

AIR QUALITY AND ETHANOL IN GASOLINE

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Ethanol in gasoline can favorably impact mobile source emissions in five main air quality areas: these areas are fine particulate matter (e.g., PM_{2.5}), carbon monoxide, toxics, ozone, and global warming. In this era of credit trading and with new data there is always a lot to do to integrate these air quality areas with respect to ethanol. For example, ethanol currently is the only compound that can be blended with gasoline to help reduce global warming; yet there is no program in place to offer any credit in this area. Below a brief overview the current situation in the other four air quality areas impacted by ethanol.

PM_{2.5}

Fine particulates can be emitted directly from vehicles (primary PM_{2.5}) or formed in the atmosphere (secondary PM_{2.5}). Ethanol can help on both fronts. Oxygen in the fuel has been shown to reduce primary exhaust particulate from cars (Mulawa et al., 1997, and Colorado, 1999) while raising aromatics has been found to increase PM (Graskow et al., 1998). The Colorado study suggests that with 3.5 percent oxygen, the PM reduction at 35F is 36 percent for the normal fleet and 64.6 percent for the high emitters studied. If the PM inventory is 50 percent from high emitters, the reduction in PM for 3.5 percent oxygen is estimated to be 50.3 percent. Since both ethanol and aromatics add octane, it can be expected that using ethanol in place of aromatics for octane would reduce primary PM_{2.5} emissions even more than had been seen in the Colorado (1999) study. Mulawa et al. (1997) also showed that PM reductions were observed from -20F to 75F and an analysis of all available data suggests the oxygen effect is proportional to the PM emission and independent of temperature.

The formation of secondary PM_{2.5} is a very complicated process currently being studied by several scientists. One notable result published by Odum et al (1997) from Caltech showed that the organic fraction of secondary PM_{2.5}, attributable to gasoline in the atmosphere could be completely accounted for by the aromatics content of the gasoline. In fact, the EPA's REMSAD model for particulates and the Caltech secondary organic aerosol model (see Griffin et al, 1999) now assume that all anthropogenic PM comes solely from aromatic compounds. Hence, the use of ethanol in place of aromatics can be expected to reduce secondary PM_{2.5} as well.

CO

Many studies have shown that the oxygen in ethanol leads to a significant reduction in mobile carbon monoxide (CO) emissions. The OSTP (1997) study notes that vehicle CO emissions are reduced from 2 to 10 percent per percent oxygen in the fuel. Moreover, emissions inventories of CO consistently show that the mobile contribution, especially in troublesome urban areas, is often as high as 90 percent. A statistical analysis of ambient CO concentrations in areas using oxyfuels indicates that these fuels appear to reduce local CO by an average of 14 percent nationally (See Whitten and Cohen, 1996).

Carbon monoxide is a major ozone precursor (National Academy, 1999). New studies (Carter et al., 2003, and Whitten, 1999 and 2001) have shown that CO can be equivalent to 25 to 50 percent of the mobile-related contribution from volatile organic compounds (VOC). A significant reduction in CO emissions is provided by the high oxygen content of ethanol. The California reformulated gasoline program does give some credit for VOC reduction due to CO from high oxygen ethanol. However, the California regulations have yet to account for new studies on CO high ozone-forming potential (e.g. Carter et al., 2003) and data that show substantial CO reduction from ethanol in new cars (Alliance, 2001). Likewise, with the partial exception of the Chicago-Milwaukee area, the federal EPA has not given any credit to ethanol as shown by these new studies. Moreover, the EPA has yet to recognize the data on new cars for its MOBILE6 emissions model.

Other studies also show that the formation of combustion chamber deposits (CCD) are strongly associated with high-boiling aromatic compounds in gasoline (See Choate and Edwards, 1993, and Price et al, 1995). Bitting et al, 1994, showed by cleaning the CCD's that emissions (of CO, hydrocarbons and NOx) seen to increase with mileage were mainly associated with CCD buildup. Ethanol should be effective in reducing CCD's when substituted for aromatics, but data is needed to show this.

Some interesting points to the oxyfuel issue are first that the impact of oxyfuels appears to be the greatest on the higher-emitting vehicles (See Mayotte et al, 1994), which can account for more than half the overall gasoline-related emissions. Pokharel et al (2001) found that 10 percent of the automobiles in the Los Angeles accounted for 73 percent of the on-road CO emissions. Second, the effect of fuel oxygen may often be more on improving catalyst efficiency (See Reuter et al, 1992) rather than just enleanment of the mixture as some have postulated. The Reuter et al. (1992) study showed that engine-out CO emissions were not significantly affected by fuel oxygen, but the tailpipe (i.e. after the catalyst) emissions were very much reduced. Assuming that ethanol improves catalyst performance is more consistent with not only the engine out versus tailpipe data, but the latest data as well (Alliance et al, 2001) that shows new cars still reducing CO in spite of having "improved" mixture control that would be expected to eliminate any enleanment from using ethanol.

Toxics

Benzene appears to be the most significant toxic compound emitted from vehicles. The EPA Complex Model indicates that benzene emissions account for nearly 70 percent of the total toxic emissions from vehicles using conventional gasoline and that exhaust benzene accounts for nearly 90 percent of the total benzene. The EPA Complex Model indicates that a 10 percent ethanol blend can reduce benzene by 25 percent compared to conventional gasoline.

In addition to a 25 percent benzene reduction, the use of 10 percent ethanol is shown by the EPA Complex Model to reduce total toxic mass emissions by 13 percent. However, the California Air Resources Board recommends that toxic mass emissions be adjusted to account for the individual potency of the toxic compounds involved. When the California potency factors are applied to the EPA Complex Model results for splash blending 10 percent ethanol into conventional gasoline the total toxics risk is predicted to be reduced by 21 percent instead of the mass-only 13 percent reduction noted above.

There are three reasons that combine to explain why adding only 10 percent ethanol to gasoline might reduce toxic benzene emissions by 25 percent or more. First, of course, there is the

dilution that occurs when ethanol is added. Second, the high octane value of ethanol allows the oil refineries to scale back on all aromatics to keep octane within the same grade of gasoline. The Caldecott tunnel study by Kirchstetter et al (1996) showed quite clearly that essentially all aromatics were, in fact, scaled back by at least 20 percent when an oxyfuel program in California went into place using only 2 percent oxygen by weight. Neither benzene itself nor aromatics in general were regulated as part of the California winter oxyfuel program in 1994. Benzene is an intermediate combustion product of other aromatics. That is, reducing aromatics alone will reduce a large fraction of the benzene exhaust emissions. And as noted below, exhaust benzene typically makes up about 90 percent of total benzene emissions (even during the summer months). The third, reason why benzene can be reduced from using ethanol is the oxygen that helps reduce all organic emissions. In summary, the three reasons why only 10 percent ethanol can reduce benzene by as much as 25 percent are based on the dilution, the octane and the oxygen provided by ethanol.

Ozone

Urban ozone formation occurs from rather complex photochemistry mainly from volatile organic compounds (VOC) and CO in the presence of nitrogen oxides (NO_x). The role that ethanol can play in an urban ozone abatement program has been the subject of several studies (See Whitten and Greenfield, 1993). Typically, ethanol blends have been considered “neutral” towards summer ozone formation when used in conventional gasoline with a 1 psi waiver in RVP volatility. This “neutrality” stems from the ability of the oxygen in ethanol to reduce carbon monoxide (CO) emissions (which are an ozone precursor) that compensate for the increased volatile organic compound (VOC) emissions due to the waiver. In reformulated gasoline (RFG) the role of ethanol is more complex due to the fact that fuel oxygen content is only one of several fuel properties considered. Also the regulations supporting RFG tend not to account for high emitters, aggressive driving, combustion chamber deposits, off-road engines, and carbon monoxide reactivity, which are areas that ethanol (with its high oxygen content) has shown advantages.

One experimental study by Mayotte et al (1994) shows that ethanol significantly reduces exhaust VOC and CO emissions compared to an equal volume of MTBE, where both oxygenates were blended to essentially the same base clear gasoline. The NO_x emissions were found in that study to not be significantly different between the two oxygenates. The extra VOC and CO reductions seen in the Mayotte et al (1994) study that could be credited to the use of ethanol were mainly due to the impact of ethanol on the higher emitting vehicles, which can account for more than half the overall gasoline-related emissions. A recent remote sensing study by Pokharel et al (2001) found that 10 percent of the vehicles in the Los Angeles area accounted for 78 percent of the on-road VOC emissions. A 1998 study of 12 vehicles by the California Air Resources Board (ARB) failed to include any higher emitting vehicles, but it did include tests involving heavy acceleration. The combined ARB tests that accounted for heavy acceleration show that even for normal-emitting vehicles CO was reduced about 10 percent due to the extra 1.5 percent fuel oxygen between 11 volume percent MTBE (i.e., 2 percent fuel oxygen) and 10 percent ethanol (i.e., 3.5 percent fuel oxygen). There is evidence showing that reformulated gasoline made with 10 percent ethanol could have a similar impact on ozone formation to that expected from the use of a reformulated gasoline made from the same clear base gasoline blended with 11 percent MTBE. In this regard, when heavy acceleration, higher-emitting vehicles, and off-road engines

are accounted for, the extra exhaust reductions of the ethanol blend would at least mitigate, if not compensate, for the additional evaporative emissions due to ethanol.

Long Term Impacts

First, Bitting et al (1994) as noted above found that combustion chamber deposits (CCD) are associated with long term emissions increases of CO, NO_x, and hydrocarbons. Bitting et al (1994) further showed that removal of CCD's at high mileage can restore emissions to low-mileage levels. Second, Choate and Edwards (1993) and Price et al (1995) have shown that these CCD's are strongly associated with high-boiling aromatic compounds in gasoline. Hence, it now appears that reformulated gasoline containing oxygenates in place of aromatics may be preventing some CCD build-up and, in turn, leading to long term *de facto* emissions reductions previously not accounted for in the more or less instantaneous effects of reformulated gasoline tested to date such as used in the Complex and Predictive Models. More studies of these effects are needed.

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