

Estimates of Air Emissions from Asphalt Storage Tanks and Truck Loading

David C. Trumbore

Asphalt Technology Laboratory, Owens Corning, Summit, IL 60501

Title V of the 1990 Clean Air Act requires the accurate estimation of emissions from all U.S. manufacturing processes, and places the burden of proof for that estimate on the process owner. This paper is published as a tool to assist in the estimation of air emissions from hot asphalt storage tanks and asphalt truck loading operations. Data are presented on asphalt vapor pressure, vapor molecular weight, and the emission split between volatile organic compounds and particulate emissions that can be used with AP-42 calculation techniques to estimate air emissions from asphalt storage tanks and truck loading operations. Since current AP-42 techniques are not valid in asphalt tanks with active fume removal, a different technique for estimation of air emissions in those tanks, based on direct measurement of vapor space combustible gas content, is proposed. Likewise, since AP-42 does not address carbon monoxide or hydrogen sulfide emissions that are known to be present in asphalt operations, this paper proposes techniques for estimation of those emissions. Finally, data are presented on the effectiveness of fiber bed jilters in reducing air emissions in asphalt operations.

INTRODUCTION

The use of asphalt is prevalent throughout recorded history. It is produced in refinery distillation towers and solvent extraction units. Asphalt is modified by several means: reacting with oxygen in blowing operations to produce roofing asphalts, emulsifying to produce an aqueous liquid at ambient temperature, blending with solvents to make asphalt cutback, or blending or even reacting with polymers to make polymer modified asphalt. In all these cases the asphalt is stored in tanks, usually fixed roof tanks, and is loaded into trucks to ship to customers.

Title V of the 1990 Clean Air Act required the accurate estimation of emissions from all U.S. manufacturing processes, and placed the burden of proof for that estimate on the process owner. In response to Title V, Owens Corning analyzed options for estimating emissions from

asphalt tanks and loading operations and this paper is the result of that study. In particular, attempts have been made to develop data to be used with existing calculation methods to estimate air emissions in asphalt operations, to develop calculation schemes that work when existing methods cannot be used, and to expand the number of pollutants estimated. The techniques described in this paper have been used by Owens Corning to estimate asphalt emissions from their asphalt plants for many Title V permit applications.

Owens Corning also evaluated appropriate emission factors for the asphalt blowing process and that analysis has been published [1].

The Emission Factor and Inventory Group in the U. S. Environmental Protection Agency's (EPA) Office of Air Quality Planning and Standards develops and maintains a database of emission factors and a series of calculation methods for estimating air emissions from manufacturing processes. These emission factors are published in a series known as AP-42 [2]. One technique published in AP-42 calculates hydrocarbon emissions from a fixed roof tank storing petroleum products [3], and another calculates emissions for loading trucks with petroleum products [4]. These techniques require data on asphalt vapor pressure and the molecular weight of the asphalt vapor. The calculations result in an estimate of the amount of hydrocarbons emitted from the process. To complete the emission estimate, these hydrocarbons need to be split into particulate emissions (PM) and volatile organic compounds (VOC), and any control device collection or destruction efficiencies need to be applied.

In the AP-42 calculation of emissions from fixed roof tanks it is assumed that the motive force pushing vapor out of the tank comes from either the pumping of liquid into the tank or the expansion of tank contents due to temperature changes. For tanks with an active ventilation system this assumption is invalid and a different method of emission estimation is required. This is especially true if an air sweep is used to control the vapor space composition to

prevent explosive conditions [5,6]. A technique to estimate emissions from these actively controlled tanks is described in the section of this paper on non AP-42 estimates.

AP-42 EMISSION ESTIMATING TECHNIQUES FOR ASPHALT EQUIPMENT

Passive vented hot asphalt tanks: AP-42 for fixed roof petroleum tanks can be used to calculate total hydrocarbon emissions from asphalt and oil tanks that are passively vented to the atmosphere. This AP-42 calculation, simply stated, determines the amount of hydrocarbon in the tank vapor space from the vapor pressure of the material in the tank at the liquid surface temperature, and then calculates the amount of vapor forced out of the tank due to liquid being actively pumped into the tank (working losses), or due to thermal expansion or contraction of tank contents driven by ambient temperature changes (breathing losses). The result is an actual weight of hydrocarbon emissions in a specified time period. A detailed description of the tank calculations is available from the EPA web site [3]. The AP-42 calculation requires a vapor pressure versus temperature curve for the asphalt, and also estimates of the vapor phase molecular weight and partition of hydrocarbons into VOC and particulate, in addition to process data like asphalt throughput, temperature, and tank level. If the tank passively breathes through a control device, then the appropriate control efficiency is applied to the VOC and particulate emissions calculated from AP-42.

Hot Asphalt Loading: The AP-42 calculation for hydrocarbon emissions from truck or rail tank car loading of asphalt is done by estimating the amount of evaporation during the loading process. The estimate takes into account the turbulence and vapor liquid contact induced by the method of loading, i.e. submerged versus splash loading. The calculation result is an emission related to the number of tons of material loaded into the truck. Vapor pressure versus temperature curve, temperature of loading, and throughputs are key variables in this calculation. Again, the hydrocarbon emission resulting from this calculation needs to be split into particulates and VOCs and control device collection and destruction efficiencies need to be applied. A detailed description of the loading calculations is available from the EPA web site [4].

DATA NEEDED FOR APPLICATION OF AP-42 TO ASPHALT EQUIPMENT

Vapor Pressure: Information on asphalt vapor pressure as a function of temperature is not readily available in the literature and its measurement is not common. However, these data are essential to use AP-42 calculations for estimating asphalt tank and loading emissions. Asphalts from different crude oil sources and from different processes will differ in composition and vapor pressure. In the extreme, every residual material used in asphalt processing would need to be measured for vapor pressure at multiple temperatures. This would entail a prohibitive amount of testing for minimal gain in accuracy of emission estimates. To provide a cost effective solution to this problem for its emission calculations, Owens Corning has

characterized the vapor pressure of three basic classes of asphalt materials, chosen by their processing history. An estimate of the vapor pressure of each asphalt class was made by measuring asphalts from multiple crude oil source in each class and using the average vapor pressure at each temperature in a regression to generate one vapor pressure equation for the class. The three classes of asphalt chosen for this analysis follow.

- Fluxasphalts, or vacuum tower bottoms that can be used in the asphalt blowing process to make specification roofing asphalts. These materials generally have a higher vapor pressure than paving asphalts.
- Paving asphalts, or vacuum tower bottoms that meet paving specifications.
- Oxidized asphalt, or vacuum tower bottoms that have been reacted with oxygen in the asphalt blowing process to increase their softening point and viscosity. Typical softening points are greater than 190°F (88°C) These materials are also called air blown asphalts and are used extensively in the roofing industry. They generally have lower vapor pressure than the other two classes.

Vapor pressure measurements described in this paper were done by the Phoenix Chemical Lab in Chicago using the Isoteniscope (ASTM D2879).

To facilitate computer calculations it is desirable to develop an equation that accurately describes the relationship of vapor pressure and temperature. Thermodynamic treatment of the dependence of vapor pressure on temperature has led to the Clausius modification of the Clapeyron equation [7].

Clausius Clapeyron Treatment of Vapor Pressure Data

$$\ln P = a - b/T$$

Where: P is the equilibrium vapor pressure of the liquid in question,
a & b are constants, and
T is the absolute temperature of the liquid in question.
Values of a & b depend on the choice of pressure and temperature units.

Table 1 and Figure 1 give an example of the agreement of this equation with vapor pressure data for oxidized asphalts from 13 sources around the country. In Figure 1, vapor pressure of each asphalt is plotted versus temperature to show the differences between asphalt's data to the Clausius Clapeyron each individual asphalt's data to the Clausius Clapeyron relationship. The correlation coefficients in Table 1 indicate that the agreement of this equation to all individual asphalt vapor pressure versus temperature data is excellent, with correlation coefficients for the individual asphalts greater than 0.9999. The agreement is also excellent for the individual asphalts making up the other two asphalt classes. Table 1 also presents the methodology to choose constants to use with the

Table I. Vapor Pressure Data for Oxidized Asphalts

Asphalt	Temperature (°F ¹)			All Data in mm Hg ²							r value ³
	200	250	300	350	400	450	500	550	575	600	
Plant A			0.39	2	7.9	26	77	225		550	-0.999922929
Plant C		0.42	2	7.9	26		180	400	670		-0.999934558
Plant H		0.43	2	7.7	25		165	410	590		-0.999939281
Plant I		0.44	1.9	7.2	22	59	140	340		680	-0.999945804
Plant K	0.43	1.7	6.1	18.5	50	115	205	510	680		-0.999660554
Plant M	0.28	1.2	4.6	15	41	97	210	460	640		-0.999948167
Plant N	0.19	0.88	3.5	12	34	85	190	430	590		-0.999965421
Plant P	0.46	1.8	6	17.5	44	96	195	410		710	-0.999948079
Plant O		0.11	0.47	1.7	5.2	13.2	34	74		142	-0.999916578
Plant J		0.16	0.64	2.2	6.2	14.8	36	72		135	-0.999838114
Plant S	0.28	1.05	3.3	9.4	23	50	105	200		350	-0.999986213
Plant S				0.28	1	3.2	10	25		58	-0.999875798
Plant X		0.1	0.4	1.5	4.7	12.5	33	75		152	-0.999930649
Class Standard	0.22	0.91	3.2	9.5	24.9	58.8	127	254	351	477	
Average Vp	0.33	0.75	2.6	7.9	22.3	54.7	122	284	634	347	-0.994026635

13459 b in Clausius Clapeyron curve for average vapor pressure data
 18.86 a in Clausius Clapeyron curve for average vapor pressure data

1. 1 °C = (°F - 32) * 5/9

2. 1 Pa = 0.0075 mm Hg

the r value is for the fit of the vapor pressure data to the Clausius Clapeyron Equation

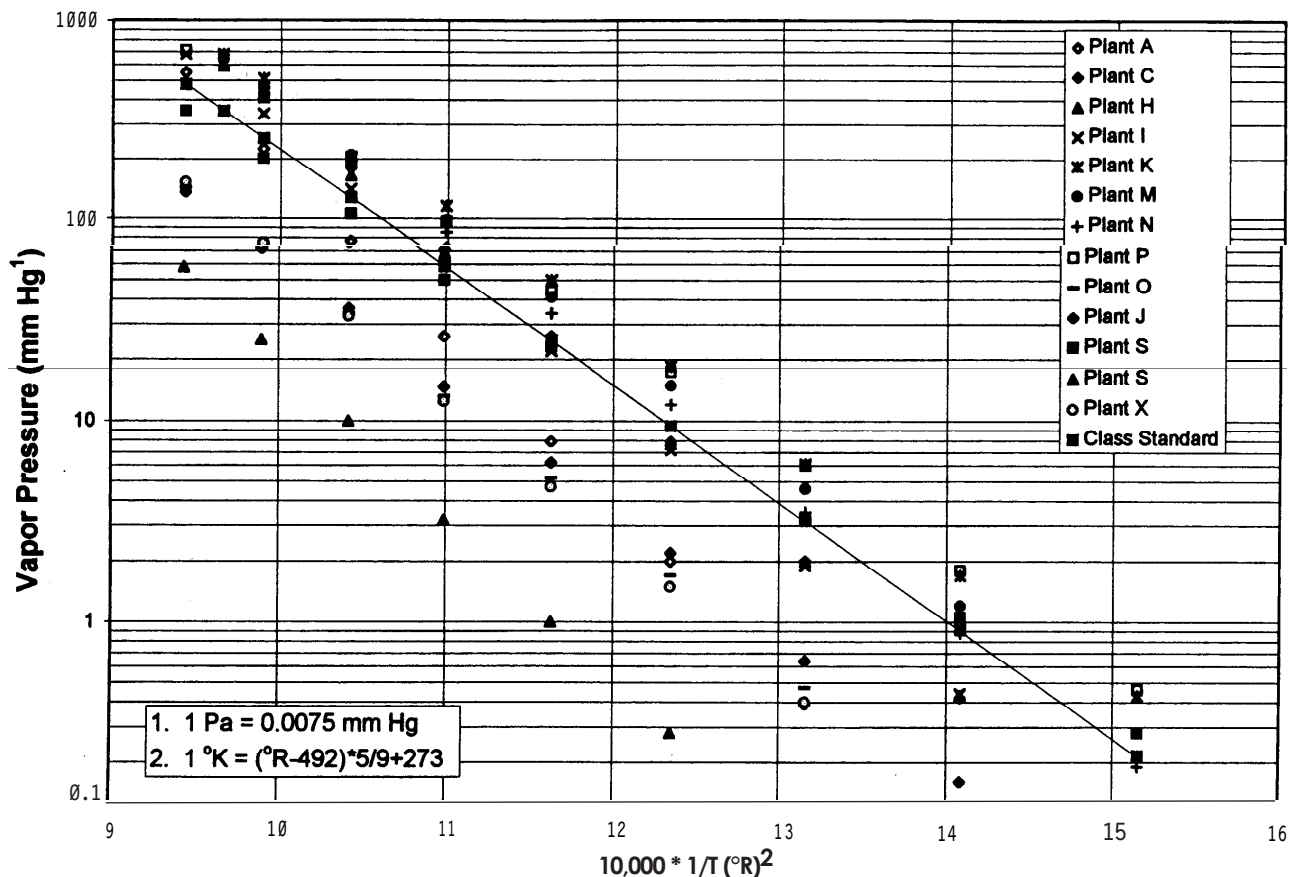


FIGURE 1. Oxidized Asphalt Vapor Pressure Data in Clausius Clapeyron Format

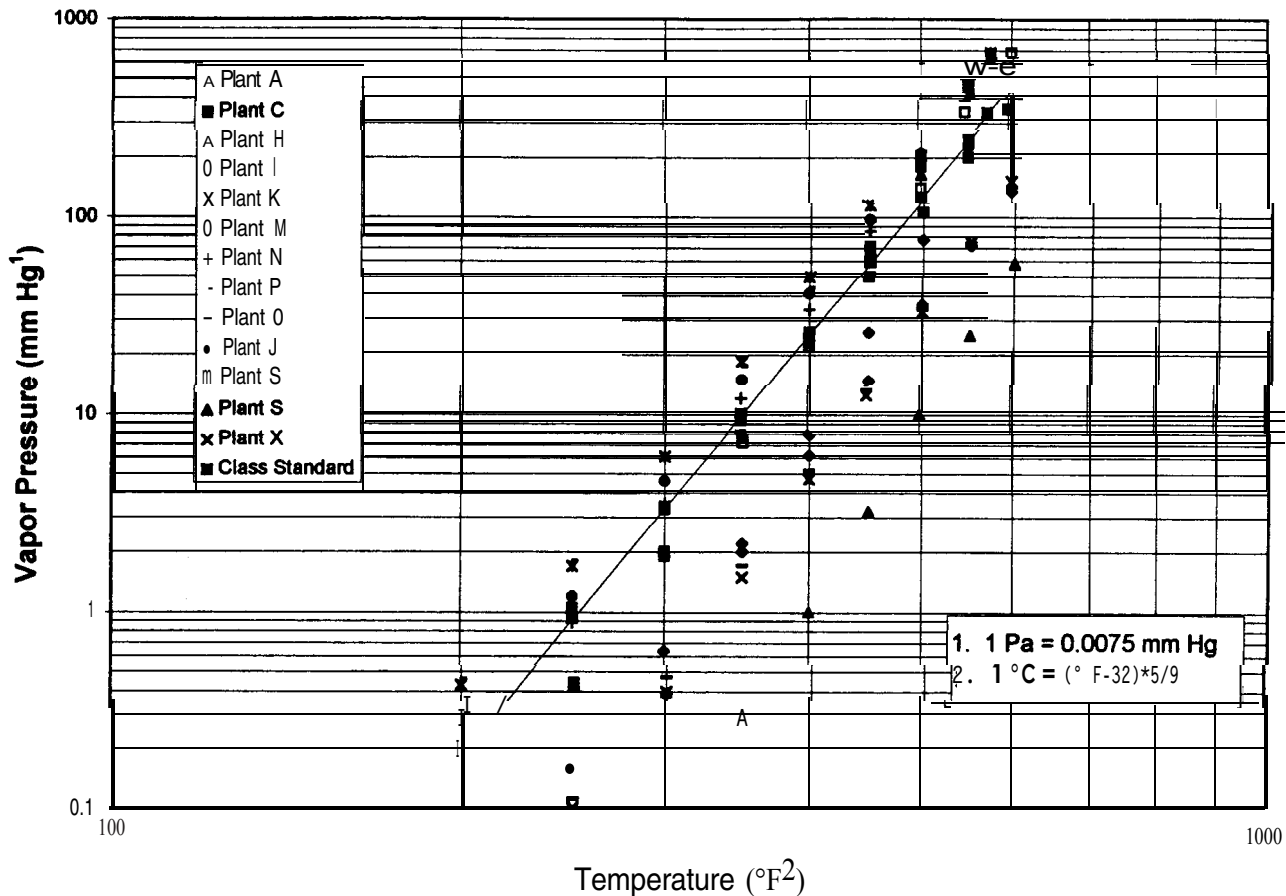


FIGURE 2. Oxidized Asphalt Vapor Pressure Data in Double Log Format

Clausius Clapeyron equation to calculate 3 representative vapor pressure at any temperature for the class of oxidized asphalts. Essentially the technique consists of averaging the vapor pressures of the 13 asphalts at each temperature and then using those averages to curve fit the data to the desired equation. This gives higher values and is more conservative than averaging the vapor pressures after the log transformation is made. The standard curve is developed by using this regression equation to calculate vapor pressures at different temperatures. and for the oxidized class that data is indicated in Table 1 and also by the straight line in Figure 1.

The form of the Clausius Clapeyron equation is somewhat cumbersome to use, especially in graphical form, and so an alternative equation was developed which used a log/log relationship to characterize the data.

Log Log Treatment of Vapor Pressure Data

$$\log Vp = A * \log(T) + B$$

where Vp is the vapor pressure.
 T is the temperature (not absolute)
 A & B are constants

Analyses of oxidized asphalts using this equation to establish the standard curve are presented in Figure 2. The agreement is also very good. with correlation coefficients for the individual asphalts greater than 0.999. Again all three

Table 2. Vapor Pressure Correlations for Asphalts

For the Clausius Clapeyron Equation
 $\ln Vp (\text{mm Hg}^1) = a - b/T (R^2)$

Class of Asphalt	a	b	n	Average correlation coefficient
Flux	18.2891	12725.60	10	-0.99976
Paving	20.7962	15032.54	8	-0.99985
Oxidized	18.8642	13458.56	13	-0.99991

For a log log Equation
 $\log Vp (\text{mm Hg}) = A * \log T (°F^3) + B$

Class of Asphalt	a	b	n	Average correlation coefficient
Flux	7.0850	-16.8999	10	0.99736
Paving	7.8871	-19.0600	8	0.99965
Oxidized	7.0607	-16.9570	13	0.99981

- 1 Pa = 0.0075 mm Hg
- 1 K = (R - 492) * 5/9 + 273
- 1 °C = (F - 32) * 5/9

Table 3. Analysis of the Molecular Weight of Asphalt Tank Vapor Spaces

Asphalt	Weighted Ave MW	Milligrams of Component in Cube Sample of Vapor																						
		<C5*	n-C5*	5-6	n-C6	6-7	n-C7	7-8	n-C8	8-9	n-C9	9-10	n-C10	10-11	n-C11	11-12	n-C12	12-13	n-C13	13-14	n-C14	14-15	n-C15	>C15*
Coating - Plant J	83	3.70	2.10	1.80	2.10	0.82	1.70	1.70	0.82	0.21	0.26	0.23	0.05	0.02	0.04	0.01	0.02	0.04	0.01	0.01	0.15	0.07	0.14	0.13
Coating - Plant J	83	7.20	0.29	2.30	3.70	1.90	3.40	3.60	2.00	0.49	0.56	0.50	0.12	0.05	0.20	0.01	0.02	0.00	0.05	0.00	0.23	0.04	0.15	0.07
Satch - Plant J	91	3.00	1.90	2.10	2.90	1.70	3.00	3.70	1.80	0.66	0.73	0.67	0.17	0.11	0.03	0.01	0.01	0.01	0.03	0.01	0.04	0.02	0.05	0.05
Coating - Plant J	97	1.80	1.20	1.10	1.20	0.48	1.00	1.20	0.59	0.16	0.27	0.27	0.09	0.04	0.03	0.02	0.03	0.03	0.10	0.01	0.37	0.10	0.31	0.25
Flux - Plant P	76	2.00	0.70	0.40	0.49	0.34	0.39	0.48	0.15	0.10	0.05	0.03	0.01	0.00	0.01	0.00	0.02	0.00	0.01	0.02	0.02	0.00	0.09	0.14
Flux - Plant P	91	3.60	1.50	1.20	1.70	1.10	1.60	2.40	0.95	0.66	0.37	0.29	0.13	0.09	0.09	0.05	0.06	0.04	0.10	0.01	0.15	0.10	0.21	0.32
Steep - Plant P	93	3.00	3.00	1.50	2.40	1.00	2.00	1.80	0.84	0.41	2.00	1.80	0.07	0.02	0.02	0.01	0.05	0.00	0.01	0.03	0.00	0.00	0.08	0.38
PBS* - Plant S	68	3.60	0.75	0.62	0.41	0.32	0.32	0.28	0.24	0.22	0.15	0.15	0.09	0.05	0.04	0.02	0.02	0.02	0.04	0.00	0.04	0.01	0.02	0.09
Steep - Plant P	85	3.70	5.40	2.70	5.10	1.60	2.30	1.10	0.41	0.12	0.06	0.04	0.01	0.02	0.00	0.01	0.01	0.00	0.10	0.00	0.14	0.00	0.13	1.00
Steep - Plant P	85	5.80	6.40	4.50	6.50	3.90	6.40	4.60	2.40	0.79	0.64	0.23	0.22	0.09	0.12	0.04	0.05	0.02	0.06	0.00	0.05	0.02	0.05	0.06
Steep - Plant P	72	3.20	1.70	0.79	1.30	0.40	0.81	0.49	0.27	0.10	0.09	0.04	0.02	0.04	0.01	0.00	0.01	0.00	0.05	0.00	0.10	0.02	0.08	0.03
PBS* - Plant S	87	3.80	1.00	1.40	1.10	0.75	0.90	1.30	0.64	0.95	0.35	0.39	0.26	0.15	0.10	0.05	0.05	0.45	0.06	0.01	0.07	0.04	0.06	0.07

MW used for Fraction 30 72 79 86 93 100 107 114 121 128 135 142 149 156 163 170 177 184 191 198 205 212 240
 used 30 (ethane) for MW of fraction less than pentane since when this is large it is heavily weighted to methane.
 *Notes: used the average MW of the two bordering n-alkanes for the intermediate peaks.
 used 240 (C17 alkane) for MW of fraction > C15 since concentration decreasing as C15 approached
 PBS refers to hard paving blend stock

classes of asphalts show similar agreement,

Vapor Pressure Summary: Table 2 gives a summary of the regression constants to be used in either of the equations discussed above to calculate the vapor pressure for the three classes of asphalt at any temperature. Also indicated are the number of asphalts that were used to develop the equation for each class. and the average correlation coefficient characterizing the agreement of the data to the form of the equation for each individual asphalt in the class.

In AP-42 for tanks, the correct temperature to use in the Table 2 equations is the asphalt surface temperature in the tank. Since the surface temperature is rarely, if ever, known with certainty, the bulk temperature should be used to estimate emissions. In a well mixed tank the bulk temperature will be a good approximation of the surface temperature. Where mixing is not effective the surface will be lower in temperature than the bulk and the use of the bulk temperature will give a conservative estimate of emissions. In AP-42 for loading trucks, the bulk temperature of the tank from which material is being loaded provides a good estimate of the actual loading temperature.

Asphalt Vapor Molecular Weight: Asphalt vapor molecular weight was determined by separation and analysis of the organic species in the vapor spaces of 12 tanks storing different types of asphalt. These profiles were obtained by drawing known volumes of the tank vapor space through a charcoal tube, sealing and freezing the tube to limit loss of the sample, and then desorbing the organic material from the charcoal with carbon disulfide and analyzing with gas chromatography using packed columns and flame ionization detectors. Analyses were performed by CHEMIR Laboratory in St. Louis. Quantitative standards were used to identify the amount of individual normal alkanes from n-pentane to n-pentadecane. Peaks eluting between the normal alkanes were assumed to be isomers of the hording alkanes, especially cyclic isomers of the lower carbon number alkane, and branched or unsaturated isomers of the higher carbon number alkane. The molecular weights for the n-alkane species and molecular weight estimates for the intermediate species were used with the amount of that material measured to calculate a weighted average vapor molecular weight for each tank, and then the twelve tanks were averaged together to get the molecular weight used for hot asphalt vapors in the AP-42 calculations. The result was a molecular weight of 84, which is used with all three classes of asphalts. This analysis is detailed in Table 3. Not enough data were available to assign different values to the three asphalt classes, however, from the table the unblown flux material in two tanks gave molecular weights which bracketed the average. as did the two paving blend stocks.

This analysis gave a lower molecular weight for the vapor space of asphalt tanks than for several petroleum solvents and fuel oils. This seems like a contradiction considering the nature of asphalt as the residuum material collected upon distillation. This contradiction is resolved by considering that asphalt is not a uniform material chemically and that the lower molecular weight materials

Table 4. PM/VOC Partition Data from Owens Corning Testing

Asphalt Plant 0	Tank A	Tank B	Tank c	
VOC Test	0.73	1.16	0.98	lb/hr ¹
PM Test	0.21	0.38	0.30	lb/hr
VOC Fraction	0.78	0.75	0.77	

Roofing Plant S Coater Results:
Measured at different points. Data indicated 22% of total emission (VOC + PM) was PM and 78% was VOC

1. 1 kg/sec = 0.0076 * lb/hr

are preferentially evaporated. More importantly, it has also been established that thermal cracking of asphalt in hot storage tanks creates low molecular weight materials which accumulate in the tank vapor spaces [5,6].

Asphalt Liquid Molecular Weight: The actual bulk asphalt molecular weight is not needed for AP-42 calculations of emissions from tanks or loading racks, but is useful in some calculations that are beyond the scope of this paper, for example using Raoult's law for crude estimates of emissions from mixtures of asphalt and other materials. Molecular weight of bulk asphalt is not a well defined material property, both because asphalt is such a complex mixture and because intermolecular interactions in the asphalt create the appearance of high molecular weight in many measurement techniques. The measured molecular weight is usually not truly representative of the covalently bonded molecules. The difficulty in getting accurate asphalt molecular weight measurements is extensively discussed in the literature [8, 9, 10]. The use of Gel Permeation Chromatography [8], Field-Ionization Mass Spectrometry [8], Vapor Pressure Osmometry [8,9,10], and Freezing Point Depression [10] have all been evaluated as methods for measuring the molecular weight of asphalt or its components. The topic is further complicated for emission calculations by the fact that many of the measurements have been made on fractions of the asphalt and not on the neat asphalt. In general, for very rough estimates, a value of 1000 [8] can be used for the molecular weight of bulk asphalt. This value should be used with the understanding that there is much variation in the true molecular weight and in the tendency for intermolecular interaction due to petroleum crude source and processing conditions.

Partition of hydrocarbon emissions that are particulate and VOC: Because of its heterogeneous nature, asphalt fumes are varied and may have components that are classified as condensed particulates (PM) or as volatile organic compounds (VOCs). It is as evident in analyzing asphalt fume results that the difference between these two classes of criteria pollutants is really defined by the method used to

test for the pollutants. Estimation schemes described in this paper calculate the sum of both (AP-42) or just the VOC component (non-AP-42 technique described below), and the partition needs to be understood to provide the best estimated values of the two pollutants. To that end, tests have been done on both asphalt tank exhausts in an Owens Corning asphalt plant and on the asphalt shingle coater exhausts in an Owens Corning roofing plant using EPA Methods 5 & 25A sampling protocols which define VOC and PM emissions in hydrocarbon fumes. Under conditions specified by the test method some fraction of the fume is captured on a filter and this is defined as a particulate emission, while a fraction of the hydrocarbon emission passes through the filter and this is defined as a VOC emission. The results of the split in the total hydrocarbon fume between VOC and particulate were approximately 78% VOC and 22% particulate in the asphalt equipment, in spite of the basic difference between a shingle coater and a storage tank. Data from these tests are given in Table 4.

NON AP-42 CALCULATIONS TECHNIQUES:

Estimation of VOC and particulate emissions from tanks with fume control: Many asphalt tanks have their fumes actively collected and treated in a control device, either a fiber bed filter or an incinerator. In these tanks it is common at Owens Corning to allow some air to pass through the tank vapor spaces to create an air sweep that controls combustible fumes well below the lower explosion limit (LEL) in order to prevent explosions. Because of the active removal of fumes in these systems, and the bleeding of air into the vapor space, the assumptions underlying the AP-42 tank calculations no longer apply. Specifically the driving force for the flow of fumes out of the tank is no longer just the working and breathing losses, and an alternative method of emission calculation is needed.

Several years ago safety concerns with asphalt tanks prompted Owens Corning to institute the periodic measurement of the combustible gas concentration in all asphalt tank vapor spaces [5]. With the advent of Title V it was recognized that these measurements could be used to estimate VOC emissions. As part of the safety program, techniques were developed to make this routine measurement simple and easy, and the result was the use of Mine Safety Appliance (MSA) combustion meters to quantify the hydrocarbon concentration in terms of the fraction (or %) of the LEL. This technique and the validation of its accuracy has been described in detail in a separate publication [6]. In addition to the combustible gas measurement, a slightly more complicated technique is also described and validated that gives the concentration of ethane, methane, and other light combustible gases separate from propane and larger hydrocarbons. This technique involves using a charcoal tube in the line between the tank and the MSA meter. The charcoal tube adsorbs all propane and higher hydrocarbons [6], with the resultant reading at the MSA meter due only to the lighter

Table 5. Fraction of Measured Combustible Gas that is not VOC or Particulate

	Asphalt Type	
	Oxidized	Unoxidized
Number tanks measured	109	47
Fraction combustible gas that is non-VOC/PM		
Average	0.52	0.23
Standard Deviation	0.12	0.23

materials. The charcoal tube technique was developed to troubleshoot excessive thermal cracking in asphalt tanks as a cause of high combustible gas levels in tank vapor spaces, and it is not routinely performed. It is important for emission calculations since the smaller combustibles found in the tank vapor spaces and measured with the charcoal tube in place (ethane, methane, hydrogen sulfide, and carbon monoxide) are not classified as VOCs because they do not react with ozone in the atmosphere. Nor are they particulate. The other hydrocarbons trapped by the tube and only measured when the charcoal tube is not present, are VOCs or particulate. Table 5 gives the results of testing of vapor spaces of oxidized and unoxidized asphalts for

these two types of combustible gas measurements. This analysis was done to see if the routine combustible gas numbers should be adjusted for significant and predictable non-VOC/PM components. For the average tank storing oxidized asphalt, 52% of the combustible gas is non-VOC/PM anti this value n-as used for this class of asphalt. For unoxidized asphalts, both paving and flux, the non-VOC/PM %LEL varied widely and was not nearly as large a fraction of the total. For these asphalts, all of the combustible gas measurement was considered to be either VOC or particulate.

Calculation of VOC & PM from combustible gas readings: Given this background the actual calculation of VOC emissions from combustion meter measurements is as follows:

- 1 Combustion meter measurements from tank vapor spaces read in %LEL are adjusted for the fraction of that reading that is non-VOC/PM. This value depends on the type of asphalt in the tank.
- 2 The adjusted %LEL is then turned into a weight per volume concentration. Hydrocarbons have a relatively constant actual LEL concentration. 45 mg/liter, when expressed on 3 weight per volume basis [11], and this constant is used to make this calculation.
- 3 The weight per volume concentration from step 2 is multiplied by the fume removal flow (in volume/time) in the tank to get the VOC emission (n-eight/time) going to

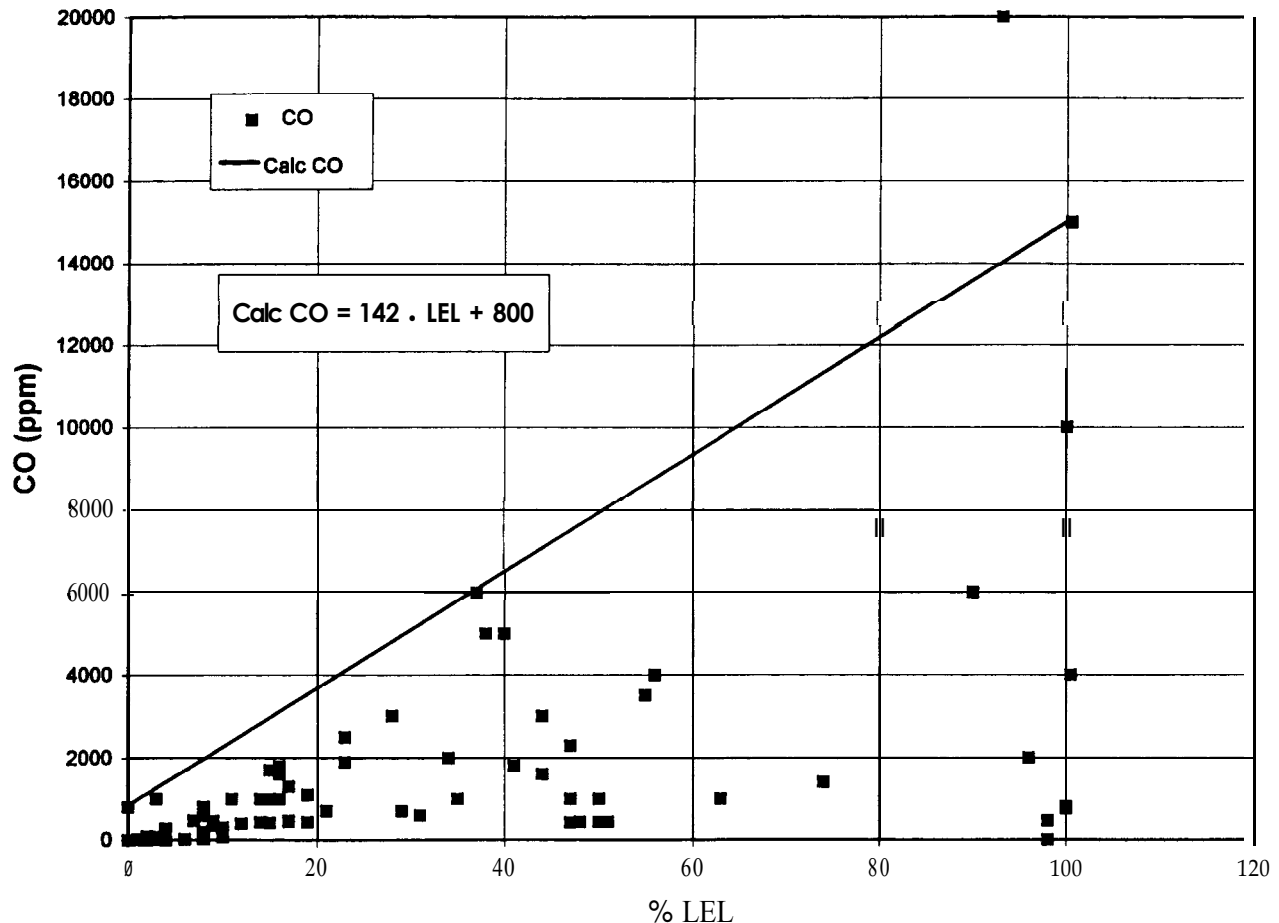


FIGURE 3. Relation of CO with % LEL Data for Oxidized Asphalts

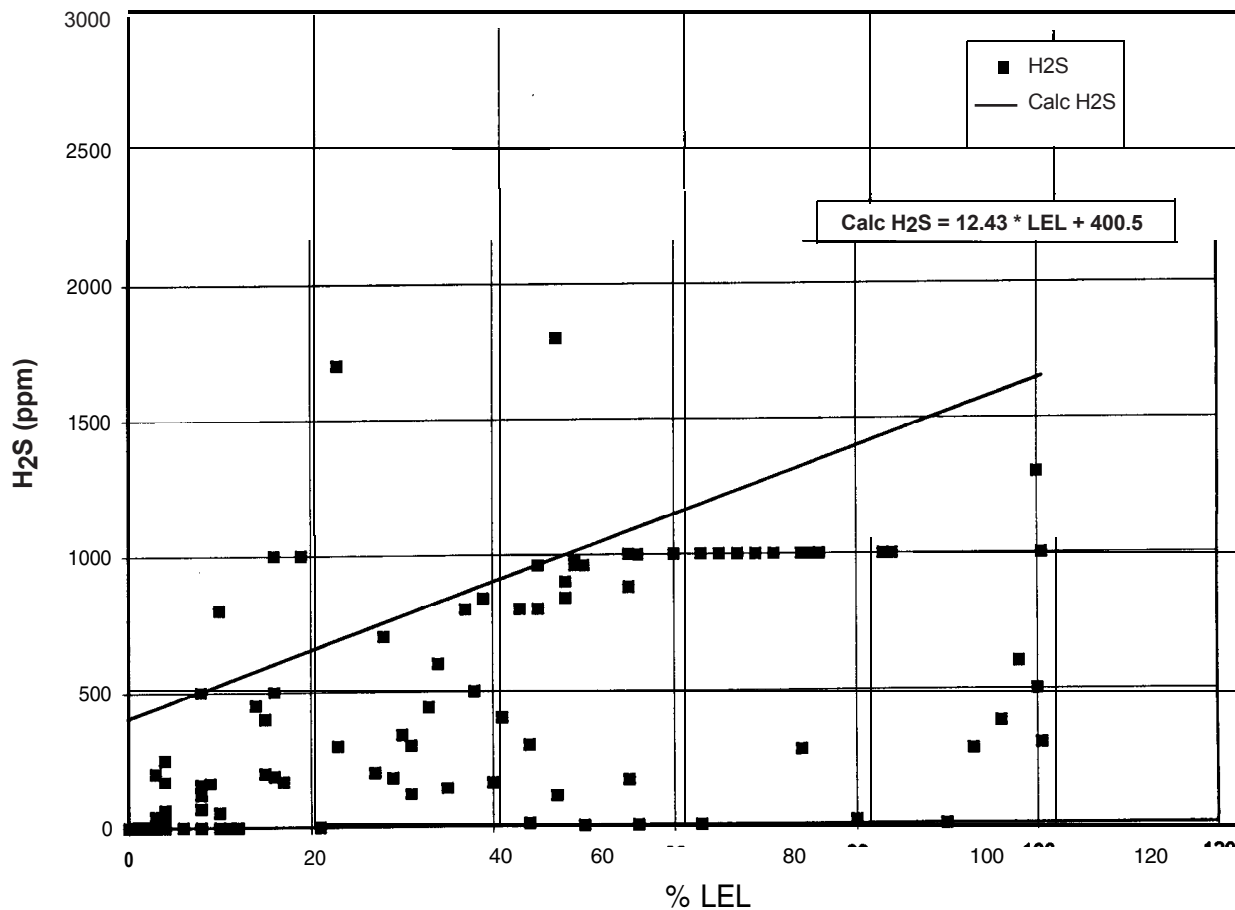


FIGURE 4. Relation of H₂S with % LEL Data for Oxidized Asphalts

a control device. It is consistent that the %LEL method measures VOC and not total hydrocarbon since the fume is drawn through a cotton filter prior to entering the combustion meter, and particulate will be filtered out.

4. The particulate emission going to the control device is estimated from the constant ratio of 22%PM/78%VOC outlined in Table 4.
5. The control device destruction efficiency is applied to both VOC and particulate emissions separately to get the final hydrocarbon based emissions from the tank. This is done after the calculation of PM emissions since the control efficiency for particulate and VOCs can be different depending on the control device.

This methodology's accuracy has been confirmed by tests in an Owens Corning asphalt plant on several

passively vented tanks while material was pumped into the tank and vapors forced out by the known pumping rate. Emissions calculated with the method outlined above were compared to tank emissions calculated using AP-42 (valid in theory in this case due to the lack of a ventilation system), and to emissions measured using EPA Method 25A. As can be seen in Table 6 the method based on actual combustion meter tests is similar to the measured VOCs while AP-42 estimates are 3 to 5 times higher.

*Estimation of CO and H₂S emissions from asphalt tanks:*As part of the safety monitoring program mentioned above. Owens Corning has also used detector tubes in asphalt tanks to measure the vapor space concentration of carbon monoxide and hydrogen sulfide [6]. These emissions are usually ignored in asphalt tanks, however, the data Owens Corning has taken clearly indicates their presence in tank vapor spaces and therefore their emission [1]. These gases are not routinely measured in Owens Corning asphalt tanks, unlike combustible gas measurements, and thus fresh data are not available for current calculation, nor are data available for every one of our tanks. To apply these data to all tanks, a surrogate measurement is necessary. Since the same mechanism, thermal cracking, that produces light hydrocarbons in asphalt tank vapor spaces also produces carbon monoxide and hydrogen sulfide, the periodic combustion meter measurement of tank vapor spaces was

Table 6. Owens Corning Tank Fume Sampling Results - VOC Emissions

	Tank A	Tank B	Tank C
VOC Method 2jA Test	0.73	1.16	0.98
% LEL Based Estimate	0.72	0.91	0.83
AP-42 Based Estimate	3.17	4.5	3.39

1. 1 kg/sec = 0.0076 *lb/hr

**Table 7. Asphalt Plant 0:
Tank Emissions of H₂S and CO**

	Tank A	Tank B	Tank C	
H₂S Data				
Actual Test	0.06	0.12	0.15	lb/hr ¹
%LEL based estimate	0.19	0.18	0.20	lb/hr
CO Data				
Actual Test	0.20	0.17	0.23	□ lb/hr
%LEL based estimate	0.74	0.85	0.83	lb/hr

1. 1 kg/sec = 0.0076* lb/hr

investigated as a surrogate for CO and H₂S Data for CO and H₂S are plotted in Figures 3 and 4. Because of the scatter of data in the correlations a representative line was chosen for each material that was more conservative than nearly all of the data, in other words a line that defined a maximum concentration of CO and H₂S that could be expected in an asphalt tank from the combustion meter measurement. The equations used in the calculation of CO and H₂S concentrations from combustion meter results

$$\text{CO (ppm)} = 142 * \%LEL + 800 \text{ for oxidized asphalt}$$

$$\text{H}_2\text{S (ppm)} = 12.43 * \%LEL + 400.5 \text{ for oxidized asphalt}$$

In unoxidized asphalt no such correlation was seen and conservative values of 500 ppm are used for both species.

To estimate an emission from this correlation the CO and H₂S concentrations are multiplied by the flow out of the tank to get emissions, and conversion factors are used to transform this into a weight per time emission. Any control device destruction efficiency is then applied. The emissions using these techniques can be significant. Limited direct measurement in an Owens Corning asphalt plant was consistent with this approach, at least in so far as that the %LEL approach was conservative. H₂S was the closer of the two estimates. Data are presented in Table 7.

One consequence of fume incineration is that one mole of H₂S in the fumes is oxidized to one mole of SO₂. The amount of H₂S oxidized to SO₂, is the amount of H₂S generated minus both the amount that escapes at the source and the amount that is not incinerated at the control device, or in effect the total uncontrolled H₂S emissions minus the emissions remaining after control. Because of the reaction with oxygen and the molecular weight differences between H₂S and SO₂, every pound (2.2 kg) of H₂S emission is oxidized to 1.88 pounds (4.14 kg) of SO₂ emission.

Loading Rack emissions of CO and H₂S: As in the tanks, %LEL versus CO and H₂S correlations are used to estimate these components in loading rack emissions. Again, with incineration, the H₂S is oxidized to SO₂. Flow out of the tank truck during loading is needed for CO and H₂S calculations. When fumes are collected, that flow can be

either the more conservative flow induced by the fume fan, or the lower and more realistic displacement of air by the asphalt being loaded. When no collection takes place that flow is the displacement of air by asphalt being loaded. Combustion meter measurements of %LELs from the tanks used for loading are used for these calculations.

EFFECTIVENESS OF FIBER BED FILTERS FOR ASPHALT FUME EMISSION CONTROL

One device used extensively to control asphalt fumes is a fiber bed filter. Fumes are actively pulled through these filters or passively breathe through these filters. Their first use at Owens Corning was to control opacity to comply with NSPS regulations, and for this application they have proven to be quite effective.

Testing was done on both asphalt tanks and on a roofing line center to determine the control efficiency of fiber bed filters for both VOC and particulate emissions. Data from the testing are summarized in Table 8. In all cases, the particulate collection in the filter exceeded 90% of the emissions in the input stream. This value agrees well with manufacturer's estimate of 95% and with the observation that these devices can eliminate opacity. However, VOC removal varied widely in the tests. With the average removal near zero, and a very large variation, it was decided that no removal of VOC by these filters could be assumed. Although organic oil is collected, this oil is considered part of the particulate fraction of the hydrocarbons in the fumes and not the VOC fraction. Indeed the lack of removal of VOCs by these filters is consistent with the method of partitioning hydrocarbons into VOC and particulate described above -- namely VOCs pass through a testing filter and particulate do not. Based on the effectiveness of these control devices to eliminate opacity it is assumed that particulate greater than 10 micron is captured by the fiber bed filter so that the total particulate emissions from the fiber bed filter are considered to be PM10 emissions.

Fiber bed filters are not considered to be a control device for CO and H₂S in tank or loading rack fume streams.

Table 8. Effectiveness of Fiber Bed Filters for Emission Control from Asphalt Tanks

Plant	Equipment	Pollutant	Control Efficiency
Asphalt 0	Tank 1	VOC	-35.7%
Asphalt 0	Tank 1	VOC	5.7%
Asphalt 0	Tank 1	VOC	43.4%
Asphalt 0	Tank 57	VOC	5.3%
Roofing I	Coater	VOC	0.0%
Asphalt 0	Tank 1	Total Particulate □	95.7%
Asphalt 0	Tank 57	Total Particulate	90.7%
Asphalt 0	Tank 1	Filterable Particulate	100.0%
Asphalt 0	Tank 57	Filterable	100.0%

Table 9. Summary of Data for Calculating Asphalt Tank Emissions

Data Type	Flux Asphalt	Paving Asphalt	Oxidized Asphalt
Clausius Clapeyron constant a for vapor pressure	18.2891	20.7962	18.8642
Clausius Clapeyron constant b for vapor pressure	12725.6	15032.54	13458.56
Log Log constant A for vapor pressure	7.085	7.8871	7.0607
Log Log constant B for vapor pressure	-16.8999	-19.06	-16.957
Asphalt vapor molecular weight	use 84 for all types of asphalt		
Asphalt liquid molecular weight	very rough estimate - 1000		
Partition of hydrocarbon fumes into particulate and VOC	use 22% particulate, 78% VOC for all types		
% fumes that are VOC or particulate, versus non VOC/PM	100%	100%	48%
Vapor space carbon monoxide (conservative estimate) ppm	500	500	142* % LEL + 800
Vapor space hydrogen sulfide (conservative estimate) ppm	500	500	12.43*%LEL + 400.5
Fiber bed filter control of VOC	use 0% for all asphalt types		
Fiber bed filter control of particulate	use 90% for all asphalt types		

1. In Vp(mm Hg) = a + b/T(°R) 1 Pa = 0.0075mm Hg, 1 °K = (°R-492)*5/9 +273
 2. log Vp (mm Hg) = A*log T(°F) + B °C = (°F - 32)* 5/9

CONCLUSIONS

Estimation of air emissions for asphalt tanks and loading racks can be done using AP-42 calculation methods given appropriate data on asphalt properties. More precise estimates of emissions, or estimates for tanks using ventilation schemes that compromise the AP-42 assumptions, can be done using a simple measurement of the combustible gas in the vapor space. Methods to do this are outlined in the paper. Data that is useful with all these methods are summarized in Table 9. These data are given for three major classes of asphalt: paving, flux and oxidized

LITERATURE CITED

1. Trumbore, D.C., "The magnitude and source of air emissions from asphalt blowing operations," *Environmental Progress*, 17, (1), pp. 53-59 (Spring 1998).
2. U.S.Environmental Protection Agency, "Introduction to 5th edition of AP-42 Emission Factors," U. S. EPA, January,1995,from the Internet at <http://www.epa.gov/ttn/chief/ap42.html> (accessed May 14, 1998).
3. U.S Environmental Protection Agency, Chapter 7.1 of the 5th edition of AP-42 Emission Factors, U.S.EPA, "Organic Liquid Storage Tanks," September, 1997, from the Internet at <http://www.epa.gov/ttn/chief/ap42.html> (accessed May 14, 1998).
4. U.S.Envoironmental Protection Agency, Chapter 5.2 of the

- 5th edition of AP-42 Emission Factors, U.S. EPA, "Transportation and Marketing of Petroleum Liquids," January, 1995, from the Internet at <http://www.epa.gov/ttn/chief/ap42.html> (accessed May 14, 1998).
5. Trumbore, D.C. and C.R.Wilkinson, "Better understanding needed for asphalt tank-explosion hazards," *Oil Gas J.*, 87, pp.38-41 (September 18, 1989).
6. Trumbore, D.C., C.R.Wilkinson, and S.Wolfersberger, "Evaluation of techniques for in situ determination of explosion hazards in asphalt tanks," *J.Loss Prev. Process Ind.*, 4, pp. 230-235 (July,1991).
7. Schmidt, A.X. and H.L. List, "Material and Energy Balance," Prentice Hall, Inc., Englewood Cliffs, New Jersey, pp. 40-41 (1962).
8. Boduszynski, M.M., "Asphaltenes in petroleum Asphalt: Composition and Formation," Chapter 7, in "The Chemistry of Asphaltenes," American Chemical Society, Washington, D.C., pp. 119-135 (1981).
9. Storm, D.A., et al., "Upper bound on number average molecular weight of asphaltenes," *Fuel*, 69, pp. 735-738 (June, 1990).
10. Speight, J.G., and S.E.Moschopedis, "Asphaltene molecular weights by a cryoscopic method," *Fuel*, 56, pp 344-345 (July, 1977).
11. Bodurtha, F.T., "Industrial Explosion Prevention and Protection," McGraw Hill, Inc, New york, New York, page 11 (1980).