AIR QUALITY AND ETHANOL IN GASOLINE

By

Gary Z. Whitten, Ph.D.
Smog Reyes

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 (NOx). 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 NOx 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.

References

Alliance, AIAM, Honda, (2001) "Industry Low Sulfur Test Program", presented at ARB Workshop, 7/2001. Available at http://www.arb.ca.gov/fuels/gasoline/meeting/2001/071201AAPrstn.pdf

Bitting, W.H., G.P. Firmstone and C.T. Keller (1994) "Effects of Combustion Chamber Deposits on Tailpipe Emissions" SAE Paper No. 940345.

Choate, P.J. and J.C. Edwards (1993) "Relationship Between Combustion Chamber Deposits, Fuel Composition, and Combustion Chamber Deposit Structure" SAE Paper No. 932812.

Carter W.P.L., G. Tonnessen, and G. Yarwood (2003) "Investigation of Reactivity Effects Using Existing Air Quality Models" Report to the American Chemistry Council (available at http://pah.cert.ucr.edu/~carter/RRWG/index.htm).

Colorado Department of Public Health and Environment, (1999) "The Impact of a 10% Ethanol Blended Fuel on the Exhaust Emissions of Tier 0 and Tier 1 Light Duty Gasoline Vehicles at 35F".

Graskow, B.R., D.B. Kittelson, I.S. Abdul-Khalek, M.R. Ahmadi, and J.E. Morris (1998) "Characterization of Exhaust Particulate Emissions from a Spark Ignition Engine" SAE Paper No. 980528.

Griffin, R.J., D.R.Cocker, and J.H. Seinfeld (1999) "Incremental Aerosol Reactivity: Application to Aromatic and Biogenic Hydrocarbons," *Environmental Science & Technology*, Vol. 33, pp 2403-2408.

Kirchstetter, T.W., B.C. Singer, R.A. Harley, G.R. Kendall and W. Chan (1996) "Impact of Oxygenated Gasoline Use on California Light-Duty Vehicle Emissions" *Environmental Science & Technology*, Vol. 30, pp 661-670.

Mayotte, S. C., C.E. Lindhjem, V. Rao and M.S. Sklar (1994) "Reformulated Gasoline Effects on Exhaust Emissions: Phase I: Initial Investigation of Oxygenate, Volatility, Distillation and Sulfur Effects" SAE Paper No. 941973.

Mulawa P., Cadle, S., Knapp, K., Zweidinger, R., Snow, R., Lucas, R., Goldbach,J., (1997) "Effect of Ambient Temperature and E-10 Fuel on Primary Exhaust Particulate Matter from light Duty Vehicles.", *Environmental Science and technology*, Vol 31, pp 1302-1307.

National Academy, 1999, Ozone-Forming Potential of Reformulated Gasoline, National Academy Press.

OSTP (1997) "Interagency Assessment of Oxygenated Fuels," Office of Science and Technology Policy, Executive Office of the President, Washington, D.C.

Odum, J.R., T.P.W.Jungkamp, R.J.Griffin, R.C. Flagan and J.H. Seinfeld (1997) "The Atmospheric Aerosol-Forming Potential of Whole Gasoline Vapor" *Science*, Vol. 276, pp 96-99.

Pokharel, S.S., G.A. Bishop, and D.H. Stedman (2001) "On-Road Remote Sensing of Automobile Emissions in the Los Angeles Area: Year 2" Univ. of Denver final report to the Coordinating Research Council, Inc., available at www.crcao.com.

Price, R.J., J.P.T. Wilkinson, D.A.J. Jones, and C. Morley (1995) "A Laboratory Simulation and Mechanism for the Fuel Dependence of SI Combustion Chamber Deposit Formation" SAE Paper No. 952445.

Reuter, R.M., J.D. Benson, V.R. Burns, R.A. Gorse, A.M. Hochhauser, L.J. Painter, B.H. Rippon, and J.A. Rutherford (1992) "Effects of Oxygenated Fuels and RVP on Automotive Emissions – The Auto/Oil Air Quality Improvement Research Program" SAE Paper No. 920326.

Whitten, G.Z. (2001) "Recent UAM Simulations on the "Reactivity" of Carbon Monoxide," for Renewable Fuels Association, 2001.

Whitten, G.Z. (1999) "Potential Extra Air Quality Benefits from Oxygenates that are not Required to Meet Reformulated Gasoline Specifications," Paper presented at the 9th CRC On-Road Vehicle Emissions Workshop, San Diego, CA, April 19-21, 1999.

Whitten, G.Z., and J.P. Cohen (1996) "Regression Modeling of Oxyfuel Effects on Ambient CO Concentrations" Systems Applications Report No. 96/78, available at *www.epe.com/OMSWWW/fuels.html#oxyfuel*.

Whitten, G. Z. and S. M. Greenfield (1993) "Photochemical Grid Modeling Study Comparing Air Quality Impacts of Ethanol and MTBE as Alternate Oxygenates in Reformulated Gasoline", presented at the Tenth International Symposium on Alcohol Fuels, Colorado Springs, Colorado (7–10 November), full text available as SAI Final Report No. 93/083 for the Council of Great Lakes Governors, Chicago, Illinois.

Ethanol's Clean Air Impact

Latest Findings

Gary Z. Whitten, Ph.D.

Five Air Quality Areas

- Global Warming
- Fine Particulates
- Carbon Monoxide
- Toxics
- Ozone

Global Warming Gases

- Ethanol is the only gasoline component that can reduce GHG gases.
- Latest Argonne study (850,000 cars)
  - Carbon Dioxide
  - Methane (cows)

Fine Particulates: $PM_{2.5}$

- Studies show primary emissions reduced by 50 percent using 10 percent blends.
- Primary linked to aromatics which ethanol can replace.
- Primary linked to deposits, which are also linked to aromatics.
- Secondary organic formation linked to aromatics which ethanol can replace.

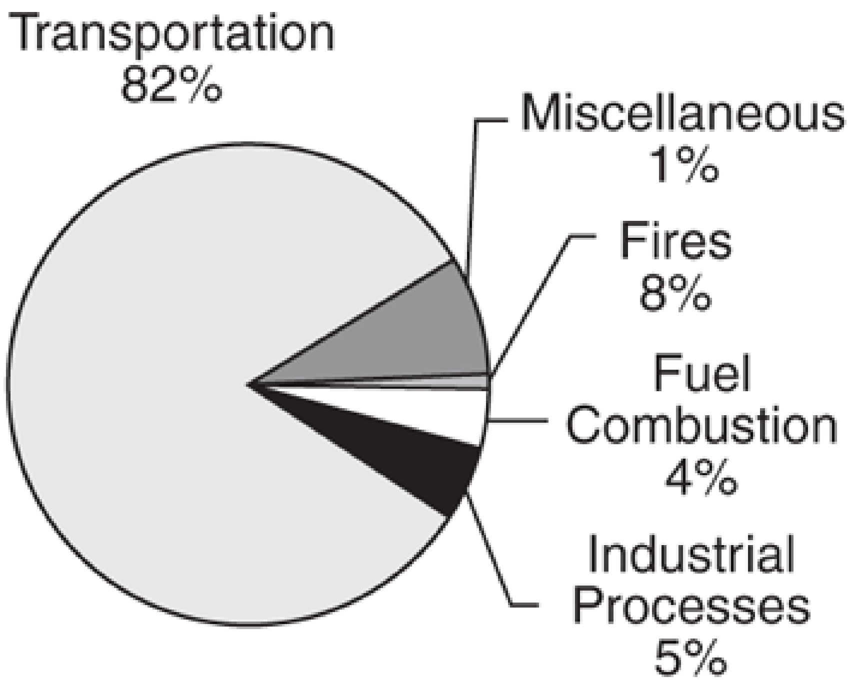
Toxics

- Main toxic is benzene.
  - Mainly from exhaust (90%)
  - Higher aromatics make benzene (65%)
- Ethanol reduces benzene.
  - Dilution
  - Substitution for aromatic octane
  - Cleaner combustion (especially high emitters)
- Acetaldehyde has low potency.
- 13% total mass reduced, 21% as potency

Carbon Monoxide

- Gas engines main source
- Ethanol significantly reduces emissions
  - Widely recognized
  - On-road 19 percent for high emitters
  - On-road normal emitters --- varies
  - Non-road 22 & 23 percent (4 & 2 stroke)
- Important ozone precursor
- Trends not so good

Figure 2-5. CO emissions by source category, 2002.



EPA Trends Report 2003
National CO Emissions (tons/yr)

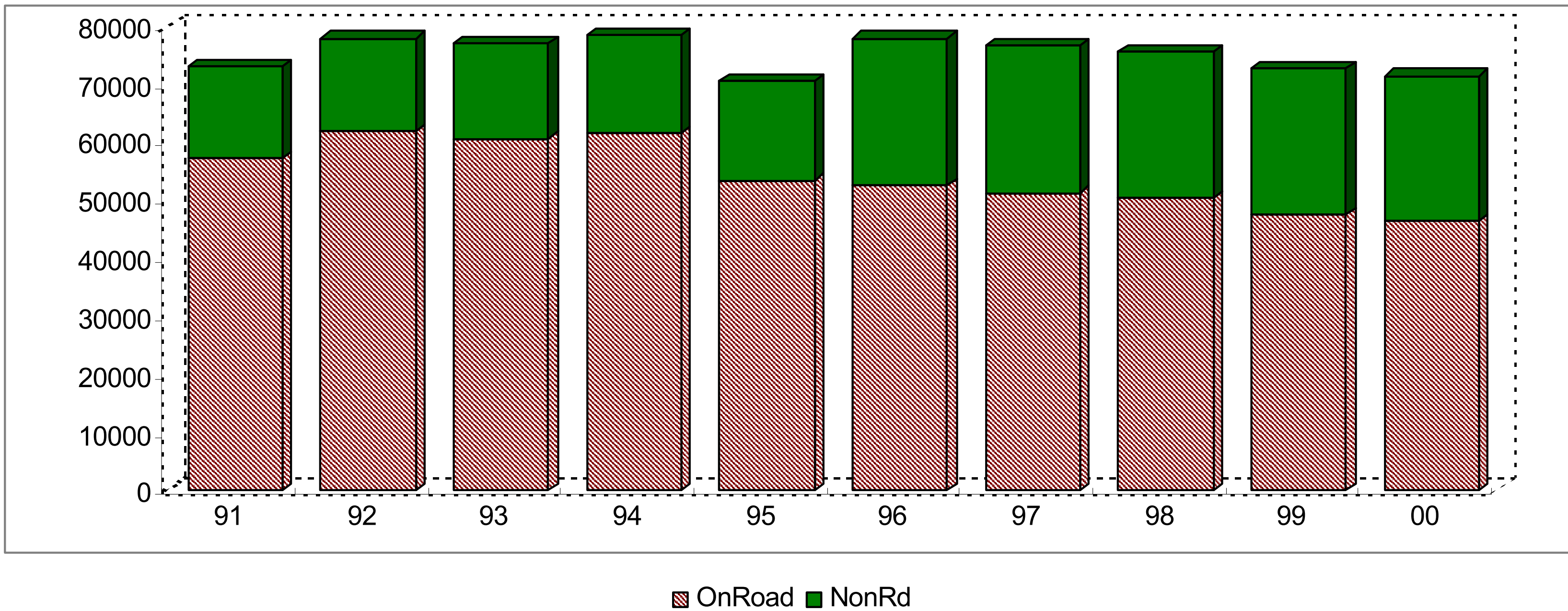
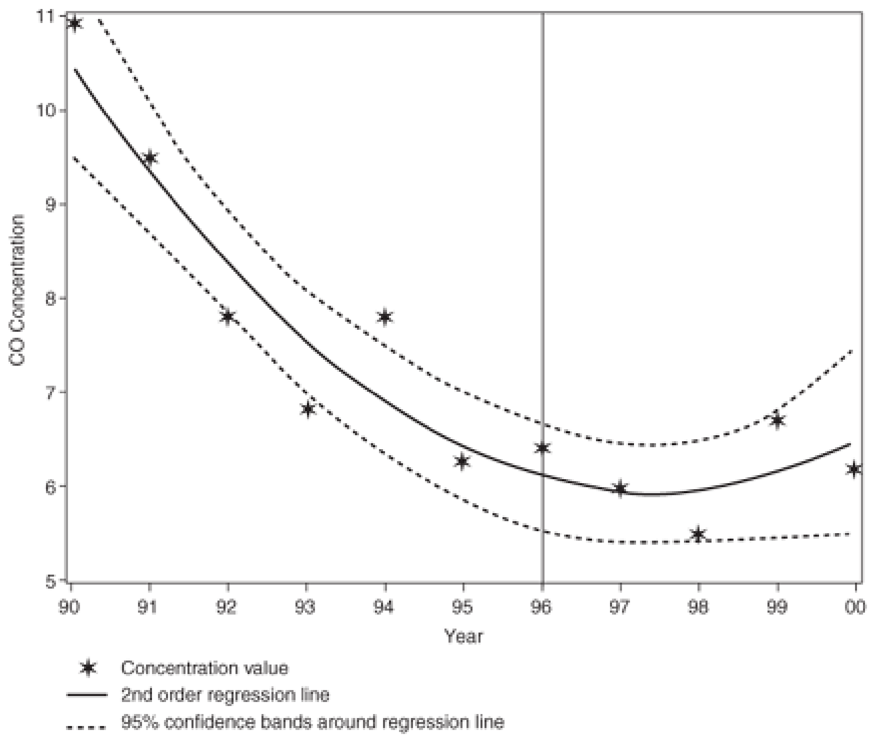
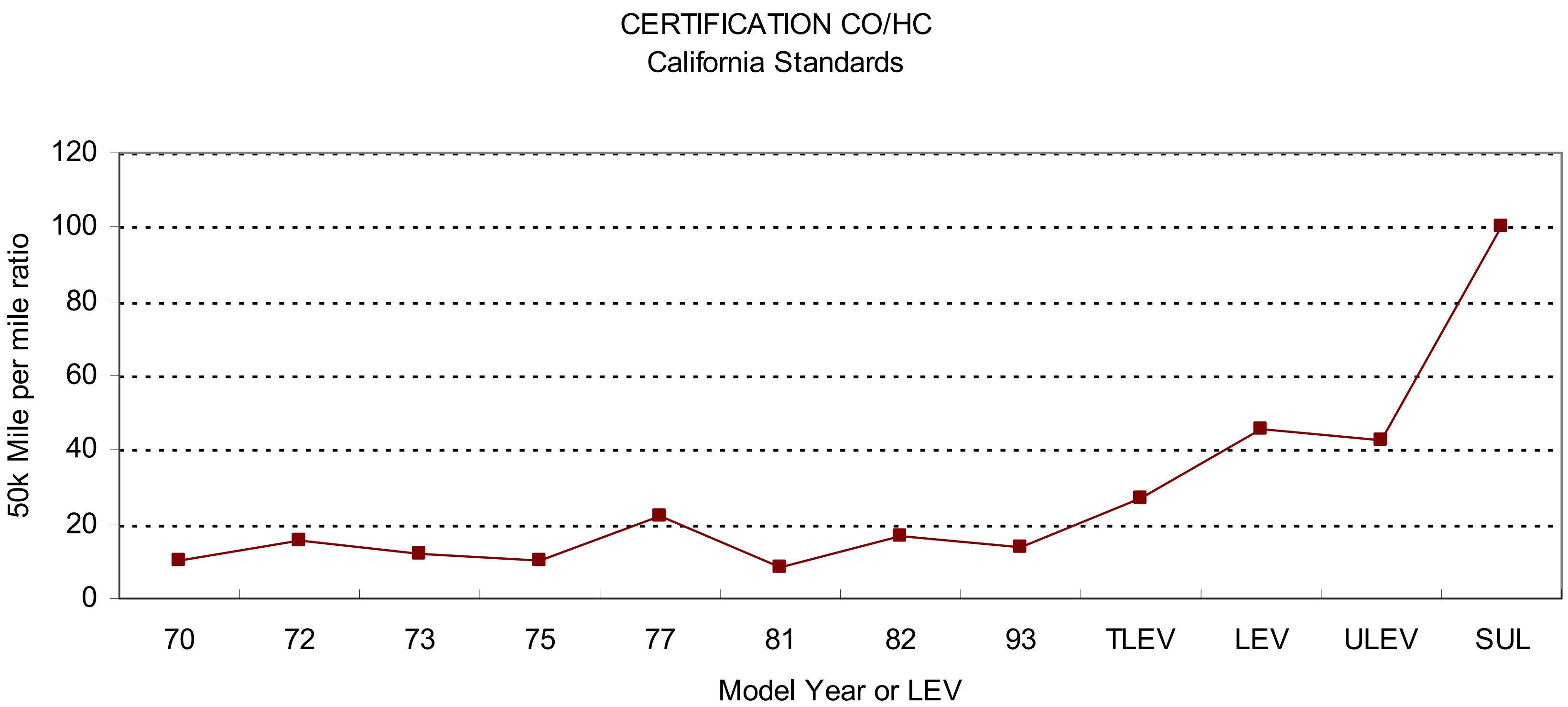


Figure 6. Example of a site with increasing trend in recent years. The vertical line indicates the year that the oxygenated gasoline requirement ended.





CERTIFICATION CO/HC
California Standards
50k Mile per mile ratio
120
100
80
60
40
20
0
70
72
73
75
77
81
82
93
TLEV
LEV
ULEV
SUL
Model Year or LEV

CO From Normal Emitters

- MOBILE6 and CARB use zero impact 1994 plus
  - Yet new data show nearly 30 percent impact from 10 percent ethanol blends
- EPA claims new car oxygen sensors negate impact
  - Air oxygen is not ethanol oxygen
  - Data show zero before but big after catalyst
  - Therefore ethanol seems to help catalyst

CO makes Smog

- In 1999 the National Academy noted that CO accounts for 20% of the combined impact of VOC and CO
- However, that NAS estimate used a simplistic 1-day box model.
- New studies using multi-day grid models show that CO can account for as much as 60%.
  - CO is one molecule, VOC represents many.

SMOG

- Conventional gasoline
  - 1 psi RVP waiver with 10 percent ethanol
    - Justified mainly by CO effect
  - MOBILE6 problems for ethanol
    - Uses zero CO impact for new ('94+) vehicles
      - New data show nearly 30 percent CO reduction
    - High RVP impact vs. little data
- Federal Reformulated Gasoline
  - Does not credit CO (except in Chicago-Milwaukee with 0.3 psi RVP credit)

SMOG –California RFG

- Regulatory model stops use of 10 percent ethanol blends
  - Due to predictions of high NOx emissions
    - Latest data showing low NOx not yet in model
      - Same study (on '94+ cars) as high CO effect
      - Current model assumes high NOx.
    - CARB model under-represents high emitters
      - Fed. Model uses separate high-emitter sub-model.
      - Such a sub-model approach for CaRFG has been shown to significantly reduce overall NOx predictions.

SMOG – California RFG

- CARB concerns about permeantion
  - Gives no CO debit (as a bonus for non-oxy)
  - Debit equal to 12.4 tons VOC (CARB model).
  - CARB now estimates permeation at 13 tons.
  - However, CARB model (like MOBILE6) gives no credit to ‘94+ cars and uses the same box model as NAS did.
  - Newer data and models show 19 to 56 tons VOC equivalent for CO debit.

Highlights to Remember

- Ethanol does not increase NOx as currently predicted by California model.
  - A new model formulation is needed with better high-emitter treatment and one that uses new data
  - This should allow use of 10 percent blends in CaRFG
- Carbon Monoxide is THE biggest single (and growing) contributor to ozone
  - New studies support more CO credit for ethanol
    - Ethanol seems to help the catalyst, not the A/F ratio