

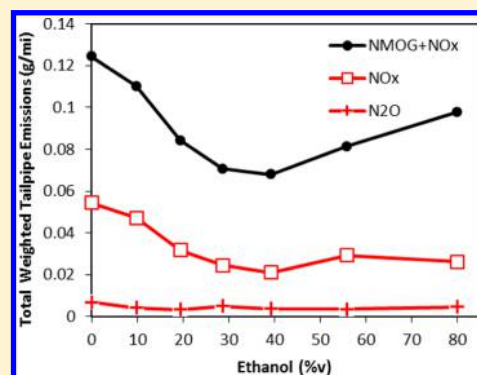
# Ethanol and Air Quality: Influence of Fuel Ethanol Content on Emissions and Fuel Economy of Flexible Fuel Vehicles

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**S** Supporting Information

**ABSTRACT:** Engine-out and tailpipe emissions of NO<sub>x</sub>, CO, nonmethane hydrocarbons (NMHC), nonmethane organic gases (NMOG), total hydrocarbons (THC), methane, ethene, acetaldehyde, formaldehyde, ethanol, N<sub>2</sub>O, and NH<sub>3</sub> from a 2006 model year Mercury Grand Marquis flexible fuel vehicle (FFV) operating on E0, E10, E20, E30, E40, E55, and E80 on a chassis dynamometer are reported. With increasing ethanol content in the fuel, the tailpipe emissions of ethanol, acetaldehyde, formaldehyde, methane, and ammonia increased; NO<sub>x</sub> and NMHC decreased; while CO, ethene, and N<sub>2</sub>O emissions were not discernibly affected. NMOG and THC emissions displayed a pronounced minimum with midlevel (E20–E40) ethanol blends; 25–35% lower than for E0 or E80. Emissions of NO<sub>x</sub> decreased by approximately 50% as the ethanol content increased from E0 to E30–E40, with no further decrease seen with E55 or E80. We demonstrate that emission trends from FFVs are explained by fuel chemistry and engine calibration effects. Fuel chemistry effects are fundamental in nature; the same trend of increased ethanol, acetaldehyde, formaldehyde, and CH<sub>4</sub> emissions and decreased NMHC and benzene emissions are expected for all FFVs. Engine calibration effects are manufacturer and model specific; emission trends for NO<sub>x</sub>, THC, and NMOG will *not* be the same for all FFVs. Implications for air quality are discussed.



## 1. INTRODUCTION

Use of ethanol as a transportation fuel in the U.S. has increased approximately 6-fold over the last 10 years (2002–2012) from 2 to 13 billion gallons per year.<sup>1</sup> Motivations for the increased use of ethanol include energy security, global climate change, and economic stimulus. In the U.S., ethanol is now blended into most gasoline at a concentration of 10%v (E10). Ethanol is also available as E85, which after a recent change in specifications, is allowed to contain as much as 83%v and as little as 51%v ethanol.<sup>2</sup> The U.S. Renewable Fuel Standard (RFS2) calls for the use of 36 billion gallons (136 billion liters) of renewable fuel by 2022 much of which would likely be ethanol.

Future blending options for ethanol in gasoline include continuation of low-level blends (E0–E15), greater use of E85 in flexible fuel vehicles (FFVs), or new use of midlevel blends (E20–E40) in FFVs or in new vehicles designed with midlevel blend-capability. Clearly there are many considerations for determining the best future fuel strategy, including fuel properties, refining sector implications, vehicle compatibility, refueling infrastructure compatibility, and transition timing.<sup>3,4</sup> One consideration is the impact of ethanol content on tailpipe emissions of NO<sub>x</sub>, volatile organic compounds (VOC), CO, and particulate matter (PM) and hence on urban air quality.<sup>5,6</sup> It is important to ensure that a future ethanol blending strategy does not hinder, and ideally supports, continuing progress in improving air quality.

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 net heating value (NHV), increased heat of vaporization (HoV), and other volatility changes.<sup>7,8</sup> These changes can have positive or negative effects that can depend on engine design, hardware, and control strategy.<sup>9</sup> In addition to direct emissions impacts, higher ethanol content fuel can also provide more efficient combustion and overall engine operation under part-load conditions<sup>10</sup> and under knock-limited higher-load conditions.<sup>11,12</sup> Designing and calibrating for optimal performance on midlevel ethanol blends represents a new consideration for FFV design. FFVs have historically been designed for operation on E0/E10 and E85 and are certified for emissions compliance by testing with E0 and E85.

While many studies have attempted to measure ethanol-related emissions changes in engines and vehicles, such studies have sometimes been performed with vehicles not intended for such fuels<sup>13</sup> (i.e., non-FFVs). When studies were performed using FFVs, it is often not reported whether the vehicle correctly determined the ethanol content in the fuel and hence was operating within appropriate parameters for the given fuel.<sup>14</sup> The literature data upon which to assess the impact of

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ethanol concentration for blends intermediate between E10 and E85 on FFV emissions is sparse<sup>13–16</sup> with reports of large,<sup>16</sup> modest,<sup>14</sup> or no<sup>13,15</sup> discernible change in NO<sub>x</sub>, VOC, and CO emissions with midlevel blends.

To improve the understanding of the effects of fuel ethanol content on vehicle emissions a comprehensive study was conducted using a 2006 model year FFV on a chassis dynamometer equipped for measurement of both engine-out and tailpipe emissions. The vehicle was operated with E0, E10, E20, E30, E40, E55, and E80 fuel, thus including the current predominant market fuel (E10), a range of possible future midlevel ethanol blends (E20–E40), and the new range for high-level ethanol blends (E55, E80). We report the effect of fuel ethanol content on engine-out and tailpipe emissions and develop a novel conceptual framework for explaining the emission trends in terms of fuel chemistry and vehicle calibration effects. The air quality impact of future increased use of ethanol in FFVs is discussed.

## 2. EXPERIMENTAL SECTION

**2.1. Fuels.** Ethanol-gasoline blends were prepared by mixing E0 gasoline (EEE certification gasoline, Haltermann) and denatured ethanol (Haltermann). Typically, 50 gallon batches were prepared in a 55-gallon drum and then mixed by rolling for 30 min. Samples were analyzed for fuel properties by Paragon Laboratories (Livonia, MI). Table 1 shows selected fuel properties.

**Table 1. Fuel Properties and PCM Inferred Ethanol Value**

fuel blend	ethanol (%v)	H:C (molar)	O:C (molar)	s.g.	NHV (MJ/kg)	RVP (kPa)	PCM inferred ethanol (%v)
E0	0.0	1.87	0.000	0.744	43.3	55	5
E10	9.8	1.90	0.039	0.749	41.5	67	5
E20	19.4	1.98	0.069	0.756	39.6	65	23
E30	28.6	2.11	0.113	0.759	38.0	65	32
E40	39.2	2.20	0.124	0.763	36.3	64	40
E55	55.8	2.31	0.212	0.771	34.2	62	55
E80	80.1	2.75	0.389	0.784	29.4	53	78

**2.2. Test Vehicle and Aftertreatment Description.** The vehicle was a model year 2006 Mercury Grand Marquis FFV equipped with a 4.6L 2-valve V8 engine with port fuel injection (PFI) and certified for U.S. Tier 2 Bin 5 emissions compliance. At the time of testing (2008), the vehicle had accumulated approximately 6,000 miles and the catalyst was aged to simulate full useful life (see Supporting Information (SI)). The vehicle was controlled by a development-level powertrain control module (PCM) integrated with a calibration tool (ATI Vision) which provided data acquisition of engine parameters during both the fuel-type learning sequence and also during standard vehicle testing on the chassis dynamometer. The PCM used the commercial calibration for the vehicle. Further details are given in the SI.

**2.3. Test Facility and Protocol.** Vehicle emission testing was conducted on a chassis dynamometer in the Vehicle Emissions Research Laboratory (VERL) at Ford Motor Company.

The test sequence for each fuel was started by draining the fuel from the previous test and then adding 5 gallons of the new fuel (approximately 25% of capacity). The vehicle was driven outdoors for approximately 20 miles (30 min) in both city and

highway conditions to allow the PCM strategy to learn (or infer) the ethanol content in the new fuel based on data from the HEGO sensors located upstream of the close-coupled catalysts. The inferred ethanol content for each fuel is shown in Table 1 and was within 3%v of the actual ethanol content for the midlevel ethanol blends (E20–E40) and E55. The PCM intentionally selected a value of E5 when detecting ethanol in the range of E0–E10 and a value of E78 for fuels with high ethanol content (representing a year-round average for typical E85).

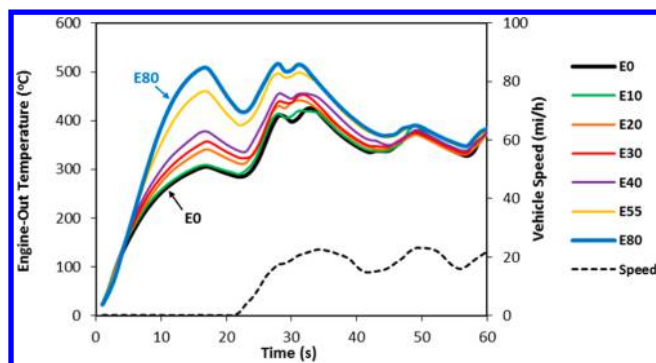
After the procedure to allow the vehicle to infer the ethanol content in the test fuel, the emissions were repeatedly tested on the chassis dynamometer over the Federal Test Procedure (FTP-75) drive cycle. A typical sequence consisted of driving one preparatory FTP-75 and US06 cycle (emissions not measured) followed by four consecutive FTP-75 emissions tests with each test preceded by a 12–17 h soak at 75 °F (24 °C). The FTP-75 test cycle consists of three phases: (1) a “cold start” phase lasting 8.4 min, (2) a “transient” operating phase lasting 14.4 min, and after a “hot soak” period with the engine turned off for 9 to 11 min, (3) a “hot start” phase lasting another 8.4 min which repeats the driving pattern of phase 1 but starts with the warmed-up engine. The tailpipe emissions from each phase are collected in separate Teflon bags, hence the common reference to “Bags 1, 2, and 3” for the three test phases. The overall test result, expressed in g/mile, is calculated using EPA-defined weighting factors (0.43, 1.0, and 0.57, respectively) applied to the emissions collected in each bag.

Tailpipe emissions were collected using a dilute-bag approach. Continuous raw engine-out exhaust emissions were recorded for total hydrocarbons (THC), CH<sub>4</sub>, CO, NO<sub>x</sub>, CO<sub>2</sub>, and O<sub>2</sub> with Horiba 7000 analyzers. Nonmethane hydrocarbons (NMHC) are calculated by subtracting CH<sub>4</sub> emissions from THC emissions, both measured by flame ionization detection (FID). Oxygenated compounds were analyzed by standard EPA impinger/cartridge methods<sup>17,18</sup> as discussed in SI. “Corrected” NMHC data are obtained by removing the FID response associated with the separately measured oxygenated compounds from the measured NMHC data. The NMOG emissions are the sum of corrected NMHC and the oxygenated compounds. N<sub>2</sub>O, ammonia, and ethene were analyzed using FTIR spectroscopy. Benzene and 1,3-butadiene, defined as toxic by the California Air Resources Board (CARB), were not measured in the present work but are discussed in the SI.

## 3. RESULTS

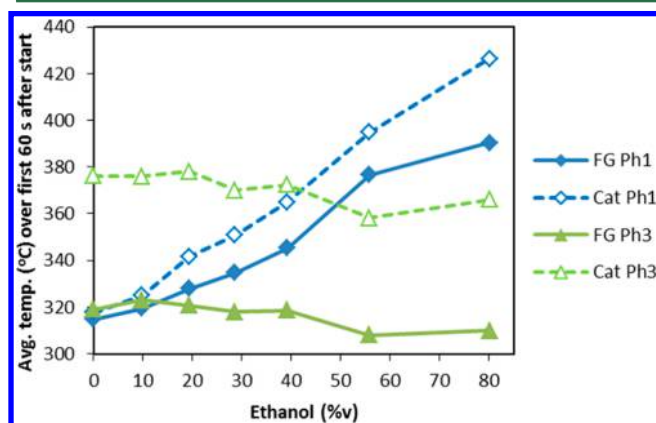
The following discussion is primarily focused on how tailpipe emissions varied with ethanol content in the test fuel over the FTP-75 test cycle, including greenhouse gas (GHG) emissions and vehicle fuel economy. Engine-out emissions data, catalyst temperatures, conversion efficiencies across the catalyst, and data for individual test phases are shown to explain the emission trends.

**3.1. Temperatures.** The cold-start portion of phase 1 of the FTP cycle contributes greatly to total emissions because the engine and catalyst have not warmed to their normal operating temperatures. Engine-out temperatures measured during the first 60 s of phase 1 are shown in Figure 1 for each fuel. The temperatures increase with increasing ethanol content in the fuel. At 15 s after starting, the engine-out temperature with E80 was approximately 190 °C higher than with E0. The exhaust gas temperature 15 s after starting the engine increased systematically with ethanol content between E0 and E80. After 45 s, the



**Figure 1.** Engine-out (catalyst feedgas) temperatures and vehicle speed during cold-start period of FTP phase 1.

temperature traces for all fuels were indistinguishable within the experimental uncertainties. Similar trends and temperature differences are observed with the catalyst midbed temperatures, except that approximately 60 s were required for the temperatures with the different fuel blends to equalize (SI Figure S1). To summarize these trends, Figure 2 shows the



**Figure 2.** Average engine-out (catalyst feedgas, FG) and catalyst midbed (Cat) temperatures during the cold-start and warm-start portion (i.e., the first 60 s) of FTP phases 1 and 3, respectively.

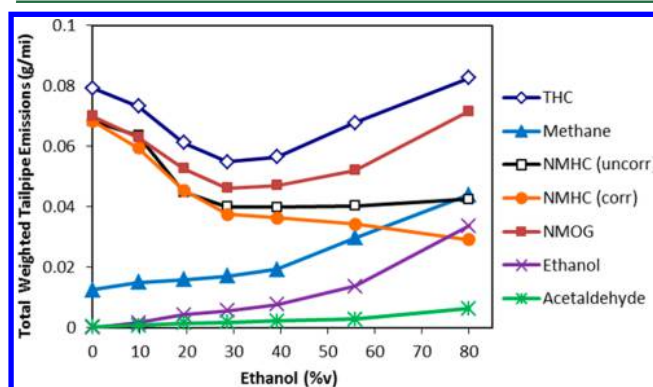
average engine-out and catalyst midbed temperatures over the first 60 s of phase 1, with average engine-out and catalyst midbed temperatures using E80 being 70 °C higher and 106 °C higher, respectively, than when using E0. Temperatures observed using midlevel ethanol blends (E20–E40) were between the E0 and E80 extremes.

The initial temperature rise with higher ethanol content fuel during the first 15 s of the cold start of phase 1 is the result of automatic calibration adjustments in the control strategy intended to generate additional heat flux from the engine to improve catalyst light-off and initial functioning. For example, to provide robust cold starting on E85, the cold-start calibration for E85 compared to E0 included a higher rpm (1615 rpm vs 1426 rpm), higher air mass flow (3.3 lb/min vs 2.5 lb/min [1.5 kg/min vs 1.1 kg/min]) and more aggressive spark retard (7 deg. ATDC vs 1 deg. ATDC). In contrast, during the warm-start period of phase 3, the control strategy senses the warmed-up state of the engine and catalyst and does not call for these calibration adjustments; thus there was no significant dependence of the engine-out and catalyst midbed temperatures on ethanol content in phase 3 (Figure 2). Calibration strategies can also yield the opposite temperature trend during cold

starting, with lower temperatures for higher ethanol content, if the emissions target (e.g., SULEV) requires such heat flux-generating actions even for E0 fuel.<sup>19</sup>

During the remainder of phases 1 and 3 (after 60 s) and during phase 2, higher ethanol content in the fuel resulted in lower engine-out temperatures and lower catalyst temperatures (SI Figure S2) in part due to the greater HoV and lower adiabatic flame temperature with ethanol.<sup>9</sup> The lower engine-out temperatures are somewhat representative of the peak combustion temperatures which affect engine-out emissions. Despite the observed differences in engine-out temperatures, the average catalyst temperatures with each fuel were well above that needed to achieve good conversion efficiency of organic compounds and NO<sub>x</sub> as described below.

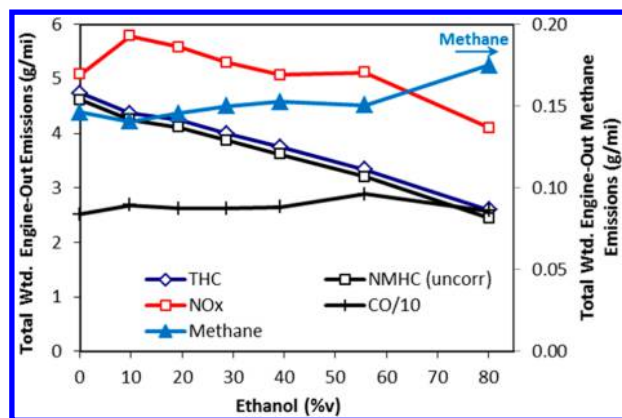
**3.2. Emissions.** Total weighted tailpipe emissions over the full FTP-75 cycle are shown in Figure 3 for various measures of



**Figure 3.** FTP cycle-weighted tailpipe emissions of THC, NMHC (both uncorrected and corrected to exclude oxygenates), NMOG, CH<sub>4</sub>, ethanol, and acetaldehyde.

organic compounds, including THC, CH<sub>4</sub>, corrected NMHC, NMOG, ethanol, and acetaldehyde. Each data point represents the average of three or four complete emissions tests. Most (80–90%) of the NMHC and NMOG emissions come in phase 1, the cold start phase, when the engine and catalyst are heating up. The emissions of THC and NMOG exhibit a clear minimum around E20–E40, 25–35% lower than for E0 and E80. This behavior is the result of two counteracting trends with increasing ethanol content, namely a decrease in hydrocarbon emissions and an increase in emissions of oxygenated compounds and methane. Emissions of unburned ethanol increase with increasing ethanol content as do acetaldehyde and formaldehyde (partial oxidation products of ethanol) particularly for the two highest ethanol content fuels (E55 and E80), see Figure 3 and SI Figure S3. The same trend is seen for methane emissions as it is formed from the decomposition of acetaldehyde over Rh catalysts used for NO<sub>x</sub> control.<sup>20</sup> Conversely, emissions of unburned hydrocarbons (oxygenate-corrected NMHC) decrease rapidly with ethanol content up to E30 and then decrease slightly for higher ethanol content. The sum of these emissions components, measured as both THC and NMOG, each yield a minimum around E20–E40 because these two trends counteract and the NMHC, ethanol, acetaldehyde, and CH<sub>4</sub> emissions increase more rapidly as they approach the extremes (E0 and E80).

The trend in tailpipe emissions of NMHC (uncorrected) shown in Figure 3 reflects changes in engine-out emissions shown in Figure 4. Engine-out NMHC (uncorrected) emissions decreased roughly linearly with ethanol content.



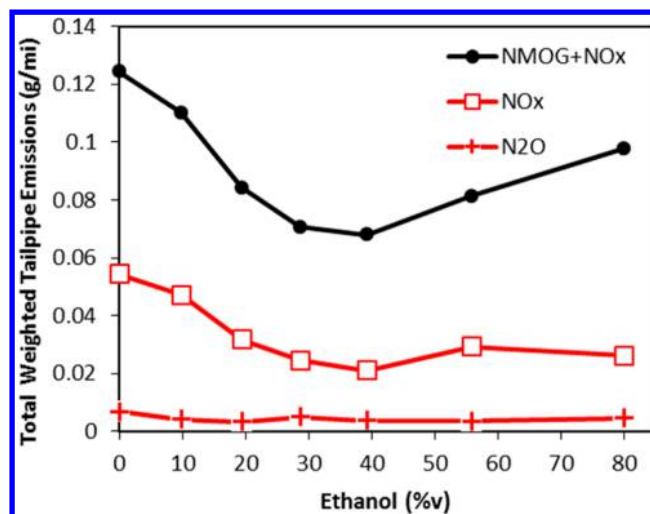
**Figure 4.** FTP cycle-weighted engine-out emissions of THC, NMHC (uncorrected),  $\text{NO}_x$ , CO, and  $\text{CH}_4$ . Carbon monoxide data are divided by 10 to allow it to be shown with the other data.

The slope of the decline is consistent with the fact that unburned fuel is the single largest contributor to engine-out emissions and the approximately 40% lower response of the FID to ethanol than to gasoline hydrocarbons.<sup>21</sup> Engine-out exhaust was not analyzed for oxygenates, thus corrected NMHC and NMOG could not be determined. The catalyst exhibited roughly constant conversion efficiency for uncorrected NMHC across all fuels for each phase and in the weighted total. Engine-out  $\text{CH}_4$  emissions were constant or slightly increasing from E0 through E55 followed by an approximately 15% increase for E85 (Figure 4) in all test phases. Note that this study was conducted with a PFI engine. Direct injection with multiple injections per combustion cycle can further reduce cold-start engine-out emissions, particularly with higher ethanol-content blends.<sup>9</sup>

There was a more pronounced trend in tailpipe emissions of  $\text{CH}_4$  (Figure 3) which reflects some decomposition of acetaldehyde to give  $\text{CH}_4$  and CO over Rh-containing catalysts.<sup>20</sup> It should be noted that even in the presence of ethanol and acetaldehyde in the exhaust the net effect of the catalyst is still to remove  $\text{CH}_4$  from the exhaust stream although the net efficiency decreases with increasing ethanol fuel content (SI Figure S4) especially in phase 1. Tailpipe ethene (SI Figure S5) emissions showed no discernible trend with ethanol content and were much lower than methane, consistent with effective ethene removal by the catalyst.<sup>22</sup>

There was little or no discernible trend of engine-out or tailpipe CO emissions with ethanol content (Figure 4 and SI Figure S6, respectively). The CO emissions by phase and corresponding catalyst efficiencies are shown in SI Figures S6–S8.

As shown in Figure 5, tailpipe emissions of  $\text{NO}_x$  were highest with E0 gasoline, decreased by approximately 50% as ethanol content increased to E20, and were essentially unchanged from E20 through E80. Engine-out  $\text{NO}_x$  emissions (Figure 4) did not change substantially from E0 to E55 and were approximately 20% lower for E80. The decrease in tailpipe  $\text{NO}_x$  emissions from E0 to E20 (Figure 5) reflects improved catalyst performance resulting from the more rapid warming to normal operating temperature (SI Figure S1). The efficiency of the catalyst in removing  $\text{NO}_x$  was lowest for E0, higher for E10, and highest for E20–E55, both as weighted totals and for each of phases 1, 2, and 3 (SI Figure S9). Conversion efficiency of  $\text{NO}_x$  by the catalyst with E80 was similar to that for E20–E55 in phase 1, but somewhat lower in phases 2 and 3, and



**Figure 5.** FTP cycle-weighted tailpipe emissions of  $\text{N}_2\text{O}$ ,  $\text{NO}_x$ , and the sum of NMOG and  $\text{NO}_x$ .

consequently also lower as the weighted total. Tailpipe emissions of  $\text{N}_2\text{O}$  (Figure 5 and SI Figure S10) showed no discernible trend while ammonia emissions (SI Figure S11) increased with ethanol content in the fuel.

The new California LEVIII emission regulations beginning in MY2014 have a combined NMOG and  $\text{NO}_x$  standard consisting of their sum on a g/mile basis. The sum of NMOG and  $\text{NO}_x$  tailpipe emissions are shown in Figure 5. As with these emissions individually, the sum of NMOG and  $\text{NO}_x$  emissions decreases from E0 to E20, with a minimum in the E20 to E55 range, and moderately higher for E80.

The majority (70–90%) of the weighted tailpipe emissions of NMOG, corrected NMHC and CO were from phase 1. Approximately 50% of  $\text{CH}_4$  and  $\text{NO}_x$  emissions occur in phase 1 with approximately 20–30% contributions from both phases 2 and 3. The importance of phase 1 reflects the cold-start of the engine and lower efficiency of the catalyst system during the time to warm and reach its optimal operating efficiency.

Greenhouse gas emissions from light-duty vehicles include  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2\text{O}$ , with the majority being  $\text{CO}_2$ . Tailpipe  $\text{CO}_2$  emissions were lower with higher ethanol content (SI Figure S12) ranging from approximately 490 to 450  $\text{gCO}_2/\text{mile}$  for E10 and E80, respectively, because the fuel carbon content (g carbon/MJ) and the vehicle fuel efficiency (MJ/mile, discussed below) change with increasing ethanol content. Tailpipe  $\text{CH}_4$  emissions (Figure 3) increased slowly from E0 to E40 and more significantly to E80, with  $\text{CO}_{2\text{eq}}$  emission values ranging from 0.3  $\text{gCO}_{2\text{eq}}/\text{mile}$  for E10 to 1.1  $\text{gCO}_{2\text{eq}}/\text{mile}$  for E80, calculated using a global warming potential of 25 for  $\text{CH}_4$ . Tailpipe emissions of  $\text{N}_2\text{O}$  (Figure 5) ranged from 3.4 to 6.9  $\text{mgN}_2\text{O}/\text{mile}$  or 1.0 to 2.0  $\text{gCO}_{2\text{eq}}/\text{mile}$ , using a global warming potential of 298 for  $\text{N}_2\text{O}$ . On a  $\text{CO}_2$ -equivalent basis,  $\text{CH}_4$  and  $\text{N}_2\text{O}$  were 0.3–0.5% of  $\text{CO}_2$  emissions.

Although emissions were the focus of this study, the volumetric fuel economy (defined here in miles per gallon) was also measured (SI Figure S13). As compared to E0, use of the midlevel blends (E20–E40) resulted in a 5–10% reduction in volumetric fuel economy, while use of E55 and E80 resulted in 15 and 25% decreases in fuel economy, respectively. As shown in SI Figure S13, these changes are 3–8 percentage points less (better) than would be predicted based on the fuel NHVs, with the improvement attributed to the HoV impact on

NHV, greater knock resistance, and nonknock limited thermodynamic efficiency improvements.<sup>10</sup>

## 4. DISCUSSION

A large body of data is presented concerning the impact of ethanol blend level on emissions from a 2006 MY FFV. The present work has two novel features. First, the number of blends investigated is approximately a factor of 2 larger than in any previous study and provides for a more detailed picture of the effect of ethanol blend level on emissions. Second, data are reported for engine-out emissions and tailpipe emissions, operating temperatures (engine-out and catalyst), and ethanol concentrations used in the engine control strategy. Comparison of these data allows for differentiation between fuel chemistry and engine calibration effects as discussed below.

**4.1. Importance of Fuel Chemistry and Engine Calibration for Tailpipe Emissions.** Increased ethanol content in the fuel affects the emissions from FFVs via two general mechanisms: fuel chemistry and engine calibration. The chemistry of a fuel impacts the emissions from an engine, with the most obvious example being unburned or partially burned fuel which is a major component of engine exhaust. Engine-out exhaust contains typically 1–3% unburned or partially burned organic fuel components. The emissions control system then removes 95–99% of these organic compounds.<sup>23</sup> The general trend of increased ethanol and acetaldehyde emissions, and decreased NMHC emissions, with increased ethanol blend level shown in Figure 3 is expected based on the dominant role of fuel chemistry in determining the tailpipe emissions of these species. On the other hand, comparison of the NO<sub>x</sub> data in Figures 4 and 5 shows the dominant role of engine calibration on the tailpipe emissions of NO<sub>x</sub>. Upon sensing greater ethanol content in the fuel, the calibration prescribed different engine operating conditions that yielded higher engine-out and catalyst temperatures during the critical cold-start period of phase 1 (Figure 1) which improved the NO<sub>x</sub> conversion efficiency of the exhaust after-treatment system (SI Figure S9). As discussed in Section 3.2, there is a pronounced minimum of THC and NMOG emissions for midlevel blends (Figure 3) reflecting the combined impact of fuel chemistry and engine calibration effects.

It is important to recognize the importance of both fuel chemistry and engine calibration in determining tailpipe emissions and to consider the fuel and vehicle together as a system. There are important differences in the nature of the fuel chemistry and engine calibration effects. The fuel chemistry effect is fundamental and the same qualitative emissions trend of increased ethanol, acetaldehyde, and CH<sub>4</sub> emissions and decreased NMHC emissions will be seen for all FFVs from all manufacturers. In contrast, the impacts of engine calibration on emissions depend on the calibration strategy and will be specific for specific vehicle models. Different manufacturers adopt different strategies and even the same manufacturer can adopt different strategies for different models. Hence, in contrast to the situation for NMHC, ethanol, acetaldehyde, and CH<sub>4</sub>, it is not possible to make general statements regarding the effect of fuel ethanol content on tailpipe emissions of NO<sub>x</sub>, THC, and NMOG for the current or future FFV fleet based on testing of a small number of existing vehicle models. The effect of fuel ethanol content on NO<sub>x</sub>, THC, and NMOG emissions for different vehicle models is *not* predictable without detailed information on engine calibrations of each model.

**4.2. Comparison with Previous Measurements of FFV Emissions.** Published studies of the impact of midlevel ethanol blends on tailpipe emissions from FFVs are relatively limited in number.<sup>13–16</sup> Haskew and Liberty<sup>15</sup> investigated the emissions from one 2006-MY and six 2007-MY FFVs using E6, E32, E59, and E85 on the FTP, US06, and LA92 cycles. The average NMHC, NMOG, CO, and NO<sub>x</sub> emissions did not exhibit an emissions trend with increasing ethanol content, with the exception of trends of decreasing NMHC and NMOG for the US06 cycle.<sup>15</sup> Karavalakis et al.<sup>13</sup> studied the emissions from a 2007-MY FFV using E10, E20, E50, and E85 fuel on the FTP cycle. They reported that there were no statistically significant trends of CO or NO<sub>x</sub> emissions with ethanol content, and that THC and NMHC increased for E85 but not for the lower blends.

Yassine and La Pan<sup>16</sup> reported decreases in emissions of THC, NMOG, CO, and NO<sub>x</sub> of 58%, 42%, 83%, and 60%, respectively, for E20 compared to E0 fuel in a 2006-MY FFV over the FTP cycle. Yanowitz et al.<sup>15</sup> investigated the emissions from 9 FFVs (model years 2002 to 2011) over the LA92 test cycle immediately after refueling with E40, having been previously adapted to E10 or E76. Average decreases in emissions of NMOG, CO, and NO<sub>x</sub> of 5%, 10%, and 8%, respectively, were reported for E40 compared to and after running on E10 fuel.<sup>14</sup>

In the present work, tailpipe emissions were measured from a 2006-MY Mercury Grand Marquis FFV fueled with E0, E10, E20, E30, E40, E55, and E80 while driven on the FTP cycle. With increasing ethanol content, the tailpipe emissions of acetaldehyde, ethanol, and methane increased, NO<sub>x</sub> and NMHC decreased, and there was no discernible effect on CO emissions. NMOG and THC emissions displayed a pronounced minimum with midlevel (E20–E40) ethanol blends that was 30–35% lower than for E0 or E80. Emissions of NO<sub>x</sub> decreased by approximately 70% as the ethanol content increased from E0 to E20–E40, with no further decrease seen with E55 or E80. As concluded in the previous section, the dependence of NO<sub>x</sub>, THC, and NMOG emissions on ethanol content is largely determined by the engine calibration and will thus vary for different vehicle models. The large scatter in different trends in the emissions of these gases reported in the literature probably reflects different engine calibration strategies for different vehicle models. The report by Karavalakis et al.<sup>13</sup> of increased NMHC emissions for E85 is inconsistent with the reports from all other studies (including the present) and is difficult to explain.

**4.3. Air Quality Implications of Increased Ethanol Use in FFVs.** Jacobson,<sup>24</sup> Cook et al.,<sup>25</sup> and Nopmongcol et al.<sup>26</sup> have conducted three-dimensional atmospheric modeling of the ozone and PM impacts of E85-fueled FFVs in the U.S. Jacobson<sup>24</sup> found that increased use of E85 increased ozone formation in urban centers such as Los Angeles but decreased ozone levels in the southeastern U.S. and in areas distant from large urban centers. Cook et al.<sup>25</sup> found that increased E85 and E10 use would adversely impact ozone levels over much of the U.S. but would decrease ozone levels over a few highly populated areas which currently have poor air quality; essentially the opposite reported by Jacobson.<sup>24</sup> Nopmongcol et al.<sup>26</sup> found that the adoption of E85 caused a negligible change in average ozone and PM concentrations in all states modeled. While the atmospheric models employed in the studies are sophisticated and there are many differences in the

models and inputs used, a key difference was the assumption regarding vehicle NO<sub>x</sub> emissions.

Formation of ozone requires the presence of NO<sub>x</sub>, organic compounds, and sunlight. The chemistry responsible for the formation of ozone in polluted air masses is complex and nonlinear. Over the majority of the U.S., a decrease in NO<sub>x</sub> emissions will lead to decreased ozone. However, contrary to intuition, in highly polluted urban areas (e.g., Los Angeles), a decrease in the emission of NO<sub>x</sub> can actually lead to increased ozone levels (with high NO<sub>x</sub> the titration reaction of NO with ozone becomes significant).<sup>27</sup> Jacobson<sup>24</sup> assumed a 30% decrease in NO<sub>x</sub> emissions for E85 compared to gasoline vehicles. Cook et al.<sup>25</sup> assumed that there was no change in NO<sub>x</sub> emissions for E85 versus gasoline vehicles but that NO<sub>x</sub> emissions were increased by more than 7% for E10 vehicles, resulting in a total NO<sub>x</sub> emissions increase for the total fleet of 3.2% in their ethanol scenario. Nopmongcol et al.<sup>26</sup> argued that dedicated E85 vehicles will have to meet the same emissions regulations as conventional vehicles and hence assumed equal tailpipe NO<sub>x</sub> emissions, but considered the impact of emissions changes associated with ethanol production and distribution and found that there was a negligible impact on ozone and PM. The results from Jacobson<sup>24</sup> and Cook et al.<sup>25</sup> illustrate the challenges in addressing ozone where, in the absence of reductions in emissions of organic compounds, changes in NO<sub>x</sub> emissions can have opposite impacts in different locations.

To reduce ozone levels in highly polluted urban areas generally requires reduction of the emissions of both NO<sub>x</sub> and organic compounds. The past four decades have seen remarkable reductions in the emissions of NO<sub>x</sub> and VOC from vehicles which have led to large decreases in ozone and PM<sub>2.5</sub> in urban areas in the U.S.<sup>28</sup> From 1970 to 2005 the emissions of NO<sub>x</sub> and VOC from the on-road gasoline fleet in the U.S. decreased by 71% and 76%, respectively, despite an approximately 3-fold increase in vehicle miles traveled.<sup>29</sup> Irrespective of ethanol blend level, the effect of increasingly stringent emission standards and vehicle fleet turnover is that emissions of NO<sub>x</sub> and NMOG from the on-road FFV fleet will continue to decrease substantially in the future. A secondary question is whether this decrease would be slightly enhanced, or slightly degraded, as a result of the use of fuel with increased ethanol content in the on-road FFV fleet. It is not possible to provide a definitive answer to this question, but two points are worthy of note. First, any such effect will be small compared to the larger trend driven by emission regulations and fleet turn over noted above. Second, the minimum in NO<sub>x</sub> and NMOG emissions for midlevel ethanol blends for the FFV tested in the present work (Figure 3) points to future opportunities for emission reductions from FFVs.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Further details on the test vehicle and aftertreatment system, the test facility and protocol, additional emissions data, fuel consumption data, air quality implications for increased ethanol use in FFVs, engine-out and catalyst temperatures, conversion efficiencies and bag-by-bag emissions for certain emissions, and tabulated emissions data used in the figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Notes

The authors declare no competing financial interest.

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