Evaporative Emissions Regulations Development

In-House Test Program
Report No. 3
Effect of Fuel Composition

by

Eric Ellsworth

Notice

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Contents

1. Introduction: This report will deal with the interrelationship of fuel characteristics and evaporative losses. The characteristics which we will try to correlate to evaporative losses are Reid Vapor Pressure (RVP), the shape of a fuel's distillation curve and weathering.

2. Summary and Conclusion: Evaluation of the effect on evaporative emission of RVP, distillation temperatures, and weathering has indicated that some general trends are present. As the RVP decreases, the evaporative losses decrease. The slope of a fuel's distillation curve will give an indication of how much fuel vapor will be generated during the hot soak mode of an evaporative emission test. The effect of weathering is largely dependent on the temperatures which a fuel encounters. Temperatures above the initial boiling point of a fuel weathers that fuel more severely because the mechanism by which the fuel weathers changes from diffusion to distillation.

Correlations and engineering assumptions can be drawn, with reasonable accuracy, from fuel composition indicators such as RVP and distillation curves. Although weathering does not indicate a particular fuel characteristic it is an indication of the change in fuel characteristics due to evaporation.

3. Technical Discussion:

3.1 Volatility: Reid Vapor Pressure (RVP) is the primary indicator of fuel volatility. The RVP for a fuel is arrived at by placing a measured amount of fuel in a special bomb (sealed container), heating the bomb to 100°F, and recording the resultant pressure. A mixture of the base fuel blend and the pressurizing agents results in a final fuel RVP. The base fuel's RVP is fixed by the type of crude oil used and the way in which it was refined. As a rule, the base fuel blend has too low a RVP to provide acceptable vehicle operation. To increase the fuel's RVP, a hydrocarbon with a high RVP, the pressurizing agent, is added to the base fuel. Materials such as butane, propane and/or pentane could be used as pressurizing agents (1).

Studies indicate that there is a relationship between RVP and total vehicle evaporative emissions (Fig. 3-1a). As the RVP of a fuel increases, the evaporative losses from a vehicle with that fuel increase (Fig. 3-1b). An analysis of the loss composition indicates more than 50% of the components are butane and pentane (1).

Also, there exists a relationship between RVP and engine performance, specifically the cold starting of an engine. As the volatility of a fuel decreases (lower RVP) the cranking time required to start the engine increases. This condition is most pronounced at low ambient temperatures, 0°F (2).

3.2 Distillation Temperatures: A typical distillation curve indicates the temperature at which various percentages of a fuel are evaporated (Fig. 3-2a). There are several methods by which a distillation curve may be arrived at such as the ASTM method or the single plate distillation method. The significant difference between these two methods is that the ASTM method allows for refluxing because equilibrium between the fuel liquid and vapor does not exist (1) (Fig. 3-2b). The shape of the distillation curve will indicate the amount of fuel evaporated from a fuel bowl during a hot soak, specifically the shape of the curve up to and including the peak carburetor bowl temperature (2).

The high temperature, approximately 150°F, encountered by the carburetor during a hot soak dictates that the mechanism for generating fuel vapor will be distillation. A model utilizing the distillation curve can predict carburetor hot soak losses (Fig. 3-2c).

$$W = \theta_{T_1} VF \left[\frac{D_{T_2} - D_{T_1}}{1 - D_{T_1}} \right] \qquad (3)$$

W = weight of fuel evaporated
T_1 = temperature of fuel in the carburetor at the beginning of the hot soak period.
T_2 = Peak temperature of fuel during the hot soak period.
θ_{T_1} = Density of fuel at T_1.
V = Volume of fuel in the carburetor bowl at the start of the hot soak period.
D_T = Weight fraction of fuel evaporated in proceeding from the initial boiling point to the temperature T during a single plate equilibrium distillation.
F = Experimentally determined diffusion loss factor, dependent primarily on total time for soak.

In this model, as the slope of the distillation curve increases between T_1 and T_2 the weight fraction of fuel evaporated increases. With the increase of the D_{T_2} terms the difference between D_{T_2} and D_{T_1} increases, thus increasing the weight of fuel evaporated. It should be noted that the D_{T_1} and $1-D_{T_1}$ terms account for fuel weathering (7) which occurs prior to the hot soak and is a constituent of running losses (Fig. 3-2c).

There is an interrelationship between RVP and fuel distillation. By plotting RVP and percent evaporated at a specific temperature a map showing equal weight of fuel evaporated can be drawn. This indicates that a trade off can be made between RVP and the shape of the fuel distillation curve which in turn could allow changes in fuel composition without changing overall vehicle losses (Fig. 3-2e). This could allow the shifting of diurnal and hot soak losses depending on which mode of loss would be more controllable.

The distillation process is also responsible for the different hydrogen-carbon ratios used when calculating the mass of evaporative emissions. An inverse relationship exists between the hydrogen-carbon ratio and the nominal molecular weight of the condensed evaporative emissions. Both the fuel tank and carburetor undergo temperature rises with the carburetor experiencing the higher peak temperatures. Because of these higher peak temperatures more of the heavier hydrocarbons, hydrocarbons with higher molecular weights, are evaporated thus the hydrogen-carbon ratio ends up being 2.20 for the carburetor losses. The hydrogen-carbon ratio for the fuel tank losses is 2.33, which is a result of the tank losses being made up of materials with low molecular weights, such as butane, pentane and hexane. Indolene test fuel has a hydrogen-carbon ratio of 1.95. The above mentioned hydrogen-carbon ratios will remain unchanged for evaporative losses as long as the Indolene test fuel composition specifications remain unchanged. (see Appendix A).

The interrelation of the shape of distillation curve and engine performance is quite complex (Fig. 3-2d). The portion of the curve which affects evaporative loss is the portion below the 50% evaporated point. This portion of fuel also affects cold and hot starting, vapor lock, engine warm-up, carburetor icing and hot stalling (6).

3.3 Weathering: The increase in specific gravity of a fuel, in an open system, over a period of time is weathering. Evaporation is the mechanism by which a fuel weathers therefore the relationship between fuel characteristics and evaporative losses also holds true for weathering. A high RVP fuel will weather at a higher rate than a low RVP fuel. Also, there is a direct relationship between the severity of weathering and time and/or temperature. As a result of the weathering a fuel will no longer have the characteristics of its initial composition, the fuel's RVP will be lower, its initial boiling point will be higher, and the front end of the distillation curve will be flatter.

Weathering will occur during soaks by diffusion and if the temperature is high enough by distillation. If repeated tests are run on a vehicle, without changing fuel, each successive test will show a lower loss due to the decreasing quantity of light hydrocarbons in that test fuel (Fig. 3-3a). It should be pointed out that diffusion is the slower of the two processes and weathering due to this mechanism is insignificant provided the vehicle does not undergo an extended soak.

4. Sample Calculation: For the purpose of illustrating the loss model the following assumptions were used:

Fuel - Mobil 1 (3)

$\theta_{T_1} = .765$ g/cc

$D_{T_1} = .5\%$

$D_{T_2} = 20\%$

$F = .75$g loss in one hour

$V = 100$cc

$T_1 = 95°F$

$T_2 = 150°F$

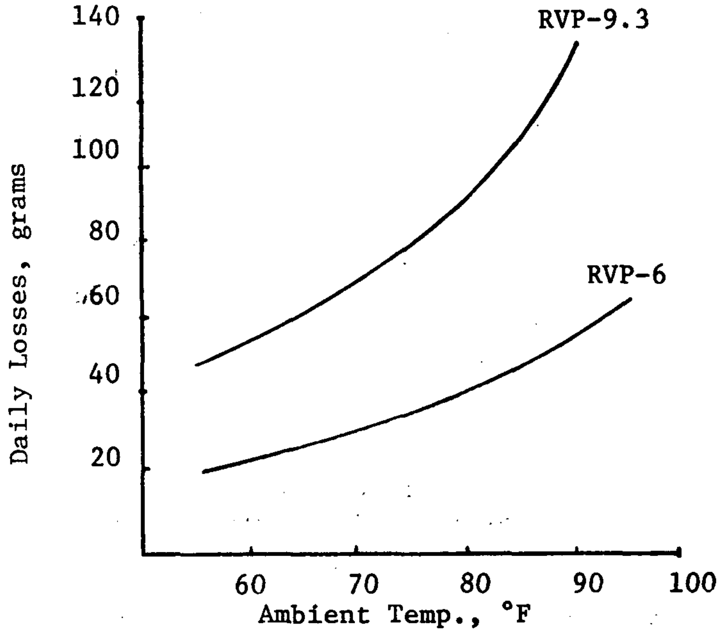
$$W = \theta_{T_1} VF \left[\frac{D_{T_2} - D_{T_1}}{1 - D_{T_1}} \right]$$

$$= (.765)\ (100)\ (.75) \left[\frac{.20 - .005}{1 - .005} \right]$$

$$= 11.24 \text{ g.}$$

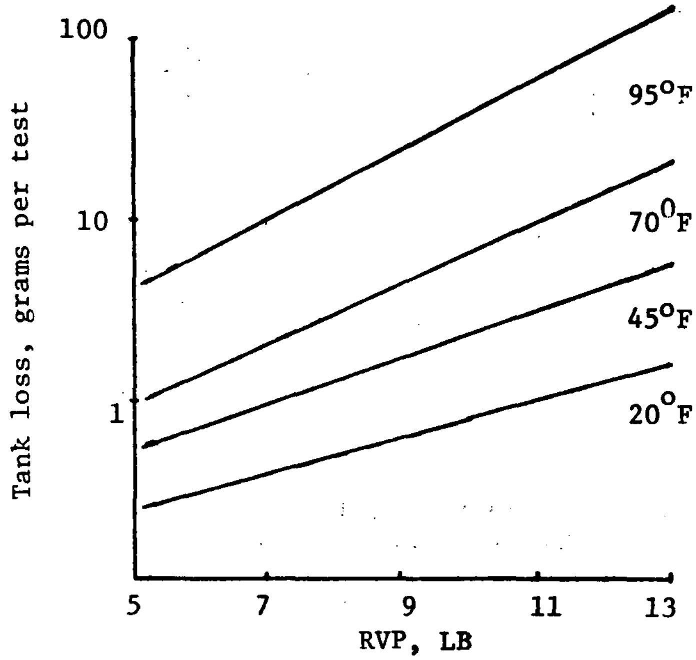
5. Closure: The primary purpose of this report is to provide an insight into the effects of fuel on evaporative emissions. Evaporative emission from vehicles can be reduced by a change in fuel composition which would supplement existing vehicle evaporative emission control systems. It should be pointed out that a major modification in fuel composition to reduce evaporative emissions could have an effect on engine operation which may require engine modifications, thus limiting the use of this fuel to new vehicles with modified engines. In addition, service stations would have to carry the modified fuel along with the standard fuel.

Figure 3-1a
Daily Losses vs. Temperature



Reference (5)

Figure 3-1b
RVP vs. Tank Losses



Reference (8)

Figure 3-2a
ASTM D86-62 Distillation Curve

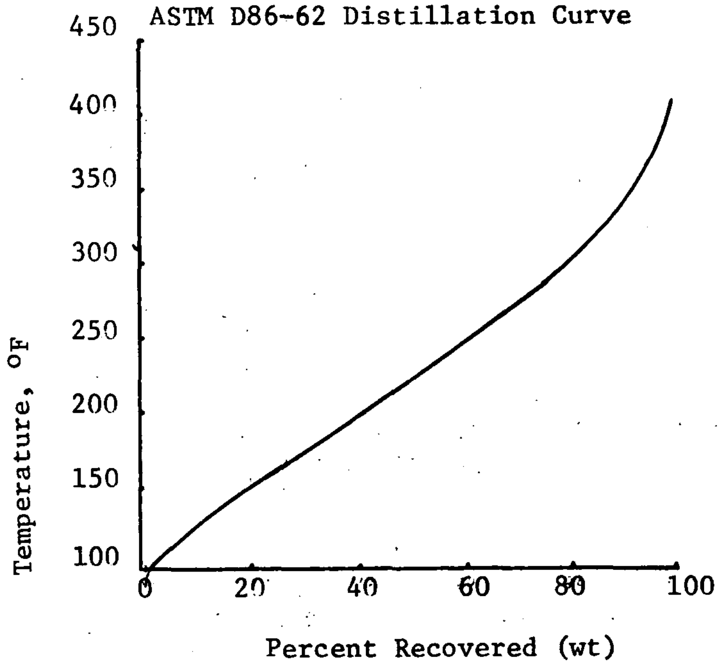
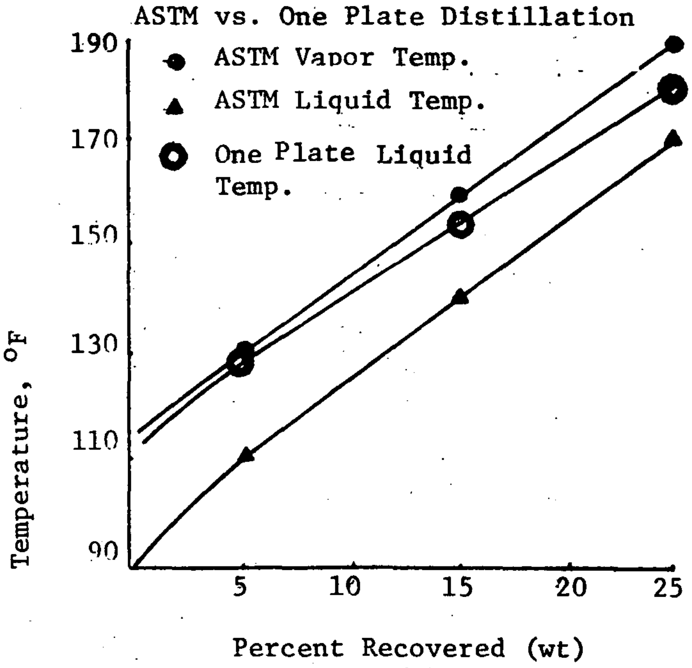
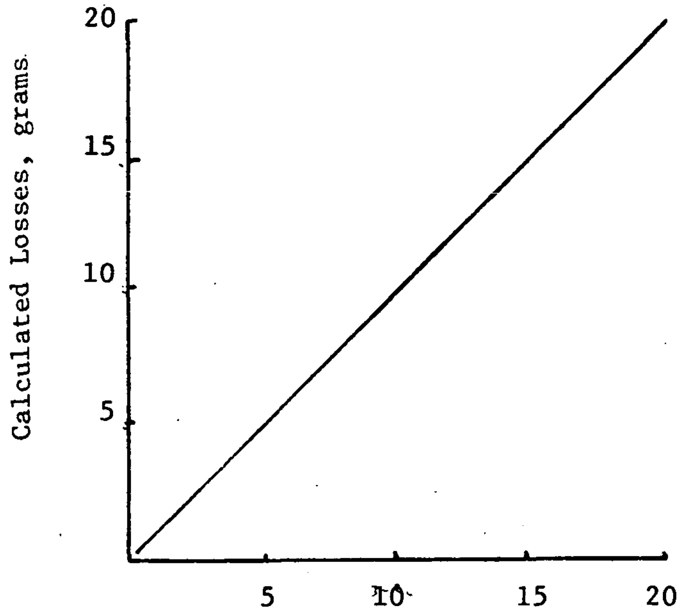


Figure 3-2b
ASTM vs. One Plate Distillation



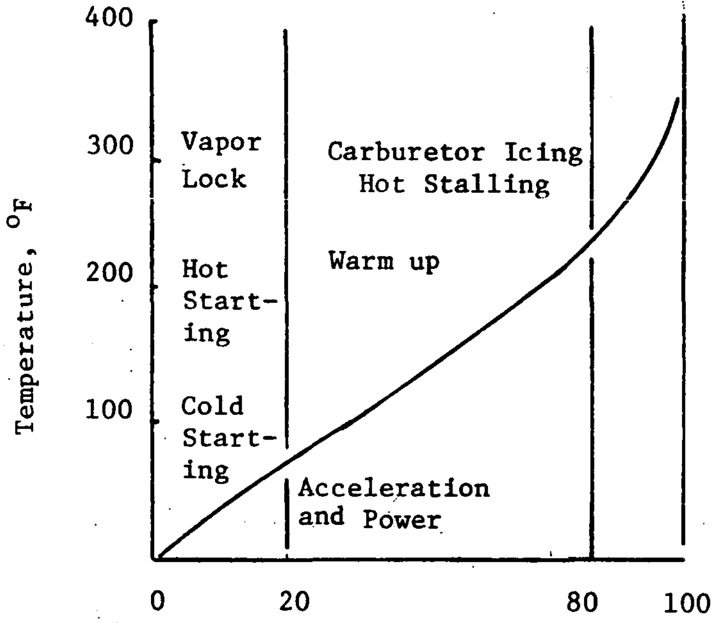
Reference (1)

Figure 3-2c
Measured vs. Calculated Losses



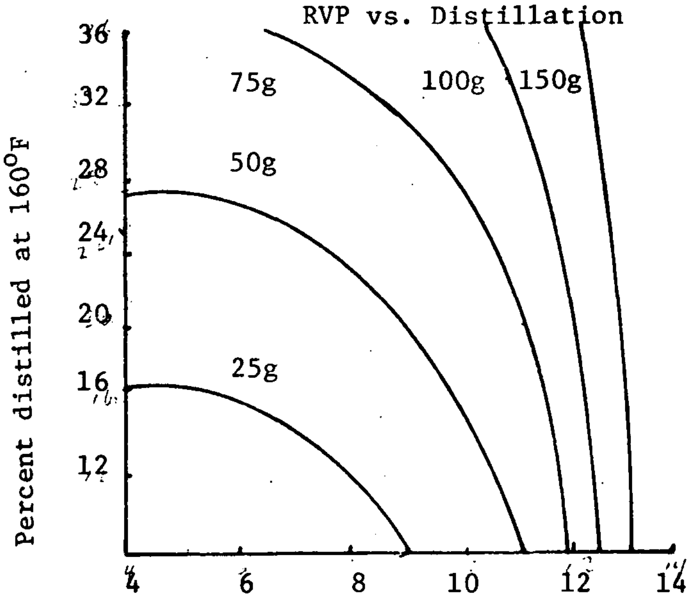
Reference (3)

Figure 3-2d
Distillation and Engine Performance



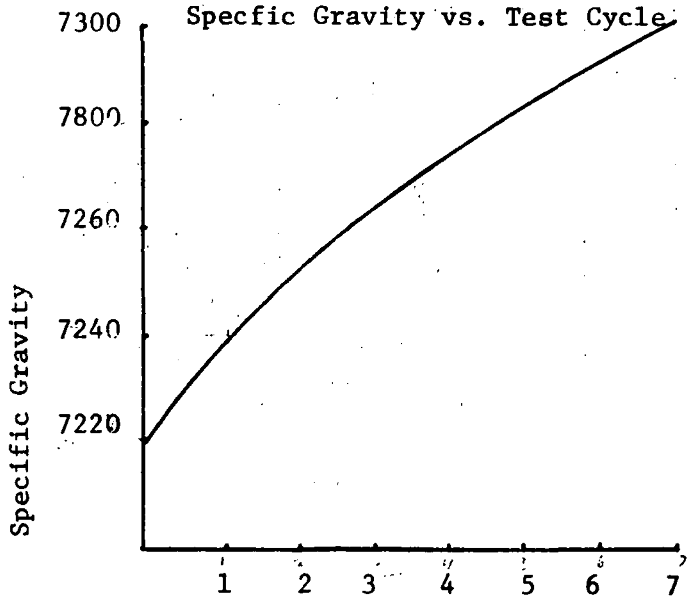
Reference (2)

Figure 3-2e
RVP vs. Distillation



Reference (3)

Figure 3-3a
Specfic Gravity vs. Test Cycle



Reference (8)

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Appendix A

AMOCO

Amoco Oil Company
2500 New York Avenue
Whiting, Indiana 46394
Research and Development Department
219-659-2700

July 16, 1975

Mr. Gary Wolfson
EPA Mobile Sources
2565 Plymouth Road
Ann Arbor, Michigan 48105

Dear Mr. Wolfson:

During June, we discussed the hydrogen-carbon (H/C) ratio for hydrocarbon vapors from the Indolene fuel now used for evaporative emission certification tests. SAE Recommended Practice J 171a, "Measurement of Fuel Evaporative Emissions from Gasoline Powered Cars and Light Trucks Using the Enclosure Technique," shows a H/C ratio of 2.33 for fuel vapors from fuel tanks and 2.20 for vapors from carburetor bowls. You wanted to determine whether the H/C ratio of vapors from Indolene certification gasoline had changed since the original estimates were developed.

I do not have any recent measurements or calculations of H/C ratios of Indolene vapors. Nevertheless, we do not believe there has been any significant change in the overall average H/C ratio of these vapors, but individual batches will vary slightly. Indolene certification fuels are still manufactured against the same strict specifications, and surveillance of recent and past gasoline liquid samples does not show any trend in H/C ratios.

If you need any additional information, please let me know.

Very truly yours,

D. K. Lawrence

D. K. LAWRENCE

DKL/vm