

**AUTOMOBILE FUEL SYSTEM VAPOR EMISSION  
FOLLOWING EVAPORATION CANISTER BREAKTHROUGH**

**Key Words:** Automobile emissions, indoor air, methanol, fuel vapor, evaporation canister

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**ABSTRACT**

Extended isothermal equilibration tests at 75°F ( $\approx 24^{\circ}\text{C}$ ) and 94°F ( $\approx 34^{\circ}\text{C}$ ) were conducted on a 1988 General Motors (GM) Corsica fuel system in a sealed housing for evaporative determination (SHED) using pure methanol fuel (M100). An initial condition of evaporation canister breakthrough loading was chosen to avoid hysteresis effects, and assure experimental repeatability. Hot Flame Ion Detection (HFID) analysis of air samples from the SHED were performed during 6-hour experiments. The concentration of methanol was found to increase continually over the duration of the experiments, but at less than a linear rate. A temperature

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dependent model was developed assuming that evaporation rate is proportional to a finite mass of fuel available for evaporation and diffusion from the fuel system. This study suggests that the hot soak emissions process, with concurrent thermal and non-equilibrated fuel system vapor concentration gradients, is unlikely to stabilize within a nominal one hour period.

## INTRODUCTION

Tailpipe emissions represent an obvious source of *ecological* pollution. Evaporative emissions from vehicles in attached garages may represent an important source of indoor (i.e. *microenvironmental*) pollution. Automobile evaporative emissions processes have been categorized by their associated vehicle operation mode - running, hot soak (cool down), diurnal (breathing), and resting losses (constant temperature, pseudo steady state). These processes are not mutually exclusive; resting losses can be concurrent with any of the others. Hot soak and resting losses may both contribute to degradation of indoor air quality during vehicle use scenarios associated with parking hot vehicles in attached residential garages. The magnitude of in-house concentration of a chemical species depends upon the emission rate of evaporating fuel, the concentration of the component species within the liquid fuel, and the air exchange rate between garage and house.

In-house and attached garage concentration of evaporated (noncombusted) fuel species from an automobile's fuel system may represent a significant component of total human exposure to these chemicals. Hot soak and resting loss phase are components of evaporative emissions applicable to attached garage vehicle use

scenarios. Each phase proceeds under the composite effects of temperature gradients and/or vapor redistribution, and evaporation canister outgassing hysteresis. A model paradigm of evaporative emissions during the hot soak and resting phase parking scenario must first succeed in isolating the functional dependence of emissions on temperature and vapor distribution gradients separately.

A methanol fuel was chosen for this study. This choice was motivated by the need to assess the potential microenvironmental concentrations of methanol vapor emitted from vehicles fueled with methanol or methanol-gasoline blends. Since the charcoal in the evaporation canister exhibits species-specific adsorption affinities (Lang and Black, 1981), evaporative fluxes from mixed species fuels display a time dependent chemical speciation. The use of M100 fuel (100% methanol), comprised of a single species, avoids this complication.

#### Role of Modeling

The functional form of vehicle evaporative emissions (i.e. source characterization) determines, in part, the time-concentration profile within an enclosed microenvironment. A model is needed that will predict source strength as a function of the independent variables, time and temperature. Specifically, a physically-based model of evaporative emissions is needed to simulate vehicle use scenarios applicable to parking a vehicle in a residential garage. The evaporative processes having greatest potential impact on indoor air quality are hot soak and resting losses, as might occur during vehicle parking in attached residential garages. The U.S. Environmental Protection Agency's Mobile Source Emission Factors Model, MOBILE5 (U.S. EPA, 1992), does not adequately define the time or

temperature dependence of evaporative emissions following vehicle parking episodes. MOBILE5 models hot soak emissions as an emitted mass *per event* - with no explicit time dependence inferred, although a one hour duration is generally assumed. Resting losses, under isothermal conditions, are assumed to be a steady state (i.e. time independent) processes, and are modeled as such by MOBILE5.

#### Background and Significance

Prior to federally mandated controls (circa 1970), evaporative emissions accounted for about 20% of automobile pollution (Black, 1991). Light duty gasoline vehicles and light duty trucks are currently required to pass evaporative emissions tests: the sum of diurnal and hot soak test emissions must not exceed 2 g (U.S. DOC, 1994). Contributions to both hot soak and resting losses originate from open-bottom evaporation canisters and from carburetors, in vehicles so equipped. While fuel injection has rapidly replaced carbureted mixing (62% of automobiles and 48% of light trucks were fuel injected in 1993 (Platte, 1993)), open bottom canisters were still present on approximately one half of all operating vehicles in 1995. Haskew et al. (1990) found that open bottom canisters can generate six times the emission flux as closed bottom canisters. Evaporation canister loading, following engine shutdown, contributes to both hot soak (thermal and pressure gradient dissipation phase) and resting (isothermal) loss emission. Canister breakthrough can occur following engine shutdown and halting of vacuum purge, in conjunction with elevated fuel tank temperature. The initial state of the canister, and its recent history, determine its capacitance to adsorb fuel vapor, and significantly affects its outgassing characteristics.

### Definitions

*Hot soak* emissions are associated with engine cool down, and are concurrent with the monotonic dissipation of pressure and thermal gradients between fuel system and ambient conditions. Hot soak emissions have been defined as being limited to the first hour following engine shutdown, after which the fuel system has presumably reached thermal and pressure equilibrium. *Resting* losses have been defined as noncombusted fuel vapor emissions from the fuel system and engine block of vehicles as a result of permeation through non-metallic conduits, seepage across imperfect seals, and vapor migration allowed by system design features such as open bottom canisters and carburetors.

### Impact of Legislation

The 1988 Alternative Motor Fuels Act (U.S. Congress, 1988) was intended to address the growing dependence of the U.S. on imported oil. The 1990 Clean Air Act Amendments (U.S. Congress, 1990) further promoted alcohol fuels and additives as part of an urban ozone, CO, and particulate abatement strategy (Black, 1991). The addition of alcohols to gasoline has resulted in a decrease of total hydrocarbon (THC) and Carbon Monoxide (CO) tailpipe emissions. Less toxic combustion products may have a direct health benefit as well, in reduced cancer incidence - an estimated 90% carcinogenicity reduction in the case of methanol fuel (U.S. EPA, 1989).

In terms of evaporative emissions, it is anticipated that M100 evaporative emissions would be 18% of that from a 9 psi gasoline (Black, 1991). The Reid Vapor Pressure (RVP) (A.S.T.M., 1982) of M100 is 4.6 psi, compared with a typical summer grade gasoline RVP of approximately 9 psi. Additionally, methanol

possesses a relatively high heat of vaporization - nearly 3 times that of gasoline. These facts would tend to indicate that a substantial reduction in evaporative fuel mass could be expected from vehicles operating on M100 fuel. However, due to engine performance and cold start limitations, M100 is a candidate fuel only for advanced technology vehicles. Gasoline-alcohol mixtures such as M85 (85% methanol, 15% gasoline) are viable fuels for the existing on-road fleet. However, the addition of alcohol to gasoline in certain ratios may increase the fuel vapor pressure, and hence the evaporation rate (Furey and Perry, 1986).

#### Scope and Limitations

The terms "hot soak" and "resting loss" are somewhat suggestive of the processes governing their emissions characteristics. The experiments conducted in support of the model development strictly replicate neither hot soak nor resting loss tests. These experiments have in common with hot soak tests an initial condition of non-equilibrated fuel system vapor distribution - with breakthrough-loaded evaporation canister representing a worst case. These experiments have in common with resting losses a constant emission temperature, and a duration extending beyond one hour. As shorthand descriptors of the evaporative emissions process conducted in these experiments, the term "isothermal saturated equilibration" experiments, or perhaps simply "saturated cold soak" might apply. The evaporative emission scenario applicable to parking in an attached residential garage is an extended hot soak of indefinite duration. The model developed here simulates a temperature dependent saturated cold soak.

The model developed in this study represents a worst case insofar as the mass

available for an isothermal saturated equilibration process. Breakthrough-loaded evaporation canisters emitting under isothermal conditions do not represent typical vehicle use evaporative processes. However, isolating temperature effects from vapor redistribution presents an opportunity to better understand the science governing evaporative losses, and apply that understanding to hot soak, resting, and diurnal evaporation. The non-isothermal conditions of hot soak emissions, concurrent with fuel system vapor redistribution, are compound processes, where the separate effects of temperature and vapor redistribution are convoluted. Resting evaporative emissions, with generally less than breakthrough-loaded canisters, emit under isothermal conditions. Uncertainty in the initial (and subsequent) distribution of fuel vapor within the fuel system represents an unknown variable.

Strict predictive capability of the model will be limited to the vehicle model and fuel to which it was calibrated. In particular, the diffusion time constant is fuel dependent. The experiments were conducted using pure methanol, and the diffusion time constant developed in the model is, therefore, specific to M100 fuel. The evaporative mass available for diffusion is design specific, and will vary with canister volume, vapor line volume, and fuel tank head space. The degree of canister loading, and recent purge/load history will also be determining factors.

### **THEORETICAL DESIGN**

A semi-empirical model of evaporative emissions is developed to simulate the emissions during parking scenarios. The model parameters, to be determined by optimization against concentration data obtained during controlled experiments, are

specific to the 1988 Corsica using M100 fuel. The model will be expected to provide estimates of evaporative emission profiles as functions of time and temperature. These emission estimates should be conservative (i.e. plausible worst case) since the intended application is in calculating upper bound indoor concentrations of methanol. The functional form of the model should be general enough to serve as a boilerplate for parking emission characteristics for an inventory of vehicles, with model parameters specific to other fuels and fuel systems being determined by regression against appropriately specific experiments.

The fuel system, defined here as the continuous path from fuel tank to evaporation canister, is modeled as a *mass capacitor* - having a finite storage capacity (i.e. breakthrough loading), and a temperature-dependent *diffusion* time constant associated with purging fuel mass exceeding an equilibrated, strongly adsorbed fuel mass. Open-bottom evaporation canister emissions under isothermal conditions are hypothesized here to be supplied by a finite reservoir of fuel. That fuel mass may exist in either vapor, liquid, or adsorbed film phase, and resides in the canister itself, the tubing feeding the canister, and the head space of the fuel tank. The effective mechanical path length for vapor diffusion from the fuel system influences both the diffusion time constant and the effective mass available for diffusion. It is expected that this design parameter varies substantially between vehicles. The chemical-dependent process of vapor adsorption onto and desorption from the charcoal canister is not explicitly modeled. This process depends upon the polarity of the chemical species, its molecular weight, and even the initial state of the charcoal - a hysteresis effect.

The mathematical development of the model is as follows: the finite fuel mass,  $M$ , is outgassed from the canister at a rate proportional to the residual (unpurged) mass,  $m$ . Stated as a first order linear differential equation:

$$\frac{dm}{dt} = -\frac{1}{\tau} m \quad (1)$$

where  $t$  is time and  $\tau$  is a temperature dependent time constant. The diffusion process is modeled as proceeding from an initial condition of fuel mass  $M$  at time 0, to a remaining mass  $m$  at time  $t$ . Integrating both sides from initial condition to variable endpoint, applying the exponential function, and rearranging yields:

$$m(t) = M \times \exp\left(-\frac{t}{\tau}\right) \quad (2)$$

Defining the source term,  $Q(t)$ , as the rate of mass discharge:

$$Q(t) = -\frac{dm}{dt} \quad (3)$$

Thus, restating the source model in its entirety:

$$Q(t) = \frac{M}{\tau} \times \exp\left(-\frac{t}{\tau}\right) \quad (4)$$

where  $\tau$  is a *diffusion* time constant.

The diffusion time constant  $\tau$  is a function of numerous physical, chemical, and mechanical factors, including the initial distribution and phase of methanol within the fuel system (from liquid methanol in the tank, to vapor in the head space

and tubing, to vapor and adsorbed methanol in the evaporation canister). Physically, consideration of the temperature dependence of  $\tau$  appears implicitly through a dependence on vapor pressure, which in turn depends on temperature i.e.  $\tau(p(T))$ . The Clausius-Clapyron Equation (Atkins, 1978) relates the equilibrium vapor pressure,  $p$ , above a pure liquid (single species chemical), to its liquid temperature,  $T$ . The Clausius-Clapyron Equation may be stated as

$$p = p^* \exp\left[ \frac{-\Delta H_{\text{evap},m}}{R} \left( \frac{1}{T} - \frac{1}{T^*} \right) \right] \quad (5)$$

where  $p^*$  is the vapor pressure at some temperature  $T^*$ ;  $\Delta H_{\text{evap},m}$  is the molar enthalpy of vaporization; and  $R$  is the gas constant. The molar enthalpy of vaporization is a linear function of temperature, and is approximately constant over the small temperature ranges of interest ( $70^\circ\text{F}$  ( $\approx 21^\circ\text{C}$ ) to  $100^\circ\text{F}$  ( $\approx 38^\circ\text{C}$ )). The temperature dependence of the Clausius-Clapyron Equation has the functional form:

$$p \propto \exp\left[ \frac{\text{const}}{T} \right] \quad (6)$$

Since the diffusion time constant,  $\tau$ , is inversely proportional to the pressure, we may substitute  $\tau$  for  $1/p$ , and restate the proportionality as an equality with the substitution of a proportionality constant  $\beta$ :

$$\tau = \beta \times \exp\left[ - \frac{\text{const}}{T} \right] \quad (7)$$

The Clausius-Clapyron Equation as applied here describes the liquid-vapor phase

equilibrium, hence temperatures are relative to the methanol freezing point temperature. Under normal ambient pressure (760 mm Hg), the liquid-vapor phase extends from  $-97^{\circ}\text{C}$  (standard atmosphere freezing point) to  $+65^{\circ}\text{C}$ , (standard atmosphere boiling point). Assigning the letter  $\gamma$  to the exponential constant in Equation (7), and translating the temperature scale relative to the methanol freezing point gives:

$$\tau = \beta \times \exp\left[ \frac{\gamma}{(T - (-97))} \right] \quad (8)$$

The constants  $\beta$  and  $\gamma$  are dependent on the molar enthalpy of vaporization of methanol, the gas constant  $R$ , as well as the fuel system design path length for emission, and the adsorption-desorption function of methanol on charcoal. Equation (8) is applicable only to methanol, and an equation of that form may be descriptive of only single species fuels (the adsorption-desorption reaction with the charcoal filter is expected to be very species dependent). Thus the model has explicit time, temperature and discharge mass dependence, while the other dependencies are taken as empirical constants, to be determined from experiment.

#### Concentration Formulation

Measurements of the SHED concentration  $\chi(t)$ , and leak rate  $v$ , enabled the indirect determination of the source strength  $Q(t)$ . The general expression for the time dependent concentration  $\chi(t)$  within a volume  $V$ , containing time varying source  $Q(t)$ , initial concentration  $\chi(0)$ , air exchange rate (i.e. leak rate) of  $v$  with external

air having background concentration  $\chi_b(t)$ , and mass removal processes with sink strength  $\Phi(t)$ , is given as:

$$\chi(t) = \frac{1}{V} \int_0^t Q(t) dt - \frac{1}{V} \int_0^t [\chi(t) - \chi_b(t)] v dt - \int_0^t [\chi(t) \times \Phi(t)] dt + \chi(0) \quad (9)$$

In Equation (9), the first term accounts for the source, the second term describes leakage, the third term describes other (non-leakage) mass removal processes (e.g. chemical reaction, surface adsorption), and the last term is the initial concentration. If the volume leak rate and other mass removal processes such as chemical reaction or surface adsorption may be neglected, then the above equation may be simplified:

$$\chi(t) = \frac{1}{V} \int_0^t Q(t) dt + \chi(0) \quad (10)$$

In terms of the derived source function:

$$\chi(t) = \frac{M}{V} (1 - \exp(-\frac{t}{\tau})) + \chi(0) \quad (11)$$

## EXPERIMENTAL PROCEDURES

### Fuel System Physical Description

A replica of a 1988 Corsica fuel system was fabricated for experiments that isolate fuel system emissions from other (e.g. engine block) sources of noncombusted fuel evaporation. The Corsica fuel system's essential components consisted of the fuel tank, the charcoal evaporation canister, and the vapor line connecting the tank

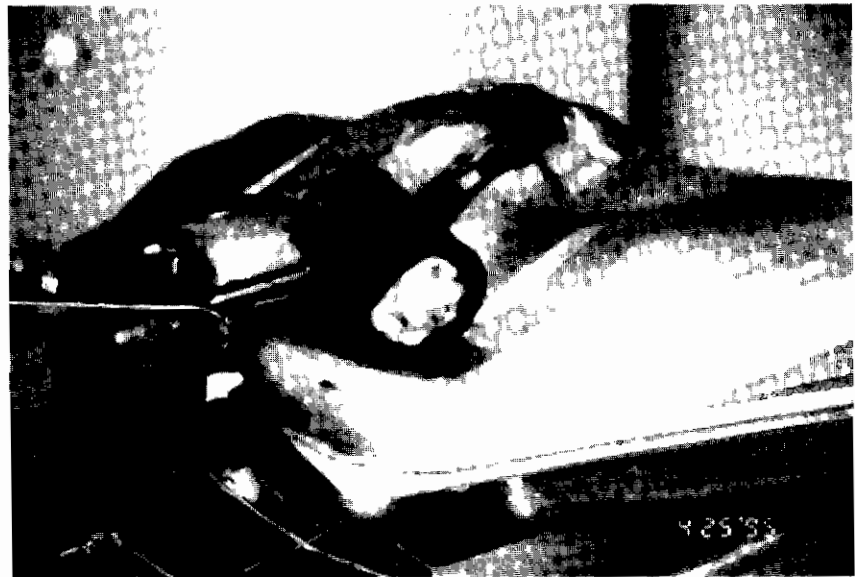


FIGURE 1  
Corsica fuel system showing tank, vapor line, and evaporation canister.

to the canister, as shown in Figure 1. The fuel tank volume was 52.2L (13.8 gal). The 1988 Corsica fuel system was designed with the fuel pump enclosed within the tank. The tank fluid ports consisted of a fuel line and return line (both sealed to the atmosphere), and a line to the evaporation canister. The evaporation canister is a plastic encased charcoal cylinder, with diameter of 9.2 cm (3 5/8 in), and height of 12.1 cm (4 3/4 in), giving a volume of 803 cm<sup>3</sup> (49 in<sup>3</sup>). The canister is open to the atmosphere at the bottom, and connected to the tank by rubber and metal tubing. The total path length from the head space of the tank, to the canister, is 71.1 cm (28 in), consisting of 48.2 cm (19 in) of stainless steel tubing attached to the tank, followed

by 22.9 cm (9 in) of rubber tubing. Canister purge during engine operation is enabled by a vacuum port at the top of the canister, and a vacuum control valve. Vacuum line and valve control line were sealed.

#### Test Facilities

Evaporative emissions tests were conducted in a 47.346 m<sup>3</sup> SHED facility. The SHED integrity was verified as part of the quality assurance plan by injecting known quantities of propane. The leakage rate of the SHED had been determined to be 0.2% per hour, or 2.63E-5 m<sup>3</sup>/s. A mixing fan operated to insure samples were representative. Manual valves controlled gas extraction through Teflon lines attached to the SHED at sampling ports. A Beckman Model 402 Hot Total Flame Ionization Detector (HFID) was used for monitoring methanol concentrations. HFID response to methanol was 75% of the response to propane. High intensity ceiling-mounted heat lamps were used (feedback controlled) to maintain SHED temperatures above ambient levels. SHED air was purged with a built in blower after each test.

#### Canister Preconditioning

The Corsica evaporation canister was preconditioned for the saturated cold soak experiments. Establishing a repeatable initial condition of the canister is critical in evaporative loss experiments. The canister preconditioning consisted of a purge of all residual adsorbed contaminants, followed by saturation to breakthrough with methanol. The evaporative canister was removed and purged with 300°F (= 150°C) Nitrogen at 20 liters per minute until incremental weight loss was less than 1 g in 30 minutes (approximately 12 hours). Canister weight was measured following purge as 413.0 g. The purged canister was re-attached to the fuel tank. Canister

breakthrough was achieved by subjecting the fuel system to progressive ramping-up of ambient temperature until a characteristic spike in ambient concentration of methanol was observed by HFID. Specifically, the progressive time at temperature ramp applied consisted of 3 hrs at 90°F (=32°C), 3 hrs at 125°F (=52°C), and 1 hr at 135°F (=57°C). Breakthrough was observed during the final hour (135°F). The canister was weighed following breakthrough, with "loaded" canister weight recorded at 530.7 g. The net loading achieved being 117.7 g, the presumed canister capacity.

#### Test Procedure

Saturated cold soak evaporative emission experiments were conducted in the SHED at two temperatures, 75°F and 94°F. A Beckman Model 402 heated flame ionization detector (HFID) was used for total hydrocarbon analysis (THC). THC data were recorded at 15 minute intervals for a 6 hour time period for each experiment. Background THC was determined prior to the start of each experiment, and subtracted from reported results. **The HFID does not respond to oxygenated compounds with the same sensitivity as pure hydrocarbons. The HFID response to methanol is 75% of the response to the calibration gas propane. Reported concentrations have been corrected for HFID response.** A fuel system temperature feedback control loop was maintained using electrical resistive heating elements attached to the bottom of the tank, and sealed thermocouple temperature probes to monitor head space and liquid fuel temperature. Following FTP convention, the fuel tank was filled to 40% capacity for all tests (U.S. DOC, 1994).

The first experiment maintained SHED air temperature at 75±1°F for 6 hours. The conditioned canister was weighed immediately prior to the experiment

and recorded as 530.7 g. The canister was reattached to the fuel tank, and the fuel system was sealed in the SHED. Samples were extracted and analyzed (HFID) every 15 minutes. At the conclusion of 6 hours, the canister weight was recorded as 528.1 g, a loss of 2.6 g. The second experiment maintained SHED air temperature at  $94\pm 3^{\circ}\text{F}$  for 6 hours. The conditioned canister was weighed immediately prior to the  $94^{\circ}\text{F}$  experiment and recorded as 525.6 g. As in the  $75^{\circ}\text{F}$  experiment, samples were extracted at 15 minute intervals and analyzed by HFID. Following the experiment, the canister was weighed and recorded as 520.4 g, a loss of 5.2 g.

### RESULTS AND DISCUSSION

In Table 1, initial and final canister weights are given for both experiments, and the canister capacity is reported as 117.7 g (canister weight at breakthrough loading minus the weight at fully purged condition). The evaporation canister weight loss during each saturated cold soak experiment was substantially less than the calculated mass of methanol in the SHED volume. Canister weight loss during the  $75^{\circ}\text{F}$  cold soak experiment was 2.6 g, while the SHED concentration at 6 hours (96.67 ppm) corresponds to 6.5 g methanol. Canister weight loss during the  $94^{\circ}\text{F}$  cold soak experiment was 5.2 g, while SHED concentration at 6 hours (269.33 ppm) corresponds to 18.2 g methanol. These results indicate that saturated cold soak losses emitted from the open bottom of the canister originate from both the more remote tubing path and/or head space of the fuel tank, as well as the canister itself. However, the canister methanol load (presumably 117.7 g) was not significantly discharged over the duration of these experiments.

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**TABLE 1**  
**Evaporation Canister Purge and Loading**

|                     | 75°F Experiment | 94°F Experiment | Breakthrough Loading |
|---------------------|-----------------|-----------------|----------------------|
| initial weight [g]  | 530.7           | 525.6           |                      |
| final weight [g]    | 528.1           | 520.4           |                      |
| net gain (loss) [g] | (2.6)           | (5.2)           | 117.7                |

Table 2 gives the measured SHED methanol concentration (ppm) as a function of time for both experiments. The concentration continued to increase through 6 hours for both experiments, although the rate of increase was declining. The sub-linear growth in the concentration may be explained as either a constant (i.e. steady state) source subject to a mass removal process (leakage, chemical reaction, or surface adsorption), or as a finite (depletable) mass of methanol available for evaporation/diffusion. The SHED leak rate of 0.2% per hour is negligible over the course of a 6 hour experiment. Furthermore, methanol is a relatively inert gas, and is not believed to undergo chemical reaction or surface adsorption to any significant degree during these experiments. Consequently, the mass removal terms in Equation (9) may be neglected, and Equation (10) may be substituted as the working equation of state, relating the concentration to the source flux.

#### Model Implementation

The model parameters  $M$ ,  $\beta$ , and  $\gamma$ , were optimized to fit the data using Quasi-Newton optimization methods (Beightler et al., 1979). The optimization was

**TABLE 2**  
**Measured and Modeled SHED Concentrations**

| Time[hrs] | 75°F HFID [ppm] | 75°F Model [ppm] | 94°F HFID [ppm] | 94°F Model [ppm] |
|-----------|-----------------|------------------|-----------------|------------------|
| 00.0      | 00.0            | 00.0             | 00.0            | 00.0             |
| 0.25      | 04.3            | 04.2             | 21.3            | 15.5             |
| 0.50      | 07.5            | 08.4             | 31.9            | 30.6             |
| 0.75      | 11.3            | 12.6             | 49.7            | 45.2             |
| 1.00      | 15.5            | 16.7             | 59.3            | 59.4             |
| 1.25      | 20.5            | 20.8             | 71.3            | 73.2             |
| 1.50      | 23.3            | 24.9             | 86.5            | 86.6             |
| 1.75      | 29.1            | 28.9             | 99.5            | 99.6             |
| 2.00      | 31.1            | 32.9             | 114.4           | 112.2            |
| 2.25      | 34.8            | 36.9             | 123.2           | 124.4            |
| 2.50      | 39.3            | 40.8             | 134.0           | 136.3            |
| 2.75      | 42.4            | 44.7             | 147.2           | 147.9            |
| 3.00      | 46.1            | 48.6             | 158.5           | 159.1            |
| 3.25      | 51.3            | 52.4             | 170.7           | 169.9            |
| 3.50      | 56.0            | 56.2             | 181.1           | 180.5            |
| 3.75      | 59.7            | 60.0             | 190.3           | 190.7            |
| 4.00      | 62.8            | 63.7             | 200.7           | 200.7            |
| 4.25      | 66.8            | 67.5             | 209.1           | 210.3            |
| 4.50      | 70.8            | 71.1             | 219.9           | 219.7            |
| 4.75      | 74.7            | 74.8             | 230.0           | 228.8            |
| 5.00      | 78.9            | 78.4             | 238.3           | 237.6            |
| 5.25      | 82.8            | 82.0             | 248.3           | 246.2            |
| 5.50      | 87.1            | 85.5             | 254.0           | 254.5            |
| 5.75      | 90.8            | 89.1             | 262.0           | 262.6            |
| 6.00      | 96.7            | 92.6             | 269.3           | 270.5            |

$$\text{Loss} = \text{Temperature} \times (\text{predicted} - \text{observed})^2 \quad (12)$$

subject to a temperature-weighted least squares loss function:

The temperature weighting factor improved the model fit at higher temperatures, where evaporative emissions are of greater interest. The model parameters were thus determined to be  $M = 31.9$  g,  $\beta = 4.107E-6$  hr, and  $\gamma = 1911$  C°. The appropriate units for  $\beta$  and  $\gamma$  are given for dimensional and scaling completeness. No physical interpretation should be inferred.  $\beta$  and  $\gamma$  are complex functions of the initial condition of the canister, as well as the fuel system design. The parameter  $M$  is interpreted as the maximum effective equilibration discharge mass for the fuel system, i.e. the mass difference between breakthrough loading and strongly adsorbed equilibrium mass. That equilibrated mass is assumed to be relatively temperature invariant over normal ambient conditions. For fuel systems having canister breakthrough as the initial condition, such mass loss should be repeatable.

#### Model Performance

The model results are given numerically for 75°F and 94°F in Table 2, for direct comparison with the measured data. The model results and data are displayed graphically as a 3-dimensional surface in Figure 2. Methanol concentration in the SHED is plotted against time and temperature. The modeled surface has been extrapolated above and below the temperature range of the experiments. Measured methanol concentrations (75°F and 94°F) are shown as solid circles. The calculated time constant  $\tau$  was 30.1 hours for the 75°F experiment, and 8.5 hours for the 94°F

CO<sub>2</sub> SOAK EMISSIONS  
Modeled Surface with Data Points

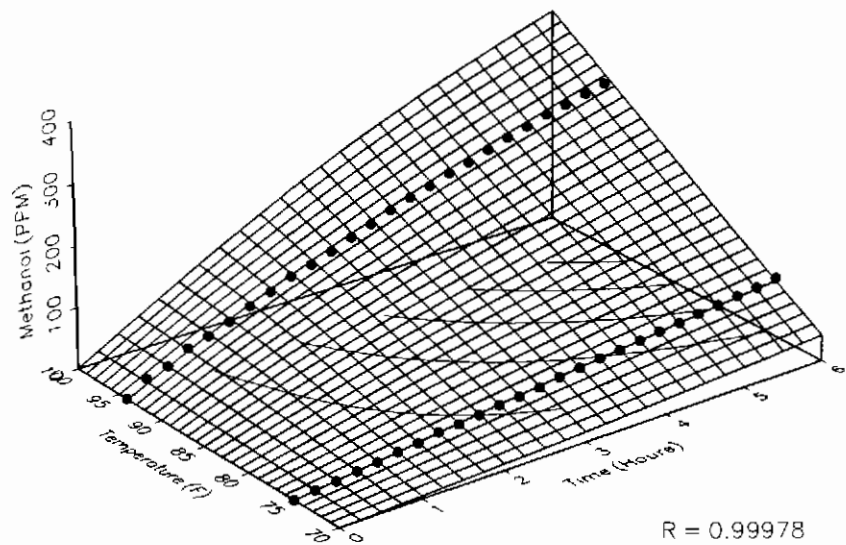


FIGURE 2

Methanol concentration in the SHED as a function of time and temperature. The modeled surface is compared with measured values at 75 and 94 °F.

experiment. The proportion of variance accounted for by the model is 99.96%. The R-statistic is reported as 0.99978.

The time and temperature dependent model, with regressed parameters  $M$ ,  $\beta$ , and  $\Upsilon$ , may then be stated as follows:

$$Q(t) = \left[ \frac{31.9 \text{ g}}{\tau} \right] \times \exp\left( - \frac{t}{\tau} \right) \quad (13)$$

where  $\tau$  is the diffusion time constant, dependent on temperature, molecular diffusivity, and liquid vapor pressure:

$$\tau = (4.107 \times 10^6 \text{ hr}) \times \exp\left[ \frac{1911 \text{ C}^\circ}{(T - (-97)) \text{ C}^\circ} \right] \quad (14)$$

### General Discussion

Hot soak evaporative emissions are modeled in MOBILE5 as evaporated mass *per event*, without explicit time dependence. This is not inconsistent with the fuel system evaporation model paradigm developed here. Resting evaporative emissions are modeled in MOBILE5 as constant in time. This, as well, is not inconsistent with the model presented here. Very low level resting emissions, as predicted in MOBILE5 (tenths to hundredths of a gram per hour), may in fact be ongoing, and would be masked by the much larger equilibration discharge of the fuel system. What is challenged here is the adequacy of a one hour hot soak experiment to characterize the hot soak process. Similarly, any model of the hot soak process that assumes that thermal equilibrium marks the completion of hot soak emissions is in error. It is both thermal equilibrium, and more importantly, fuel system vapor redistribution equilibrium, that leads to steady state emissions.

Evidence of vapor redistribution within the fuel system was observed during these experiments. The canister weight loss during saturated cold soak did not account for the total SHED ambient mass of methanol. Methanol migration from deeper in the fuel system - including the tank itself - must have been available for diffusion, and responsible for contributing the difference. While the methanol in the fuel tank (21.2 L) represents a near infinite source of methanol (relative to the order of magnitude of the flux), the path for evaporation may be sufficiently long that, under constant temperature conditions, the diffusible mass may have a limit which is approached asymptotically. Thus the mass effectively available for diffusion into the ambient environment - the model parameter  $M$  - may be a function of the fuel

system design, not the quantity of liquid fuel in the tank. It is expected that the total path length from the fuel tank head space to the canister open bottom will be an independent variable in the total mass available for diffusion, and would be expected to be specific to a fuel system's design.

Lang and Black (1981) have questioned the adequacy of the one hour hot soak. Using several different fuels, they found that cumulative emissions measured during two hour extended hot soak tests ranged from 10% to 43% above the first hour's emissions alone. Stump et al. (1990) found that hot soak emissions had not reached steady state even after a four hour extended test. Since thermal gradients can create vapor concentration gradients, it should be expected that the attainment of thermal equilibrium

be a necessary, but not a sufficient condition for steady state emissions. The nominal one hour hot soak may or may not be sufficient time to attain *thermal* equilibrium, depending on convection and radiative transfer effectiveness. These experiments have

shown that vapor redistribution within the fuel system is an important component of evaporative emissions, and the effective time constant characterizing this process is generally much greater than one hour.

#### Indoor Air Quality

One significant aspect of the functional form of parking episode evaporative emissions is in how it impacts indoor air quality. A given evaporative mass, emitted into a closed but leaky enclosure over a short time interval, will result in a higher

concentration; whereas the same mass released over a longer time interval will result in a lower, albeit more chronic, concentration. Lorang (1989) estimated peak garage concentration of methanol at  $75 \text{ mg/m}^3$  (60ppm at  $100^\circ\text{F}$  ( $\approx 38^\circ\text{C}$ )) for hot soak emissions from a vehicle with malfunction emission factor of 2.3 times certification compliance. Concentration estimates (U.S. EPA, 1988) have been made as well by the Health Effects Institute (15 minute average of  $200 \text{ mg/m}^3$  (159 ppm) for worst case conditions) and by Southwest Research Institute (peak concentrations of  $153 \text{ mg/m}^3$  (122 ppm) for poorly ventilated garage with malfunction factor offset of 4.6). The experiments described here were conducted in an enclosure approximately  $2/3$  of the volume of a one car garage. No residential garage would be as well sealed as the SHED. It is interesting to note, however, that the Corsica saturated cold soak evaporative emission model, with initial conditions (breakthrough loading) noted, predicts a concentration of approximately 230 ppm in a *sealed* garage of volume  $70 \text{ m}^3$  at 6 hours in  $100^\circ\text{F}$  ambient temperature. Chronic ambient concentration of methanol corresponding to adverse physiological effects in humans may be as low as  $4.5 \text{ mg/m}^3$  (3 ppm) (Harvey et al., 1984). Such low concentrations would be easily attainable, for limited durations, in a poorly ventilated garage. Short term exposure scenarios (perhaps 15 minutes) would be more applicable to hot soak emission / parking episodes. The American Conference of Governmental Industrial Hygienists established a threshold limit value (TLV) of  $260 \text{ mg/m}^3$  (207 ppm at  $100^\circ\text{F}$ ) for 8 hour exposures (U.S. EPA, 1988). The U.S. Environmental Protection Agency has adopted this value as its threshold level of concern.

### **SUMMARY AND CONCLUSIONS**

A model paradigm of the fuel system as mass capacitor, having a temperature dependent diffusion time constant, is successful in describing the isothermal vapor discharge following breakthrough-loading for a single species fuel. Evaporation canister discharge contributes to both hot soak and resting loss phases of vehicle use scenarios. Vapor redistribution within the fuel system is an important component of evaporative emissions, and the effective time constant characterizing this process is generally much greater than one hour. Thus the hot soak emissions process, with concurrent thermal and non-equilibrated fuel system vapor concentration gradients, is unlikely to stabilize within a nominal one hour period. Insofar as canister outgassing contributes to resting loss, those losses are not constant.

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### **DISCLAIMER**

This paper has been reviewed in accordance with the United States Environmental Protection Agency's peer and administrative review policies and

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approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

### REFERENCES

- American Soc. for Testing Materials, Standard Test Method for Vapor Pressure of Petroleum Products (REID Method), ASTM: D323-82, (1982).
- Atkins, P.W., Physical Chemistry, Freeman and Co. Press, San Francisco, (1978), pp. 174-181.
- Beightler, C.S., Phillips, D.T., and Wilde, D.J., Foundations of Optimization, 2nd Edn, W.Fabrycky and J.Mize, Eds, Prentice-Hall, Englewood Cliffs, N.J., (1979), pp. 34-35.
- Black, F.M., Crit. Revs. Environ. Contrl, 21(5), 373-410 (1991).
- Black, F.M., International Fuels and Lubricants Meeting and Exposition, Toronto, Canada, SAE 912413, (1991).
- Furey, R.L., and Perry, K.L., International Fuels and Lubricants Meeting and Exposition, Philadelphia, PA, SAE 861557, (1986).
- Harvey, C.A., Carey, P.M., Somers, J.H., and Garbe, R.J., International Fuels and Lubricants Meeting, Baltimore, MD, SAE 841357, 331-346 (1984).
- Haskew, H.M., Cadman, W.R., and Liberty, T.F., Government/Industry Meeting, Washington, DC, SAE 901110, (1990).
- Lang, J.M., and Black, F.M., International Congress and Exposition, Detroit, MI, SAE 810438, (1981).
- Lorang, P.A., Conference on Methanol as an Alternative Fuel Choice: An Assessment, Johns Hopkins Foreign Policy Institute, Washington, DC, (1989).
- Platte, L., U.S. EPA, Ann Arbor, MI, personal communication, (1993).
- Stump, F.D., Knapp, K.T., and Ray, W.D., J. Air Waste Management Assoc., 40, 872-880 (1990).
- U.S. Congress, Alternative Motor Fuels Act of 1988, Public Law 100-494, 100th Congress, 102 STAT. 2441, October 14, 1988.

U.S. Congress, Clean air Act Amendments of 1990, Report 101-952, U.S. Government Printing Office, Washington, D.C., October 26, 1990.

U.S. Dept. of Commerce, Protection of the Environment, Federal Register, CFR 40(86), July 1, 1994.

U.S. Environmental Protection Agency, Summary and Analysis of Comments on the Notice of Proposed Rule-making for Emission Standards and Test Procedures for Methanol-Fueled Vehicles/Engines, Office of Mobile Sources, Ann Arbor, MI (1988).

U.S. Environmental Protection Agency, Analysis of the Economic and Environmental effects of Methanol as an Automotive Fuel, Office of Mobile Sources, Ann Arbor, MI, (1989).

U.S. Environmental Protection Agency, User's Guide to MOBILE5, EPA Report No. EPA-AA-TEB-92-01, Office of Mobile Sources, Ann Arbor, MI (1992).

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