

## **DETERMINATION OF RATES OF PRODUCT CONSUMPTION AND SOOT FORMATION DURING COMBUSTION OF SOLVENTS COMMONLY CARRIED BY RAIL**

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(Received June 1, 1985; accepted in revised form October 1, 1985)

### **Summary**

A two-phase study of the combustion of solvents carried in large quantity by rail was performed. The first phase involved development of protocols and apparatus for determining the amounts of soot produced and heats of combustion for several commonly carried commodities under varying conditions of oxygen availability. In the second phase, the rate of product consumption, hereafter referred to as the "burnrate", was measured for solvents under controlled conditions. This paper presents a description of the combustion apparatus, the protocols used and the burnrate data obtained. The possibility of developing a predictive model for burnrate or amount of soot generated based on physical and chemical properties of the solvent is explored.

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### **Introduction**

In 1983, there were over 8500 Hazardous Materials Incident Reports filed with the Department of Transportation's Hazardous Materials Information System [1]. Of these incidents, 825 involved commodities shipped by rail. Over 115,000 gal plus 1,015 lbs of combustible liquids and 442,000 gal plus 141,000 lbs of flammable liquids were spilled in rail accidents in that year. (The units are taken as reported from the HAZMAT file.) Table 1 shows amounts of some commonly carried commodities involved in rail spills in 1983. It must be emphasized that most spills did not result in fire. According to the "1984 Emergency Response Guidebook" [2] issued by DOT to personnel responding to rail accidents, the procedure for serious fires is to evacuate personnel in the immediate vicinity and areas downwind and to let the fire burn itself out. Two pieces of data required to evaluate this "let-burn" option are: a) the products of combustion, to assess toxicity of the plume and permit estimation of a safe evacuation distance; and b) how fast the fuel is consumed, to determine how long the fire will last.

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TABLE 1

Amounts of some commonly carried commodities spilled during rail transit in 1983

| Commodity              | HAZMAT code <sup>a</sup> | Quantity spilled |
|------------------------|--------------------------|------------------|
| Benzene                | 2070                     | 13 gal           |
| Toluene                | 10340                    | 25,000 gal       |
| Xylenes                | 10890                    | 4 gal            |
| Styrene monomer        | 9874                     | 21 gal           |
| Butyraldehyde          | —                        | none reported    |
| Acetone                | 1010                     | 97 gal           |
| Methyl ethyl ketone    | 7040                     | 6 gal            |
| Methyl isobutyl ketone | —                        | none reported    |
| Alcohols <sup>b</sup>  | 1190                     | 132,000 gal      |
| Acrylonitrile          | 1140                     | 8 gal            |
| Ethyl acetate          | 4660                     | 1 gal            |
| Butyl acetate          | 2470                     | 3 gal            |

<sup>a</sup>DOT Hazardous Materials Information System code number.<sup>b</sup>Not otherwise specified.

Although a great deal of work has been performed on various aspects of combustion, most studies concentrate on either fundamental mechanisms of combustion and soot generation [3-7] or the toxicity of the combustion products [8-11]. Gases such as methane or ethylene [12,13], polymers [14-16], and natural products (e.g., wood [17]) have been studied. Results of combustion experiments are dependent upon the conditions under which they were obtained [18-20]. Correct evaluation of the let-burn option requires an internally-consistent dataset containing the heats of combustion, burnrates and the rates of soot production, as well as the composition of the gaseous and particulate combustion products for solvents burned under controlled conditions.

This report focuses on the prediction of the rate at which commonly carried solvents burn. Product analysis will be the subject of a future report. Two sets of experiments were required to obtain the necessary information on the combustion properties of the solvents and the effects of the conditions surrounding the burn. Calorimeter studies were performed to determine the effects of oxygen availability on the heats of combustion and the amounts of soot produced from combustion of organic solvents. These data were used as a basis for evaluating the design of an "open-burn" system, a combustion chamber constructed to permit control of burn conditions. Using it, solvents were burned and the rates of solvent consumption (burnrates) determined. Trends in the data are presented and the correlation of the results with physical and chemical properties of the solvents is discussed. The possibility of using the data to obtain a predictive model of burnrate is explored.

## Experimental procedure

### Reagents

Gases were obtained from Linde Corporation (Union Carbide, Linde Division, Danbury, CT). All gas concentrations are calculated as percent by volume. Solvents were obtained from Fisher Scientific (Atlanta, GA). Solvents for combustion were reagent grade except for the "xylenes", which was a commercial solvent grade mixture of the type shipped by rail.

### Calorimetry

A Parr Model 1341 Oxygen Bomb Calorimeter, standardized with benzoic acid, was used in this study. The system was calibrated using ASTM D-240 [21]. This procedure was modified for studies of reduced oxygen availability by reducing the pressure of oxygen used to charge the calorimeter from 30 atm to as low as 1.2 atm. A comparison of the experimental values for the heats of combustion of seventeen solvents of various type gave a mean experimental error of  $-0.49\%$  relative to the literature values.

In many cases, particularly at reduced oxygen concentrations, the solvent burned to completion but left significant amounts of carbonaceous in the sample cup. Deposits on the walls of the calorimeter were negligible. The residue was weighed and corrected for the residue from the tape used to seal the liquid in the cup. This value, reported as the percent of original mass of solvent burned, is called the "sootmass" and provides a means of estimating the relative amount of soot produced from the combustion of each solvent.

### Open-burn system

The scenario illustrated in Fig. 1 was employed for experimental design. The tankcar was assumed to have a single breach in the shell through which air entered and exhaust gases exited. Because of this air flow pattern, it was assumed that a dynamic equilibrium was reached between air influx rate, product volatilization, total heat released during combustion, and exhaust

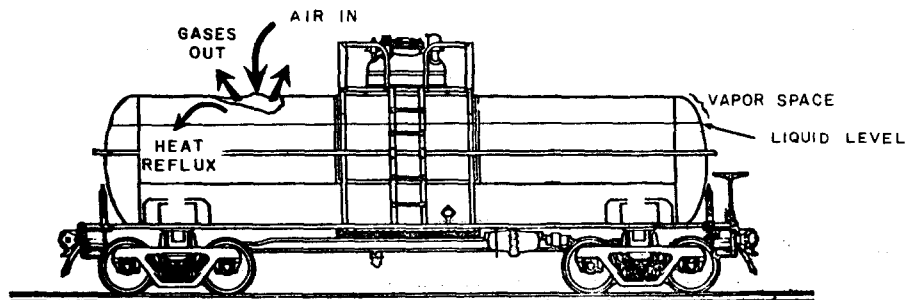


Fig. 1. Tankcar Scenario. Ambient conditions: atmospheric pressure, 1 atm; oxygen pressure, 159 torr; temperature, 25°C, relative humidity, constant.

gas flow. The sample was assumed to be liquid at room temperature (25°C), and on fire. Conditions surrounding ignition of the sample were not considered. Additionally, the following environmental assumptions were made: (1) all burns would occur in normal air (20.9% oxygen); (b) the ambient pressure would be one atmosphere; (c) the relative humidity would be constant during the burn; and (d) burning conditions could range from a minimum of air required for combustion to a condition of unlimited supply. Based on the constraints derived from this scenario, the furnace design had to allow for direct control of three key variables: oxygen concentration, air flow rate, and the sample temperature.

The combustion chamber, designed from the above considerations, is illustrated in Fig. 2. It consisted of a cylinder of 0.64 cm thick stainless steel, 20 cm inside diameter and 61 cm high. A demountable stainless steel funnel which terminated in a 3.5 cm inside diameter tube was affixed to the top. Pressurized laboratory air (20.9% oxygen) was passed through desiccant and 4A molecular sieves before entering a gas-dilution manifold which consisted of a set of flowmeters and precision metering valves. To obtain reduced oxygen

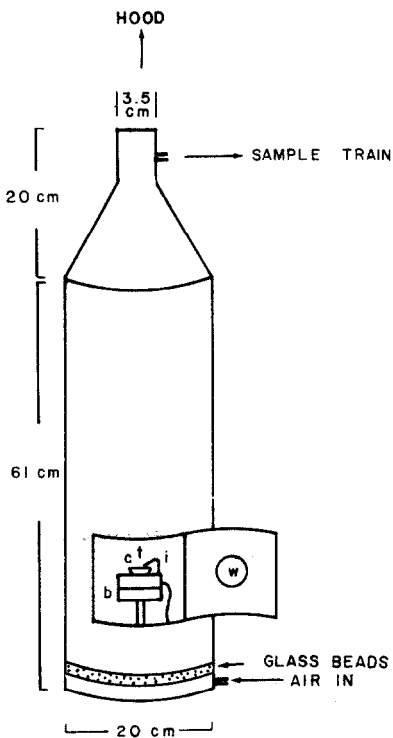


Fig. 2. Schematic diagram of combustion chamber used in the open-burn experiments. The sample block (b), crucible (c), igniter wire (i), thermocouple (t) and windowed door (w) are shown.

concentrations, the purified air was diluted volumetrically with nitrogen from a gas cylinder. The air entered at the base of the cylinder through a coiled, perforated copper tube below a 0.65 cm thick bed of glass beads. A windowed door located approximately 15 cm from the base allowed observation of, and access to, the sample. A 7.00( $\pm$ 0.05) ml aliquot of the solvent to be burned was transferred volumetrically to a platinum crucible. When using less than 21% oxygen, the entire chamber was flushed with the air/nitrogen mixture for two minutes prior to ignition of the sample, and correction was made for evaporative loss of sample during the interval. Any effect of the shape or the surface area of the crucible (7.07 cm<sup>2</sup>) was minimized by the use of the same crucible for all burns. The crucible rested in a 7.5 × 10 × 5 cm aluminium block fitted with a resistive heater to control the sample temperature prior to ignition. A Nichrome igniter wire ran through the block to a position above the sample well. Iron-constantan thermocouple wires were placed in the sample block, above the sample, and on the funnel. The thermocouples were connected through a selector switch to a strip-chart recorder. The burn was initiated by turning on a Variac controlling the igniter wire voltage until the sample ignited, as indicated by the thermocouple above the sample, which was monitored during the burn. Since the thermocouple was in a fixed position and the level of solvent decreased during the burn, the signal produced was not a true measure of the flame temperature and was not used as such.

#### *Experimental conditions*

In order to determine a set of standard conditions under which to conduct the experiments, two sets of organic solvents were used to characterize the open-burn system: normal alkanes and simple alcohols. These solvents are liquid at room temperature and reasonably flammable, which are the characteristics of many commodities shipped in rail tankcars. For these experiments, the sample block was maintained at 25°C. The rate of product consumption depends on the surface area of the liquid and the burnrates are therefore reported in units of mass per unit area per unit time (mg/cm<sup>2</sup>/min).

The data in Table 2 show the effect of air flow rate on burnrates of the model compounds. The presence of intramolecular oxygen significantly affected combustion of a solvent. For example, the alcohols were less affected by flow rate of the air supplied than the alkanes. At any given flow rate, the burnrate decreased with increasing molecular weight of the solvent in either series. For all subsequent studies, a flow rate of 10.0 lpm was selected as the standard condition. This inlet flow produced a face velocity within the range of the equipment used for collection of the combustion products for future analysis.

The effect of oxygen concentration on burnrates for the test solvents is shown in Table 3. At any given oxygen concentration, the burnrate followed the same trends as above; however, the burnrate decreased rapidly

TABLE 2

Effect of flowrate of normal (21% oxygen) air on burnrates of hydrocarbons and alcohols

| Compound   | Burnrate (mg/cm <sup>2</sup> /min) |         |          |              |
|------------|------------------------------------|---------|----------|--------------|
|            | 5.0 lpm                            | 7.5 lpm | 10.0 lpm | 15.0 lpm     |
| Pentane    | 62                                 | 86      | 107      | 146          |
| Hexane     | 47                                 | 73      | 90       | 99           |
| Heptane    | 30                                 | 38      | 46       | 44           |
| Decane     | N <sup>a</sup>                     | N       | N        | N            |
| Methanol   | 52                                 | 60      | 65       | 64           |
| Ethanol    | 41                                 | 48      | 48       | 48           |
| 2-Propanol | 36                                 | 41      | 49       | 46           |
| 1-Butanol  | N                                  | N       | 40       | <sup>b</sup> |

<sup>a</sup>Did not ignite or failed to burn to completion.<sup>b</sup>Experiment not performed.

TABLE 3

Effect of oxygen concentration on burnrates (mg/cm<sup>2</sup>/min) of hydrocarbons and alcohols (air flow = 10.0 lpm)

| Compound   | Percent oxygen |                |       |
|------------|----------------|----------------|-------|
|            | 10.5%          | 15.7%          | 20.9% |
| Pentane    | N <sup>a</sup> | 55             | 107   |
| Hexane     | N              | 32             | 90    |
| Heptane    | N              | I <sup>b</sup> | 46    |
| Decane     | N              | N              | N     |
| Methanol   | N              | 68             | 65    |
| Ethanol    | N              | I              | 48    |
| 2-Propanol | N              | I              | 49    |
| 1-Butanol  | N              | N              | 40    |

<sup>a</sup>Did not ignite.<sup>b</sup>Did not burn to completion.

with decreasing oxygen content. For the n-alkanes, a 25% decrease in oxygen halved the burnrate. At 10.5% oxygen, all solvents failed to ignite. These results are similar to studies of the combustion of polymers, wood, and organic liquids at similar oxygen concentrations [17] and for epoxy fibers at elevated (20–100%) oxygen concentrations [9].

## Results and discussion

### Calorimetry

Table 4 lists the energy released under conditions of varying oxygen pressure added to the bomb calorimeter for twenty (20) commodities commonly carried by rail. Whereas it may not be technically rigorous, this value is referred to as the "heat of combustion", which usually indicates that the value was obtained under conditions where oxygen is present in large excess. The effect of oxygen availability on the heat of combustion is as expected for most compounds. The general trend is an increase in the heat released as the air-to-fuel ratio increases. Oxygen containing species were less seriously affected by reduction in oxygen availability than other classes, as shown in the data in column 8 of Table 4. This value represents the percent decrease in the heat of combustion from 30.2 to 5.2 atm of oxygen. The effect of intramolecular oxygen is to significantly reduce the

TABLE 4

Heats of combustion (cal/g) under differing conditions of oxygen availability

| Compound             | Literature value <sup>a</sup> | Atmospheres of oxygen |                |       |       |      | % change |
|----------------------|-------------------------------|-----------------------|----------------|-------|-------|------|----------|
|                      |                               | 30.2                  | 20.2           | 15.2  | 10.2  | 5.2  |          |
| Methanol             | 5417                          | 5450                  | 5433           | 5382  | 5250  | 5385 | 1        |
| 2-Propanol           | 7899                          | 7913                  | 7942           | 7884  | 7863  | 5662 | 28       |
| 1-Butanol            | 8628                          | 8586                  | 8543           | 8423  | 8427  | 5818 | 33       |
| Ethyl acetate        | 6093                          | 5977                  | 6051           | 5966  | 5958  | 5461 | 10       |
| Vinyl acetate        | —                             | 5446                  | 5703           | 5714  | 5710  | 5550 | -2       |
| Butyl acetate        | 7295                          | 7405                  | 7315           | 7353  | 7276  | 5997 | 18       |
| MEK <sup>b</sup>     | 8100                          | 8000                  | 7978           | 7949  | 7916  | 6237 | 23       |
| MIBK <sup>c</sup>    | —                             | 8918                  | 8888           | 8827  | 8772  | 5625 | 37       |
| Butyraldehyde        | —                             | 8005                  | 8075           | 8078  | 8035  | 5513 | 31       |
| Acetone              | 7367                          | 7319                  | 7344           | 7258  | 7338  | 5144 | 30       |
| Acrylonitrile        | 7931                          | 7846                  | 7796           | 7846  | 7980  | 6107 | 23       |
| Chloroform           | 747                           | 1007                  | N <sup>d</sup> | N     | N     | N    | —        |
| Hexane               | 11546                         | 11426                 | 11410          | 11459 | 10745 | 5964 | 48       |
| Cyclohexane          | 11132                         | 11038                 | 11041          | 11082 | 10349 | 5987 | 46       |
| Benzene              | 10012                         | 9983                  | 9979           | 9823  | 9208  | 6137 | 38       |
| Toluene              | 10154                         | 10089                 | 10098          | 10068 | 8464  | 5365 | 47       |
| Xylenes <sup>e</sup> | 10268                         | 10155                 | 10204          | 10045 | 8629  | 5153 | 50       |
| Aniline              | 8728                          | 8631                  | 8659           | 8630  | 7552  | 5234 | 40       |
| Styrene              | 10054                         | 9959                  | 10065          | 9954  | 8952  | 5160 | 49       |
| Phenol               | 7764                          | 7656                  | 7680           | 7712  | 7492  | 6052 | 22       |

<sup>a</sup>Reference [22].

<sup>b</sup>Methyl ethyl ketone

<sup>c</sup>Methyl isobutyl ketone

<sup>d</sup>Did not ignite.

<sup>e</sup>Literature value is the average of the three isomers.

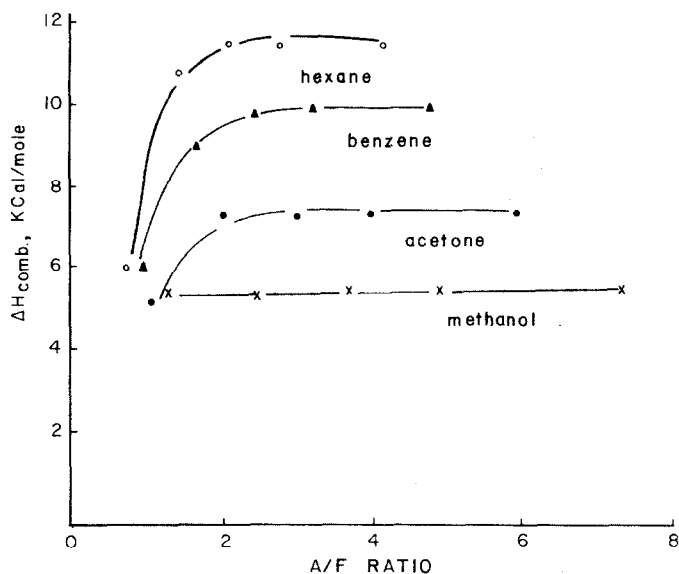


Fig. 3. Effect of oxygen availability (as A/F ratio) on the heats of combustion of solvents from four chemical groups.

TABLE 5

Soot formation (expressed as the percent of original mass) under conditions of differing oxygen availability

| Compound      | Atmospheres of oxygen |      |      |      |      |
|---------------|-----------------------|------|------|------|------|
|               | 30.2                  | 20.2 | 15.2 | 10.2 | 5.2  |
| Methanol      | 0.0                   | 0.0  | 0.21 | 0.74 | 2.03 |
| 2-Propanol    | 0.0                   | 0.0  | 0.08 | 0.23 | 3.93 |
| 1-Butanol     | 0.0                   | 0.0  | 0.09 | 0.0  | 2.02 |
| Ethyl acetate | 0.0                   | 1.36 | 2.54 | 1.10 | 3.29 |
| Vinyl acetate | 0.0                   | 0.0  | 0.0  | 0.0  | 4.32 |
| Butyl acetate | 0.0                   | 0.0  | —    | 0.53 | 1.82 |
| MEK           | 0.0                   | 0.11 | 0.22 | 0.47 | 5.53 |
| MIBK          | 0.0                   | 0.32 | 0.18 | 0.34 | 2.51 |
| Butyraldehyde | 0.20                  | 0.12 | 0.29 | 0.25 | 4.75 |
| Acetone       | 0.0                   | 0.28 | 0.18 | 4.09 | 5.39 |
| Acrylonitrile | 0.36                  | 0.29 | 0.22 | 0.81 | 3.31 |
| Hexane        | 0.0                   | 0.0  | 0.53 | 3.57 | 6.28 |
| Cyclohexane   | 0.0                   | 0.15 | 0.43 | 6.80 | 4.00 |
| Benzene       | 0.0                   | 0.0  | 0.24 | 6.63 | 34.1 |
| Toluene       | 0.17                  | 0.16 | 0.36 | 16.2 | 21.5 |
| Xylenes       | 0.0                   | 0.25 | 0.72 | 7.8  | 20.6 |
| Aniline       | 0.0                   | 0.24 | 1.05 | —    | 16.7 |
| Styrene       | 0.0                   | 0.0  | 4.52 | 10.4 | 42.1 |
| Phenol        | 0.0                   | 0.58 | 0.92 | 1.83 | 10.4 |



effect of changes in the externally supplied oxygen. Aromatic species exhibited the most significant decrease in the heat of combustion; however phenol, which contains oxygen, was the least affected aromatic. All of the solvents tested failed to burn to completion between 1 and 5 atm of oxygen. The amount of oxygen in the bomb for each test was used to calculate the stoichiometric air-to-fuel ratio, and the data are plotted for four solvents in Fig. 3.

The amount of soot formed during combustion of the solvents was calculated from the weight of the residue in the sample cup. The percent of original mass present was termed the percent "sootmass". The data are presented in Table 5 and plotted against air-to-fuel ratio in Fig. 4 for selected solvents. The data in Table 5 can be compared across a row to show the increase in soot production with decreasing oxygen availability. When compared from top to bottom in a column, the data show the effect of molecular structure on soot production. Oxygen-containing species show the least amount of soot formation at 5.2 atm, with aromatics producing the most soot. Phenol again shows the effect of intramolecular oxygen, in this case as a reduction in the amount of soot produced. Aniline also produces less soot than purely hydrocarbon aromatics, though the effect is not as great as for phenol. This suggests that any model of burnrate or soot production must include a correction for the molecular composition of the solvent.

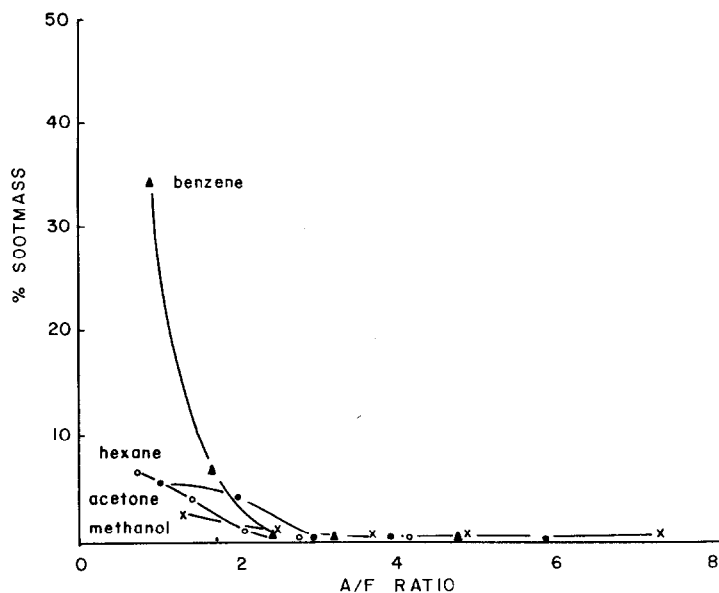


Fig. 4. Effect of oxygen availability (as A/F ratio) on the amounts of soot produced (as % of the original mass of solvent burned) from combustion of solvents from four chemical groups.

*Open-burn system*

The burnrates of sixteen solvents were measured under conditions of varying oxygen content in air supplied at a constant rate. The data are presented in Table 6. The effects of oxygen availability observed in the calorimeter studies are similarly apparent in the open-burn results. A decrease in the percent oxygen of the air stream reduces the burnrate, the effect being less on oxygen-containing species. Indeed, methanol was the only solvent to burn to completion at 10.5% oxygen. The effect was largest for the aromatics, two of which failed to burn to completion at 15.7% oxygen. Aromatics, as observed in the calorimeter study, produce the most soot. The consistency of the trends in the open-burn data and the calorimeter results supports the validity of the furnace design.

*Correlation of burnrate and soot production with physical and chemical properties of the solvent*

Trends observed in the experimental results indicated that a model to predict the burnrate or soot production of a compound might be obtained using as input the physical and chemical properties of the solvent. Accord-

TABLE 6

Burnrates of solvents in the open-burn system at different oxygen concentrations (air flow = 10.0 lpm)

| Compound                   | Burnrate (mg/cm <sup>2</sup> /min) |                 |                 |
|----------------------------|------------------------------------|-----------------|-----------------|
|                            | 20.9%<br>Oxygen                    | 15.7%<br>Oxygen | 10.5%<br>Oxygen |
| Methanol                   | 65                                 | 59              | 57              |
| 2-Propanol                 | 49                                 | 42              | N <sup>a</sup>  |
| 1-Butanol <sup>b</sup>     | 40                                 | 27              | N               |
| Ethyl acetate              | 82                                 | 34              | N               |
| Butyl acetate              | 31                                 | 32              | N               |
| MEK                        | 71                                 | 42              | N               |
| MIBK                       | 51                                 | 30              | N               |
| Butyraldehyde              | 68                                 | 34              | N               |
| Acetone                    | 79                                 | 51              | N               |
| Acrylonitrile <sup>b</sup> | 86                                 | 50              | N               |
| Hexane                     | 90                                 | 41              | N               |
| Cyclohexane                | 58                                 | 31              | N               |
| Benzene                    | 123                                | 54              | N               |
| Toluene                    | 81                                 | I <sup>c</sup>  | N               |
| Xylenes                    | 51                                 | I               | N               |
| Styrene <sup>b</sup>       | I                                  | N               | N               |

<sup>a</sup>Did not ignite.

<sup>b</sup>Sample at 35°C.

<sup>c</sup>Did not burn to completion.

ingly, the twenty-two physical and chemical parameters listed in Table 7 were compiled [22–24]. Also included in Table 7 are the experimentally obtained burnrates and percent sootmass data. Statistical methods have been developed to interpret large datasets. A commercial package of statistics programs, called SAS [25], was run on an IBM 370/3033 mainframe computer. The technique of Factor Analysis was used to reduce the number of dependent variables (the parameters) to the independent variables, or Factors which they represent. The number of Factors needed to explain the variance in the original set of parameters is determined by the computer. The Factors are ranked according to the amount of the variance for which they account. Thus, Factor 1 can be interpreted to be the most important independent variable. The method also determines the “weight” or relative importance of each of these Factors for each parameter. The physical significance of the Factors can be inferred from the types of parameters which have similar weights. In this case, a weight of 0.90 or greater for a Factor was considered to be sufficient to use the parameter to assign physical significance to a Factor.

The data from Table 7 were analyzed using a rotated (Varimax Rotation) factor method. The resulting matrix was rearranged to the form shown in Table 8. Four Factors were needed to account for the variance in the data. The parameters were divided into five groups, or Clusters, based on the calculated weights for the Factors. These five Clusters were then used to assign the four Factors a physical significance.

The parameters in Cluster 1 are related to the “flammability” of the solvent and show high weights for Factor 1. Factor 1 is therefore interpreted to indicate a “flammability” component to the dataset. The parameters in Cluster 2 are measures of the “volatility” of the solvent. Evaporation factor has a high weight for Factor 1. The remaining parameters have moderate weights for both Factors 1 and 2, indicating that volatility itself is not an unique Factor in explaining the variance in the matrix of physical and chemical properties used in this analysis. Volatility does contribute to the flammability of a solvent, however, as indicated by the high correlation of evaporation factor with Factor 1. The four parameters in Cluster 3 are related to the composition of the solvent and show high weights for Factor 2, which is therefore interpreted to represent a “composition” component. Since refractive index is a measure of the aromaticity of the solvent it is therefore also composition-dependent and has a high weight for Factor 2. Factor 3, as represented by the Cluster 4 parameters, is interpreted to be a “mass-conversion” term which results from the mixture of units used in the parameters. The remainder of the parameters, some of which are listed in Cluster 5, did not meet the 0.9 significance level with any Factor, though melting point gave the highest weight for Factor 4. Due to the low weights, a physical meaning to Factor 4 cannot be assigned from these data. The results of this analysis indicate that the physical and chemical properties of solvents found in the literature actually represent only 3–5

TABLE 7

Physical and chemical properties of commonly carried solvents

| Parameter                           | Benzene | Toluene | Xylenes | Cyclohexane | Hexane |
|-------------------------------------|---------|---------|---------|-------------|--------|
| Molecular weight, (g/mol)           | 78.1    | 92.1    | 106.2   | 84.2        | 86.2   |
| Melting point, (°C)                 | 5.5     | -95.0   | -19.6   | 6.5         | 97.5   |
| Boiling point, (°C)                 | 80.1    | 110.6   | 140.0   | 80.7        | 69.0   |
| Density, (g/mL)                     | 0.8787  | 0.8660  | 0.8670  | 0.7781      | 0.6600 |
| Refractive index, (R.I. units)      | 1.4691  | 1.4691  | 1.4995  | 1.4266      | 1.3751 |
| Dielectric constant, (20°C)         | 2.28    | 2.38    | 2.40    | 2.03        | 1.89   |
| Dipole moment, (gas phase, debye)   | 0.0     | 0.36    | 0.31    | 0.0         | 0.0    |
| Heat of vaporization, (cal/mol)     | 10245   | 9368    | 9904    | 7830        | 7627   |
| Heat of combustion, (cal/mol)       | 10012   | 10154   | —       | 11132       | 11546  |
| Hildebrand constant, (unitless)     | 9.20    | 8.90    | 8.76    | 8.20        | 7.30   |
| Threshold limit value, (ppm) — 1978 | 10      | 100     | 100     | 300         | 100    |
| Threshold of smell, (ppm)           | 5.0     | 5.0     | 4.0     | 0.4         | —      |
| Vapor pressure, (mm Hg)             | 76.0    | 22.0    | 5.0     | 78.0        | 120    |
| Volatility, 20°C, (mg/l)            | 325     | 111     | 29      | 360         | 565    |
| Evaporation factor, (ether = 1)     | 3.0     | 6.1     | 13.5    | —           | 8.7    |
| Lower ignition limit, (vol.%)       | 1.2     | 1.2     | 1.0     | 1.2         | 1.2    |
| Upper ignition limit, (vol.%)       | 8.0     | 7.0     | 7.6     | 8.3         | 7.4    |
| Flash point, (°C)                   | -11.0   | 4.4     | 23.5    | -18         | -20    |
| Ignition temperature, (°C)          | 555     | 535     | 465     | 260         | 240    |
| % Carbon, (wt./wt.)                 | 93.3    | 91.3    | 90.5    | 85.6        | 83.6   |
| % Hydrogen, (by wt.)                | 7.75    | 8.75    | 8.75    | 14.4        | 16.4   |
| % Oxygen, (by wt.)                  | 0.0     | 0.0     | 0.0     | 0.0         | 0.0    |
| <i>Experimental data</i>            |         |         |         |             |        |
| Burnrate (mg/cm <sup>2</sup> /min)  | 123     | 81      | 51      | 58          | 76     |
| % Sootmass (% original wt.)         | 34.1    | 21.5    | 20.6    | 4.00        | 6.28   |

fundamental characteristics. Selection of parameters with the highest weight for each of the Factors should produce a model with no more than 3–5 variables.

Burnrates for eleven of the solvents were then added to the matrix, as was the percent sootmass at 5.2 atm oxygen (from the calorimeter study). A correlation matrix was then generated using a SAS routine. Table 9 shows the correlation coefficients of these two experimental observations with the above parameters. Comparison of Tables 8 and 9 shows that burnrate is most significantly affected by those parameters related to volatility and flammability (Factor 1) whereas sootmass correlates more strongly with composition-dependent parameters (Factor 2). The parameter having the highest correlation level with sootmass was dipole moment. This serves to illustrate the reasons for the seemingly poor correlations for burnrate and the potential for misleading interpretations due to the small size of the dataset. Since most species were either hydrocarbons (dipole moment approximately zero) and oxygenated species (e.g. alcohols, with large dipole moments), the correlation may not actually be as significant as it appears.

The solvents selected for this discussion are the most commonly carried rail commodities and represent a wide range of chemical classes (alcohols;

| Methanol | 2-Propanol | 1-Butanol | Acetone | Butyraldehyde | Ethyl acetate |
|----------|------------|-----------|---------|---------------|---------------|
| 32.0     | 60.1       | 74.1      | 58.1    | 72.1          | 88.1          |
| -97.8    | -88.5      | -90.0     | -94.0   | -99.0         | -83.6         |
| 64.7     | 82.5       | 117.5     | 56.5    | 74.8          | 77.1          |
| 0.7866   | 0.7808     | 0.8100    | 0.7880  | 0.8016        | 0.9020        |
| 1.3288   | 1.3776     | 1.3993    | 1.3588  | 1.3843        | 1.3723        |
| 33.6     | 18.3       | 17.1      | 20.7    | 13.4          | 6.02          |
| 1.70     | 1.66       | 1.66      | —       | —             | 1.78          |
| 9377     | 10064      | 10970     | 7641    | —             | 8301          |
| 5417     | 7899       | 8628      | 7366    | —             | 6093          |
| 14.5     | 10.0       | 13.6      | 9.78    | —             | 8.88          |
| 200      | 200        | 50        | 1000    | —             | 400           |
| 5.0      | 100        | 25.0      | 100     | —             | 50            |
| 96.0     | 32.0       | 4.3       | 175     | —             | 73            |
| 168      | 105        | 17        | 556     | —             | 350           |
| —        | —          | 33.0      | 2.1     | —             | 2.9           |
| 5.5      | 2.0        | 1.4       | 2.5     | —             | 2.1           |
| 44.0     | 12.0       | 11.3      | 13.0    | —             | 11.5          |
| 12       | 11.7       | 37        | -18     | -6.7          | 7.2           |
| 455      | 425        | 340       | 540     | —             | 460           |
| 37.5     | 60.0       | 66.0      | 62.0    | —             | 54.5          |
| 2.6      | 13.4       | 13.8      | 10.4    | —             | 9.2           |
| 49.9     | 26.6       | 22.2      | 27.6    | —             | 36.3          |
| 63       | 45         | 40        | 79      | 68            | 82            |
| 2.03     | 3.94       | 2.02      | 0.00    | 4.75          | 3.29          |

aldehydes; normal and substituted aromatics; cyclic, saturated and unsaturated hydrocarbons). This diversity is responsible for the low correlation coefficients seen in Table 9. Correlation matrices run on compounds within a chemical class, however, gave significantly higher correlation coefficients. This suggested that within a compound type, it may indeed be possible to predict burnrate or soot production from a limited number of physical and chemical parameters.

#### *Development of a model for burnrate of simple hydrocarbons and alcohols*

A set of simple hydrocarbons (pentane, hexane, heptane and octane) and alcohols (methanol, (ethanol was excluded since it contained 5% water), n-propanol, n-butanol) was used to develop a simple predictive model for burnrate using the Generalized Linear Model approach from SAS. It is assumed that the burnrate is a linear function of one or more of the parameters in the dataset. The computer generates the best-fit line from the parameters, starting with the one which accounts for the largest variance in the dataset, and adding terms until the correlation coefficient approaches unity. For the model compounds, the parameter which gave the best one-dimensional prediction of burnrate was, not unexpectedly, boiling point

TABLE 8

Rotated factor pattern for the most significant parameters in each Factor

| Parameter                          | Factor 1 | Factor 2 | Factor 3 | Factor 4 |
|------------------------------------|----------|----------|----------|----------|
| <b>Cluster 1 (flammability)</b>    |          |          |          |          |
| Flash point                        | 0.98     | 0.08     | 0.10     | -0.14    |
| Ignition temperature               | -0.93    | -0.36    | 0.09     | 0.03     |
| Evaporation factor                 | 0.95     | -0.03    | -0.31    | 0.01     |
| <b>Cluster 2 (volatility)</b>      |          |          |          |          |
| Boiling point                      | 0.82     | -0.48    | 0.23     | -0.25    |
| Dielectric constant                | 0.17     | 0.47     | -0.85    | -0.16    |
| Dipole moment                      | 0.72     | 0.58     | 0.36     | -0.08    |
| Volatility                         | -0.85    | 0.44     | -0.26    | 0.18     |
| Hildebrand constant                | 0.84     | 0.08     | -0.52    | 0.08     |
| <b>Cluster 3 (composition)</b>     |          |          |          |          |
| Heat of combustion                 | 0.05     | -0.99    | -0.05    | 0.10     |
| % Oxygen                           | 0.14     | 0.98     | -0.09    | -0.12    |
| % Carbon                           | -0.15    | -0.96    | 0.14     | 0.16     |
| Refractive index                   | -0.00    | -0.93    | 0.37     | 0.00     |
| <b>Cluster 4 (mass conversion)</b> |          |          |          |          |
| Molecular weight                   | 0.21     | -0.26    | 0.92     | -0.20    |
| Density                            | -0.12    | -0.05    | 0.97     | 0.22     |
| <b>Cluster 5 (not assignable)</b>  |          |          |          |          |
| Melting point                      | -0.23    | -0.38    | 0.17     | 0.88     |
| Heat of vaporization               | 0.74     | -0.53    | 0.02     | 0.39     |
| Threshold limit value              | -0.58    | 0.57     | -0.49    | -0.29    |

(BP) ( $r = 0.889$ ). The % carbon (% C) was added to the linear model, raising the correlation coefficient to 0.968. Addition of molecular weight ( $MW$ ) increased the correlation to 0.989 and the inclusion of auto-ignition temperature ( $IGN T$ ) gave a correlation coefficient for the linear model of burnrate of 0.999. The resulting linear equation for predicting burnrate was:

$$\text{Burnrate} = -0.143 (\text{BP}) + 1.67(\% \text{ C}) - 2.18 (MW) - 0.357 (IGN T) + 240.7$$

As expected, terms related to volatility, flammability, composition and a mass conversion term were included in the model.

One way to estimate the accuracy of the model, is to successively remove each compound from the dataset and recalculate the equation. The new coefficients are used to predict back the removed value. The difference between the calculated and observed values for burnrate is the error of the prediction. The relative error for the predicted burnrate of the compounds

using the above equation is: methanol, 0.0%; n-propanol, -1.3%; n-butanol, +2.0%; pentane, +1.6%; hexane, -0.4%; heptane, +0.7%; and octane, -0.8%. These are within experimental error. Thus, at least for simple datasets, prediction of the rate of product consumption can be obtained with good accuracy.

Using the same coefficients to predict burnrate for the compounds in Table 7 (excluding butyraldehyde, for which the auto-ignition temperature was not found), the results deteriorate. The average error in the predicted burnrate, relative to the observed, is -22%, with a standard deviation of 94% and a range of errors from -150% to +159%. Additionally, molecular weight becomes statistically invalid in the model (99% probability that it would fail the student's *T* test).

One hundred and thirtyeight compounds, of which approximately half are flammable or combustible liquids, account for over 98% of the mass of commodities shipped by rail. As indicated above, these compounds represent a variety of chemical classes. In order to obtain a valid and more

TABLE 9

Correlation of burnrate and soot production with selected physical and chemical properties of the solvent burned

| Parameter                | Correlation coefficient |            |
|--------------------------|-------------------------|------------|
|                          | Burnrate                | % Sootmass |
| Evaporation factor       | -0.77                   | -0.47      |
| Flash point              | -0.57                   | -0.15      |
| Volatility               | 0.51                    | -0.06      |
| Dipole moment            | -0.56                   | -0.98      |
| Refractive index         | 0.21                    | 0.81       |
| % Hydrogen               | -0.54                   | -0.73      |
| % Carbon                 | 0.32                    | 0.71       |
| Ignition temperature     | 0.49                    | 0.65       |
| % Oxygen                 | -0.24                   | -0.61      |
| Vapor pressure           | 0.42                    | -0.18      |
| Boiling point            | -0.37                   | 0.35       |
| Hildebrand constant      | -0.36                   | 0.35       |
| Dielectric constant      | -0.34                   | -0.53      |
| Density                  | -0.29                   | 0.49       |
| Heat of vaporization     | -0.19                   | 0.31       |
| Heat of combustion       | 0.17                    | 0.39       |
| Upper ignition limit     | -0.15                   | -0.38      |
| Treshhold of smell       | -0.15                   | 0.47       |
| Molecular weight         | -0.09                   | 0.43       |
| Treshhold limiting value | 0.05                    | -0.59      |

generalized model for the prediction of burnrate (or sootmass), additional data are required. The list of compounds studied is currently being expanded to approximately 50 solvents including normal, branched and substituted aliphatics and aromatics; acetates; acrylates; alcohols; aldehydes; ketones; and chlorinated solvents. Given this larger dataset containing burnrate and sootmass from several compounds in each chemical group, it should be possible to develop a more general model using the above methods. To date the largest problem arises from the lack of consistent data on the chemical and physical properties of the solvents.

### Acknowledgements

This work was supported jointly by the Research and Test Department, Association of American Railroads, Washington, DC, and the Environmental Emergency Technology Division, Technical Services Branch, Environmental Protection Service, Ottawa, Ont. The input of Mr. Gerald Meier from AAR was particularly helpful. Mr. David Jossi, of Wilson Hill Associates is acknowledged for his assistance in obtaining the HAZMAT data. Portions of this work were presented at the Technical Seminar on Chemical Spills, Toronto, Ont., October, 1983 and at the Hazardous Materials Spills Conference, Nashville, TN, April, 1984.

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