and perhaps carbon dioxide (CO_2) and its effects on health and environmental ecology are very severe [2]. In 2006, transport accounted for 13% of global GHG emissions while 23% of global CO_2 emissions from fuel combustion are transport-related whereas transport related carbon monoxide (CO) emissions are expected to increase by 57% worldwide in the period 2005–2030 [2]. For e.g. in Lagos, Nigeria, CO from non fossil sources are relatively small compared to engines operating on fossil fuels especially trucks and generators [3]. This increased gasoline consumption are triggered by population growth and increase in number of vehicles per capita. These promote more exhaust emissions from combustion of gasoline consequently affected by fuel grade, vehicle age, vehicle model, engine size, fuel type and delivery system, catalytic converter, vehicle maintenance and road network and country of origin [4]. For e.g. Japanese and German cars would be most likely to fail Jordanian and possibly Californian emission tests. In Cairo, Egypt, investigations of gasoline combustion emissions (pollutants) from vehicles confirmed CO_2, Hydrocarbon (HC), Nitrogen oxides (NOx) and CO as major pollutants [4].

Also in Nigeria, fuel emissions, open fires and restricted ventilation contribute to high ozone while non methane volatile organic compound (NMVOC) emissions are higher in India and China compared to most countries [5].

The Nigerian GDP rebased economy recently surpassed South Africa, [4] making it the largest economy on the continent. On the other hand, growing concerns of automotive exhaust emissions remain unchecked and worsened by bad roads, traffic congestion, malfunctioning vehicles, aldulterated fuel and presence of sub-standard spare parts [5]. Motorcycle exhaust emissions in Uyo, Akwa Ibom state Nigeria reveals that CO, Sulphur (IV) oxide (SO_2), Oxygen (O_2), Hydrogen sulphide (H_2S), Ammonium (NH_4) and Chlorine (Cl_2) are some of the major air pollutants [6]. Moreover exhaust emissions from gasoline fuelled motorcycles are of higher concentrations in total hydrocarbon (THC) and CO than gasoline/methanol blend but lower in formaldehyde while the concentration of NOx increased in the fuel blend whereas BTEX emissions: (Benzene, Toluene, Ethyl-benzene, p,m,o-Xylene) from gasoline combustion in motorcycles are higher in concentration than emissions from the fuel-blends [7]. Emissions from traffic in developing nations contribute about 50-80% Nitrogen (IV) oxide (NO_2) and CO emissions, for e.g. assessment of air quality in Kano city, Nigeria along high traffic roads showed high levels of these pollutants indicating automobile exhaust emissions as mainstream air pollutants [8]. Similarly, contributions from emissions of power generating equipments due to inadequate power supply and its implications in Port Harcourt, Nigeria showed CO to be 20,175.3 tons per year and CO_2 about 34,718.22 tons per year from gasoline generators and proposed inventory of emissions [9]. Also Pollution is a major problem in the entire Niger delta region of Nigeria [10], traffic emissions and other combustion processes releases toxic substances: VOCs, oxides of carbon, nitrogen, sulphur, particulate matter (PM) and heavy metals (HM) at levels exceeding national and international guidelines and will constitute a bigger challenge if it continues unabated and unchecked [10].

Motor vehicle exhausts are also sources of trace metals, smaller amount of ions and carbonaceous aerosols [10]. For e.g. heavy metals (HM) in Particulate Matter ($P.M_{2.5}$) are notorious in Changsha, China and significant in spring with higher than normal concentrations with vehicular emissions, fuel combustion pollution as major contributors [11]. However diesel and gasoline exhaust emissions differ in composition; diesel engines emit higher amount of PM, elemental carbon (EC), and ultrafine particles (UFPs) compared to gasoline vehicles which releases a higher fraction of Organic Carbon (OC). A number of polycyclic aromatic hydrocarbons (PAHs) have also been reported to be present in vehicle exhaust with inherent health risks [12]. The effects of air pollutants on health are very complex; they affect the human health severely damaging the cardiovascular and respiratory system. Methane is a more potent GHG than CO_2 [13] whose atmospheric concentration can be affected by wind dispersion speed and other meteorological parameters like wind direction and temperature [14]. But using remote sensing absorption spectroscopy techniques combined with Automatic Number Plate Recognition for vehicle identification showed that emissions of CO, HC, Nitrogen monoxide (NO) and smoke pollutant from petrol cars have being observed to decline with the introduction of each successive Euro emissions standard from Euro 1 onwards [15]. This review introduces the problems of automotive exhaust emissions and the effects of exhaust emissions. It also evaluated the forms and sources of pollution with emphasis on gasoline combustion emission. Further discussions reviewed characterisation of exhaust emissions with focus on gasoline automotives, controls for exhaust emission especially CO_2, present challenges and practical solutions.

II. EFFECTS OF EXHAUST EMISSIONS

Gasoline is the fuel in liquid form used in internal combustion engine (ICE) of spark ignition type predominantly in automobiles and automotives made of complex hydrocarbon and blended components [16]. In the USA, a study of its lifecycle and regulation to ensure performance and less environmental and health consequences confirmed that Companies seeking to register gasoline or gasoline additives into the U.S. commerce must submit to Environmental Protection Agency (EPA) a chemical description of their product. This information allows EPA to determine the likely combustion products and other emissions that may be released into the environment including toxicity tests; yet evaporative emissions and non evaporative emissions are only minimised [16]. Moreover exhaust emissions depend on factors such as: the engine combustion design and operating conditions, the fuel grade and lubricant, the state of maintenance, and local road conditions [17]. In Europe about 20% of all CO_2 emission comes from road transport [18] and concerns over exhaust emissions have been part of the apprehension, especially CO_2 being a GHG in automotive markets globally. Although methane (CH_4) & N_2O emissions can have a global warming impact with as much as 1% - 3% emissions from a given vehicle, CH_4 is converted to CO_2 and H_2O generally increasing the emission levels of CO_2 emitted from automotive exhaust. However, ethanol blends if used as an alternative fuel has no significant difference in emission of CO_2 while Compressed Natural Gas (CNG) and Liquid Petroleum Gas (LPG) could reduce CO_2 exhaust emissions. Vehicle technologies, strict legislation, quotas and incentives may have emerged to reduce exhaust emissions but evidence still shows that laboratory measured emissions are different from real time on road exhausts emission measurements.[18]. Analysis of 60 office workers and truck drivers exposed to traffic related $PM_{2.5}$ and its correlation to lung infection in Beijing, China showed that Si, Ti, Al, and Ca of $PM_{2.5}$ were common among truck drivers and negligible in office workers a pointer that occupational exposure could be indicators of toxicity levels of particulates. Pollutants emitted by motor vehicles such as CO, CO_2, NOx, HC, and SO_2, lead (Pb) and suspended particulate matter (SPM) are very toxic to humans and leads to environmental and economic losses.[20]. These exhaust gases are responsible for pollution. The ICE requires the chemically correct Air Fuel ratio. In petrol engines, the gases comprise a mixture of unburnt hydrocarbons (UBHC), CO and NOx, if in excess quantities, vehicular pollution is caused contributing to atmospheric pollution. The principal emissions from gasoline vehicles are crankcase blowby emissions making up of 40% in a four stroke engine and less than 1% in 2 stroke engines [20]. Also evaporative emissions make up 20% in a four stroke engine and exhaust emissions up to 60% and as high as 97% in a two stroke engine with evaporative emission only 3%.

In pursuant of improved clean air act regulations for fuel and fuel additive registration [21], the petroleum producing industry, additive producers, and makers of oxygenates conducted comparative toxicology testing on evaporative emissions of gasoline alone and gasoline containing fuel oxygenates were able to mimicking real world exposures which indicated levels of genotoxicity, subchronic toxicity, reproductive toxicity, neuro and immune toxicity, simultaneously. However atypical and typical gasoline blends, consist of fuels or fuel additives that contain elements such as antioxidants and metal deactivator other than carbon, hydrogen, oxygen, nitrogen, and sulphur [22]. Also research on the extent of gasoline exposure to both workers and consumers has been for several decades. These hazard and exposure data provide useful data set for the purposes of gasoline risk assessment and a regulatory purpose which includes measures to minimise exhaust gas emissions of CO_2. In a study to evaluate health assessment of gasoline and fuel oxygenate vapours on subchronic inhalation toxicity, rats were exposed via inhalation to vapour condensates of either gasoline or gasoline combined with various fuel oxygenates to determine whether their use in gasoline affects the hazard level of evaporative emissions.[23]. The results showed evidence that the use of the studied oxygenates is unlikely to increase the hazard of evaporative emissions during refuelling, compared to those from gasoline alone indicating that regulated exhaust emissions are the major cause of air pollution [23]. CO has been attributed to car exhaust suicide through poisoning in the USA and Great Britain in the 1960's, and in the 1990's it accounted for fourth leading method of committing suicide in Sweden [24] but has been on the decline since the introduction of car emission control in USA and its removal in domestic gas in Britain.

Research in Isfahan, metropolis in Central Iran showed correlation with previous researches that vehicle exhausts, lubricants, weathered materials from road surfaces, tire particles, and atmospherically deposited materials are responsible for PAHs and heavy metal concentrations in the surface of road dust within urban areas [25], therefore characterizing the anthropogenic sources of heavy metals and PAHs in road dust is significant in quantifying levels of pollution. Similarly HMs in road dust samples which can cause siliceous disease of the lungs was been determined in Yola, Adamawa state, Nigeria. In addition automobile emission, metal welding and exhaust from generators have been identified as the major contributors in Nigeria [26]. Also, particle size and surface area can influence the negative effect of pollutants as demonstrated in the characterization study of combustion particles from vehicle exhaust and wood smoke [27] which showed that combustion particles from vehicle exhaust are characterised by a larger surface area to mass and a lower content of OC and PAHs, as compared to wood smoke particles.

Another Study also confirmed that particle toxicity increases with surface area while a high content of OC and PAHs have been associated with increased inflammatory responses. Additionally toxic effects of particulate matter from exhaust emissions affects populations of ecosystem due to their complex physicochemical characteristics [17]. In a country like Nigeria, gasoline exhaust emissions had become the major air pollutants in the atmosphere and not diesel exhaust emissions. The likelihood of more harmful toxicological effect will be significant due to smaller particle diameter [28]. The three major emission phases are gaseous phase, soot particles, and semivolatile organics. They have been shown to cause oxidative damage to lungs and brains in rats by increasing DNA single strand break, promoting lipid peroxidation and oxidative protein damage and decreasing activities of Superoxide dismutasein in lungs and brains. In contrast, diesel fuelled vehicles have higher particulate emissions than gasoline fuelled vehicles due to PAH content in the fuel contributing significantly to emissions from traffic sources [29]. But its occurrence in the atmosphere is a major concern because of their mutation and carcinogenic potentials. Therefore there should be a need for controls either through air quality regulations or exhaust emission controls [30].

In regulation and control of toxic exhaust emissions, seasonal variation has continued to play an important role from roadside to tunnels [31] even to non road side emission and vehicular emission has been identified as a predominant contributor to high variation of PAH. Moreover vehicular transport is now recognized as urban air pollution source. Associated with urban pollution are the 5 ring coarse PAHs of $PM_{2.5-10}$ and fine $PM_{2.5}$ particulates at urban sites known to cause lung cancer. Thus to protect public health is to reduce exposure to vehicular traffic emissions [32].

Analyses of VOCs vehicular emission measurement of a tunnel in Hong Kong contributed to photochemical smog due to released photochemical oxidant precursors and formation of ground level O_3 in many urban areas of the world. The smog is a complex mixture of O_3, NO_2, nitric acid (HNO_3), aldehydes reacting with NOx and HC while ozone formation precursors like ethane, propane and toluene are associated with gasoline fuelled vehicles [33]. Benzene and other VOCs have also been noted to be of higher indoor concentration in southern Europe than the Northern Europe possibly due to volatization. The guideline for benzene concentration in Flanders region Belgium is at $2\mu gm^{-3}$ and China to be $90\mu gm^{-3}$ showing a large difference in safety limit margins. But since natural dispersive forces produce exchange between indoor and outdoor environment, then it means that fuel and solvent related pollutants are more abundant in countries with no strict implementation of exhaust emissions of pollutants [34].

Motorcycle is a major source of transportation in some countries and emissions from motorcycle exhaust is a source of PAH. Carcinogenic Benzo [a] pyrene [32, 34, 35, 36] has been found in motorcycle exhausts and vehicular exhausts and may be due to the highly toxic VOCs generated from incomplete combustion from motorcycle, its exhaust emission is significantly more toxic than BTEX [22]. Also powered two wheelers has been a popular transportation mode in Southern Europe like Italy. Incomplete combustion from powered two wheelers are known carcinogenic contributors of VOCs like 1,3 Butadiene however, their depleting ozone effect is negligible when compared with respect to CO_2 [37,38].

Research also confirms that the main pollutant in vehicle beside VOCs concentrations under static conditions, include HC, CO_2, SO_2, NOx, PM and various C_7-C_{12} alkanes, however factors, such as [38,39] vehicle model, Vehicle age, temperature, air exchange rate, and environment airflow velocity affects them. A recent work investigating air quality in Multi-Storey Car Parks and exhaust emissions also proved that the main harmful exhaust emissions based on the motor vehicles are gases such as CO, HC, and NOx [40]. These pollutants increases in closed environments like poor ventilated car parks but below threshold limit value (TLV) in temporary car parks and thus do not pose any danger in health risk [40]. Studies in India verified that aldulterated fuels still finds its way into the market causing emissions of significant higher levels of HC, CO and NOx and SPM. HC and CO have been observed to be higher in petrol aldulterated with kerosene but with reduced BTEX emissions [41] while petrol ethanol blends had reduced CO, HC, NOx vehicular emissions compared to unleaded fuels. The exhaust gases from ICEs are complex mixtures consisting principally of the products of complete combustion or incomplete combustion and its major constituent are H_2O, CO_2, N_2, O_2, CO and H_2 and [42] minor constituents including oxides of SOx, NOx, aldehydes, organic acids, HC and smoke and small amounts of the oxidation products derived from the fuel and lubricant. Because the exhaust-gas concentration and its constituent is not indicative of the contribution of the constituent to the overall air-pollution problem due to wide variations in exhaust-gas flow rate with different engine types and automotive sources [42] under different operating conditions; the amount of the constituent exhaust gases discharged per unit time therefore plays an important role and driving conditions has remarkable effect on the emission rate of all constituents [42].

III. FORMS AND SOURCES OF EXHAUST EMISSIONS

The transport sector is a major source of air pollution and CO_2 emissions. These emissions will increase sharply as the global vehicle fleet is projected to grow between 2 to 3 billon vehicles by 2050 mainly in developing countries contributing over 50% of urban air pollution [1,2]. A comparative estimation into road vehicle exhaust emission in Genoa Italy from 1992-2010 and air quality showed a sharp 7% increase in vehicle number and 22% increase in mileage. Total emissions decreased for CO, HC, NOx, CO and PM due to improved technologies and rigid European legislation while NO_2 remained almost unchanged [43]. A study investigating source apportionment of

VOCs in an industrial area in Nanjing, China using their large differences in their atmospheric photochemical activities was used as a tracer for combustion sources indicated [44] that the sources are mainly automobile emission sources, combustion sources, and industrial and volatilization sources with marked seasonal variations. Similarly, source apportionment study of gaseous and particulate PAHs from traffic emission in Shanghai, China using tunnel measurement identified the main sources of the gaseous PAHs to be combustion engine and combustion of fuel traffic related emissions based on PAH used as a chemical tracers of traffic exhaust [45]. An early Preceding research on combustion engine running on gasoline when compared with engine running on methanol demonstrated that engine emissions are dependent on running conditions and different condition produces different results, however HC are found in both exhausts but lower in methanol engine also higher concentration of methanol and aldehydes are obtained in methanol engine exhaust [46] agreeing with a more recent research that ethanol blends reduces CO and HC but with increases CO_2 and NOx emissions [47].

In a similar study of motorcycle Exhaust and evaporative emissions from motorcycles fuelled with ethanol/gasoline blends, it was observed that regulated emissions of CO and THC decreased while NOx increased but regulated emissions of VOCs decreased with increases in carbonyls [48]. Subsequently biofuel consisting of gasoline ethanol blends operated in a gasoline injector engine with installed alcohol injector produced different exhaust emissions at different engine loads and driving conditions [49] while biodiesel in contrast is not suitable as fuel for ICES, [50] though it serves as an alternative fuel for compression ignition engines (CIE) with attendant sulphur content and reduction of CO_2 emissions [51, 52]. Moreover investigations carried out on the emissions and performance characteristics of a H_2/O_2-gasoline fuelled Spark Ignition engine (SIE) reduced THC and CO emissions but increased levels of NOx a precursor of photochemical smog, [53] also the effect of air fuel stoichiometry ratio on emissions studied on oil fired furnace demonstrated that automotive exhaust emissions occur within a fairly narrow band of mixtures and can be reduced by changes in design for efficient combustion.[54].

Gasoline grades are popular with ICEs and its composition affects combustion and exhaust emissions. A comparative analysis of gasoline showed that Nigerian gasoline due to its chemical composition is most likely to be below international standard among Holland and Kuwait gasoline samples although low in sulphur content [55]. In reducing exhaust emissions on new gasoline blends in Mexico using physicochemical properties, a reduction of CO, THC and NOx was achieved at sulphur levels of 89ppm and 34ppm because if at such low concentration catalytic converter increases efficiency [56] and in reducing emissions from automobile exhausts, Mexican government has directed the use of gasoline/ethanol as fuel improvement research showed decrease in CO, HC and NOx [57]. Another study on the effects of octane number and fuel systems on the performance and emissions of a spark ignition engine indicated that lower octane gasoline grade emitted higher concentrations of THC and CO at higher engine loads [58]. On the alternative, the effects of gasoline/diesel blended fuel on combustion and exhaust emissions when investigated, indicated that higher gasoline fraction of up to 40% resulted to incomplete combustion while lower fractions had tendency for emission reductions [59] furthermore profiling of emission of diesel and gasoline cars at city traffic junction using no load conditions demonstrated that a diesel exhausts emit higher particle peak number concentrations compared to gasoline exhaust emissions on volumetric basis. Also increasing engine speed increases CO and NOx emissions of both cars but fuel lean conditions of diesel engines leads to reduction in HC emissions [60].

Also emissions studied on the flow of traffic at traffic junctions made remarkable impact on vehicular emissions confirming that CO, NO_2 and PM emissions at road intersections increases but unaffected at roundabouts with continuous traffic movement except at weekend days [61] although the emissions come from light duty vehicles (LDV), however, in U.K with large fleet of light duty diesel engines have made a significant reduction in both NO and smoke emissions since the transition from Euro III to Euro IV vehicles [15]. Moreover engine loads and vehicle speed are closely linked to fuel consumption and pollutant emission rates [1] as well as driving conditions. An investigation of gasoline direct Injection engine (GDIE) particulate emissions rates in the real world driving conditions using standard driving cycles shows that the ratio of semi-volatile particles to total particle number is generally higher during acceleration followed by the idle operating mode. More particles per kilometre are produced during acceleration compared to cruise conditions [62]. The use of Methyl-cyclopentadienyl Manganese Tricarbonyl (MMT) in GDIE as antiknock and to improve octane rating increases the total particulate mass (TPM) and number concentrations and increases CO and NOx emissions while HC decreases significantly with the increase of MMT content in the test fuels, although phased out in 2004 [63, 64]. Research on the effect of different alcohol fuel use on the performance, emission and combustion characteristics of a gasoline engine when compared with gasoline fuel showed that NOx, HC and CO emissions increased while CO_2 emissions increased [64] although MMT has been phased out while that of gasoline/methanol blends in passenger cars at 15% methanol by volume showed that THC and CO decreased while NOx increased and formaldehyde almost doubled whereas unregulated carbonyls and VOCs increased at 19% and 23% [65].

Dispersion also plays an important role in emission sources as statistics shows 20,000 tonnes of hydrocarbons released into waterways from boats on two stroke engines on studies of the mixing and dispersion of emissions from a vessel using organic dye as tracer showed that initial concentration of pollutants decreases with time due to dispersion [66]. The Ocean going Vessels alone in Hong Kong have contributed 0.07% NOx, 0.05% SO_2, and 0.06% PM_{10} out of the global total shipping emissions as at 2007 [67]. In the U.S alone, generator use has climbed in recent years, from an estimated 9.2 million units in 2002 to 10.6 million units in 2005, a study investigating the dispersion and indoor CO exposure associated with running a generator indoors in an enclosed shed found that for consistent weather conditions it would take about 2 hours for the emission to reach most rooms of the house at dangerous levels [68]. Similarly vehicular emissions are also known sources of HMs. HMs such as Cu, Zn, Cd Pb in $PM_{2.5}$ from Changsha, China in spring using peripheral component analysis (PCA) showed sources are from fuel combustion, vehicular emissions and other pollutant sources [69] likewise a study of road traffic emissions using simultaneous measurements of HMs at street and roof level, enabling calculations of emission factors using a tracer technique demonstrated that annual concentrations of Cd, Ni, As and Pb had decreased significantly while 80% of road emissions of Ni and 40% of Zn are from road traffic emissions [70]

Review of vehicle related metals and PAHs in the UK environment as a continuing source of persistent pollutants in the environment confirmed that while other pollution sources are reducing, automobiles have remained a major source of Cu, Zn, and PAH [71]. Study reveals that different fluorescence spectra will arise from the exhausts of different combustion systems when operated with the same fuel. This suggests that the routes of formation/oxidation of organic species depend on combustion conditions [72] thus rain water samples analysed showed a strong absorption band below 250nm, with shape similar to those observations in condensed combustion-water samples indicating predominance of traffic emissions [72] and a major source of urban pollution [73]. Toronto, Southern Ontario Oxidants Study of 1992 was used to determine some of the factors leading to the production of high ozone levels in the Windsor to Quebec corridor. Results showed that HC distributions measured in the urban area had vehicle exhaust as the most contributing source [74] even previous research has identified the major PAH source from traffic emissions are from traffic mainly from diesel vehicles leading to recent shift to lighter diesel fuel vehicles [12,27,29,75].

As traffic emissions continue to unsettle the world, nations continue to seek divers solutions. In Delhi, India under the proposed road map of emission standards and vehicular technology for on-road vehicle emissions from two wheelers, 4 stroke engines and CNG, $PM_{2.5}$ emissions in 2030 will be halved, CO emissions will reach three times, and VOC and NOx emissions will at least stabilize compared to 2014 estimates [76]. In Malaysia, the presence of high concentrations of Benzo perylene at all locations suggested a source indicator for traffic emission. Diagnostic ratio analysis and PCA also suggested substantial contributions from traffic emission with minimal influence from coal combustion and natural gas emissions [77]. Additionally the use of catalytic converters in vehicles gives cleaner exhaust compositions and emissions with characteristics that are distinct from those obtained in the absence of catalytic converters [78]. Furthermore, a laboratory and an on-road study of exhaust particles of modern gasoline vehicles indicated that under transient driving conditions gasoline vehicles can emit particles consisting of the lubricant oil originating compounds, also particles are emitted during acceleration and steady speed conditions but also during engine braking when the fuel is not injected into the combustion chamber [79] and in two powered wheelers it has been noted that the modern technology used to lower regulated compounds would have a negative effect on unregulated compounds like carbonyls and organic aerosol producing more harmful pollutants [80] while two stroke carburettor motorcycle exhaust emission is dominated by submicron particulates [35]. Carbonyl emissions ranging from $2.3E^{-01}$ to $4.8E^{-01}$ gkg^{-1} fuel dominated by formaldehyde have also been found in exhaust nozzle of aircraft while PM emission indices are found to increase from $1.1E^{-02}$ to $2.05E^{-01}$ gkg^{-1} of fuel with increase in power from idle to 85% [81]. Thus sources and forms of automotive exhaust varies for e.g. vehicle surveillance program in Southern California noted that the contribution of emissions from malfunctioning vehicles to total fleet emissions increased from 16% to 32% for the 1995 fleet to the 2003 fleet even as percentage of malfunctioning vehicles in the fleet decreased from 10% to 5%. Malfunctioning vehicles are mostly vehicles that are at least 10 years old and generally have higher acetylene emission rate ratios. The successful identification and control of these malfunctioning vehicles will become increasingly important for improving mobile source emission estimates and reducing future tailpipe emissions [82].

IV. CHARACTERISATION OF EXHAUST EMISSION

Characterisation of exhaust emissions requires extensive laboratory work. From the table 1 below the early laboratory work involved the use of IR spectrum and old analytical techniques [83, 84]. By 2001, GC coupled to Mass Spectrometer or Flame ionization Detector and other specialised equipments had become popular [85, 86, 87, 88] and researchers pursued specific objectives. Heavy metals were uncommon but became research areas due to toxicity levels and development of more specialised instruments [81, 87, 88, 89, 90]. By the time awareness became a trajectory; several researches emerged to solve the emerging challenges presented by exhaust emissions [91, 92, 93, 94, 95, 96]. Also more advanced combustion engines needed to be tested and more advanced procedures became the norm been advancement and modification and improvement from already known techniques [97, 98, 99, 100, 101]. With the advancement in emission measurement and introduction of Euro III and Euro IV cars, the levels of emission needed to be measured accurately and toxicological levels quantified [102, 103, 104, 105, 106] moreover the use of fuel blends became acceptable and researches move to reduce emission and improve performances [107, 108, 109, 110, 111, 112] and today ICPMS and GCMS/FID have become advanced instruments for analyses of exhaust gas emissions: VOCs, PAH, PM, HMs from exhaust while gases of concern are CO, CO_2, NOx, THC and HC and usually analysed with exhaust gas analyzers. But a systematic characterisation of exhaust emissions will initially involve the determination of physicochemical properties of the fuel. Samples are taken and analysed using ASTM or approved methodologies [20,113]. Further analyses may be carried out to determine the chemical composition of gasoline or fuel [114, 115, 116, 117] which usually contain HC fractions C_8-C_{12} and BTEX. A Gas chromatography coupled to flame ionization detector (FID) or mass spectrometer may be then utilized to determine the VOCs concentrations of the exhaust emissions [[33, 37, 65, 91, 92, 98, 99, 118, 119, 120]. Determination of particulate matter in exhaust emissions are often carried out along with determination of polycyclic aromatic hydrocarbon [17, 31, 89,101]. CO_2 and other gaseous pollutant have been identified as a major exhaust pollutant and continual measurement [57, 83, 84, 92, 93, 95, 105, 106] has remained ongoing and major focus on CO_2, CO and NOx exhaust emissions. Fuels contain elements, other elements in additives and antiknocks other than carbon which are transformed during combustion and the effluent gases contain metallic products in addition to CO_2 and $H_2 0$. Therefore the determination of heavy metals from exhaust emissions [17, 70, 90, 94, 112] formed a major focus for scientist due to heavy metal poisoning and toxicity levels in the atmosphere. However some bio-indicators like moss and lichen are being used to indicate the levels of bio-toxicity of HM in the environment. [94,118,119,121].

However from the table 1 below, it can be seen that the recent focus on exhaust emissions is the testing of engine performance relative to emission reduction.

Table 1: Analyses and characterisation of automotive exhaust emissions

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AUTHOR	OBJECTIVE	SOURCE	FUEL	AREA	INSTRUMENT	GASES	METAL	STATISTICAL ANALYSIS	TOXCITY	REF S/N
Twiss S.B et al., 1955	Exhaust gas analysis of hydrocarbon	Engine manifold & Exhaust Analysis	Gasoline	Stationary dynamometer	IR spectroscopy Thermocouple Manometer	CO_2,CO, HC, NOx, UHC	No	IR spectrum & Excel software	Non dispersive IR gas analyzer recommended. Both results agree.	83
Martin A. Elliot et al., 1955	Determination of exhaust composition	(Motor coaches) Gasoline exhaust. Diesel exhaust Propane exhaust.	Gasoline Diesel Propane	Stationary	Mass spectrometer Orsat analysis Phenylhydrazine ferricyanide, Phenol disulfonic acid method	CO, CO_2, N_2, O_2, H_2, SO_2, SO_3, HCHO, CH_3OH & smoke	No	Simple diagrams	Exhaust gas constituent alone not indicative of overall air pollution	84
Dennis Schuetzle et al., 1983	Vehicle emissions & biological testing correlation	Vehicle exhausts	Gasoline/diesel	Chassis dynamometer	HPLC, Dilution tube sampling of vehicle, fluorescence GC-MS	NO_2,CO, CO2, NOx, PAH, C_8-C_{18}, Nitro-PAH, OXY-PAH,	NO	Microsoft excel	No correlation of vehicle exhaust & mutagenicity	103
Alan Gertler et al., 1997	Characterisation of vehicle emissions ozone correlation	HDDV, LDV, HD SPARK IGNITION	Gasoline/diesel	Tunnel measurement (cassia tunnel)	Toddler bag samplers Gas Analyzers	CO, NMHC, NOx,	No	MOBILE 4.1C MOBILE 5C	MOBILE ratios of CO/NOx & NMHC/NOx in agreement	104
H. Wingfors et al., 2001	PAH Characterisation	Road Traffic (HDV & LDV)	Gasoline/diesel	Urban Traffic tunnel	Gravimetric method Sohxlett extraction HPLC GCFID	PAH, HCs, PM1, 2.5 & 10um, TSP	No	PCA, PLS Multivariate analysis	PAH mainly from Diesel Vehicles	85
Stephen Harris S.J et al., 2001	Characterisation of PM & distribution	Gasoline/diesel engines	Gasoline/diesel	Tunnel dilution & tailpipipe sampling, exhaust	Scanning mobility particle sizer (SMPS)	PM	no	Coagulation model Excel software	Soot oxidation a major determinant	86

				tube						
Cohen, D.D. et al., 2005	Investigate before, during and after trial of MMT introduction	Exhaust emissions	gasoline	Basin area and urban area	Particle induced X ray & y ray emission, Particle elastic scattering, Rutherford back scattering	$PM_{2.5}$	Mn, Al, Si, K,Pb	Paris-winsten regression & spearman correlations , Excel software	Continous monitoring where DDT is used	87
Hei-Hsien Yang et al., 2005	PAH particle size distribution characterisation	2 stroke carburettor Motorcycle exhaust	Gasoline/diesel	European driving cycles: Idle Cruising Acceleration deceleration	MOUDI impactor GC-MS	21 PAH	No	Excel software	Submicron particulates dominates motorcycle exhaust	35
Anette et al., 2006	Physicochemical characterisation	Vehicle exhaust /wood smoke	Gasoline/diesel	MOTROWAY TUNNEL urban	TEM/HR/TEM, EELS & SAED/GC-MS/TOTA	16PAH/EC/OC/TC	NO	SPSS ANOVA	Undetermined/ Mutagenic/ Carcinogenic	88
Michael.D. Geller et al., 2006	Physicochemical & Redox Characteristics of PM	Renault Laguna , Peugeot 306, & Honda accord Passenger cars	Gasoline/diesel	Chassis dynamometer using New European Driving Cycle (NEDC)	CVS, fine articulate sampler , Condensation particulate counter, thermal optical transmittance, HPLC, scanning mobility particle counter	EC, OC, PAH, PM	Ni, Zn, Be, Li,Mg, Al, S, K, Ca, V, Cr, Na	Excel software	Toxicity level need to be reviewed upwards	89
Vassilakos Ch. Et al., 2007	Variations of HM in PM_{10}	Ambient air	Unknown	Urban & sub-urban	Air quality monitoring stations Horiba APNA 360 ozone analyser, FAAS, EMS Andersen Instruments automatic sampler.	Aerosols, PM_{10}, NO, NO_2, O_3	Cd, Pb, Ni, As, Hg	Excel software	Dispersive winds affect ambient gaseous pollutants	90
Harshit Agrawal et al.,	Chemical Characterisation of PM in	Aircraft Exhausts nozzles	Aviation fuel	4 different engine	HPLC-DAD, Thermal/optical Carbon	EC, OC, carbonyl emissions, PAH, n	Cr,Al, S, Si, Fe,	Excel software	Types of engine affects metal distribution	81

2008	Aircraft engines			power testing on wing at ground run up closure	aerosol analyzer, XRF, ICP-MS	alkanes, dioxins, CO_2				
Ying Liu et al., 2008	Source profiling of VOCs	Exhaust Gasoline vapour burning & petrochemical industry etc	Gasoline, diesel coal & biomass & petrochemicals	Chassis dynamometer ECE driving cycles & urban driving cycles	GC-FID/MS CVS	92 VOCs	No	Excel software	1,3 butadiene as exhaust tracer while n butane, trans-butane & n-pentane as gasoline vapour tracer	91
Johansson .C. et al., 2009	Quantify road traffic emissions and HM	Road traffic emission	Unknown	Urban air in street canyons & road tunnel	MAD, ICPMS ICPOEMS	NOx tracer	Cd, Pb, Ni, As, Zn, Cr, Cu, Mn, Sb, Mo, W	COPERT III Gaussian air quality model	Exhaust emission a major Ni, Zn Pb a major ambient contributor	70
Vouitsis.E. et al., 2009	Physicochemical characterisation of PM in LDV	Gasoline/diesel vehicle exhaust 3 types of LDV	Gasoline/diesel	Urban, road, motorway & Mild accelerations	Condensation particle counter, Scanning mobility particle sizer Constant volume sampling, ion chromatography, HPLC/FD EDXRF	CO_2 as a trace gas PAH, PM, aerosol	Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, P, Pb, Sb, Se, Sn, Ti, Zn, Te,	Excel software	PM emissions are most often unrelated to ecotoxixity	17
Ho K.F et al., 2009	Determination of Vehicular emission of VOCs in a tunnel	Vehicle exhaust : LDT HDT LPG	Gasoline/diesel	Direct measurement in road Tunnel. Two Monitoring station	Hydrogen gas Methanizer, GCFID GCMSD	110 VOCs CO, CO_2, OCS, CH_4, NMHCs,CS_2	No	Excel software	Ethane, toluene, n-butane, propane & i pentane most abundant	33
D.A Thornhill et al.,	Quantify gasoline/ diesel vehicle	Vehicle emissions	Gasoline/diesel	On road (city roadways)	Non dispersive IR & Aerodyne	CO, CO_2, NO, NO_2, NH_3, HCHO,	no	Positive Matrix Factorization receptor	Gasoline produces more CO & NOx while diesel more	105

2010	emissions			Aerodyne mobile laboratory	IR, photometer, PTR-MS, QC-TILDAS	Benzene, PM, BC, Toluene, Acetone, aldehyde		model	VOCs. idling in measurements should be accounted for.	
N. Seshaiah, 2010	To achieve Performance & lower emissions in blends	Spark Ignition engine	Gasoline/kerosene Gasoline/ethanol	Laboratory experimental test rig	Orifice meter, burette, gas flow meter, orsat apparatus	CO_2, CO,	No	Microsoft excel	Kerosene blends gives more emissions	106
D.Balaji et al., 2010	To determine emissions & performance in Isobutanol Blend.	Spark ignition engine	Gasoline/isobutanol Gasoline/ethanol	Eddy current dynamometer	Sun glass Analyzer MGA 1200 (NDIR)	CO, CO_2, NOx, HC,	No	Microsoft excel	Blends reduced CO & CO_2 but NOx increased	107
Dhanapal Balaji et al., 2010	Exhaust emission & combustion of unleaded gasoline & additives	Spark ignition engine	Gasoline/ethanol	Eddy current dynamometer	Sun glass IR Analyzer	CO, CO_2, NOx, HC,	No	Microsoft software	Ethanol in gasoline reduces emissions	108
Adam, T.W et al; 2011	Chemical composition, Emission factors & ozone formation potentials	LDV exhausts (dual fuel cars)	LPG/gasoline	Chassis Dynamometer	REMPI-TOFMS HPLC GC-FID	CO_2, CO, NOx, THC, carbonyls, Volatile hydrocarbons	No	LABVIEW Excel software	Chemical composition of emissions affects vehicle performance	92
G.A. Rhys-Tyle et al., 2011	Significance of emission standards in LDV	LDV	Gasoline/diesel	Instrumentation intercepted primarily light vehicle exhaust plumes. Total of 94328 matches. 54599 valid emissions matched to vehicle identification	Pre-existing Data collected using road side remote sensing absorption spectroscopy techniques combined with Automatic number plate recognition (ANPR) (IR and UV)	CO, CO_2, HC, NO, smoke	No	Vehicle registration plate number software matched against Driver & vehicle registration database (DVLA)(UK)	Petrol cars had Successive downward emission trend with introduction of emission standards from EURO 1 onwards	93

Bajpai .R. et al., 2012	Determine Road emission & HM level	Ambient air	Bioindicator (Lichen Thallus)	urban	UV scanning spectrophotometer, ICPMS	No	As, Al, Cd, Cr, Cu, Fe, Pb, Zn,,	LSD-test One way ANOVA,	Concentrations increases near roadside	94
Clairotte .M. et a., l 2012	EURO 2-Emission compliance of Powered two wheelers (mopeds)	Exhaust emission	Gasoline/diesel	Chassis dynamometer	FTIR spectrometer, REMPI-TOF-MS MAAP Condensation particle counter CO_2 analyzer	CO_2, CHA, N_2O, organic Aerosol, carbonyls PAH	No	PCA Multivariate analysis	After treatment may be potentially harmful	80
KIM J.Y et al., 2012	Determination of seasonal variation of roadside PAHs	Roadside &ambient air	Gasoline/diesel	Monitoring station	GC-MS	16 PAH particulate & Gaseous	No	Excel software	Toxicity level could be a concern	31
Janaka Gunawardena et al., 2012	City Traffic contributions of PAH & HM from exhaust	Diesel vehicles Petrol vehicles	Gasoline/diesel	City heavy traffic (street and city park area)	High volume polyurethane foam. Total sampling volume GCMS ICPMS	PAH, TSP	Zn, Pb Cd, Mn, Ni, Cu, Cr	MCDM e.g. PROMETHEE & GAIA Microsoft excel	Traffic sources are major PAH contributors	109
Yenny Gonzalez et al., 2013	Comparative study of UFP in vehicle exhaust, ship emissions &oil refinery	Vehicle exhaust Ship emissions, Oil refinery	Diesel engines Gasoline engines Ships refinery	Entries & exits at harbour, refinery area, City main roads	Gas analyzers, ultra fine condensation particle counter (UCPC) Multiple angle absorption photometer	$PM_{2.5}$, $PM_{2.5-10}$, BC, NOx, SO_2, SO_3, CO, O_2	No	Microsoft excel	UFPs background linked to vehicle, ship & refinery are major source	110
Sekimoto et al., 2013	Characterisation of nitromethane & time resolved Determination	Automotive Exhaust (gasoline passenger car + diesel trucks)	Gasoline/diesel	Stationary	Proton transfer reaction mass spectrometer/ chassis dynamotor PTR-MS	Nitromethane, CO_2, CO, NOx	No	Excel software	Nitromethane suppressed in gasoline due catalytic converter	95
Drew R. Gentner et al.,	Chemical Quantification, emission	Gasoline/diesel exhaust, non	Gasoline/diesel	Tunnel measurement.	GC-MS, GC-FID, IR spectromete	N butane to N pentadecane .	No	SAPRC-07 MIR MOIR Excel	Gasoline a major contributor of pollution & Organic	96

2013	factors & ozone formation potential	tailpipe gasolin e exhaust			r	(C_4-C_{15}), SOA, VOCs, branched alkanes, Cycloalkan es, Tri/Bicyclo alkanes NOx, PAH		software	compounds from motor vehicles has high ozone potential	
Sutthic ha Nilrit et al., 2013	Emission factors of CH_4 & CO_2 in vehicles	HDDV, LDDV, LDGV	Gasoline/d iesel	Chassis dynamo meter	Bag sampling system Constant volume sampling NDIR, Methane analyzer & FID	CH_2 & CO_2	No	Microsoft software	Can be used to evaluate GHG emissions factors	111
Farouk Alkurd i et al., 2013	PAH exhaust emission characteri sation	Exhaust emissio ns (mini vans, Passeng er cars, buses)	Gasoline/d iesel 3 gasoline 3 diesel	In service vehicles	HPLC with UV Visible detectors Fluorescenc e detectors	15 PAH	No	Excel software	Catalytic converter gave cleaner emissions	78
Peipei Dai et al., 2013	Characteri se exhaust & evapourati ve emissions	Exhaust & evapour ative emissio n (passen ger cars)	Gasoline/ methanol blends	Stationa ry (dynam ometer)	Motor exhaust gas analyser, HPLC GC-MS Thermal desorption	THC, VOCs, NOx, carbonyls, methanol	No	Excel software	Evapourative emission a major source of HC emissions	65
Dallma nn et al., 2014	Characteri se chemical compositi on	Heavy duty diesel trucks & light duty gasolin e vehicles	Gasoline/d iesel	On Road urban (1 KM tunnel)	Soot Particle aerosol mass spectromete r (SPAMS) with Laser Vaporizer	$PM_{2.5}$/BC/ OA Organic aerosol	Zn. Ca, Ph, Mg, K, Na, S	SQUIRREL PIKA	Unclassified Most OA in gasoline are lubricant derived	97
Moren o A.I et al., 2014	Chemical Characteri sation	treatme nt plant	Solid waste	Municip al area: landfills , leachate pond & biogas leaks	Fluorimetri c method Diffuse sampling Ogawa passive Samplers MX6 Ibrid portable detector. GC/MS	H_2S, C2S, NH3, VOCs Dimethyl sulphide, Methyl mercaaptan	No	Microsoft excel	Exhaust emissions are Main Contributors	98
Carme n R et	Determine VOCs and	Ambien t air	unknown	Urban area	Tenax T.A catridges	29 VOCs 24 VOCs	No	Excel software	Road Traffic source.	99

al., 2014	PM main sources	pollutants		low traffic Rural traffic	SCK Catridges GC-MS Optical particle counter	PM2.5-10>10			VOCs in urban > VOCs in Rural	
Stephan Weinbruch, et al., 2014	Quantification of Exhaust emissions of Particulate traffic/resuspension component	Road vehicles	Gasoline/diesel	2 monitoring stations (Urban area)	Electro Microscopy (SEM/EDX /HRSEM))	PM_1, $PM_{10,}$ $PM_{2.5}$	Silicates, Ca sulphates, Carbonates, Fe oxides/ hydroxide	READY HYSPLIT 4 software,	Lower concentration of Exhaust particles compared to resuspension particles	100
Marcel Hernandez et al., 2014	Determination of emission & fuel economy in gasoline/ethanol blends	Exhaust emissions of 3 LDV	Gasoline Ethanol	Cold start Hot start Constant speed Real in city driving	Ignition calorimeter Gas analyzer ASTM method	CO, CO_2, NOx, UHC,	No	Excel software	Premium blend had lowest emission of CO, NOx, HC	57
Perrone et al., 2014	PAH, n alkanes & Phenols in different European classes of vehicles	5 Private cars 5 Light duty vehicles Chassis dynamometer, Warm start conditions Cold start conditions	Gasoline/diesel	In service vehicles using EU Standard urban driving traffic (UDC) EU standard extra urban driving cycle (EUDC)	GC-MS HPLC-UV	PM, PAH & n alkanes	No	Excel software	PAH changes with fuel use. Oldest vehicle had highest levels of unregulated emissions and still in circulation	101
Short .D. eta al., 2015	Evaluate emissions of GDI & PFI in blends	GDI vehicles & PFI vehicles	Gasoline/iso butanol/ methanol blends	Single Roll Emission dynamometer	A Pieburg AMA 4000 bench, Condensation particulate counter, MAAP, APM analyzer	PM, BC, WSOC, droplet surface tension	No	Online particle characterization Excel software	Operating conditions affect emission	102
Neghmeh Soltani	PAH & HMs in road dust	Traffic load & Land	Undefined traffic road dust	commercial Agricult	GCMS ICPMS	13 PAH	As, Cd, Cu,	SPSS	PAH linked to Traffic & high cancer risk.	112

et al., 2015	& cancer correlation	use		ural Industrial etc			Pb, Zn, Ni, Cr, Co, Sb			

V. CONTROLS OF EXAHSUT EMISSIONS

Automotive manufacturers and scientists have continued to improve combustion process and reduce exhaust emissions from automotive engines. Turbocharging technologies has become popular in reducing CO_2 and increase engine efficiency during combustion and continuous improvement of turbocharged gasoline engine sought through research and development [122]. The size of particles formed during combustion is dependent on the time spent in the formation and oxidation zones and a research investigated how the location of air inlet affected particulate formation by changing the temperature of combustion inlet, it was observed that CO decreases with increasing temperature with higher CO_2 production [123]. Also studies on vehicular pollutants emission and CO_2 emission reductions using Real-time monitoring and early warnings for vehicle exhaust emission factors showed that NOx are usually emitted at high temperature and CO at low temperature and there is a correlation for early warning and monitoring data of the vehicle exhaust emissions [124]. Therefore it is important to ensure that the temperature of the reactants is very close to the temperature of the products, since real combustion processes in ICEs occur in combustion chambers where both the volume and the internal energy are time-variant [125]. Moreover exhaust gas recirculation (EGR) has become a popular exhaust emission control measure, because when this exhaust gas is re-circulated in the cylinder, the UBHC in exhaust gas burns because of sufficient O_2 available in combustion chamber and reasonably high intake temperatures [126]. EGR has also been used to assist in achieving decreased PM formation and reduced gaseous emissions with pre-mixed hydrogen and carbon dioxide introduced into the EGR stream to generate a gas composition representative of reformate [127]. Also an investigation of the exhaust emission characteristics of small amount of hydrogen added to gasoline air mixtures showed that HC emissions decreased significantly while an increase in the air-fuel ratio leads to a significant reduction in CO and HC emissions [128] and improves engine performance [129].

Furthermore fuel injection strategy on low temperature combustion with gasoline performed on independently adjustable intake/exhaust gas recirculation (EGR), and common-rail injection system while keeping other engine components intact showed that NO_X emission could be well controlled by either the single or double injection strategy with sufficient boost and EGR though double injection strategy emits more CO and THC emissions than the single injection strategy [130]. In addition, in a dual injection bi-fuel spark ignition engine, the HC, NOx and CO_2 emissions will reduce when using gasoline or ethanol fraction in direct injection. While the NOx and CO_2 emissions increases and HC increases When using 2,5 dimethylfuran (DMF) [131]. Emission reduction has also been investigated by equipping gasoline/methanol fuel vehicles with dilution air refine system (DAR) performed on sealed Housing for evapourative determination (SHED) on chassis dynamometer, measured by a constant volume sampling (CVS) system and tested over the New European Driving Cycle (NEDC) showed that THC and CO decreased while NOx, VOCs and Carbonyls also increased [65] while gasoline/ethanol blended fuel spark ignition engine (SIE) illustrated that concentration of CO and HC in the exhaust pipe decreased by introducing ethanol blends, but CO_2 and NOx emissions increased [47, 132] and gives best emission control of HC and CO at 20% [133] whereas the use of CNG in particular as an alternative fuel lowers CO_2 emissions, but ethanol blends generally show no change in CO_2 emissions but an increase in volumetric fuel consumption.[134].

A combined application of gasoline and diesel blends using an ultra-low sulphur diesel with a cetane number of 51 and a high-quality gasoline with a octane number of 97 as the test fuel to prepare six blends with different volume fraction of gasoline using EGR was effective in reducing NOx and smoke emissions simultaneously with minimal fuel consumption [59]. Using fuels that were blended from standard gasoline refinery blending streams, but without any special chemicals, the impact of olefin content in gasoline on modern vehicles and its toxic emission when studied, showed that changing the olefin content had relatively low impact on exhaust emissions such as THCs, NOx, and CO emissions and recorded slight increase in levels of 1,3 butadiene [135]. Work on effects of gasoline properties on exhaust and evaporative emissions on LDV using seven fuels formulated with distillate fractions selected aromatic, paraffinic and olefinic refinery components to produce a test fuel matrix giving different effects showed that emissions of modern cars are usually reduced in warm engine conditions by catalysts, consequently emissions are significantly higher during the cold start [136]. Accordingly, the concentrations of HMs in Lichen and Moss have been used as bio-indicators of roadside and exhaust emissions [94,137,138].

Catalytic exhaust after-treatment has also been employed to control exhaust emissions in spark-ignition. The noble metals (Pt, Pd, Rh) used are impregnated into a highly porous alumina washcoat of about 20-40µm thick and applied to the passageway walls [139]. Also alumina washcoat also contains other components, which function as catalytic promoters or stabilizers against ageing. Cerium is normally present in high quantities in the washcoat because ceria compounds have high oxygen storage capacity and lantanas have proper basicity and large ionic size [139] moreover modern studies on the vehicle related air pollution suggest that improved air quality standards could be achieved by monitoring and controlling the current technology [140]. This evident was observed in a research using series of low noble-metal content monolithic catalysts for exhaust purification of small gasoline engines, and it was found that the PtRh-

OSM/Al_2O_3, (OSM: oxygen storage material) catalyst with $Ce_{0.5}Zr_{0.5}$-MnO_x(3%MnO_x) OSM held low light-off temperature for CO, HC, and NO while the three catalysts easily met the exhaust's temperature range of (300 – 700°C) of small gasoline engines and efficiently controlled exhaust emission of small gasoline engines e.g. water pump, power machine [141]. Experimental investigations have revealed that combustion chamber using ceramic material attaining an adiabatic condition with Optimum Cooling can reduce the emissions of CO, CO_2, HC and smoke when compared to base engine [142].

The Intergovernmental Panel on Climate Change (IPCC) estimates that the terrestrial biosphere could mitigate between 10 and 20% of the world's fossil fuel emissions by 2050 as scientific evidence indicates significant risks around CO_2 induced climatic change [143]. The IPCC estimates further that average CO_2 concentration may rise to 570 ppm by the year 2100 causing a rise of about 1.9 ^{0}C in average temperature and 3.8m in the global mean sea level. Therefore CO_2 capture and sequestration (CCS) has emerged in reducing CO_2 emissions [144]. The use of activated carbon (AC) material evenly packed inside the adsorption column forming the reaction bed where CO_2 is adsorbed at low pressures has been reported [144] including CO_2 capture on primary amine groups entrapped in AC at low temperatures, demonstrated that the impregnation of amino clay (H_2N-CL) nanoparticles into AC can be a useful method for selective CO_2 adsorption at 273 and 298 K at 1 atm [145].
The use of amino acid salt solutions (AAS) and regeneration using hollow fibre membrane contactor showed that AAS have enhanced CO_2 absorption/stripping performances when compared to Monoethanol amine (MEA) [146] while CO_2 absorption with membrane contactors indicated that membrane contactors may provide significant improvements in offshore CO_2 capture, both from gas turbine, flue gas and in sweetening of natural gas [147] and simulation studies of MEA in a based packed column demonstrate CO_2 recovery increased with the flow rate of absorbent and absorption height but decreased as the lean CO_2 loading of the absorbent increases and very high recovery rate [148]. Although Chilled ammonia process and Corti process are two main processes that utilize ammonia as solvent but the composite membrane contactor in particular, can achieve promising performance for CO_2 post-combustion capture by ammonia [149] as confirmed by the use of novel hollow fibre membrane contactor that integrates absorption and stripping using a non volatile reactive absorbent polyamidoamine (PAMAM) dendrimer generation and an ionic liquid. This absorbent showed high CO_2 absorption capacity.[150]. Furthermore comparison of amines and ammonia as aqueous solutions for post-combustion CO_2 capture showed that aqueous ammonia has much loading capacity, higher absorption and lower energy for regeneration, while NH_3 has better resistance to oxidative or thermal degradation relative to MEA [151].

Thus among various CO_2 capture technologies including adsorption, physical absorption [152] which is popular in industry and in post-combustion CO_2 capture pilot plant emission studies [153], plus chemical absorption e.g. chemical absorption using aqueous alkanolamine solutions for instance, MEA is proposed to be the most applicable technology for CO_2 capture before 2030 [152] and this primary, secondary, and tertiary amines for CO_2 capture can be designed for various mesoporous CO_2 adsorbents[154]. As a consequence, current research on physical adsorption focuses on how to improve the CO_2 adsorption capacity and selectivity via two ways: to improve surface area and pore structure of the carbonaceous adsorbents for e.g. the use of Zeolites is affected by size, charge density. Metal organic frameworks (MOFs) also have high surface area, controllable pore structures and tuneable pore surface properties which can be easily tuned by changing either the metallic clusters or the organic ligands chemical composition of cations in their porous structure [[152].

A precipitating potassium carbonate (K_2CO_3)-based solvent absorption process has been developed for CO_2 from industrial sources. CO_2 removal rate was between 5 and 15% depending upon operating conditions and removal efficiency is limited by the height of the pilot plant packed column also removal rates are expected to improve with the addition of a rate promoter as well as higher concentrations of K_2CO_3 [155]. In contrast, there is CCU by biological system and converting it to complex molecules is becoming promising and the list of such microorganism are increasing e.g. algae, cyanobacteria, clostridia etc and there has been proposal that these biological CCU organisms can be incorporated into chemical or physical absorption [156]. Finally several opportunities exist for CO_2 combustion capture and utilisation. popular with post combustion process is chemical absorption, adsorption, membrane separation, and cryogenic distillation while the use of selexicol, rectisol, flour purisol is common in pre-combustion capture of CO_2 and finally oxy-combustion technology through the use air separation, combustion and CO_2 recycle and cleaning and CO_2 capture [157] but this review has emphasised post combustion process by exhaust pipes during combustion of gasoline.

VI. CONCLUSION

Transportation control measures through mobile source abatement can reduce CO_2 pollution through implementation of transportation control measures that can decrease motor vehicle trips, and vehicle mile travel congestion reduction by encouraging off-peak period travels under more optimal conditions and encouraging the use of transportation modes other than single occupant vehicle travel [158]. Although decrease in vehicular emissions has been notable in Cities especially Los Angeles, USA [159] data collected between 2001 and 2002 of Vehicular emissions of gasoline and diesel vehicles were the second major contributor to $PM_{2.5}$, following secondary aerosols, with about 20% contribution to total mass in both sites [159] it would also be notable that developing Motor Vehicle Exhaust Emission Standards in California has been on for several decades [160] as adopted by the California Board of Public Health on December 4, 1959 [160]. In the EU for e.g. the legal instrument for regulation of PM is through EU directive wherein member States are obligated to meet the emission limits and air quality standards but the legal means to achieve this at national level are left to their individual discretion [161], while in a country like Nigeria environmental policy needed to continually improve and implement sustainable transport development lack enforcement [162] and in nations like India the optimism of reducing future pollution should not be hinged primarily on emission standards, but also on an efficient and strictly enforced vehicle testing program [163]. In summary it is obvious that much of the reported analyses have been carried out in the USA or Europe, and there is lack of reliable information on traffic emissions in areas with high population density in Africa, Asia and South America and there is need to fill the gap [164]. Finally, new developments in engine and catalyst technologies have engineered a tremendous progress in emission control from exhaust, fuel economy and performance of automotive engines ,but the increasing complexity in modern engine designs may bring with it new challenges for more continual approach in research, development, policy and standards implementation [165].

VII. RECOMMENDATIONS

1) There has been significant need to fit the exhaust emission measurements into the stoichiometry of gasoline combustion using stoichiometric equations.
2) There have been absences of simple colorimetric absorbents (indicators) that can indicate toxic levels of exhaust emissions for motor users.
3) There has been significant need for cheaper metals or dopants beside the noble metals to be used in catalytic exhaust after treatment.
4) There is need to source cheaper and biodegradable material or local materials that are useable as washcoat in catalytic exhaust after treatment.
5) There is also the need to significantly research in isotopic labelling to actually differentiate if CO_2, HC and other UBHC are carbon 12 or 14 isotope.
6) Research should also be expanded to source cheaper chemical exhaust emissions adsorbents/absorbents with local material precursors.
7) Development of a laboratory device that can trap and store CO_2 and reusable since most laboratory reactions evolve CO_2
8) There have been the absences of traffic emissions or vehicle emission computer programs to simulate and predict exhaust emissions in Africa region e.g. use of computer program on road transport emissions (COPERT III).
9) There is therefore need to apply advanced statistical tools like multivariate analysis or PCA to test the correlation and significant trends and patterns in exhaust emissions.

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