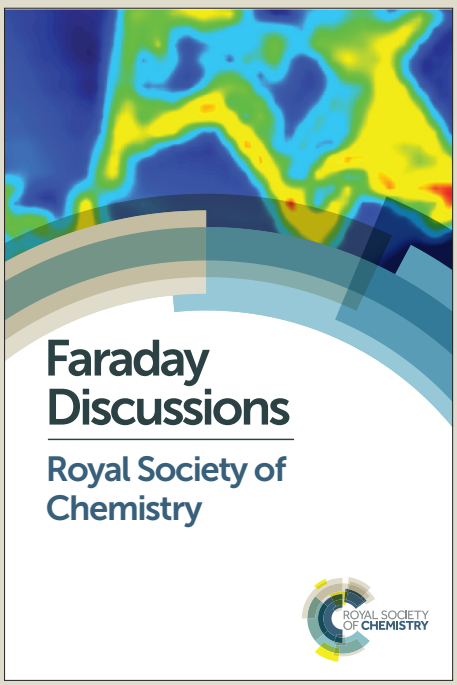
Faraday Discussions

Accepted Manuscript

This manuscript will be presented and discussed at a forthcoming Faraday Discussion meeting. All delegates can contribute to the discussion which will be included in the final volume.

Register now to attend! Full details of all upcoming meetings: http://rsc.li/fd-upcoming-meetings



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/faraday_d

Biofuels, Vehicle Emissions, and Urban Air Quality

Timothy J. Wallington, James E. Anderson, Eric M. Kurtz, Paul J. Tennison
Research & Advanced Engineering, Ford Motor Company, Dearborn, Michigan 48121-2053, USA

Abstract

Increased biofuel content in automotive fuels impacts vehicle tailpipe vehicle emissions via two mechanisms: fuel chemistry and engine calibration. Fuel chemistry effects are generally well recognized, while engine calibration effects are not. It is important that investigations of the impact of biofuels on vehicle emissions consider the impact of engine calibration effects and are conducted using vehicles designed to operate using such fuels. We report the results of emission measurements from a Ford F-350 fueled with either fossil diesel or a biodiesel surrogate (butyl nonanoate) and demonstrate the critical influence of engine calibration on NO_x emissions. Using the production calibration the emissions of NO_x were higher with the biodiesel fuel. Using an adjusted calibration (maintaining equivalent exhaust oxygen concentration to that of the fossil diesel at the same conditions by adjusting injected fuel quantities) the emissions of NO_x were unchanged, or lower, with biodiesel fuel. For ethanol, a review of the literature data addressing the impact of ethanol blend levels (E0-E85) on emissions from gasoline light-duty vehicles in the U.S. is presented. The available data suggest that emissions of NO_x, non-methane hydrocarbons, particulate matter (PM), and mobile source air toxics (compounds known, or suspected, to cause serious health impacts) from modern gasoline and diesel vehicles are not adversely affected by increased biofuel content over the range for which the vehicles are designed to operate. Future increases in biofuel content when accomplished in concert with changes in engine design and calibration for new vehicles should not result in problematic increases in emissions impacting urban air quality and may in fact facilitate future required emissions reductions. A systems perspective (fuel and vehicle) is needed to fully understand, and optimize, the benefits of biofuels when blended into gasoline and diesel.

1. Introduction

Driven by a desire to improve energy security, address global climate change, and provide economic stimulus for rural communities, the use of biofuels in transportation has increased substantially over the past 10-20 years. Ethanol and biodiesel are the two most commercially important biofuels. Ethanol is produced commercially by the fermentation of sugars from corn, sugar cane, and cellulose. Biodiesel is

produced from the trans-esterification of plant oils and animal fats. There are several routes to convert biomass into fuel for diesel engines and the nomenclature can be confusing. Fatty acid methyl esters (FAMEs) made from transesterification of plant oils or animal fats make up the majority of biomass-derived diesel fuel both in the U.S. and globally. The American Society of Testing Materials Standards (ASTM) defines biodiesel as "a fuel comprising mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats that meets the requirements of ASTM D 6751" [1]. Biodiesel is distinct from hydrocarbons produced from hydrotreating (and sometimes isomerizing) vegetable oils or animal fats which are referred to as "hydrotreated vegetable oil (HVO)" or "renewable diesel". There is interest in thermochemical conversion to produce biomass-to-liquid (BTL) fuels. One BTL option is gasification of biomass to give synthesis gas (mixture of CO and H_2) which can be converted into alkanes via the Fischer-Tropsch synthesis. The Fischer-Tropsch synthesis produces a mixture of straight-chain alkanes; it is well suited to the production of high-cetane diesel fuel. Another BTL option is the pyrolysis of biomass to produce bio-oil which could be blended with conventional oil and processed in a refinery. Renewable diesel and BTL are hydrocarbons and as such are effectively fungible with fossil diesel. Biodiesel is not fully fungible with fossil diesel as it has properties that differ substantially from fossil diesel.

The global production of biofuels increased by approximately a factor of four from 16 to 71 Mtonne oil equivalent between 2004 and 2014 [2]. Although growing rapidly, the production of biofuels is still small when compared to the 4221 Mtonne of oil produced in 2014 [2]. On a global basis ethanol accounts for the majority, approximately two thirds, of biofuel production, however there are important regional differences with biodiesel and HVO accounting for the majority, approximately 75%, of biofuel production in Europe. Ethanol is mainly used in blends with gasoline. Biodiesel is mainly used in blends with fossil diesel (commonly B2 [2%v biodiesel] or B20 [20%v biodiesel] in the U.S.). Ethanol use in fuel in the U.S. has increased approximately 4-fold over the last 10 years (2004-2014) [3] where it is now blended into most gasoline at a concentration of 10%v (E10). Ethanol is also available as E85, which is

allowed to contain as much as 83%v and as little as 51%v ethanol [4]. In Brazil ethanol has been available as E18-E27 blends (gasohol) in recent years or as hydrous ethanol. Gasoline in the EU commonly contains 5%v ethanol, with E10 and E85 available in some locations. The U.S. Renewable Fuel Standard (RFS2) calls for an increase in use from approximately 13.4 billion gallons of ethanol and 1.4 billion gallons of biodiesel in 2014 to 36 billion gallons (136 billion liters) of renewable fuel by 2022, much of which would likely be ethanol. The European Union Renewable Energy Directive 2009/28/EC includes a target of 10% contribution by renewable sources such as biofuels in transportation fuel by 2020.

While the future trajectory of the global biofuel industry is hard to forecast, current regulations and concerns related to energy security, global climate change, and economic development for rural communities suggest long-term and increased use of biofuels. There are many important considerations for future fuel strategy, including fuel properties, refining sector implications, vehicle compatibility, refueling infrastructure compatibility, and transition timing [5,6]. An important consideration is the impact of biofuel content on tailpipe emissions of NO_x, volatile organic compounds (VOC), CO, and particulate matter (PM) and hence on urban air quality [7,8]. It is important to ensure that the current, and any future increased, biofuel use in automotive fuel does not hinder, and ideally supports, continuing progress in improving air quality.

There have been numerous studies on both engines and vehicles that have attempted to assess the influence of biodiesel on emissions. Almost universally, those studies have shown a reduction in PM with increasing biodiesel blend; however, there is significant variation in the effect of biodiesel on NO_x emissions. The most widely held belief is that there is a slight increase in NO_x with biodiesel [9,10]. However, several recent publications have suggested that the influence of biodiesel on NO_x is not a direct result of the fuel, but is due to the interaction of the properties of biodiesel with the engine calibration and control strategy [11,12,13]. To investigate this further we conducted vehicle testing to assess the change

in emissions relative to diesel fuel when an oxygenated fuel is tested both with a production calibration and control strategy and with one that accounts and compensates for the properties of the oxygenated fuel.

Likewise, there have been numerous studies of the effect of ethanol fuel content on engine-out and vehicle tailpipe NO_x, non-methane hydrocarbons, PM, and mobile source air toxic emissions. Several of these studies include measurements from vehicles that were misfueled, such as using >E10 fuel in a vehicle designed and calibrated to operate on E0-E10. A transition to a future using more biofuel would include building the infrastructure to handle and use such fuels including vehicles designed to operate on the fuels. Studies of the effects of misfuelling are not relevant to addressing the question of how the future use of higher amounts of biofuels in vehicles designed for such fuels would impact emissions and hence air quality. To provide more clarity in future discussions of the effect of ethanol fuel on emissions and air quality we review and discuss the available data concerning the effect of ethanol blend content on vehicle emissions.

2. Experimental - Vehicle testing with butyl nonanoate and fossil diesel fuels

Vehicle testing was performed with three different fuels: two fossil diesel fuels ("diesel A" and "diesel B") from a commercial supplier and butyl nonanoate (BN, $C_8H_{17}C(O)OC_4H_9$) synthesized by Michigan State University (MSU). Butyl nonanoate has been studied as a possible biodiesel fuel with desirable cold flow properties [14]. Diesel B is used for U.S. certification of vehicles for emissions and fuel economy. Diesel A is a diesel fuel with higher aromatic content. Properties of the three fuels are listed in Table 1.

Table 1. Properties of the fuels used in vehicle testing

	Diesel A	Diesel B	Butyl nonanoate
Net Heating Value [MJ/kg]	42.6	42.9	35.2
Density [g/cm^3]	0.856	0.846	0.864
Carbon [%wt]	0.871	0.870	0.740
Hydrogen [%wt]	0.129	0.130	0.124
Oxygen [%wt]	<0.005	<0.005	0.136
Aromatics [%v]	34	29	-
Saturates [%v]	63	68	-
Olefins [%v]	3	3	-
Kinematic Viscosity, 40°C [mm^2/s]	2.39	2.43	2.10
Distillation, T10 [°C]	214	207	254
Distillation, T50 [°C]	253	256	254
Distillation, T90 [°C]	312	313	255
Cetane Number	42	44	47

A 2011 Ford F-350 with a 6.7L diesel engine was tested on a chassis dynamometer using the three fuels over three different emissions test cycles: the cold-start Federal Test Procedure (FTP-75) representative of city driving, the highway fuel economy test (HWFET) representative of light highway driving, and the supplemental FTP test (US06) representative of aggressive driving including highway driving. Averages of emissions over 2 sets of tests are shown, with the exception of butyl nonanoate using the baseline calibration for which only 1 set of tests was conducted. FTP-75 data are bag-weighted averages for the three test phases. All tests were run at a vehicle test weight simulating a vehicle curb weight and payload totaling 9500 lbs (4300 kg). Standard emissions measurements of total hydrocarbon (THC), CO, and NO_x, were taken as well as PM measurements with a Dekati Mass Monitor (DMM). Measurements were taken at the engine-out location (also known as the catalyst feedgas location). For the two diesel fuels the production engine calibration was used. The production calibration was developed from emissions, performance, and fuel economy testing on multiple fuels, including diesel A and B. For the butyl nonanoate fuel, one set of tests was run utilizing the production calibration and two sets of tests were run with a modified calibration that compensated for differences in fuel net heating value (NHV), density, and oxygen content. The modified calibration adjusted the fuel quantities in each fuel pulse (for pilot, main,

and post injections) to maintain an exhaust oxygen concentration equivalent to that with fossil diesel at the same operating conditions [15].

3. Results - Vehicle testing with butyl nonanoate and fossil diesel fuel

To better illustrate the emissions trends, the emissions data are normalized to those obtained using "Diesel A" using the production calibration. Figure 1 shows the engine out, bag-weighted emissions of THC, CO, NO_x, and PM measured in the FTP-75 testing for the three fuels using the production calibration, and for butyl nonanoate using the adjusted calibration. As seen in Figure 1, butyl nonanoate had lower THC emissions than diesel A with the production calibration. With the adjusted calibration, THC emissions for butyl nonanoate increased but were still lower than diesel A and similar to diesel B. Similar results are seen for CO, with lower CO emissions for butyl nonanoate with the production calibration, and CO emissions equivalent to those observed with diesel A with the adjusted calibration. The trend is very different for NO_x. With the production calibration, NO_x emissions for butyl nonanoate were higher than the fossil diesel fuels but with the adjusted calibration were reduced compared to both fossil diesel fuels. The PM emissions benefits of butyl nonanoate are clearly evident in Figure 1. PM emissions were approximately 90% lower than the fossil diesel fuels with the production calibration. The adjusted calibration results in an increase in PM emissions for butyl nonanoate, but they were still 70% lower than for the baseline diesel fuel.

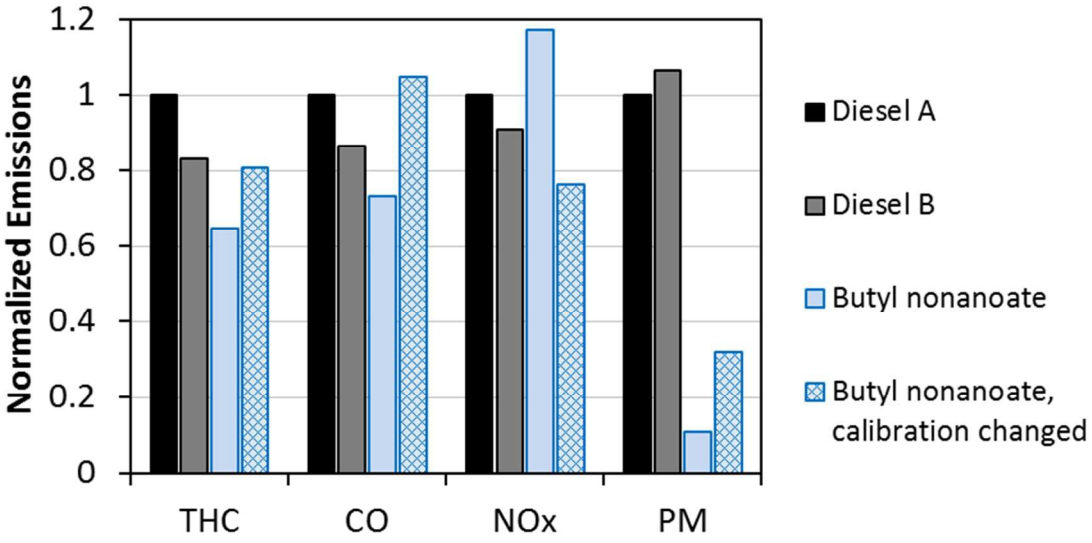


Figure 1. Engine-out emissions of THC, CO, NOx, and PM for the Federal Test Procedure (FTP-75 bag-weighted average) for the three fuels after engine calibration with diesel A. The right-most bar represents emissions for butyl nonanoate after adjusting the calibration to account for heating value differences as described in the text. All emissions (mg/mile) are normalized to the emissions for diesel A with the original calibration.

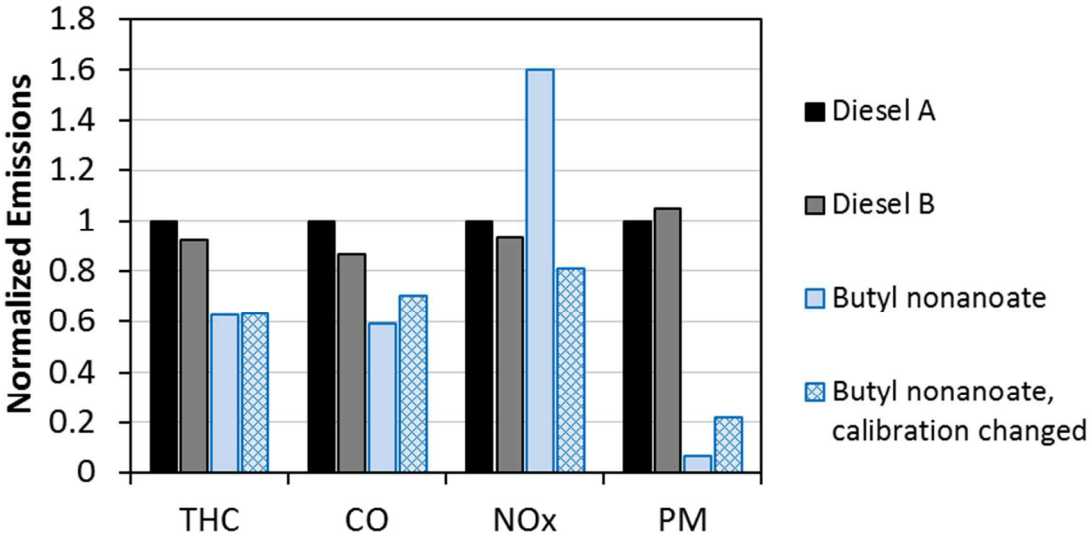


Figure 2. Engine-out emissions of THC, CO, NOx, and PM for the Highway Fuel Economy Test (HWFET) for the three fuels for the three fuels after engine calibration with diesel A. The right-most bar represents emissions for butyl nonanoate after adjusting the calibration to account for heating value differences as described in the text. All emissions (mg/mile) are normalized to the emissions for diesel A with the original calibration.

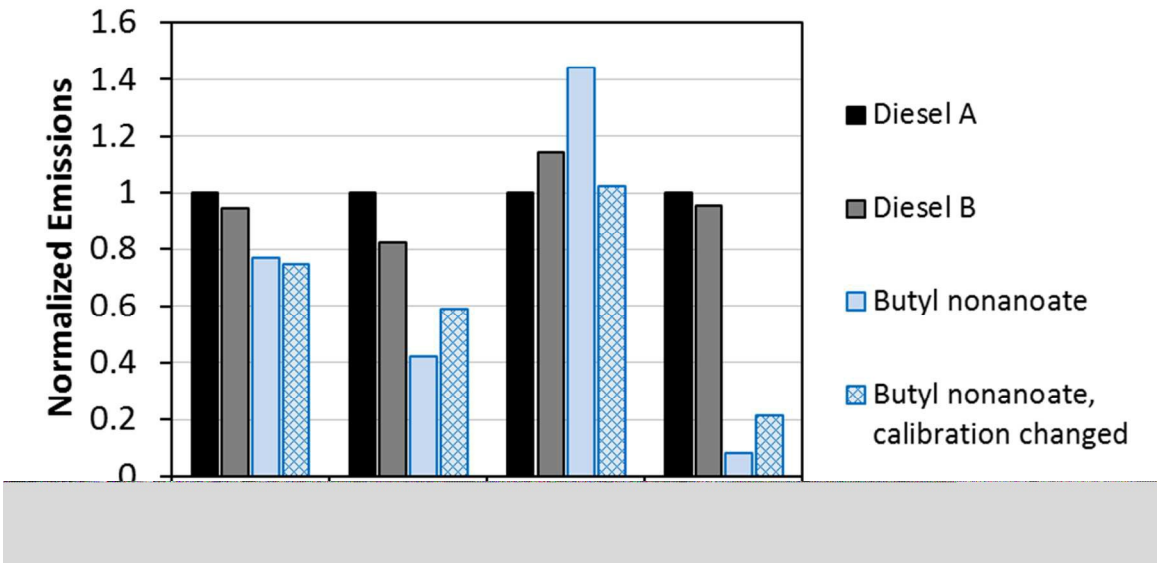


Figure 3. Engine-out emissions of THC, CO, NOx, and PM for the US06 driving cycle for the three fuels for the three fuels after engine calibration with diesel A. The right-most bar represents emissions for butyl nonanoate after adjusting the calibration to account for heating value differences as described in the text. All emissions (mg/mile) are normalized to the emissions for diesel A with the original calibration.

Figure 2 shows the results from emissions testing on the highway fuel economy test (HWFET). The overall trends in the HWFET data are similar to the FTP-75 data in Figure 1, but with more substantial differences in the emissions changes. As can be seen in Figure 2, butyl nonanoate with either calibration results in lower emissions of THC, CO, and PM relative to diesel A and B. Note that the engine responds differently to the initial engine and catalyst temperatures in the hot-start HWFET and cold-start FTP-75. When temperature sensors determine that the engine and catalyst are not starting in warmed-up condition, the calibration initiates engine operation in a catalyst warm-up mode which utilizes post injection and other actions to facilitate catalyst warm-up and thereby reduce cold-start emissions. No such warm-up mode is employed for starting under warmed-up conditions. These operational differences have an impact on emissions for cold starting and hot starting. The NO_x data clearly show the dramatic effect the calibration changes can have on engine-out emissions. With no calibration changes NO_x emissions for butyl nonanoate are 60% higher than the baseline case, while with the calibration changes the NO_x emissions are 20% lower than baseline. This fuel property-based calibration adjustment leads to a 50%

reduction in NO_x emissions and results in a substantial NOx emissions reduction instead of an emissions increase relative to the baseline fuel. The PM emission trends for the HWFET cycle were similar to those for the FTP cycle; a >90% reduction in PM for butyl nonanoate with the baseline calibration and a slight increase (but still 80% lower than the baseline) for the tests with the adjusted calibration.

Results from the supplemental FTP test, US06, are shown in Figure 3. The US06 is similar to the HWFET in that it involves warmed-up conditions for starting. Overall the results generally follow the same trends seen in both the FTP-75 testing and the HWFET testing. For both the US06 and HWFET cycles, THC and CO emissions for butyl nonanoate are lower than the fossil diesel fuels with both calibrations. Similarly, PM emissions are 90% and 80% lower with the production and adjusted calibrations, respectively. Emissions of NO_x with butyl nonanoate show an increase for the production calibration and a decrease back to the baseline fossil diesel level with the adjusted calibration.

In general, the emissions results for the biodiesel surrogate (butyl nonanoate) using the production engine calibration confirmed the typically reported findings of higher NOx and lower PM relative to fossil diesel fuels [10], though the NOx emissions increase (20-60%) and PM emissions decrease (90-95%) were greater than typically reported, perhaps due to the lack of unsaturation in butyl nonanoate and its somewhat higher oxygen content (14%wt) compared to conventional biodiesel from plant oils and animal fats (typically ~11%wt oxygen). Emissions of THC and CO with butyl nonanoate were also reduced by 20-40% relative to the baseline diesel. However, after adjusting the calibration to compensate for the different fuel properties of butyl nonanoate, NOx emissions were significantly decreased relative to the baseline production calibration, causing NOx emissions to change from being 20-60% *higher* than the fossil diesel baseline to 0-20% *lower* than the baseline on the three emissions test cycles. These calibration changes for butyl nonanoate also resulted in negligible to modest increases in THC and CO emissions (0-20% for THC and 10-30% for CO), but these emissions were still considerably less than or (in one case) similar to the fossil diesel baseline. Likewise, the 90-95% reduction in PM emissions for butyl nonanoate with the baseline calibration was somewhat diminished by the adjusted calibration, but

were still 70-80% less than the baseline diesel fuel. These results highlight the importance of engine calibration effects on emissions for biodiesel or other biofuels which have properties that are different from fossil diesel fuel.

As described previously [11,13,16] NO_x emission increases reported for biodiesel are primarily related to higher peak temperatures during combustion caused by an increase in the intake oxygen concentration for a given EGR rate with an oxygenated fuel and a shift in the calibration settings to lower EGR rate and higher injection pressure and pressure caused by the need for increased fuel quantity to compensate for the energy density difference of the fuel. PM emissions reductions for biodiesel are primarily related to fuel oxygen content promoting higher oxygen content at the flame liftoff length as well as reduced content of aromatic hydrocarbons and other soot-prone chemical structures.

Therefore, increased biodiesel content for diesel engines can provide the well-accepted reductions in PM and other emissions, and need not result in problematic increases in NO_x emissions if, in a forward-looking fashion, vehicles have been appropriately designed and calibrated for these fuels. Optimal outcomes for emissions and efficiency for introduction of future fuels and vehicles requires a systems level perspective involving both fuel and vehicle considerations.

4. Literature review of effect of ethanol fuel content on vehicle emissions

Understanding the effects of ethanol fuel content on vehicle emissions reported in the literature is complicated by many factors, not least of which being the different ethanol blending strategies employed. When preparing ethanol blends there are two general approaches; splash-blending and match-blending. As the name implies, in splash-blending the base gasoline blendstock is fixed and the desired ethanol level is simply added (splashed) into the base gasoline. In splash-blending the ethanol-gasoline blend compositions are clearly defined, and effects on emissions are *relatively* straightforward to interpret. In contrast in match-blending the blendstock composition is modified for each ethanol-gasoline blend to

match one or more fuel properties (e.g., octane number, vapor pressure). For emission measurements using match-blending, the ethanol-gasoline blend compositions are often not clearly defined. The effects on emissions depend on which fuel properties are matched and what modifications are made, making emission trends difficult to interpret. As an example, Graham et al. [17] reported increases in emissions of 1,3-butadiene and benzene for E10 compared to E0 fuel. It is difficult to understand how increased ethanol fuel content would lead to increased 1,3-butadiene and benzene emissions. As noted by Graham et al. [18], the observed emission trend probably reflected the higher benzene and aromatic content in the E10 fuel rather than its higher ethanol content.

Higher ethanol content in gasoline affects several fundamental fuel properties that can impact emissions, including increased oxygen content, decreased volumetric energy content typically measured as NHV, increased heat of vaporization (HoV), and other volatility changes [18,19]. These changes can have positive or negative effects that depend on engine design, hardware, and control strategy [20]. In addition to direct emissions impacts, higher ethanol content fuel can also provide more efficient combustion and overall engine operation under part-load conditions [21] and under knock-limited higher-load conditions [22,23]. Conventional gasoline vehicles in the U.S. are designed to operate on E0-E10 and have been certified for emissions compliance by testing with E0 fuel, but now transitioning to E10 as part of U.S. Tier 3 and California LEV-III emissions regulations. Flexible fuel vehicles (FFVs) are designed for operation on E0-E10 and E85 and have been certified for emissions compliance by testing with E0 and E85. While many studies have attempted to measure ethanol-related emissions changes, some studies are performed with vehicles not intended for such fuels, e.g., using >E10 blends in vehicles designed to operate on E0-E10 [24,25,26]. In Table 2 we exclude the results from such studies involving vehicle misfuelling. Finally, we note that there have been large advances in the efficiency of engine and emission control systems over the past few decades and we restrict our review to literature concerning 2000 model year (2000MY) vehicles or later. Given the different vehicle technologies involved it is convenient to separate the discussion of variation of ethanol fuel content over the ranges E0-E10 and E0-E85.

4.1 Effect of E0-E10 on vehicle emissions

The "EPAct/V2/E-89" study conducted by the U.S.E.P.A. [26] provides the most comprehensive dataset available to assess the effect of variation of ethanol blend over the range E0-E10 on vehicle emissions. The EPAct/V2/E-89 study used 15 different MY2008 vehicles with 17 different E0/E10 test fuels. Five fuel properties were varied in the study; ethanol volume, aromatic content, RVP, T50, and T90. T50 and T90 are the temperatures at which 50 and 90% of the fuel has evaporated for the standard ASTM D86 distillation test. A full chemical speciation was provided for each of the fuels. The chemical speciation allows calculation of the fuel particulate matter index [27] which is a predictive model of PM emissions based on the chemical composition of the fuel. Figure 4 shows plots of vehicle NMOG and NOx emissions versus fuel T50, and Figure 5 shows vehicle PM emissions versus fuel PM index [27], for E0 and E10 fuels in the EPAct/V2/E-89 study. As can be seen from Figures 4 and 5 there is a general trend of decreased NMOG and NOx emissions with increasing T50, and increased PM emissions with fuel PM index, but there is no discernable dependence of NMOG, NOx, or PM emissions with ethanol content over the range E0 to E10. Within that data set, U.S.E.P.A. [28] showed an apparent PM increase for some vehicles with increasing ethanol content, however others showed no effect.

Recently, George et al. [29] reported VOC emissions from 1 conventional 2008MY and 2 flexible fuel 2008MY vehicles using summer and winter grade E0 and E10 for vehicle operating temperatures of -7^{o}C and 24^{o}C. George et al. [29] reported that there was no statistically significant difference in the sum of VOC emissions, the sum of the maximum incremental reactivity weighted ozone forming potentials of VOC emissions, or the sum of mobile source air toxic emissions between vehicles fueled with E0 or E10. The available data suggest that over the range E0 to E10 there is no discernable influence of ethanol fuel content on emissions of NMOG, NO_x, or PM from light-duty vehicles.

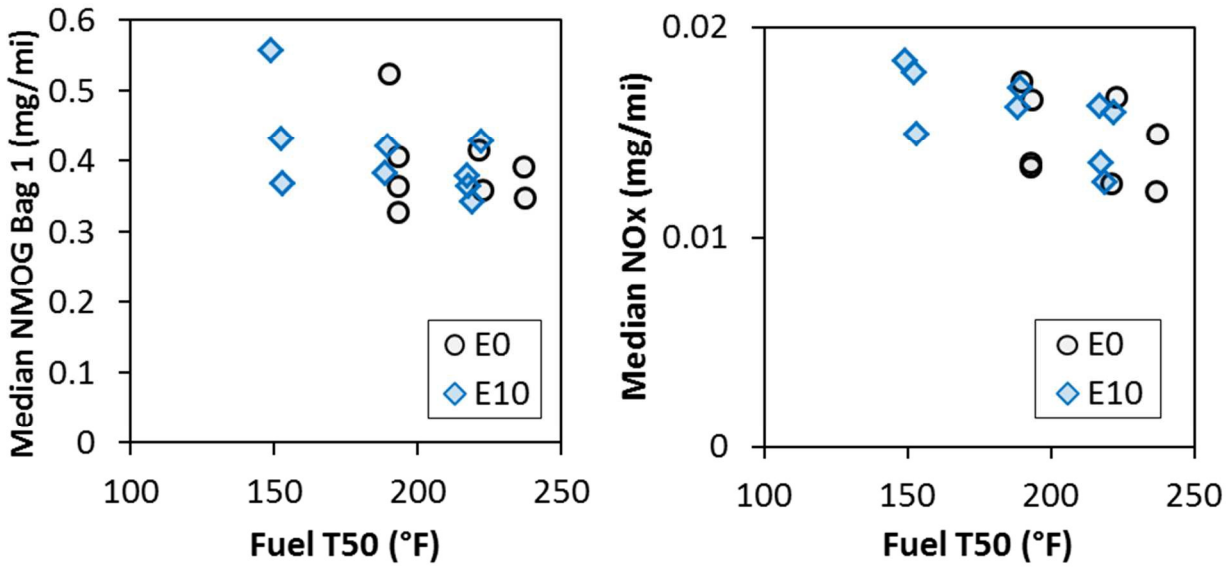


Figure 4: NMOG and NOx emissions from E10-capable vehicles on LA92 cycle when fueled with either E0 (black circles) or E10 (blue diamonds) as functions of fuel T50.

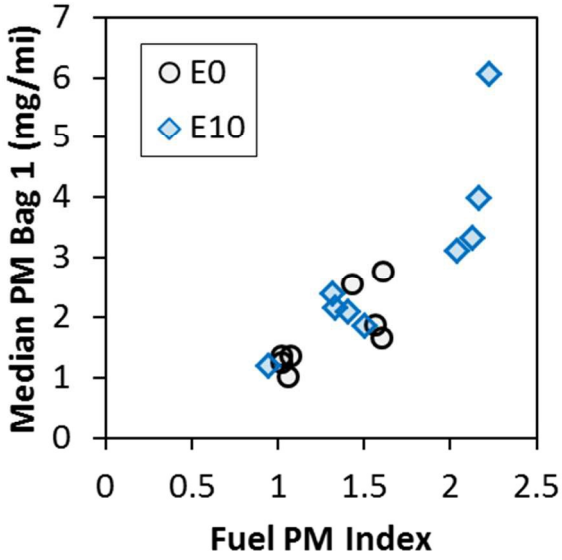


Figure 5: PM emissions from E10-capable vehicles on LA92 cycle (bag 1) when fueled with either E0 (black circles) or E10 (blue diamonds) as functions of fuel T50.

4.2 Effect of E10-E85 on vehicle emissions

The literature data upon which to assess the impact of ethanol concentration for blends intermediate between E10 and E85 on FFV emissions [24,29,30,31,32,33,34,35] are summarized in Tables 2 and 3. From inspection of Table 2 it is clear that there is a substantial range of results reported in the literature. Given that the bulk of organic compounds present in vehicle exhaust are unburned or partially burned fuel, it is to be expected that increasing the ethanol fuel content would lead to increased emissions of ethanol and its oxidation products acetaldehyde and formaldehyde, and decreased emissions of gasoline components and their oxidation products. Consistent with these expectations, there is general agreement in the literature data that increased ethanol fuel content leads to increased emissions of ethanol and acetaldehyde and decreased emissions of non-methane hydrocarbons (NMHC). There is also agreement that increased ethanol levels lead to comparable, or decreased, levels of NO_x and CO emissions. There is no consensus on the trend for total hydrocarbon emissions with one study reporting an increase [24], one reporting a decrease [33], and one reporting a minimum at about E40 [34] which probably reflects differences in conversion of acetaldehyde to methane on rhodium catalysts in the different vehicles [34]. There is also no consensus on the effect of ethanol fuel content on the ozone forming potential of VOC emissions calculated by weighting the VOC emissions by their maximum incremental reactivity factors [36]. One study reported no trend in ozone-forming potential [29] while another reported a factor of approximately 2 increased ozone-forming potential [35] with increased ethanol fuel content. Literature data for the effect of ethanol on PM emissions [31,37,38,39] are given in Table 3. As seen from Table 3, there is general agreement that for modest increases in ethanol content there is not a discernable effect on PM emissions but large increases in ethanol lead to decreased PM emissions.

The impact of increased ethanol fuel content on mobile source air toxic (MSAT) emissions has been reviewed recently by Stein et al. [20]. Regulations in California require measurement of tailpipe emissions of the toxic compounds 1,3-butadiene, benzene, formaldehyde, and acetaldehyde and that the potency-weighted sum of these compounds is below a limit that is based on the corresponding value for

the certification fuel. Tailpipe measurements show increased emissions of formaldehyde and acetaldehyde and decreased emissions of 1,3-butadiene and benzene as ethanol fuel content is increased. There was no discernable trend of the toxicity weighted sum of 1,3-butadiene, benzene, formaldehyde, and acetaldehyde with ethanol fuel content [20]. The available data indicate that emissions of NO_x, NMOG, PM, and MSATs from modern vehicles are not adversely affected by increased ethanol fuel content over the range for which the vehicles are designed to operate.

Table 1: Literature data for E0-E85 ethanol fuel content impacts on VOC, CO, and NOx vehicle emissions.

Study	Scope	Impact of increased ethanol on tailpipe emissions
Graham et al. (2008) [17]	One 2002MY, one 2004MY FFV E0, E85 FTP cycle	NO_x and NMHC decreased by 45% and 48% Formaldehyde and acetaldehyde increased by 73% and 2540%. No discernable change in CO or NMOG emissions.
Haskew and Liberty (2011) [32]	One 2006MY, six 2007MY FFVs E6, E32, E59, E85 Match blended (vapor pressure) FTP, US06, LA92 test cycles	Average NMHC, NMOG, CO, NOx emissions did not exhibit an emissions trend with increasing ethanol content, with exception of decreasing NMHC and NMOG for US06 cycle.
Karavalakis et al. (2012) [24]	One 2007MY FFV E0, E10, E20, E50, E85 Splash blended FTP cycle	No statistically significant trends for CO or NOx emissions; THC and NMHC increased for E85 but not for lower blends.
Yassine and La Pan (2012) [33]	One 2006MY FFV E0, E20 Splash blended FTP cycle	THC, NMOG, CO, NOx decreased by 58%, 42%, 83%, and 60%, respectively, for E20 compared to E0.
Yanowitz et al. (2013) [30]	Nine (2002-2011)MY FFVs E10, E40, E76 LA92 cycle	Tested immediately after refueling with E40 having been previously adapted to either E10 or E76. Average decreases in NMOG, CO, and NOx emissions of 5%, 10%, and 8% for E40 compared to E10 fuel.
Karavalakis et al. (2014) [31]	One 2013MY, one 2014MY FFV E10, E51, E83 Match blended FTP, UC cycles	NMHC, CO, and PM decreased, acetaldehyde increased, no trend for THC and NOx with increased ethanol.
Hubbard et al. (2014) [34]	One 2006MY FFV E10, E20, E30, E40, E55, E80 Splash blended FTP cycles	Acetaldehyde, ethanol, and methane emissions increased, NOx and NMHC decreased, no discernable effect on CO emissions. NMOG and THC emissions had minimum (30-35% lower than E0 or E85) for E20-E40.
George et al. (2015) [29]	Two 2008MY FFVs E0, E10, E85 (summer & winter) Match blended (vapor pressure) LA92 cycle	NMHC decreased, acetaldehyde increased, no trend in VOC (NMOG) emissions, no trend in ozone-formation potential with increased ethanol.
Suarez-Bertoa et al. (2015) [35]	One 2012MY FFV E5, E10, E15, E85 Splash blended WLTC cycle	NOx emissions decreased by 30-55%, CO, CH_4, formaldehyde, acetaldehyde, and ethanol emissions increased by 65%, 150%, 100%, 120%, and 350%, ozone-formation potential increased by factor of 2 for E85 versus E5-E15.

FTP, Federal Test Procedure; UC, Unified Cycle also known as the LA92 cycle; US06, high acceleration aggressive cycle also referred to as the supplemental FTP cycle; WLTP, worldwide harmonized light vehicles test procedure

Table 2: Literature data for E0-E85 ethanol fuel content impacts on PM vehicle emissions.

Authors	Scope	Tailpipe emissions
He et al. (2010) [37]	One 2009MY engine/emission system E0, E10, E20 Splash blended 10 steady state engine operating modes	Compared to the baseline gasoline (E0), E10 does not significantly change PM emissions, while E20 and BU12 both reduce PM emissions under the conditions studied.
Storey et al. (2010) [38]	One 2007MY vehicle E0, E10, E20 Splash blended FTP, US06 cycles	No significant change in PM emissions from E0 to E10. From E0 to E20, the average mass emissions declined 30% and 42% over the FTP and US06 cycles, respectively.
Maricq et al. (2012) [39]	Light-duty truck, 3.5-L V6 E0, E10, E17, E32, E45 fuels FTP test cycle	"As the ethanol level in gasoline increases from 0% to 20%, there is possibly a small (<20%) benefit in PM mass and particle number emissions, but this is within test variability. When the ethanol content increases to >30%, there is a statistically significant 30%–45% reduction in PM mass and number emissions observed for both engine calibrations."
Karavalakis et al. (2014) [31]	One 2013-MY, one 2014-MY FFV E10, E51, E83 fuels FTP, UC cycles	"Particulate matter (PM) mass, number, and soot mass emissions showed strong reductions with increasing alcohol content in gasoline. Particulate emissions were found to be clearly influenced by certain fuel parameters including oxygen content, hydrogen content, and aromatics content."

5. Vehicle emissions and urban air quality

To place into context the impacts of increased biofuel content on vehicle emissions and urban air quality it is useful to consider the historical trend of vehicle emissions and urban air quality. To illustrate the trend for light-duty vehicles, Figure 6 shows the combined hydrocarbon and NO_x emissions in units of g/mile. The data for 1957-1967 and 1967-1971 are emissions measured for vehicles representative of the on-road U.S. fleet [40]. The data for 1975-2025 are the California, Federal U.S., and EU regulatory requirements that vehicle manufacturers are required to meet for new vehicles [41]. The red line shows a 10% annual reduction to aid visual inspection of the data trend. As illustrated in Figure 6, the per-vehicle per-mile emissions from light duty vehicles have been decreasing at a rate of approximately 10% per year, have decreased by orders of magnitude over the past 50 years, and will continue to decrease consistent with existing regulations. Reductions in emissions from the on-road fleet lag behind those shown for new vehicles in Figure 6 reflecting the 10-20 years taken for turnover of the vehicle fleet.

As the result of actions taken to reduce emissions from vehicles and other sources there is a clear trend of improving air quality in U.S. cities [42]. From 1970 to 2014 the number of vehicle miles traveled in the U.S. *increased* by 172% but the aggregate emissions of CO, Pb, NO_x, VOCs, PM10, PM2.5 and SO_2 *decreased* by 69% [42]. Levels of O_3, PM, CO, NO_2, and SO_2 have decreased substantially in urban air in U.S. cities over the past several decades [42]. While remarkable progress has been made in improving air quality, more progress is needed. In 2014 more than 57 million people in the U.S. lived in areas which did not meet one or more of the National Ambient Air Quality Standards for ozone, PM, SO_2 or Pb [42]. As discussed above the available data suggest that emissions of NO_x, non-methane hydrocarbons, PM, and mobile source air toxics from modern gasoline and diesel vehicles are not adversely affected by increased biofuel content over the range for which the vehicles are designed to operate. We highlight the importance of engine calibration as a critical factor determining vehicle emissions. Considerable engineering efforts go into the optimal design and calibration of engines and their aftertreatment systems to meet increasingly rigorous tailpipe emissions standards. Calibrations optimized for conventional fuels

are not likely to be optimal for biofuels which typically have physical and chemical properties which differ significantly from fossil fuels. The fuel and the vehicle need to be thought of as one system. The available data suggest that increased biofuel content together with changes in engine design and calibration for new vehicles to accommodate increased biofuel content should not result in problematic increases in emissions impacting urban air quality and may in fact enable future emissions reductions in new vehicles designed for these fuels. As discussed above, vehicles need to be operated on fuels for which they were designed. Older vehicles in the on-road fleet need to be provided with appropriate fuels and there may be challenges to convert the existing infrastructure to accommodate substantially higher biofuel blends. A discussion of such challenges is beyond the scope of the present study. Further research is needed using a systems perspective to better understand, and optimize, the benefits of biofuels when blended into gasoline and diesel.

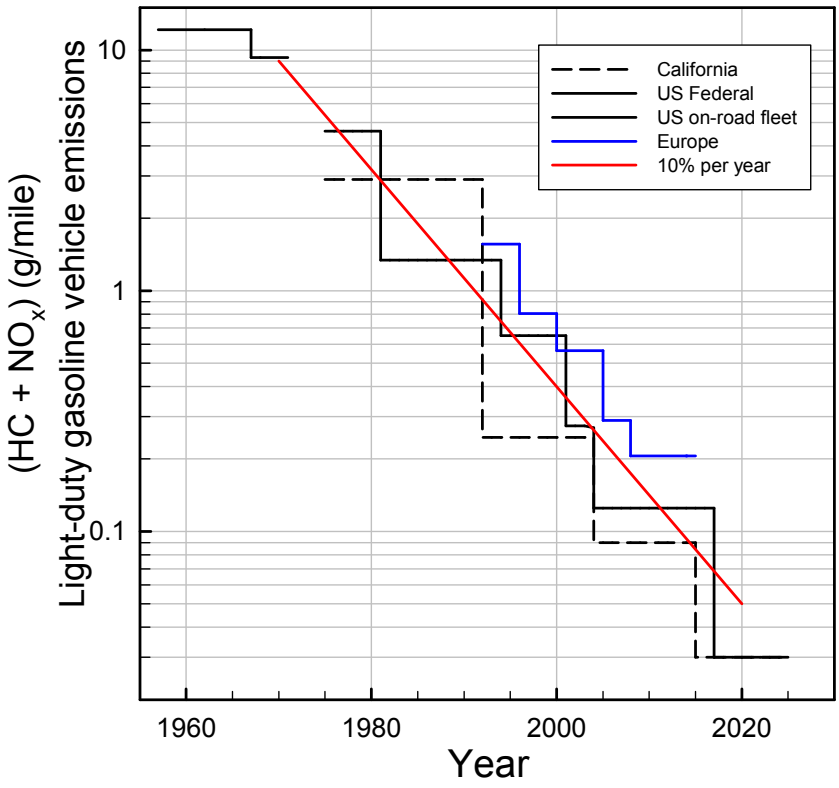


Figure 6: Emission standards from gasoline light-duty vehicles. Data taken from Fegraus et al. [40] and TransportPolicy.net website (http://transportpolicy.net). See text for details.

DISCLAIMER

ACKNOWLEDGEMENTS

Butyl nonanoate was synthesized and provided by Prof. Dennis Miller and Dr. Lars Peereboom of Michigan State University. This material is based upon work supported by the Department of Energy under Award Number DE-FC26-07NT43278.

References

1. ASTM D6751-15b. Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, ASTM International, West Conshohocken, PA, 2015

2. BP Statistical Review of World Energy June 2015, **2015**, British Petroleum, www.bp.com

3. U.S. Energy Information Administration, Monthly Energy Review March 2015, http://www.eia.gov/totalenergy/data/monthly/

4. ASTM International, Standard Specification for Ethanol Fuel Blends for Flexible-Fuel Automotive Spark-Ignition Engines, ASTM D 5798-11, Rev. 2011.

5. Anderson, J.E.; Baker, R.E.; Wallington, T.J.; Ginder, J.M., Implications of the 2007 Energy Independence and Security Act for the US Light-Duty Vehicle Fleet, SAE Technical Paper 2009-01-2770, **2009**, doi:10.4271/2009-01-2770.

6. Anderson, J.E.; DiCicco, D.M.; Ginder, J.M.; Kramer, U.; Leone, T.G.; Raney-Pablo, H.E.; Wallington, T.J., High Octane Number Ethanol-Gasoline Blends: Quantifying the Potential Benefits in the United States, *Fuel*, **2012**, *97*, 585-594.

7. U.S. Environmental Protection Agency, 2011. Biofuels and the Environment: First Triennial Report to Congress. EPA/600/R-10/183F

8. Gaffney, J.S.; Marley, N.A., The Impacts of combustion emissions on air quality and climate: from coal to biofuels and beyond, *Atmos. Environ.*, **2009**, *43*, 23-36.

9. Knothe, G.; Sharp, C.A.; Ryan, T.W., Exhaust Emissions of biodiesel, petrodiesel, neat methyl esters, and alkanes in a new technology engine, *Energy & Fuels*, **2006**, *20*, 403-408.

10. A Comprehensive Analysis of Biodiesel Effects on Exhaust Emissions, EPA Draft Technical Report, EPA420-P-02-001, October 2002.

11. Kurtz, Eric M.; Kuhel, D.; Anderson, J.E.; Mueller, S.A., A comparison of combustion and emissions of diesel fuels and oxygenated fuels in a modern DI diesel engine, *SAE Int. J. Fuels Lubr.*, **2012**, *5*, 1199-1215, doi:10.4271/2012-01-1695.

12. Eckerle, W.A.; Lyford-Pike, E.J.; Stanton, D.W.; LaPointe, L.A.; Whitacre, S.D.; Wall, J.C., Effects of methyl ester biodiesel blends on NOx emissions, SAE Technical Paper, **2008**, 2008-01-0078.

13. Snyder, D.B.; Adi, G.H.; Hall, C.H.; Shaver, G.M., Control-variable-based accommodation of biodiesel blends, *Int. J. Engine Res.*, **2011**, *12*, 564-579.

14. Lown, A. L.; Peereboom, L.; Mueller, S. A.; Anderson, J. E.; Miller, D. J.; Lira, C. T., Cold flow properties for blends of biofuels with diesel and jet fuels, *Fuel*, **2014**, *117*, 544-551.

15. Kurtz, E., Brehob, D. D., Vigild, C. W., Dronzkowski, D. J., Pilbeam, J., Anderson, J. E., Compensation for oxygenated fuels in a diesel engine, US patent #8046153 issued on 10/25/2011.

16. Eckerle, W.; Lyford-Pike, E.; Stanton, D.; LaPointe, L.; Whitacre, S.D.; Wall, J.C., Effects of methyl ester biodiesel blends on NO_x emissions, *SAE Int. J. Fuels Lubr.*, **2009**, *1*, 102-118, doi:10.4271/2008-01-0078.

17. Graham, L.A.; Belisle, S.L.; Baas, C.-L., Emissions from light duty gasoline vehicles operating on low blend ethanol gasoline and E85, *Atmos. Environ.*, **2008**, *42*, 4498-4516.

18. Andersen, V.F.; Anderson, J.E.; Wallington, T.J.; Mueller, S.A.; Nielsen, O.J., Distillation curves for alcohol−gasoline blends, *Energy & Fuels*, **2010**, *24*, 2683-2691.

19. Andersen, V.F.; Anderson, J.E.; Wallington; T.J., Mueller, S.A.; Nielsen, O.J., Vapor pressures of alcohol−gasoline blends, *Energy & Fuels*, **2010**, *24*, 3647-3654.

20. Stein, R.A.; Anderson, J.E.; Wallington, T.J., An overview of the effects of ethanol-gasoline blends on SI engine performance, fuel efficiency, and emissions, *SAE Int. J. Engines*, **2013**, *6*, 470-487, doi:10.4271/2013-01-1635.

21. Jung, H.; Shelby, M.H.; Newman, C.E.; Stein, R.A., Effect of ethanol on part load thermal efficiency and CO_2 emissions of SI engines, *SAE Int. J. Engines*, **2013**, *6*, 456-469, doi:10.4271/2013-01-1634.

22. Stein, R.A.; Polovina; D., Roth, K.; Foster, M.; Lynskey, M.; Whiting, T.; Anderson, J.E.; Shelby, M.H.; Leone, T.G.; VanderGriend, S., Effect of heat of vaporization, chemical octane, and sensitivity on knock limit for ethanol - gasoline blends, *SAE Int. J. Fuels Lubr.*, **2012**, *5*, 823-843, doi:10.4271/2012-01-1277.

23. Jung, H.; Shelby, M.H.; Leone, T.G.; Anderson, J.E.; Collings, T., Fuel economy and CO_2 emissions of ethanol-gasoline blends in a turbocharged DI engine, *SAE Int. J. Engines*, **2013**, *6*, 422-434, doi:10.4271/2013-01-1321 .

24. Karavalakis, G.; Durbin, T.D; Shrivastava, M.; Zheng, Z.; Villela, M., Impacts of ethanol fuel level on emissions of regulated and unregulated pollutants from a fleet of gasoline light-duty vehicles, *Fuel*, **2012**, *93*, 549-558.

25. Karavalakis, G.; Short, D.; Vu, D.; Villela, M., Asa-Awuku, A.; Durbin, T.D., Evaluating the regulated emissions, air toxics, ultrafine particles, and black carbon from SI-PFI and SI-DI vehicles operated on different ethanol and iso-butanol blends, *Fuel*, **2014**, *128*, 410-421.

26. U.S. EPA Office of Transportation and Air Quality, Assessing the effect of five gasoline properties on exhaust emissions from light-duty vehicles certified to Tier 2 standards: Analysis of data from EPAct Phase 3 (EPAct/V2/E-89), EPA-420-R-13-002, April 2013.

27. Aikawa, K.; Sakurai, T.; and Jetter, J., Development of a predictive model for gasoline vehicle particulate matter emissions, *SAE Int. J. Fuels Lubr.*, **2010**, *3*, 610-622.

28. Butler, A. D.; Sobotowski, R. A.; Hoffman, G. J.; Machiele, P., Influence of fuel PM Index and ethanol content on particulate emissions from light-duty gasoline vehicles, SAE Technical Paper 2015-01-1072, **2015**.

29. George, I.J.; Hays, M.D.; Herrington,J.S.; Preston, W.; Snow, R.; Faircloth, J.; George, B. J.; Long, T.; Baldauf, R.W., Effects of cold temperature and ethanol content on VOC emissions from light-duty gasoline vehicles, *Environ. Sci. Technol.*, **2015**, *49*, 13069-13074.

30. Yanowitz, J.; Knoll, K.; Kemper, J.; Luecke, J.; McCormick, R.L., Impact of adaptation on flex-fuel vehicle emissions when fueled with E40, *Environ. Sci. Technol.*, **2013**, *47*, 2990-2997, doi: 10.1021/es304552b.

31. Karavalakis, G.; Short, D.; Russell, R.L.; Jung, H.; Johnson, K.C.; Asa-Awuku, A.; Durbin, T.D.; Assessing the impacts of ethanol and isobutanol on gaseous and particulate emissions from flexible fuel vehicles, *Environ. Sci. Technol.*, **2014**, *48*, 14016-14024.

32. Haskew, H.M.; Liberty, T.F., Exhaust and evaporative emissions testing of flexible-fuel vehicles, CRC Report E-80, August 2011.

33. Yassine, M.K.; La Pan, M. 2012, Impact of ethanol fuels on regulated tailpipe emissions. SAE Technical Paper 2012-01-0872.

34. Hubbard, C.P.; Anderson, J.E.; Wallington, T.J., Ethanol and air quality: Influence of fuel ethanol content on emissions and fuel economy of flexible fuel vehicles, *Environ. Sci. Technol.*, **2014**, *48*, 861-867.

35. Suarez-Bertoa R.; Zardini, A.A.; Keuken, H.; Astorga, C., Impact of ethanol containing gasoline blends on emissions from a flex-fuel vehicle tested over the Worldwide Harmonized Light duty Test Cycle (WLTC), *Fuel*, **2015**, *143*, 173-182.

36. Carter, W.P.L., Development of ozone reactivity scales for volatile organic compounds, *J. Air Waste Manage. Assoc.*, **1994**, *44*, 881-889.

37. He, X.; Ireland, J.C.; Zigler, B.T.; Ratcliff, M.A.; Knoll, K.E.; Alleman, T.L.; Tester, J.T., The impacts of mid-level biofuel content in gasoline on SIDI engine-out and tailpipe particulate matter emissions, SAE Technical Paper 2010-01-2125, **2010**, doi:10.4271/2010-01-2125.

38. Storey, J.M.; Barone, T.; Norman, K.; Lewis, S., Ethanol blend effects on direct injection spark-ignition gasoline vehicle particulate matter emissions, *SAE Int. J. Fuels Lubr.*, **2010**, *3*, 650-659, doi:10.4271/2010-01-2129.

39. Maricq, M.M.; Szente, J.J.; Jahr, K., The impact of ethanol fuel blends on PM emissions from a light-duty GDI vehicle, *Aerosol Sci. Technol.*, **2012**, *46*, 576–583.

40. Fegraus, C.E.; Domke C.J.; Marzen, J., Contribution of the vehicle population to atmospheric pollution, Society of Automotive Engineers Technical Paper 730530, **1973**.

41. TransportPolicy, http://transportpolicy.net/, accessed November 2015.

42. U.S.E.P.A., Air Quality Trends, 2015, http://www.epa.gov/airtrends/, accessed November 2015.