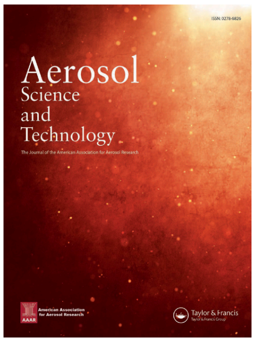

Aerosol Science and Technology

ISSN: 0278-6826 (Print) 1521-7388 (Online) Journal homepage: www.tandfonline.com/journals/uast20

Toxic Potential Evaluation of Particulate Matter Emitted from a Constant Speed Compression Ignition Engine: A Comparison between Straight Vegetable Oil and Mineral Diesel

Avinash Kumar Agarwal, Tarun Gupta & Abhishek Kothari

To cite this article: Avinash Kumar Agarwal, Tarun Gupta & Abhishek Kothari (2010) Toxic Potential Evaluation of Particulate Matter Emitted from a Constant Speed Compression Ignition Engine: A Comparison between Straight Vegetable Oil and Mineral Diesel, Aerosol Science and Technology, 44:9, 724-733, DOI: 10.1080/02786826.2010.486386

To link to this article: https://doi.org/10.1080/02786826.2010.486386

Aerosol Science and Technology, 44:724–733, 2010

ISSN: 0278-6826 print / 1521-7388 online
DOI: 10.1080/02786826.2010.486386

Toxic Potential Evaluation of Particulate Matter Emitted from a Constant Speed Compression Ignition Engine: A Comparison between Straight Vegetable Oil and Mineral Diesel

Avinash Kumar Agarwal,[1] Tarun Gupta,[2] and Abhishek Kothari[1]
[1]*Department of Mechanical Engineering, Indian Institute of Technology Kanpur, Kanpur, India*
[2]*Department of Civil Engineering, Indian Institute of Technology Kanpur, Kanpur, India*

This study was primarily focused on analyzing particulate matter coming out of engine exhaust from diesel and straight vegetable oils (SVO) for the following parameters: (1) Benzene soluble organic fraction (BSOF), (2) Metal traces, and (3) Particulate surface morphology. Hence, the exhaust from a small compression ignition (CI) engine emitted under varying engine load conditions at constant engine speed was extensively analyzed for its chemical constituents and PM morphology. Two fuels, namely mineral diesel and straight vegetable oil, were tested with this engine and the engine emissions were compared in order to assess their relative toxic potential. One of the major findings of this study suggested that by preheating, viscosity of vegetable oil can be lowered to the level of mineral diesel, and vegetable oil gives better particulate emission results than mineral diesel in terms of lower toxic metal emissions as well as less soot formation.

INTRODUCTION

Particulates produced by compression ignition are always of concern to engine manufacturers because they influence engine performance and wear; however, nowadays because of their impact on the human health, they have become a major concern to the manufacturers. The main concerns about particulates are environmental impact, adverse health effects, decreased visibility, and soiling of buildings. A strong relationship between exposure to internal combustion engine related air pollutant emissions and adverse human health impacts is now well established (Kunzli et al. 2000; Krzyzanowski et al. 2005; Schlesinger et al. 2006). More than 40 components of the engine exhaust have been listed as toxic air contaminants (TACs) by the Californian Air Resources Board (CARB 1998).

Using straight vegetable oils (SVO) in diesel engines is not a new idea. Rudolf Diesel first used peanut oil as a fuel for demonstration of his newly developed compression ignition (CI) engine in year 1910. Later with the availability of cheap petroleum, crude oil fractions were refined to serve as "diesel," a fuel for CI engines. Nowadays, due to limited resources of fossil fuels, rising crude oil prices, and the increasing concerns for environment, there has been renewed focus on vegetable oils and animal fats as an alternative to petroleum fuels.

Vegetable oil is easily available worldwide. It is a renewable fuel with short carbon cycle period (1–2 years compared to millions of year for petroleum fuels) and is environment friendly (Peterson and Hustrulid 1998). These are the triggering factors for research all over the world to consider vegetable oils and their derivatives as alternative to petroleum diesel. However, a major disadvantage of vegetable oil is its viscosity, which is an order of magnitude higher than that of mineral diesel. The fuel injection system of new technology engines is sensitive to fuel viscosity changes. High viscosity of the vegetable oil leads to poor fuel atomization, which in turn may lead to poor combustion, ring sticking, injector cocking, injector deposits, injector pump failure, and lubricating oil dilution by crank-case polymerization (Agarwal and Das 2001; Agarwal et al. 2003). Viscosity of the vegetable oils must be reduced in order to improve its engine performance. Heating, blending with diesel, and transesterification are some of the methods used to reduce viscosity of vegetable oils.

Straight vegetable oil is an important fuel resource. It is also an oxygenate fuel. In the case of straight vegetable oil, its viscosity and low calorific values at same density as diesel makes it a poor alternative fuel but a good and easily available fuel. Injector coking due to higher fuel viscosity is the major problem with this alternative fuel. Oxygenates are burned neat or more typically as oxygenate–diesel blends and their particulate suppressing properties are well documented. Before choosing any particular oxygenate as a renewable fuel for technical feasibility, a wide range of criteria other than reliable clean burning combustion must be checked. Examples of that criteria can be ignitability, long-term stability, corrosiveness, polymerization

---

Received 28 October 2009; accepted 7 March 2010.

Address correspondence to Avinash Kumar Agarwal, Indian Institute of Technology Kanpur, Kanpur 208016, India. E-mail: akag@iitk.ac.in

compatibility, toxicity, lubricity (Geller and Goodrum 2004), solubility in diesel (Zhao et al. 2005), viscosity, volatility (Vertin et al. 1999), and degradability. There is also susceptibility to injector nozzle coking (Labeckas and Slavinskas 2005), especially in the case of straight vegetable oils utilization. If bulk fuel properties such as density and viscosity are altered, then certain effects might be observed not in the combustion, but in the geometry of fuel spray, the atomization of the fuel, or even in the flow characteristics of fuel within the injector nozzle.

Composition of Particulate

Diesel exhaust is a complex mixture of organic and inorganic compounds and gas, liquid, and solid phase materials. Diesel particulate matter consists of an elemental carbon core with several organic compounds (soluble and insoluble in organic solvents), sulfates, nitrogen oxides, heavy metals, trace elements, and irritants (such as acrolein, ammonia, acids, fuel vapors, unburned lubricating oils, moisture) absorbed to its surface. They include classes of compounds such as aldehydes, alkanes, and alkenes (both straight and branched chain), and aromatic compounds (single rings, substituted, and poly-nuclear). Any of these species may also contain functional groups such as carbonyl (C=O), hydroxyl (OH), and nitro (NO_2). These organic compounds originate primarily from the unburned fuel and the lubricating oil, although some may be formed during the combustion process and/or reaction with catalysts. The inorganic species include sulfur, oxygen, carbon, and nitrogen-containing compounds such as sulfate (SO_4), carbon monoxide (CO), elemental carbon, and oxides of nitrogen (NO_X). Some of these compounds may also have their origin from the fuel, especially those containing sulfur and carbon (Johnson et al. 1994). About 90% of diesel particulate encompass a size range from 7.5 nm to 1.0 μm (Baumgard and Johnson 1992). The carcinogenic effect related to diesel exhaust particles is now considered to have at least two components, one related to the inorganic "carbon core" or SOL (solid or insoluble) portion and the other due to the adsorbed organics or BSOF (benzene soluble organic fraction) portion. Several recent laboratory studies with rats have indicated that the SOL portion is probably essential for tumor formation for initiation (Mauderly et al. 1991, 1992; Heinrich 1993; Nikula et al. 1993). The associated BSOF, particularly the poly-nuclear aromatic hydrocarbons (PAH) and the nitro-PAH, could have a contribution to the overall carcinogenic effect (Atkinson and Arey 1994). Therefore BSOF is generally considered to be a marker of toxicity.

Metallic elements emitted from engine include silicon, copper, calcium, zinc, lead, manganese, and chromium (Hare 1977). Calcium, phosphorous, and zinc are normally present in engine lubricating oil as organo-metallic additives. In one study, calcium was found to be the dominant metallic element in diesel particulate matter, with levels ranging from 0.01 to 0.29% (w/w). Phosphorous, silica, and zinc were the next most abundant species found and sodium, iron, nickel, barium, chromium, and copper were barely present and were below detection limits of the instrument (Springer 1997). Silicon, iron, zinc, calcium, and phosphorous were observed and together constituted up to about 0.5% of total diesel particulate matter with emission rate of 1.02 mg/ km reported as engine transient test emissions of metals for a medium duty truck (Norbeck et al. 1998).

Health Effects

Researchers have carried out tests using animals and models to determine the mechanisms associated with pulmonary cancer caused by diesel exhaust particles. In 1996, a study carried out by Sjogren et al. used multivariate statistical methods to identify factors that affect the biological potency of the exhaust, analyzed physical and chemical characteristics of particulate matter emitted and performed an Ames test to evaluate the mutagenicity potential of the exhaust. A study conducted for inhalable total suspended particulates (TSP) from the urban area, diesel and gasoline exhaust particles, and urban street dusts suggested that the deposition of metals (like Iron) on the lower airway would probably generate hydroxyl radicals, which would trigger the production of oxygen free radicals and finally cause both acute and chronic lung injuries (Valavanidis et al. 2000). Metals originating from combustion sources like As, V, Cu, and Zn can initiate epidermal growth factor (EGF) receptor signaling in a human airway epithelial cell line suggesting inflammation and they can probably also show synergistic effects in the presence metals like Fe, Pb, and Mn originating from other environmental sources like steel mills. Few recent findings have indicated that these metals activate epidermal growth factor receptor (EGFR) and lead to increases in the levels of guanosine triphosphate-bound Ras in human lung cells (Wu et al. 2001).

In one study, healthy human volunteers were exposed for short duration to concentrated ambient particles (Ghio 2000). The aerosols were extensively characterized and detail measurements of several health parameters were carried out. A subsequent principal component analysis linked specific water-soluble components of the PM collected on filters to both the neutrophil influx and elevation in blood fibrinogen. A sulfate/iron/selenium factor, which may be attributed to photochemical air pollution, was associated with the neutrophil increase in the lavage, while a copper/zinc/vanadium factor, which was likely related to various combustion processes, was linked to increase in blood fibrinogen (Ghio 2004).

This study is focused on analyzing particulate matter coming out of engine exhaust from diesel and straight vegetable oils for the following parameters: (1) Benzene soluble organic fraction (BSOF), (2) metal traces, and (3) particulate surface morphology. Therefore, the objectives of the present article is to characterize the compression ignition (CI) engine exhaust under varying engine load conditions at constant engine speed and assess their relative toxic potential.

TABLE 1
Experimental engine specifications

Manufacturer	Kirloskar Oil Engines Ltd, India
No. of cylinders	One
Combustion system	Direct injection
Bore/Stroke (mm)	102 / 116 mm
Engine displacement (cc)	948 cc
Compression ratio	17.5
Nozzle opening pressure	200–205 bars
Rated power	7.4 kW (10.0 hp) at 1500 rpm
Engine weight and fly wheel weight	127 kg and 64 kg
Starting	Hand start with cranking handle

EXPERIMENTAL SETUP

For the comparative study of straight vegetable oil and mineral diesel, a small single cylinder, direct injection, constant speed engine (Make: Kirloskar Oil Engines Limited, Pune; Model: DM10) (Figure 1) was used. This engine is typically used in agriculture sector for irrigation purposes as-well-as in small decentralized engine gensets. A schematic diagram of the engine with alternator and heat exchanger devised for the purpose of using straight vegetable oils is shown in Figure 1. The heat exchanger uses the waste heat of the exhaust gases in order to pre-heat the vegetable oils so that their viscosity comes in a range closer to mineral diesel. A single phase AC alternator was used for loading the engine to desired levels. The electricity thus generated by the alternator was consumed in a specially fabricated load bank. Engine specifications are given in Table 1.

Experiments were performed at different loads at constant speed since this engine always operates at constant speed due to the restriction of producing the same amount of voltage across the alternator terminals. To characterize emissions, the engine was operated on some specific operating points.

TABLE 2
Filters selection for different investigations

S. No.	Investigation	Type of filter	Sampling duration
1	Trace metals	AQ F/A (047) Tissue-quartz	5–7 min
2	Benzene Soluble Organic Fraction	AQ F/A (047) Tissue-quartz	30–35 min
3	Scanning Electron Micrograph	GF/A (047) Glass fiber	30 min

Particulate matter emitted from the engine tail pipe after dilution through partial dilution tunnel was collected through Tissue-Quartz filter (QF/A, 47 mm, Make: Whatman products), specified in NIOSH method 5040 for Elemental Carbon (Diesel Particulate) (Table 2). Filters were kept in desiccators for 12 h before and after sample collection, which made sure the precise mass of particulate matter. Glass vessels were thoroughly cleaned with 4% concentrated $HNO_3$and MIlli-Q water.

Test Methods

Initially, filter papers were desiccated for 12 h in anhydrous silica gel desiccators and then weighed. For collecting a sample, one filter paper was placed in filter holder assembly of the partial dilution tunnel used in the experimental setup. After running the engine at desired load and speed and collecting the particulates through partial flow dilution tunnel for a predetermined period of time, the filter papers were removed carefully from the filter assembly and again kept in desiccators. These filter papers were then analyzed for characterization of metals and BSOF in particulates.

Estimation of Metals in Mineral Diesel, Straight Vegetable Oil, and Lubricating Oil

The sample preparation of mineral diesel, straight vegetable oil, and lubricating oil was carried out using fast responsive

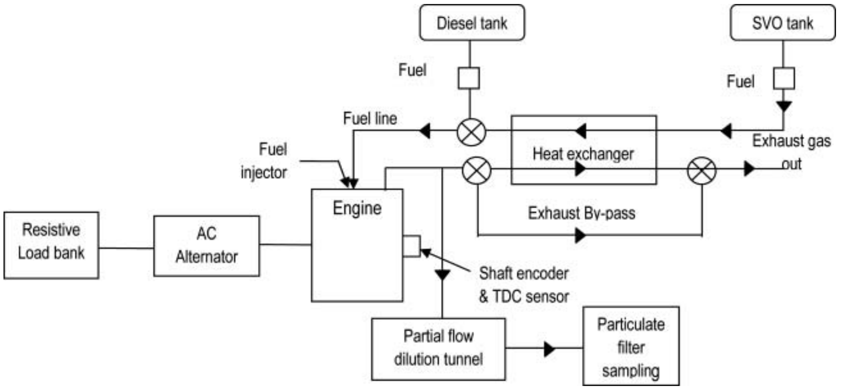

FIG. 1. Schematic diagram of single cylinder agricultural engine setup with a heat exchanger.

temperature controlled furnace. 0.5 g of any fuel or lubricating oil was taken in an inert vessel to which 9 ml of concentrated HNO_3 was added. USEPA 3052 method was used for this digestion. Temperature of each sample was raised to 180°C in 5.5 min and then kept constant at 180°C for another 9.5 min. After digestion, the acid was measured and was diluted three times with Milli-Q water and further stored in inert bottles. This solution is then filtered by 0.22 μm filter. Concentrations of Ca, Cd, Cr, Fe, Mg, Ni, Na, Pb, Zn, and Cu were determined in all above samples using ICP-Optical Emission Spectrometer (USEPA method 3052).

Heavy Metal Analysis in Particulates

In the present study, sample extraction was carried out using the hot plate digestion method (USEPA SW-846, method 3015). This digestion procedure is used for preparing samples, which are to be analyzed by ICP-OES (Make: Thermo, USA; Model 6300 duo ICAP). One half of the sample laden filter was cut into small pieces using plastic scissors and then put into a inert bottle, in which 15 ml of concentrated HNO_3 was added. The remaining half of the filter paper was taken in a similar way into another bottle. Temperature of each sample was raised to 175°C in less than 5.5 min and maintained at 175°C for more than 4.5 min. After digestion, the acid from the two vessels was combined and filtered through a 0.22 micron Millipore filter paper. The filtrate was measured and diluted 3 times with Milli-Q water and then further stored in inert bottles. Reference was taken as analytical blank filter paper and 30 ml of conc. HNO_3 (Suprapure, Merck), 10% of blanks from the same lot of filter papers were used to get a best representative average blank concentration. By the above described method, concentrations of Ca, Cu, Cr, Mg, Fe, Na, Ni, Pb, and Zn were analyzed by ICP-OES.

Inductively coupled plasma-optical emission spectrometry (ICP-OES) is an analytical technique used for the detection of trace metals. It is a type of emission spectroscopy that uses inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic to a particular element.The intensity of this emission is indicative of the concentration of the element within the sample. Argon gas is used to create the plasma. A peristaltic pump delivers an aqueous or organic sample into a nebulizer, where it is atomized and introduced directly inside the plasma flame. The sample immediately collides with the electrons and other charged ions in the plasma and is broken down into charged ions. The various molecules break up into their respective atoms, which then loose electrons and recombine repeatedly in the plasma, giving off the characteristic wavelengths of the elements involved, which are compared with those emitted by pure standards to derive elemental concentrations in the given sample.

Benzene Soluble Organic Fraction in Particulates

Before sampling, filters were desiccated for about 12 h. After sample collection using partial flow dilution tunnel, particulate laden filters were kept for desiccation for another 12 h and their final weight was noted. Filters papers were cut into small pieces using metal scissors and then placed into a reagent bottle, thereafter 20 ml of benzene was added to it. This reagent bottle was kept in ultrasonic bath for 20 min thereafter sample was decanted and filtered through 0.45 micron Millipore filter paper. The filtrate was collected in a 100 ml beaker. The procedure was repeated with another 10 ml of benzene in the same reagent beaker. These 100 ml beakers were covered with aluminum foil having holes and were kept in oven at 40°C for 12 to 18 h until the sample dried. The initial and final weight of the beaker was measured to estimate the total mass of benzene soluble organic fraction in the sample (ASTM 2001). In order to check the reference concentration, blank filters were used to benzene extraction as per the same ASTM standard.

RESULTS AND DISCUSSION

Metals in Mineral Diesel, Straight Vegetable Oil, and Lubricating Oil

The results of the metals analysis in mineral diesel, straight vegetable oil, and lubricating oils are given in Table 3. The SVO selected for the present investigation is Karanja oil, which is essentially a surplus non-edible vegetable oil from tree-origin and has been recommended by planning commission of India as one of the potential biodiesel feedstock oils (Agarwal et al. 2009; Bajpai et al. 2009; Murugesan et al. 2009; Srivastava et al. 2008).

Ten percent nos. analytical blank filters are used for determining metal concentrations in blank filters using the ICP-OES spectrophotometer. All the data presented in this article has been corrected for the average blank readings.

Metals in Engine Exhaust Particulates

Experimental study showed that concentrations of Fe, Mg, Ca, and Na were much higher than those of Cu, Ni, Pb, and Zn.

TABLE 3
Concentration of various metals in diesel, straight vegetable oil, and lubricating oil samples

Metals	Diesel (μg/g)	Karanja oil (μg/g)	Lubricating oil (μg/g)
Ca	902.3	271.4	2046.8
Co	2.3	7	2.6
Cr	58.7	19.8	76
Cu	9	2	4.3
Fe	402.3	326	827
Mg	1162.3	468.2	3618.1
Ni	31.8	ND	76
Pb	8	2	8
Zn	271	167.8	832.4

Calcium (Ca)

Figure 2 shows Ca concentration in milligrams per gram of exhaust particulate matter. As shown in the figure, K20 exhaust shows the maximum Ca concentration, followed by diesel exhaust and lowest Ca concentration was seen in heated K100 exhaust. All these curves showed decreasing trend with increase in load.

Heated K100 exhaust particulate showed very low Ca concentration ranging from 4 to 18 mg/g, whereas 20 percent blend of Karanja oil (K20) exhaust particulate showed the maximum Ca concentration ranging from 21 to 51 mg/gm. Lubricating oil and diesel has Ca in relatively large quantities, hence presence of Ca in diesel exhaust particulate is obvious. However K20 exhaust (K20E) shows maximum Ca concentration. K20 has 80% mineral diesel so all the metals presents in the diesel are present in K20 exhaust. Due to addition of 20% unheated SVO, viscosity of the blend rises. The viscosity of different fuels at 40°C is as follows:

Viscosity of Diesel @ 40°C = 2.61 cSt,
Viscosity of Karanja oil @ 40°C = 37.0 cSt,
Viscosity of K20 @ 40°C = 8.3 cSt

This higher viscosity of K20 leads to poor spray characteristics, larger droplet size, and hence higher momentum of droplets. Due to this, fuel droplets strike cylinder liner walls causing dilution of the lubricating oil film present on liner walls and thus partial combustion/pyrolysis of the lubricating oil. Dilution of oil film causes higher wear of liner walls in the cylinder and the lubricating oil gets mixed with fuel, thus the burning of fuel mixed with higher mounts of lubricating oil gives very high levels of metal concentrations in exhaust particulate. Lubricating oil contains very high level of Ca concentration as compared to any fuel as seen from Table 3.

Copper (Cu)

Figure 2 presents Cu concentration in particulates drawn from diesel, K20, and heated K100 exhaust at varying load conditions. K20 exhaust particulate show the highest Cu concentration with diesel exhaust particulate having values very close to it. One possible reason for higher concentration of copper in K20 exhaust particulate can be higher viscosity of K20, as explained earlier. Kinematic viscosity of K20 is relatively higher (8.3 cSt @ 40°C) in comparison to kinematic viscosity of mineral diesel (2.61 cSt @ 40°C). Higher viscosity of K20 leads to poor spray characteristics and larger droplet size which leads to mixing of fuel with lubricating oil and finally burning of lubricating oil. Heated K100 exhaust particulates show the lowest or close to zero Cu concentration while the exhaust particulates from diesel and K20 are very close to each other.

Magnesium (Mg)

Figure 2 presents Mg concentration in particulates drawn from mineral diesel, K20, and heated K100 exhaust at varying load conditions. K20 exhaust particulates show the highest Mg concentration at all engine loads except no load condition. Heated K100 exhaust particulates show the lowest Mg concentration among them. From Table 3, we can see diesel has 1.1623 mg/g, Karanja oil 0.4682 mg/g, and lubricating oil 3.6181 mg/g magnesium.

Iron (Fe)

Figure 2 presents iron concentration in particulates drawn from diesel, K20, and preheated K100 exhaust at varying engine load conditions. K20 exhaust particulates show the highest iron concentration, which very sharply goes down with increasing engine load. For loads above 40%, DE and K20 exhaust both shows the same concentration of Fe. Preheated K100 exhaust particulate show the lowest Fe concentration among them. K100 exhaust has relatively high Fe concentration at no load and then it decreases very sharply on increasing the engine load.

Sodium (Na)

Figure 2 presents sodium concentration in particulates drawn from diesel, K20, and heated K100 exhaust at varying engine load conditions. Diesel exhaust particulates show the highest sodium concentration.

Nickel (Ni)

Figure 2 presents nickel concentration in particulates drawn from diesel, K20, and preheated K100 exhaust at varying engine load conditions. Only diesel exhaust particulate show the presence of nickel. Since only lubricating oil and mineral diesel have nickel as a constituent. So absence of nickel in preheated K100 was expected. Though lubricating oil has Ni content but inherent lubricating properties of vegetable oil prevent presence of Ni in exhaust particulate.

Lead (Pb)

Figure 2 presents lead concentration in particulates drawn from diesel, K20, and preheated K100 exhaust at varying load conditions. Diesel exhaust particulates show the average high lead concentration. From Table 3, it can be noticed that diesel has 8 μg/g, Karanja oil has 2 μg/g, and lubricating oil has 8 μg/g lead. Heated K100 shows very low Pb concentration for all load conditions.

Zinc (Zn)

Figure 2 presents zinc concentration in particulate drawn from diesel, K20, and preheated K100 exhaust at varying engine load conditions. Diesel exhaust particulate show the highest zinc concentration. From Table 3, diesel has 271 μm/g, Karanja oil 167.8 μg/g, and lubricating oil has 832.4 μg/g Zn as a constituent. Though lubricating oil has very high concentration of zinc, K20 showed consistently lesser zinc content than diesel exhaust particulate. Heated K100 showed very low Zn concentration for all load conditions.

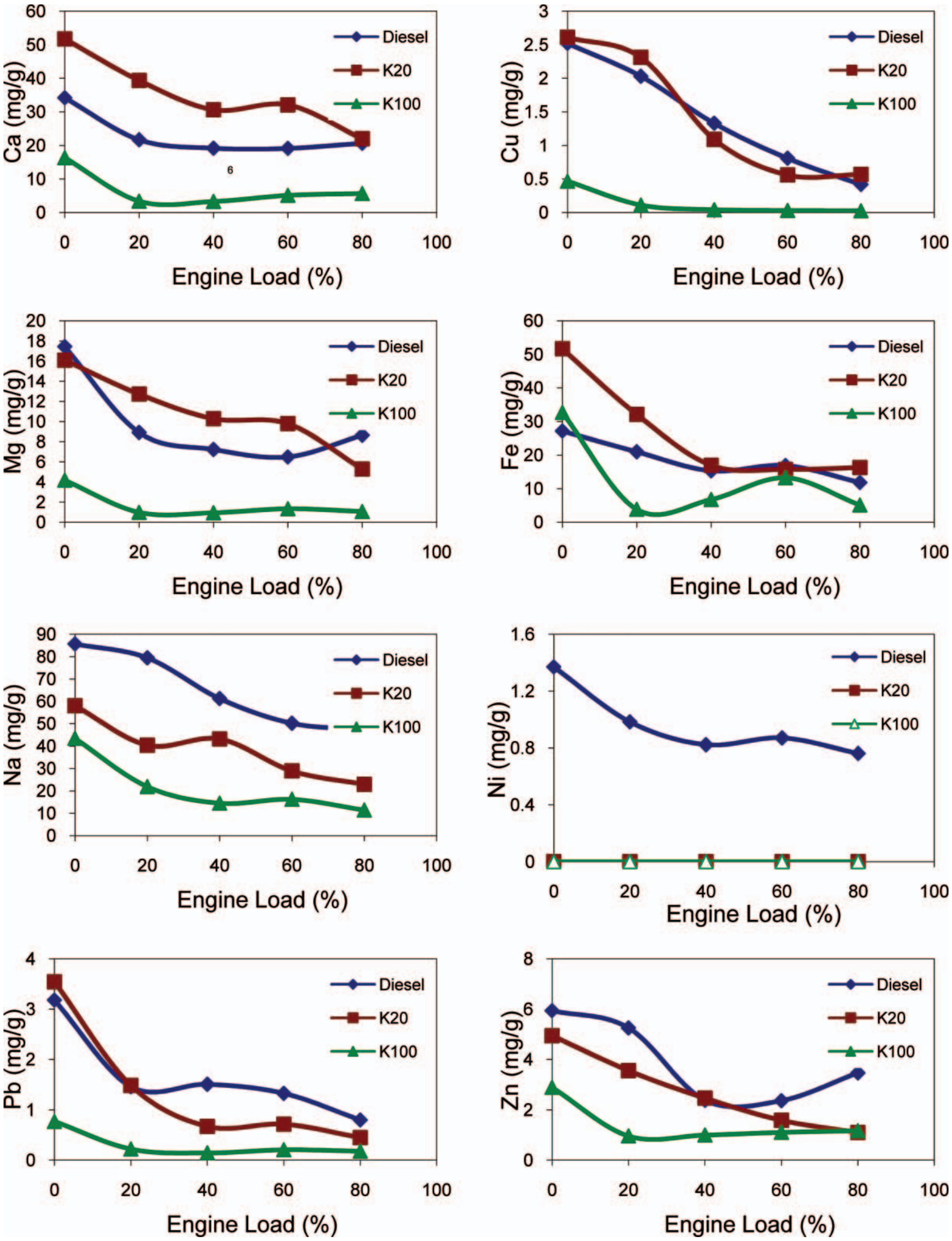

FIG. 2. Concentration of various metals in exhaust particulates with varying engine load conditions.

Ca, Mg, and Na are not harmful to humans at the engine emission concentrations presented above. All the curves for the metals of different fuels follow the same trend of having the highest concentrations of metals at the lowest engine loads and with a continuously decreasing trend, lowest values being for either 60% or at 80% rated loads. For diesel, lowest metal concentrations are found at 60% rated loads as combustion quality was observed to be relatively inferior for loads higher than 60% rated load.

K20 has generally shown the highest concentrations for many of the metals among three fuels used, namely, heated K100, K20, and mineral diesel. A most obvious reason for this is mixing of fuel with lubricating oil, which leads to increased viscosity of fuel blend, and higher engine component wear. K100, if heated properly to 65–70°C at injector, has viscosity very close to mineral diesel. Heated K100 at no load condition gives relatively higher level of concentration compared to higher load conditions and the steepness of curve between no load and 20% rated load condition is maximum. For no load condition, preheating of vegetable oil to required temperature is not efficient because the exhaust temperatures are also low and amount of exhaust is low too. Hence, even if the temperature is kept stabilized for mineral

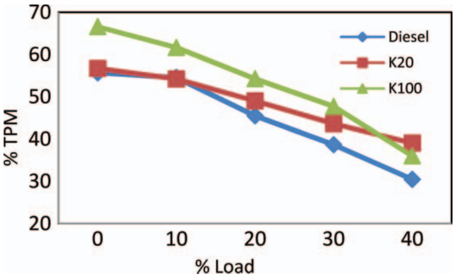

FIG. 3. SOF percentage in terms of mass of TPM with varying load conditions.

diesel at no load, after switching to K100, it starts decreasing, and this can be one of the reasons for relatively higher metal concentration at no load condition.

Metal concentration for heated K100 is the lowest because vegetable oil contains very low metal concentrations. Viscosity of heated SVO is equivalent to mineral diesel, hence no operational problems related to fuel injection system were observed and mixing of fuel with lubricating oil was also not an issue. SVO is an oxygenated fuel, hence stability of combustion at higher load is superior to mineral diesel and the amount of smoke coming out of engine is less for heated K100. K20 is also an oxygenated fuel and it contains more oxygen than mineral diesel but gives more smoke than mineral diesel due to its increased fuel viscosity.

The absence of incombustible ash in SVO makes them a nonparticipant responsible for metal emissions. Since SVO are essentially composed of purely organic compounds, it leads to no contribution toward ash fraction and also their sulfur levels are low or negligible, which results in no contribution to the sulfate fraction. These are some welcome facts which make SVO a desired partial replacement for mineral diesel.

Benzene Soluble Organic Fraction (BSOF)

As it is shown in the Figure 3, heated K100 shows the highest SOF percentage in terms of mass of particulate matter. Lowest SOF percentage among heated K100, K20, and diesel is for the mineral diesel exhaust particulate matter.

Curves for all three fuels follow the same trend and all the curves have their maximum value at the start and it goes down with an increase in engine load. BSOF percentage for K20 remains close to mineral diesel for low load conditions but as the load increases, i.e., amount of fuel injected increases, kinematic viscosity (Karanja 37.0 cSt and diesel 2.61 cSt@ 40°C) of 20% SVO comes into the picture, and amount of unburned fuel increases, i.e., BSOF percentage increases.

Figure 3 shows that heated K100 gives higher percentage of BSOF for low load conditions and it comes down as load increases. For low load operating conditions exhaust is not very hot, hence preheating of K100 in heat exchanger by heated engine exhaust is not sufficient, this situation persists until 20% load condition. For loads higher than 20%, preheating of K100 oil is sufficient but BSOF percentage for SVO remains still on the higher side; one of the reasons for that can be low calorific value of Karanja oil (i.e., Diesel 43.06 MJ/Kg, Karanja Oil 41.66 MJ/Kg). Low calorific value for Karanja implies larger quantities of fuel to be injected for the same amount of power to be produced. For 80% load condition, combustion stability comes into the picture, which proves to be better in the case of heated K100 hence less unburned hydrocarbons.

Past studies also suggest observation of variable effects on the organic fraction: e.g., the particulate mass is lower but the carbonaceous organic ratio remains unchanged, suggesting that both the fractions are proportionally decreased (Yeh et al. 2001); or there is no consistent trend (Litzinger et al. 2000). More commonly filter deposits are “wetter” and lighter in colors (Suppes et al. 1999), both observation suggests greater organic fraction (Sidhu et al. 2001), i.e., preferential reduction in soot (Lapuerta et al. 2005) or perhaps of greater gas to particle conversion among organic compounds than with diesel. Filter deposits may also become lighter simply because the reduction in carbonaceous particulate allows lubricant derived organic particulate to become more prominent by proportion or increase in organic particulate out weighs the decrease in carbonaceous particulate (Bechtold et al. 1991). Smoke readings responding to blackness register only decrease in carbonaceous particulates (Grimaldi et al. 2002). Contrary trends between hydrocarbon and organic particulates (Romig et al. 1996) suggest subtle differences in gas to particle conversion and in volatilities between oxygenates and diesel fuel, e.g., with vegetable oils, the organic fraction has a larger contingent of high molecular weight compounds than with diesel (Trapel et al. 2005).

The soot suppression seems not to arise simply through displacing diesel fuel; and it might equally proceed through discouraging soot formation or encouraging soot oxidation as both routes, accomplishing the same aim. Another argument can be the combustion process particularly if fuel rich regions are simply furnished with more oxygen (Rakopoulos and Antonopoulos 2006) and oxidizing rather than pyrolytic reactions are there. In this understanding, the mixture is in effect leaned through the internal oxygen present (via the fuel), contrary to external oxygen (via the air), which has no part in excess oxygen.

Particulate Surface Morphology

Scanning electron microscopy (SEM) provides analysis of particulate size, and microscopic structure of the particulates (Figure 4). Particulate samples were collected from the engine using three fuels (mineral diesel, preheated K100, and K20) at five different load operating conditions.

Particulate surface morphology changes with engine load and fuel composition, e.g., granular with fine spherules are emitted at high speeds and whereas granular but bigger size particles are emitted at high load conditions. Layered and plate-like structures are emitted at low speed and low load conditions.

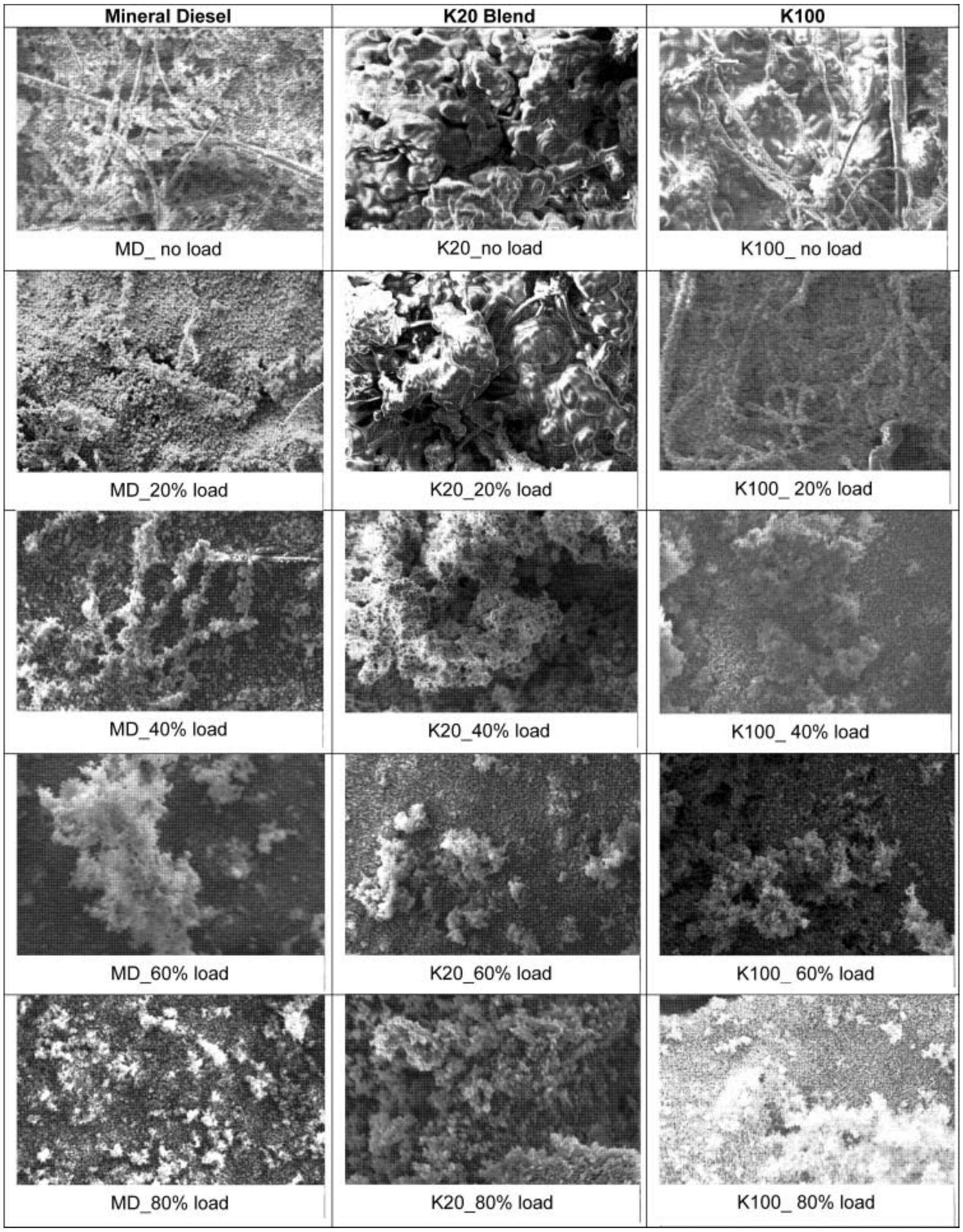

FIG. 4. SEM micrographs of particulates at different engine loads for different fuels.

SEM images for all the particulates samples are taken at 1000× magnification. Filters were exposed for the same (approximately) duration through filter assembly connected in partial dilution tunnel.

For no load and 20% load operating condition K20 shows heavy carbon deposits on the filter paper, preheated K100 and mineral diesel shows particulate loading in comparable levels. Preheated K100 shows slightly bigger agglomerates than mineral diesel, which suggests more soot formation in case preheated K100. At 40% load operating condition again K20 shows maximum soot deposition, where as preheated K100 still shows slightly more deposition than mineral diesel but much less deposition when compared to K20. At 60% load preheated K100 shows less deposition than even mineral diesel; K20 still shows maximum soot deposition. At 80% load operating condition K20 shows very heavy carbon deposits compared to preheated K100 and mineral diesel. Preheated K100 and mineral diesel shows comparable carbon deposits on the filter sample; granular size for mineral diesel seems slightly bigger compared to preheated K100.

Mineral diesel and preheated K100 samples show comparable particle agglomeration. Their granular structure and particle sizes also look very comparable. For both fuels, as load increases, amount of particles settled on filter surface increases.

For preheated K100 at 40% load, the biggest sized particles can be seen whereas this happens for mineral diesel at 60% load after this as load increases particle size also decreases.

CONCLUSIONS

This study was carried out for characterizing the particulate emissions from vegetable oil (Karanja) and its blends vis-à-vis mineral diesel in order to compare their relative toxic potential in terms of their toxic chemical constituents and PM morphology. Experiments were performed to investigate the benzene soluble organic content produced by vegetable oil and its blends with respect to mineral diesel BSOF values. Findings suggest that vegetable oils emit more BSOF in engine exhaust particulate matter, irrespective of how it was being used. Study to characterize their metal emissions showed that property of having less metal content in vegetable oil can only be useful if somehow its (straight or in blend form) viscosity can be decreased to mineral diesel levels. Otherwise, higher viscosity of vegetable oil leads to poor air–fuel mixture formation, mixing of lubricating oil with fuel, hence high metal concentrations in engine exhaust particulate. If by preheating, viscosity of vegetable oil can be lowered to level of mineral diesel, vegetable oil gives better particulate emission results than mineral diesel, e.g., low metal emissions, less soot formation. Significant improvements were observed at higher loads where preheated vegetable oil emission results were much better than mineral diesel. Study showed that if vegetable oil was used directly even in the small percentage like K20, it worsen the emissions of mineral diesel and degrades engine performance by poorer combustion inside the combustion chamber and excess soot formation.

REFERENCES

Agarwal, A. K., and Das, L. M. (2001). Biodiesel Development and Characterization for use as a Fuel in Compression Ignition Engines. *J. Eng. Gas Turb. Power* 123:440–447.

Agarwal, A. K., Bijwe, J., and Das, L. M. (2003). Effect of Biodiesel Utilization on Wear of Vital pArts in Compression Ignition Engine. *J. Eng. Gas Turb. Power* 125:604–611.

Agarwal, A. K., and Rajamanoharan, K. (2009). Experimental Investigations of Performance and Emissions of Karanja oil and its Blends in a Single Cylinder Agricultural Diesel Engine. *Appl. Ener*. 86(1):106–112.

ASTM. (2001). D-4600-87: Standard Test Method for Determination of Benzene Soluble Particulate Matter in Workplace Atmosphere.

Atkinson, R., and Arey, J. (1994). Atmospheric Chemistry of Gas-Phase PAH: Formation of Atmospheric Mutagens. *Environ. Health Perspect*. 104(S4): 117–126.

Bajpai, S., Sahoo, P. K., and Das, L. M. (2009). Feasibility of Blending Karanja Vegetable Oil in Petro-Diesel and Utilization in a Direct Injection Diesel Engine. *Fuel* 88:705–711.

Baumgard, K. J., and Johnson, J. H. (1992). The Effect of Low Sulfur Fuel and a Ceramic Particle Filter on Diesel Exhaust Particle Size Distributions. *SAE Trans*. 101:691–699.

Bechtold, R. L., Timbario, T. J., Miller, M. T., and Urban, C. (1991). Performance and Emissions of a DDC 8V 71 Transit Bus Engine Using Ignition Improved Methanol and Ethanol. SAE Paper No. 912356.

CARB. (1998). Proposed Identification of Diesel Exhaust as a Toxic Air Contaminant. Part A: Exposure Assessment. Californian Air Resources Board, 103 pp.

Geller, D. P., and Goodrum, J. W. (2004). Effects of Specific Fatty Acid Methyl Esters on Diesel Fuel Lubricity. *Fuel* 83:2351–2356.

Ghio, A. J., Kim, C., and Devline, R. B. (2000). Concentrated Ambient Particles induce Mild Pulmonary Inflammation in Healthy Human Volunteers. *Am. J. Respir. Crit. Care Med.* 162:981–988.

Ghio, A. J., and Huang, Y. C. T. (2004). Exposure to Concentrated Ambient Particles (CAPs): A Review. *Inhal. Toxicol.* 16:53–59.

Grimaldi, C. N., Postrioti, L., Battistoni, M., and Millo, F. (2002). Common Rail HSDI Diesel Engine Combustion and Emissions with Fossil/Bio-Derived Fuel Blends. SAE Paper No. 2002-01-0865.

Hare, C. T. (1977). Characterization of Diesel Engine Gaseous Particulate Matter. Final Report, prepared by South West Research Institute contract no. 68-02-1977.

HEI. (1995). *Diesel Exhaust: A Critical Analysis of Emissions, Exposure and Health Effects*. Health Effects Institute, Cambridge, MA, 294 pp.

Heinrich, U. (1993). Carcinogenic Effects of Solid Particles, in *Toxic and Carcinogenic Effects of Solid Particles in the Respiratory Tract*. Proceedings of the 4th International Inhalation Symposium, Hanover, Germany, U. Mohr, D.L. Dungworth, J.L. Mauderly, and G. Oberdorster, eds. ILSI Press, Washington, DC, pp. 57–73.

Johnson, J. H., Bagley, S. T., Gratz, L. D., and Leddy, D. G. (1994). A Review of Diesel Particulate Control Technology and Emission Effects. *SAE Trans*. 103:210–244.

Krzyzanowski, M., Kuna-Dibbert, B., and Schneider, J. (eds). (2005). Health Effects of Transport-Related Air Pollution. World Health Organization.

Kunzli, N., Kaiser, R., Medina, S., Studnicka, M., Chanel, O. Filliger, P., Herry, M., Horak, F., Puybonnieux-Texier, V., Quenel, P., Schneider, J., Seethaler, R., Vergnaud, J. C., and Sommer, H. (2000). Public-Health Impact of Outdoor and Traffic-Related Air Pollution: A European Assessment. *Lancet* 356:795–801.

Labeckas, G., and Slavinskas, S. (2005). Performance and Exhaust Emission Characteristics of Direct-Injection Diesel Engine When Operating on Shale Oil. *Energy Conversion and Manage.* 46:139–150.

Lapuerta, M., Armas, O., Ballesteros, R., and Fernandez, J. (2005). Diesel Emissions from Bio-Fuels Derived from Spanish Potential Vegetable Oils. *Fuel* 84:773–780.

Litzinger, T., Stoner, M., Hess, H., and Boehman, A. (2000). Effects of Oxygenated Blending Compounds on Emissions from a Turbo Charged Direct Injection Diesel Engine. *Intl. J. Engine Res.* 1:57–70.

Mauderly, J. L., Griffith, E. C., Henderson, R. F., Jones, R. K., and McClellan, R. O. (1991). Evidence from Animal Studies for the Carcinogenicity of Inhaled Diesel Exhaust, in *Nitro-Arenes*, PC Howard et al., eds. Plenum Press, New York, pp. 1–13.

Mauderly, J. L. (1992). Diesel Exhaust, in *Environmental Toxicants: Human Exposures and Their Health Effects*, Lippmann, M., ed. Van Nostrand Reinhold, New York, pp. 119–162.

Murugesan, A., and Umarani, C. (2009). Subramanian R. and Nedunchezhian N., Bio-Diesel as an Alternative Fuel for Diesel Engines—A Review. *Renewable and Sustainable Energy Rev.* 13:653–662.

Nikula, K. J., Snipes, M. E., Barr, E. F., Griffith, W. C., Henderson, R. F., and Mauderly, J. L. (1993). Influence of Particle-Associated Organic Compounds on the Carcinogenicity of Diesel Exhaust, in *Toxic and Carcinogenic Effects of Solid Particles in the Respiratory Tract*. Proceedings of the 4th International Inhalation Symposium. Hanover, Germany, U. Mohr, D.L. Dungworth, J.L. Mauderly, and G. Oberdorster eds. ILSI Press, Washington, DC.

Norbeck, J. M., Durbin, T. D., and Truex, T. J. (1998). *Measurement of Primary Particulate Matter Emissions from Light Duty Motor Vehicles.* University of California, Riverside, CA.

Peterson, C. L., and Hustrulid, T. (1998). Carbon Cycle for Rapeseed Oil Biodiesel Fuels. *Biomass and Bioenerg*. 14:91–101.

Rakopoulos, C. D., and Antonopoulos, K. A. (2006). Multi Zone Modeling of Diesel Engine Fuel Spray Development with Vegetable Oil, Biodiesel or Diesel Fuels. *Energy Conversion and Manage*. 47:1550–1573.

Romig, C., and Spataru, A. (1996). Emissions and Engine Performance from Blends of Soya and Canola Methyl Esters with ARB#2 Diesel in a DDC6V92TA MUI Engine. *Bioresource Technol*. 56:25–34.

Schlesinger, R. B., Kunzli, N., Hidy, G. M., Gotschi, T., and Jerrett, M. (2006). The Health Relevance of Ambient Particulate Matter Characteristics: Coherence of Toxicological and Epidemiological Inferences. *Inhal. Toxicol.* 18:95–125.

Srivastava, P. K., and Verma, M. (2008). Methyl Ester of Karanja Oil as an Alternative Renewable Source Energy. *Fuel* 87:8–9.

Sidhu, S., Graham, J., and Striebich, R. (2001). Semi Volatile and Particulate Emissions from Combustion of Alternative Diesel Fuels. *Chemosph*. 42:681–690.

Sjogren, M., Li, H., Banner, C., Rafter, J., Westerholm, R., and Rannug, U. (1996). Influence of Physical and Chemical Characteristics of Diesel Fuels and Exhaust Emissions on Biological Effects of Particle Extracts: A Multivariate Statistical Analysis of Ten Diesel Fuels. *Chem. Res. Toxicol.* 9:197–207.

Springer, K. J. (1997). Charcterization of Sulfate, Odor, Smoke, POM and Particulates from Light Duty and Heavy Duty Diesel Engines—Part IX. Report prepared by South West Research Institute, EPA/460/3-79/007.

Suppes, G. J., Lula, C. J., Burkhart, M. L., and Swearingen, J. D. (1999). Type Performance of Fischer-Tropsch Liquids (FTL) in Modified Off-Highway Diesel Engine Test Cycle. SAE Paper No. *1999-01-1474*.

Trapel, E., Mayer, C., Schulz, C., and Roth, P. (2005). Effects of Biodiesel Injection in a DI Diesel Engine on Gaseous and Particulate Emission. SAE Paper No. 2005-01-2204.

USEPA SW-846, method 3015. (1995): A Microwave Assisted Acid Digestion of Aqueous Samples and Extracts.

USEPA method 3052. (1997). Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices.

Valavanidis, A., Salika, A., and Theodosopoulou, A. (2000). Generation of Hydroxyl Radicals by Urban Suspended Particulate Air Matter. The Role of Iron Ions. *Atmos. Environ.* 34:2379–2386.

Vertin, K. D., Ohi, J. M., Naegeli, D. W., Childress, K. H., Hagen, G. P., Mccarthy, C. I., Cheng, A. S., and Dibble, R.W. (1999). Methyl and Methyl Diesel Blended Fuels for Use in Compression Ignition Engines. SAE Paper No. 1999-01-1508.

Wu, W. D., Samet, J. M., Ghio, A. J., and Devlin, R. B. (2001). Activation of the EGF Receptor Signaling Pathway in Airway Epithelial Cells Exposed to Utah Valley PM. *Am. J. Physiol-Lung C*, 281:L483–L489.

Yeh, L. I., Rickeard, D. J., Schlosberg, R. H., Duff, J. L. C., Caers, R. F., and Bateman, J. R. (2001). Oxygenates: an Evaluation of Their Effects on Diesel Emissions. SAE Paper No. 2001-01-2019.

Zhao, X., Ren, M., and Liu, Z. (2005). Critical Solubility of Dimethyl Ether (DME + Diesel Fuel and Dimethyl Carbonate (DMC) + Diesel Fuel. *Fuel* 84:2380–2383.