Studies on the evaporation of crude oil and petroleum products
II. Boundary layer regulation

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Abstract

Experiments were conducted to determine if oil and petroleum evaporation is regulated by the saturation of the air boundary layer. Experiments included the examination of the evaporation rate with and without wind. It was found that evaporation rates were similar for all wind conditions, but lower for the no-wind conditions. Experiments where the area and mass varied showed that boundary layer regulation was not dominant for petroleum products. Under all experimental and environmental conditions, oils or petroleum products were not found to be strictly boundary-layer-regulated. Experiments on the rate of evaporation of pure compounds showed that those larger than decane were not boundary-layer-regulated. Many oils and petroleum products contain few compounds smaller than decane, and this explains why their evaporation is not strictly boundary-layer-limited. Comparison of the air saturation levels of various oils and petroleum products shows that the saturation concentration of water, which is strongly boundary-regulated, is significantly less than that of several petroleum hydrocarbons. Lack of boundary layer regulation for oils, after a short initial time period, is shown to be a result of both this higher saturation concentration, as well as a low (below boundary layer value) evaporation rate. © 1998 Elsevier Science B.V.

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1. Introduction

Evaporation of a liquid can be considered as the movement of molecules from the surface into the vapour phase above it. The layer of air above the evaporation surface is known as the boundary layer [1]. This is the air layer most directly affected by the surface and by oil evaporation. The characteristics of this air layer can influence evaporation. In water, the air regulates the evaporation rate. Air can hold a variable amount of water, depending on temperature, as expressed by the relative humidity. Under conditions where the boundary layer is not moving (no wind) or has low turbulence, the air immediately above the water quickly becomes saturated and evaporation slows or ceases [2,3]. In practice, the actual evaporation of water proceeds at a small fraction of the maximum rate because of the saturation of the boundary layer. The boundary layer physics is then said to regulate the evaporation of water. This regulation manifests itself in the sensitivity of evaporation to wind or turbulence. When turbulence is weak or absent, evaporation can slow down by orders-of-magnitude. The molecular diffusion of water molecules is at least 1×10^3 times slower than turbulent diffusion [2].

Evaporation can then be viewed as consisting of two fundamental components — basic evaporation itself and regulation mechanisms. Basic evaporation is that process consisting of the evaporation of the liquid directly into the vapour phase without any regulation except that by the thermodynamics of the liquid itself. Regulation mechanisms are those processes that serve to regulate the final evaporation rate into the environment. For water, the main regulation factor is the boundary layer regulation discussed above. The boundary layer regulation is manifested by the limited rate of diffusion, both molecular and turbulent diffusion, and by saturation dynamics. Molecular diffusion is based on the exchange of molecules over the mean free path in the gas. The rate of molecular diffusion for water is about 1×10^5 slower than the maximum rate of evaporation permitted, purely from thermodynamic considerations [2]. The rate for turbulent diffusion, the combination of molecular diffusion, and movement with turbulent air is 1×10^2 slower than that for maximum evaporation. In fact, in water, maximum evaporation is not known and has only been estimated by experiments in artificial environments or by calculation [3].

If the evaporation of oil was like that of water and was boundary-layer-regulated, one could write the mass transfer rate in semi-empirical form (also in generic and unitless form) as:

$$E \approx KCT_u S \tag{1}$$

where E is the evaporation rate in mass per unit area, K is the mass transfer rate of the evaporating liquid presumed constant for a given set of physical conditions, sometimes denoted as k_g (gas phase mass transfer coefficient, which may incorporate some of the other parameters noted here), C is the concentration (mass) of the evaporating fluid as a mass per volume, T_u is a factor characterizing the relative intensity of turbulence, and S is a factor that relates to the saturation of the boundary layer above the evaporating liquid. The saturation parameter, S, represents the effects of local advection on saturation dynamics. If the air is already saturated with the compound in question, the evaporation rate approaches zero. This also relates to the scale length of an evaporating

pool. If one views a large pool over which a wind is blowing, there is a high probability that the air is saturated downwind and the evaporation rate per unit area is lower than that for a smaller pool. It should be noted that there are many equivalent ways of expressing this fundamental evaporation equation.

Much of the pioneering work for evaporation work was performed by Sutton [4], who proposed the following equation based largely on empirical work:

$$E = K C_s U^{7/9} d^{-1/9} Sc^{-r}, \tag{2}$$

where C_s is the concentration of the evaporating fluid (mass/volume), U is the wind speed, d is the area of the pool, Sc is the Schmidt number and r is the empirical exponent. Other parameters are defined as above. The terms in this equation are analogous to the very generic Eq. (1). The turbulence is expressed by a combination of the wind speed, U, and the Schmidt number, Sc. The Schmidt number is the ratio of kinematic viscosity of air (ν) to the molecular diffusivity (D) of the diffusing gas in air, i.e., a dimensionless expression of the molecular diffusivity of the evaporating substance in air. The coefficient of the wind power typifies the turbulence level. The value of 0.78 (7/9), as chosen by Sutton [4], represents a turbulent wind, whereas, a coefficient of 0.5 would represent a wind flow that was more laminar. The scale length is represented by d and has been given an empirical exponent of $-1/9$. This represents, for water, a weak dependence on size. The exponent of the Schmidt number, r, represents the effect of the diffusivity of the particular chemical, and historically was assigned values between 0 and 2/3 [1].

This expression for water evaporation was subsequently used by those working on oil spills to predict and describe oil and petroleum evaporation. Much of the literature follows the works of Mackay and Matsugu [5], and Stiver and Mackay [6]. Mackay and Matsugu [5] corrected the equations for hydrocarbons using the evaporation rate of cumene. Data on the evaporation of water and cumene have been used to correlate the gas phase mass transfer coefficient as a function of wind speed and pool size by the equation:

$$K_m = 0.0292 U^{0.78} X^{-0.11} Sc^{-0.67}, \tag{3}$$

where K_m is the mass transfer coefficient in units of mass per unit time and X is the pool diameter or the scale size of evaporating area. Stiver and Mackay [6] subsequently developed this further by adding a second equation:

$$N = k_m AP/(RT), \tag{4}$$

where N is the evaporative molar flux (mol/s), k_m is the mass transfer coefficient at the prevailing wind (m/s), A is the area (m^2), P is the vapour pressure of the bulk liquid (Pa), R is the gas constant (8.314 J K^{-1} mol^{-1}), and T is the temperature (K).

Thus, boundary layer regulation was assumed to be the primary regulation mechanism for oil and petroleum evaporation. This assumption was never tested by experimentation, as revealed by the literature search [7]. The implications of these assumptions are that evaporation rate for a given oil is increased by: (i) increasing turbulence, (ii) increasing wind speed, and (iii) increasing the surface area of a given mass of oil.

These factors can then be verified experimentally to test if oil is boundary-layer-regulated or not. These factors formed the basis of experimentation for this paper.

2. Experimental

The evaporation rate was measured by weight loss using an electronic balance. The balance was a Mettler PM4000. The weight was recorded using a Toshiba 3100, a serial cable to the balance and a modified version of the software program, 'Collect' (Labtronics, Richmond, Ontario).

Measurements were conducted in the following fashion. A tared petri dish of defined size was loaded with a measured amount of oil. At the end of the experiment, vessels were cleaned and rinsed with dichloromethane and a new experiment started. The weight loss dishes were standard glass petri dishes from Corning. A standard 139-mm-diameter (ID) dish was used for most experiments. For the experiments in which area was a variable, dishes of other diameters were employed. Diameters and other dimensions were measured using a Mitutoyo digital vernier calliper. The lip, height of the dish above the oil with the 139-mm dish varied from 2 to 10 mm depending on depth of the fill. For the other dishes, the lip varied from 2 to 20 mm.

Measurements were done in one of three locations: inside a fume hood, inside a controlled temperature room, or on a counter top. Many experiments were conducted in the fume hood, where there was no temperature regulation. Temperatures were measured using a Keithley 871 digital thermometer with a thermocouple supplied by the same firm. Temperatures were taken at the beginning and the end of a given experimental run.

The constant temperature chamber (room) employed was a Constant Temperature model constructed in 1993. It could maintain temperatures from $-40°C$ to $60°C$ and regulate the chosen temperature within $\pm 1°C$.

Table 1
Properties of the test liquids

Test liquid	Description	Density (g/ml)	Boiling point (°C)
ASMB	Alberta Sweet Mixed Blend, a common crude oil in Canada	0.839	Initial: 37
Water		1	100
FCC heavy	A highly cycled refinery intermediate containing few components	0.908	
Gasoline	Standard automotive gasoline	0.709	Initial: 5
Benzene	Pure hydrocarbon-C_6	0.879	80.1
Dodecane	Pure hydrocarbon-C_{10}	0.749	213
Undecane	Pure hydrocarbon-C_{11}	0.742	196
p-xylene	Pure hydrocarbon-C_8	0.861	139
Nonane	Pure hydrocarbon-C_9	0.722	151
Decane	Pure hydrocarbon-C_{10}	0.73	174
Heptane	Pure hydrocarbon-C_7	0.684	98
Octane	Pure hydrocarbon-C_8	0.703	126
Decahydron	Decahydronaphthalene - pure hydrocarbon-C_{10}	0.893	195
Tridecane	Pure hydrocarbon-C_{13}	0.755	226
Hexadecane	Pure hydrocarbon-C_{16}	0.773	287

In experiments involving wind, air velocities were measured using a Taylor vane anemometer (no model number on the unit) and a Tadi, 'Digital Pocket Anemometer'. Measurements were taken at the closest position above the glass vessel floor and at the lip level. These velocities were later confirmed using a hot wire anemometer and appropriate data manipulations of the outputs. The anemometer was a TSI-Thermo Systems model 1053b, with power supply (TSI model 1051-1), averaging circuit (TSI model 1047) and signal linearizing circuit (TSI model 1052). The voltage from the averaging circuit was read with a Fluke 1053 voltmeter. The hot wire sensor (TSI model 1213-60) was angled at 45°. The sensor probe resistance at 0°C was 7.21 Ω and the sensor was operated at 12 Ω for a recommended operating temperature of 250°C. Data from the hot wire anemometer was collected on a Campbell Scientific CR-10 data logger at a rate of 64 Hz.

Evaporation data were collected on the Toshiba 3100 laptop computer and subsequently transferred to other computers for analysis. The 'Collect' program records time and the weight directly. Data were recorded in ASCII format and converted to Excel format. Curve fitting was performed using the software program 'TableCurve' (Jandel Scientific, San Raphael, CA).

Oils were taken from supplies of Environment Canada and were supplied by various oil companies for environmental testing. Table 1 lists the properties and descriptions of the test liquids [8].

3. Results and discussion

Table 2 lists the experiments performed and the results in terms of the best-fit equations. These were done by curve fitting using the program TableCurve, as noted above. The best fit was done on the basis of the simplest equation fitting with the highest regression coefficient (R^2). The results are presented in the order of the experimental series.

3.1. Wind experiments

Experiments on the evaporation of oil with and without wind, were conducted with three oils, ASMB (Alberta Sweet Mixed Blend), gasoline, FCC Heavy Cycle, and with water. Water formed a baseline data set since much is known about its evaporation behaviour [2,3]. Regressions on the data were performed and the equation parameters calculated, as shown in Table 3. Curve coefficients are the constants from the best fit equation (Evap = a ln(t), t = time in min, for logarithmic equations or Evap = $a\sqrt{t}$, for the square root equations. Data were calculated separately for percentage of weight lost and absolute weight. Both values show the small relative upward tendency with respect to wind effects. The plots of wind speed vs. the evaporation rate (as a percentage of weight lost) for each oil type are shown in Figs. 1–4. These figures show that the evaporation rates for oils and even the light products, gasoline and FCC heavy cycle, are

Table 2
Experimental summary

Date	Experimental purpose	Oil type	Total time (h)	Pan area (cm²)	Initial thickness (mm)	Temperature (°C)	Wind (m/s)	Variable	Variable value	R^2 best equation	Best equation
June 21	Thickness	ASMB	15	151	0.65	212	0	thickness	0.65	0.991	ln
June 23	Thickness	ASMB	22	268	0.72	21	0	thickness	0.72	0.978	ln
June 24	Thickness	ASMB	23	270	1.3	21.8	0	thickness	1.3	0.97	ln
June 25	Thickness	ASMB	182	151	0.63	22.6	0	thickness	0.63	0.99	ln
July 2	Thickness	ASMB	15	151	1.59	22.4	0	thickness	1.59	0.937	ln
July 3	Thickness	ASMB	51	151	1.78	21.9	0	thickness	1.78	0.975	ln
July 5	Thickness	ASMB	65	151	2.14	24.4	0	thickness	2.14	0.954	ln
July 9	Thickness	ASMB	25	151	2.69	23.8	0	thickness	2.69	0.952	ln
July 16	Thickness	ASMB	73	151	2.84	21.7	0	thickness	2.84	0.96	ln
July 20	Thickness	ASMB	36	151	4.55	22.8	0	thickness	4.55	0.963	ln
Aug. 30	Thickness	ASMB	18	151	9.08	20.1	0	thickness	9.08	0.879	ln
Sept. 1	Thickness	ASMB	73	151	7.61	20.3	0	thickness	7.61	0.886	ln
Sept. 4	Thickness	ASMB	217	151	5.21	40	0	thickness	5.21	0.937	ln
Sept. 13	Thickness	ASMB	64	151	1.53	22.1	0	thickness	1.53	0.981	ln
Sept. 16	Thickness	ASMB	56	151	3.21	17.8	0	thickness	3.21	0.952	ln
Sept. 18	Thickness	ASMB	47	151	1.33	19.2	0	thickness	1.33	0.987	ln
Sept. 20	Thickness	ASMB	23	151	0.59	18.8	0	thickness	0.59	0.988	ln
Sept. 21	Thickness	ASMB	25	151	0.63	20.1	0	thickness	0.63	0.985	ln
Sept. 22	Thickness	ASMB	71	151	1.96	23.1	0	thickness	1.96	0.976	ln
Oct. 15	Thickness	ASMB	32	151	2.54	18.6	0	thickness	2.54	0.977	ln
Oct. 16	Thickness	ASMB	89	151	5.27	22.9	0	thickness	5.27	0.98	ln
Oct. 20	Thickness	ASMB	76	151	1.43	20.4	0	thickness	1.43	0.993	ln
Oct. 23	Thickness	ASMB	66	151	1.39	20.3	0	thickness	1.39	0.986	ln
Oct. 26 1994	Thickness	ASMB	88	151	2.8	19.1	0	thickness	2.8	0.962	ln
Feb. 7	Area	ASMB	50	16	7.45	24.2	0	area	16 cm²	0.969	ln
Feb. 9	Area	ASMB	25	16	3.72	23.9	0	area	16 cm²	0.96	ln
Feb. 10	Area	ASMB	21	16	1.58	8	0	area	16 cm²	0.72	ln
Feb. 11	Area	ASMB	25	16	0.79	24.6	0	area	16 cm²	0.791	ln
Feb. 12	Area	ASMB	50	62	3.84	22.5	0	area	62 cm²	0.992	ln
Feb. 14	Area	ASMB	22	62	1.92	15.6	0	area	62 cm²	0.996	ln
Feb. 15	Area	ASMB	26	62	1.58	25.3	0	area	62 cm²	0.982	ln
Feb. 16	Area	ASMB	23	62	0.79	23.8	0	area	62 cm²	0.994	ln
Feb. 17	Area	ASMB	24	161	1.48	21	0	area	161 cm²	0.987	ln
Feb. 18	Area	ASMB	23	161	0.79	25.2	0	area	161 cm²	0.973	ln
Feb. 19	Area	ASMB	50	161	1.58	23.9	0	area	161 cm²	0.941	ln
Feb. 21	Area	ASMB	83	161	3.7	19.1	0	area	161 cm²	0.933	ln
Feb. 26	Area	ASMB	50	161	2.22	21	0	area	161 cm²	0.99	ln
Feb. 28	Area	ASMB	25	161	0.74	20	0	area	161 cm²	0.953	ln
Mar. 01	Area	ASMB	74	206	1.58	18	0	area	206 cm²	0.984	ln
Mar. 04	Area	ASMB	20	206	0.79	21	0	area	206 cm²	0.974	ln
Mar. 05	Area	ASMB	51	206	1.16	19.5	0	area	206 cm²	0.963	ln
Mar. 07	Area	ASMB	44	151	1.58	20.5	0	area	151 cm²	0.993	ln
Mar. 09	Area	ASMB	26	151	0.79	19	0	area	151 cm²	0.994	ln
Mar. 10	Wind	ASMB	23	151	1.58	22.9	1.45	wind	1.0 m/s	0.98	ln
Mar. 11	Wind	ASMB	24	151	1.58	22	1.45	wind	1.0 m/s	0.972	ln
Mar. 12	Wind	ASMB	42	151	3.16	21.1	1.45	wind	1.0 m/s	0.99	ln

Table 2 (continued)

Date	Experimental purpose	Oil type	Total time (h)	Pan area (cm^2)	Initial thickness (mm)	Temperature (°C)	Wind (m/s)	Variable	Variable value	R^2 best equation	Best equation
Mar. 14	Wind	ASMB	46	151	3.16	21.2	1.45	wind	1.0 m/s	0.993	ln
Mar. 16a	Wind	Water	3	151	1.32	21.8	1.45	wind	1.0 m/s	0.997	linear
Mar. 16b	Wind	Water	3	151	1.32	21.8	1.45	wind	1.0 m/s	0.997	linear
Mar. 16c	Wind	Water	3	151	2.65	21.8	1.45	wind	1.0 m/s	0.999	linear
Mar. 16d	Wind	ASMB	21	151	1.58	22.1	1.65	wind	1.6 m/s	0.981	ln
Mar. 17	Wind	ASMB	22	151	1.58	21.4	1.65	wind	1.6 m/s	0.949	ln
Mar. 18	Wind	ASMB	23	151	1.58	21.4	1.65	wind	1.6 m/s	0.996	ln
Mar. 19	Wind	ASMB	46	151	3.16	22.7	1.65	wind	1.6 m/s	0.986	ln
Mar. 21	Wind	ASMB	20	151	1.58	22.8	1.65	wind	1.6 m/s	0.977	ln
Mar. 22a	Wind	Water	I	151	1.32	21.7	1.65	wind	1.6 m/s	0.998	linear
Mar. 22b	Wind	ASMB	17	151	1.58	23.9	1.65	wind	1.6 m/s	0.978	ln
Mar. 23a	Wind	Water	3	151	1.32	22.2	1.65	wind	1.6 m/s	0.999	linear
Mar. 23b	Wind	Water	5	151	2.65	23.6	1.65	wind	1.6 m/s	0.989	linear
Mar. 23c	Wind	ASMB	22	151	1.58	24.3	1.65	wind	1.6 m/s	0.981	ln
Mar. 24a	Wind	Water	1	151	1.32	23.4	1.85	wind	2.1 m/s	0.998	linear
Mar. 24b	Wind	ASMB	44	151	3.16	23	1.85	wind	2.1 m/s	0.991	ln
Mar. 26	Wind	ASMB	6	151	1.58	21.7	1.85	wind	2.1 m/s	0.993	ln
Mar. 26b	Wind	ASMB	39	151	3.16	20.4	1.85	wind	2.1 m/s	0.993	ln
Mar. 28a	Wind	Water	2	151	1.32	21.8	1.85	wind	2.1 m/s	0.994	linear
Mar. 28b	Wind	Water	5	151	2.65	22.6	1.85	wind	2.1 m/s	0.998	linear
Mar. 28c	Wind	ASMB	12	151	1.58	22.4	1.85	wind	2.1 m/s	0.993	ln
Mar. 29	Wind	FCC heavy	32	151	2.92	21.7	1.85	wind	2.1 m/s	0.987	square root
Mar. 30a	Wind	Gasoline	1	151	1.87	22.6	1.85	wind	2.1 m/s	0.983	ln
Mar. 30b	Wind	Gasoline	2	151	3.74	22.4	1.85	wind	2.1 m/s	0.975	ln
Mar. 30c	Wind	FCC heavy	22	151	1.46	22.3	1.85	wind	2.1 m/s	0.996	square root
Mar. 31	Wind	ASMB	21	151	1.58	23.4	3.8	wind	2.5 m/s	0.981	ln
April 1a	Wind	Water	1	151	1.32	22.4	3.8	wind	2.5 m/s	0.997	linear
April 1b	Wind	Water	2	151	2.65	22.2	3.8	wind	2.5 m/s	0.999	linear
April 1c	Wind	Gasoline	0	151	1.87	22.2	3.8	wind	2.5 m/s	0.984	ln
April 1d	Wind	Gasoline	1	151	3.74	21.9	3.8	wind	2.5 m/s	0.994	ln
April 2a	Wind	Water	3	151	1.32	21.7	0	wind	0	0.999	linear
April 2b	Wind	FCC heavy	47	151	2.92	21.4	3.8	wind	2.5 m/s	0.994	square root
April 4	Wind	FCC heavy	39	151	1.46	22	3.8	wind	2.5 m/s	0.997	square root
April 6	Wind	ASMB	34	151	1.58	22.5	3.8	wind	2.5 m/s	0.993	ln
April 7	Wind	ASMB	18	151	3.16	21	3.8	wind	2.5 m/s	0.997	ln
April 8a	Wind	Water	1	151	1.32	22	3.8	wind	2.5 m/s	0.986	linear
April 8b	Wind	Water	2	151	2.65	22.9	3.8	wind	2.5 m/s	0.994	linear
April 8c	Wind	FCC heavy	19	151	1.46	23	3.8	wind	2.5 m/s	0.992	square root
April 9a	Wind	Gasoline	1	151	1.87	22.1	1.65	wind	1.6 m/s	0.996	ln
April 9b	Wind	Gasoline	3	151	3.74	22.4	1.65	wind	1.6 m/s	0.983	ln
April 9c	Wind	FCC heavy	40	151	2.92	22.3	1.65	wind	1.6 m/s	0.997	square root
April 11a	Wind	Gasoline	1	151	1.87	21.8	1.45	wind	1.0 m/s	0.992	ln

Table 2 (continued)

Date	Experimental purpose	Oil type	Total time (h)	Pan area (cm^2)	Initial thickness (mm)	Temperature (°C)	Wind (m/s)	Variable	Variable value	R^2 best equation	Best equation
April 11b	Wind	Gasoline	2	151	3.74	22.1	1.45	wind	1.0 m/s	0.973	ln
April 11c	Wind	FCC heavy	21	151	1.46	23.1	1.45	wind	1.0 m/s	0.99	square root
April 12	Wind	FCC heavy	51	151	2.92	24.2	1.45	wind	1.0 m/s	0.996	square root
April 14	Wind	FCC heavy	46	151	1.46	24	0	wind	0	0.986	square root
April 16a	Wind	Water	3	151	1.32	23.9	0	wind	0	0.999	linear
April 16b	Wind	FCC heavy	87	151	2.92	23.9	0	wind	0	0.996	ln
April 20a	Wind	Water	8	151	2.65	25	0	wind	0	0.999	linear
April 20b	Wind	Water	16	151	2.65	25.1	0	wind	0	0.998	linear
April 21a	Wind	Gasoline	7	151	1.87	22.5	0	wind	0	0.92	ln
April 21b	Wind	Gasoline	17	151	3.74	22.5	0	wind	0	0.944	ln
April 22a	Wind	Water	6	151	1.32	23	0	wind	0	0.99	linear
Sept. 22a	Pure compound	Benzene	2	151	1.51	23.9	0	rate		0.999	linear
Sept. 22b	Pure compound	Dodecane	45	151	1.77	23.3	0	rate		0.999	linear
Sept. 24	Pure compound	Undecane	46	151	1.79	24.3	0	rate		0.999	linear
Sept. 26a	Pure compound	p-Xylene	7	151	1.54	24	0	rate		0.989	linear
Sept. 26b	Pure compound	Nonane	11	151	1.83	24	0	rate		0.999	linear
Sept. 27	Pure compound	Decane	19	151	1.81	22.3	0	rate		0.998	linear
Sept. 28a	Pure compound	Heptane	3	151	1.94	18.5	0	rate		0.999	linear
Sept. 28b	Pure compound	Octane	3	151	1.88	20.4	0	rate		0.997	linear
Sept. 28c	Pure compound	Deca hydro napthalene	18	151	1.48	21	0	rate		0.996	linear
Oct. 6	Pure compound	Tridecane	23	151	1.79	21.1	0	rate		0.986	linear
Oct. 8	Pure compound	Hexadecane	167	151	1.71	15	0	rate		0.847	linear

not increased by a significant amount with increasing wind speed. In most cases, there is a rise from the 0-wind level to the 1 m/s level, but after that, the rate remains relatively constant. The evaporation rate after the 0-wind value is nearly identical for all oils. The FCC heavy cycle shows the biggest jump in evaporation rate from the 0-wind level to that of the higher winds. The oil evaporation data can be compared to the evaporation of water, as illustrated in Fig. 4. These data show the typical relationship of the water evaporation rate with the wind speed (evaporation varies as $U^{0.78}$, where U is wind

Table 3
Data from the wind tests

Date	Type	Loading (g)	Curve coefficients[a]		Wind (m/s)	Date	Type	Loading (g)	Curve coefficients		Wind (m/s)
			% evaporation	Absolute weight					% evaporation	Absolute weight	
April 25	ASMB	20	4.22	0.844	0	Nov 22	FCC heavy[b]	20	0.414	0.117	0
Mar. 10	ASMB	20	5.28	1.06	1	April 11c	FCC heavy	20	0.887	0.178	1
Mar. 11	ASMB	20	5.3	1.06	1	Mar 30c	FCC heavy	20	0.8	0.161	2.1
Mar. 16d	ASMB	20	5.19	1.04	1.6	April 4	FCC heavy	20	1.13	0.225	2.5
Mar. 17	ASMB	20	5.27	1.05	1.6	April 8c	FCC heavy	20	0.905	0.181	2.5
Mar. 18	ASMB	20	5.15	1.03	1.6						
Mar. 21	ASMB	20	5.63	1.13	1.6	Nov 22	FCC heavy	20	0.414	0.2	0
Mar. 22b	ASMB	20	5.47	1.09	1.6	April 12	FCC heavy	40	0.66	0.264	1
Mar. 23c	ASMB	20	5.54	1.11	1.6	April 9c	FCC heavy	40	0.669	0.268	1.6
Mar. 26	ASMB	20	5.78	1.16	2.1	Mar 29	FCC heavy	40	0.557	0.223	2.1
Mar. 28c	ASMB	20	5.52	1.11	2.1	April 2b	FCC heavy	40	0.785	0.314	2.5
Mar. 31	ASMB	20	5.82	1.16	2.5						
April 6	ASMB	20	5.52	1.1	2.5	April 3a	Gasoline	20	12.2	3.36	0
						April 11a	Gasoline	20	19.5	3.9	1
Jul. 20	ASMB	40	4.09	2	0	April 9a	Gasoline	20	19.7	3.93	1.6
Mar. 12	ASMB	40	4.77	1.91	1	Mar 30a	Gasoline	20	18.2	3.64	2.1
Mar. 14	ASMB	40	4.77	1.91	1	April 1c	Gasoline	20	21.6	4.32	2.5
Mar. 19	ASMB	40	4.9	1.96	1.6						
Mar. 24b	ASMB	40	4.85	1.94	2.1	April 3b	Gasoline	40	12.2	6	0
Mar. 26b	ASMB	40	4.99	2	2.1	April 11b	Gasoline	40	16	6.4	1
April 7	ASMB	40	5.21	2.08	2.5	April 9b	Gasoline	40	16.6	6.65	1.6
						Mar 30b	Gasoline	40	15.4	6.15	2.1
April 2a	Water	20	0.186	0.0372	0	April 1d	Gasoline	40	16.6	6.64	2.5
April 16a	Water	20	0.179	0.0357	0						
April 22a	Water	20	0.178	0.0356	0	April 20a	Water	40	0.088	0.0354	0
Mar. 16a	Water	20	0.592	0.118	1	April 20b	Water	40	0.0778	0.0311	0
Mar. 16b	Water	20	0.612	0.112	1	Mar 16c	Water	40	0.34	0.136	1
Mar. 22a	Water	20	0.512	0.102	1.6	Mar 23b	Water	40	0.312	0.137	1.6
Mar. 23a	Water	20	0.515	0.103	1.6	Mar 28b	Water	40	0.316	0.127	2.1
Mar. 24a	Water	20	0.7	0.14	2.1	April 1b	Water	40	0.56	0.224	2.5
Mar. 28a	Water	20	0.603	0.12	2.1	April 8b	Water	40	0.602	0.241	2.5
April 1a	Water	20	1.02	0.206	2.5						
April 8a	Water	20	1.04	0.209	2.5						

[a] Note that the curve coefficients are the coefficients from single parameter equations, e.g., a in $Y = a \ln(t)$.
[b] The equations used are square root (FCC heavy) and linear (water).

speed). This, by itself, would indicate that the oils used here are somewhat boundary-layer-regulated, but only to the degree that the effect is seen in moving from 0-wind to 1 m/s, and not thereafter.

Fig. 5 shows the rates of evaporation compared to the wind speed for all the liquids used in this study. The lines shown are those calculated by linear regression using the graphics software, Sigma Plot (Washington, DC). This clearly shows that water evapora-
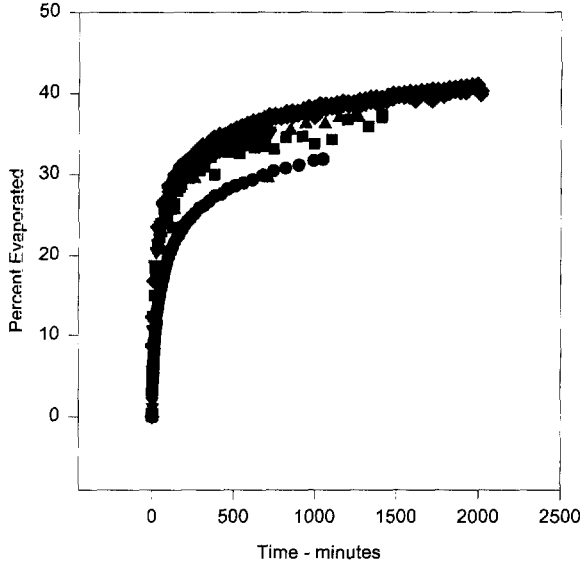
Fig. 1. Evaporation of ASMB with varying wind velocities.

tion rate increased, as expected, with increasing wind velocity. The oils, ASMB, FCC heavy cycle and gasoline, do not show a significant increase with increasing wind speed. The increase may only be a result of the increase in evaporation in going from the
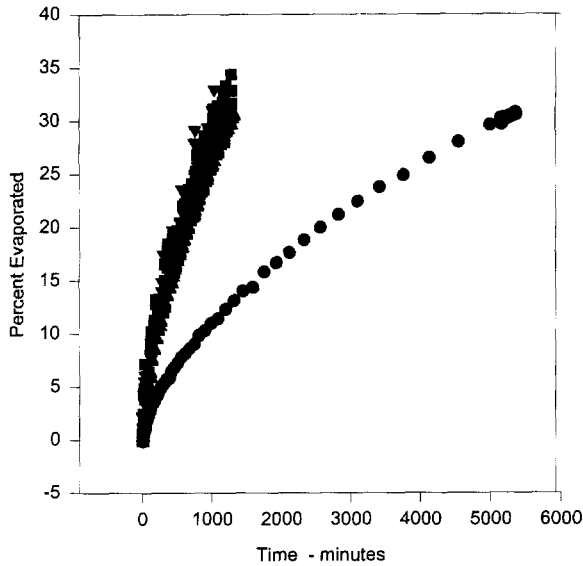

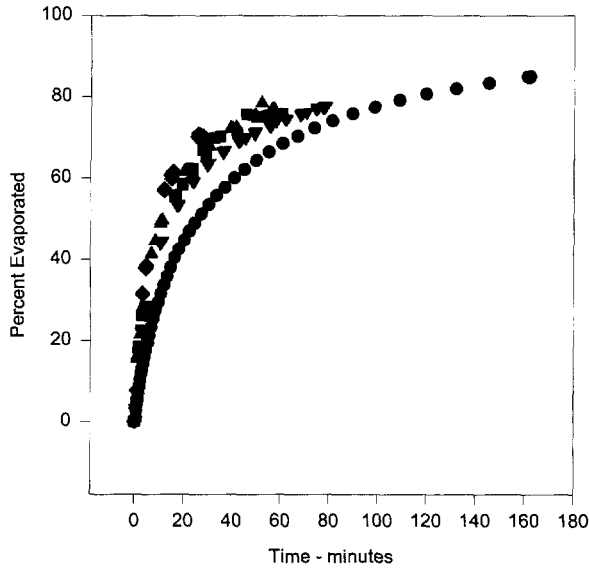Fig. 2. Evaporation of FCC heavy cycle with varying wind velocities.

Fig. 3. Evaporation of gasoline with varying wind velocities.

0-wind level to the other levels. In any case, they do not show the $U^{0.78}$ relationship that water shows.

All the above data show that oil is only slightly, if at all, boundary-layer-regulated,
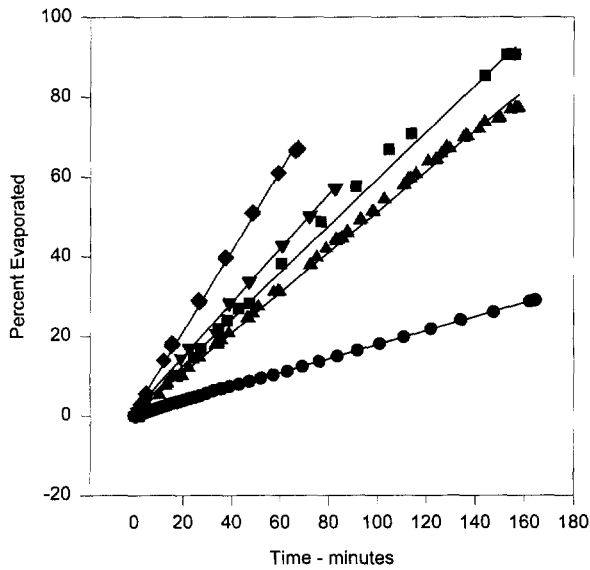
Fig. 4. Evaporation of water (20 g) with varying wind velocities.
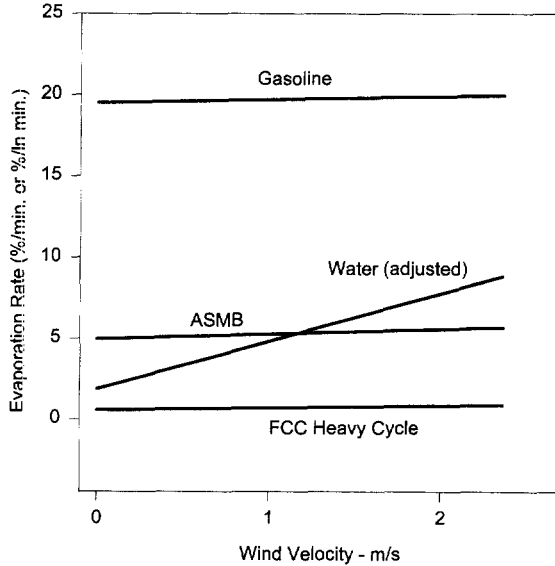
Fig. 5. Correlation of evaporation rates and wind velocity.

perhaps only affecting the very initial rates after turbulence is applied. Water shows the classic boundary layer regulation.

3.2. Evaporation rate and area

ASMB was also used to conduct a series of experiments with varying evaporation area. The mass of the oil was kept constant so that the thickness of the oil would also vary. However, the greater the area, the lesser the thickness, and both factors would increase oil evaporation if it were boundary-layer-regulated. Data are illustrated graphically in Fig. 6. These data show at best, a very weak correlation of thickness and area with evaporation rate. Because of the relationship between volume, thickness, and area, the upward tendency shown in Fig. 6 may be due to correlation with thickness or volume rather than a slight increase in area. Because of the poor correlation between area and evaporation rate, it can be concluded that evaporation rate is not highly correlated with area, and that the evaporation of oil is not boundary-layer-regulated to any significant degree.

3.3. Study of mass and evaporation rate

ASMB oil was again used to conduct a series of experiments with volume as the major variant. Alternatively, thickness and area were held constant to ensure that the strict relationship between these two variables did not affect the final regression results. Fig. 7 illustrates the relationship between evaporation rate and volume of evaporation
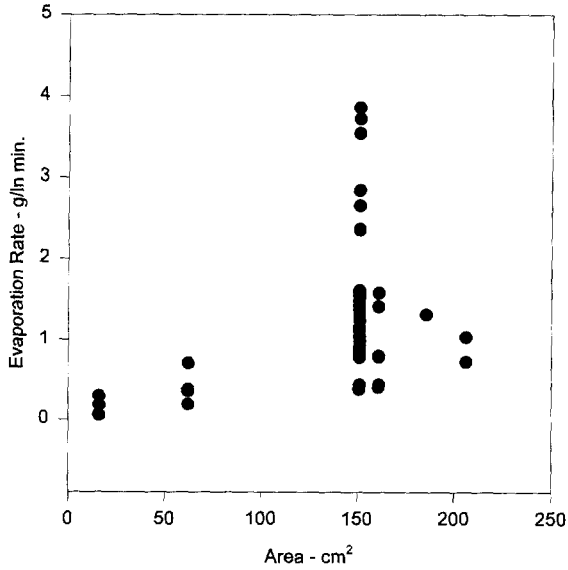
Fig. 6. Correlation of area with evaporation rate.

material (also equivalent to mass of evaporating material), showing a strong correlation between oil mass (or volume) and evaporation rate. This suggests zero or little boundary layer regulation. It also shows that any tendencies observed in the area tests described above, may have been due to volume/mass factors rather than area.
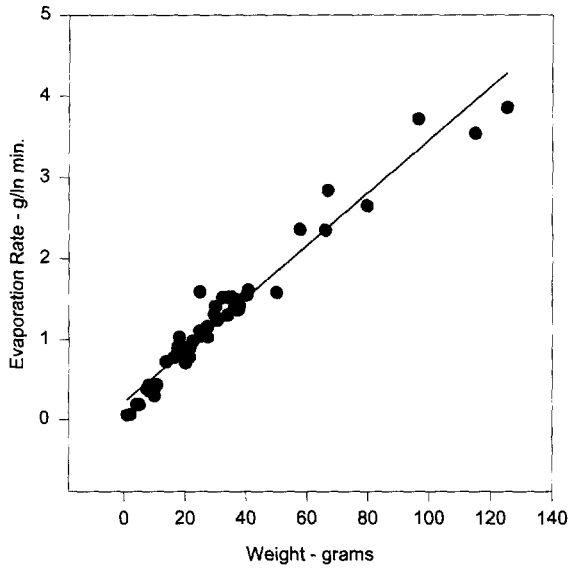

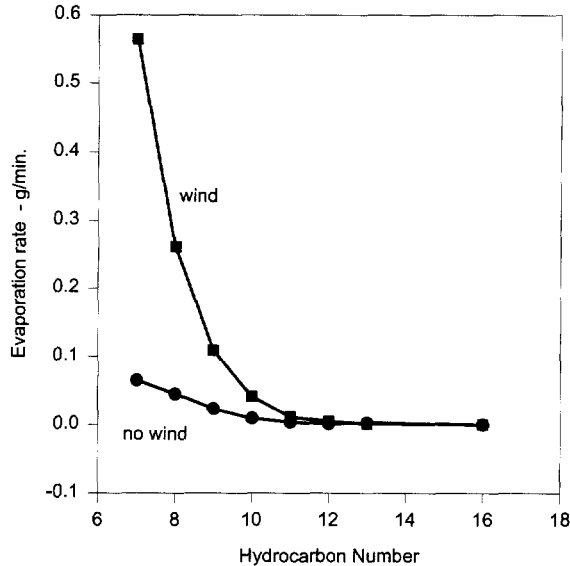
Fig. 7. Correlation of mass with evaporation rate.

Fig. 8. Evaporation rate of pure compounds.

3.4. Study of the evaporation of pure hydrocarbons with and without wind

A study of the evaporation rate of pure hydrocarbons was conducted to test the classic boundary layer evaporation theory as applied to the hydrocarbon constituents of oils. The evaporation rate data are illustrated in Fig. 8. This figure shows that the evaporation rates of the pure hydrocarbons have a variable response to wind. Heptane (hydrocarbon number 7) shows a large difference between evaporation rate in wind and no-wind conditions, indicating boundary layer regulation. Decane (carbon number 10) shows a lesser effect and hexadecane (carbon number 16) shows a negligible difference between the two experimental conditions. This experiment shows the extent of boundary regulation and the reason for the small or negligible degree of boundary regulation shown by crude oils and petroleum products. Crude oil contains very little material with carbon numbers less than decane, often less than 3% of its composition [9]. Even the more volatile petroleum products, gasoline and diesel fuel, only have limited amounts of compounds more volatile than decane, and are also not strongly boundary-layer-regulated.

3.5. Comparisons

An examination of specific evaporation rates of the products used in the previous experiments was performed. Data from the ASMB-20 g loading experiments were taken for comparison. The instantaneous evaporation rate was calculated from the weight loss at each time point recorded. This rate, with units in g/min, changes constantly over the oil evaporation period. For those tests with wind higher than 1 m/s, the noise level

Table 4
Instantaneous evaporation rates of ASMB with varying winds

Wind = 0 m/s		Wind = 1 m/s		Wind = 1.6 m/s		Wind = 2.1 m/s	
Time	Minimum rate (g/min)	Time	Rate (g/min)	Time	Rate (g/min)	Time	Rate (g/min)
0	0.05	*0*	*0.1456*	0	0.2125	0	0.1375
2	*0.075*	6.2	0.1152	*0.2*	*0.51528*	0	0.2875
2.2	0.0625	12.2	0.0313	0.4	0.31111	0.4	0.425
2.4	0.03333	19.1	0.0153	0.6	0.31111	*0.6*	*0.47358*
2.6	0.04167	20.5	0	1.5	0.28611	0.8	0.39858
3.1	0.05	31.7	0.0372	01.8	0.00833	1	0.31844
3.4	0.05417	35.8	0.0264	7.7	0.0875	1.8	0.2601
4	0.04583	43.7	0.0171	8.7	0.04086	1.9	0.11156
4.4	0.0475	52.2	0.0132	10.2	0.0356	4.3	0.12823
5.2	0.05208	71	0	15.8	0.0349	4.4	0.06923
5.7	0.04167	92.5	0	18.5	0.03462	18	0.01
6.8	0.04033	106.3	0.005	19.5	0.03208	18.1	0.08271
7.4	0.04449	113.2	0.0041	32.7	0.03116	24.8	0.02066
9.7	0.04071	123.2	0.0024	33.5	0.0236	32.2	0.03528
11.6	0.03813	135.8	0.0192	43.3	0.01834	37.7	0.01861
12.7	0.03396	151.1	0.0104	45.7	0.01012	49.5	0.01907
15.3	0.03114	167	0.0051	47.2	0.02043	72.6	0.00865
16.8	0.02899	180.5	0.0045	57.6	0.03762	98.7	0.07669
18.4	0.03361	202.9	0.0047	58.3	0.02876	123.2	0.01197
20.2	0.02997	220.1	0.0016	80.2	0.02876	147.7	0.0896
22.2	0.02698	239.9	0.0026	82.5	0.02819	172.2	0.03497
24.4	0.02974	263.5	0.0032	82.8	0.01435	185.2	0.00352
26.8	0.02725	290.4	0	107.2	0.02099	221.1	0.05883
29.4	0.02496	318.6	0.001	132.1	0.00609	244.6	0.04106
32.3	0.02464	357.4	0	157	0.00093	294.8	0.03375
42.9	0.02227	382.9	0	181.9	0.00093	295	0.01169
51.9	0.02154	432.2	0.0047	203.2	0.00863	319.3	0.07556
57	0.02272	462.2	0.0016	207.5	0.02229	346	0.06027
75.8	0.02346	533.5	0.0019	229	0.03019	392.8	0.07486
83.4	0.02177	558.2	0.0017	256.5	0.00101	410.1	0.00079
121.9	0.01905	623.3	0.0006	274.3	0.00108	417.9	0.07378
134	0.0162	691	0.0008	306.1	0.02727	430.8	0.04045
178.3	0.00694	746.4	0.0001	307	0.02412	442.5	0.03376
215.7	0.00394	820	0.0007	331	0.01623	466.2	0.00876
286.9	0.00294	921.4	0.001	353.6	0.02577	491.6	0.043
315.5	0.00279	995.1	0.0006	380.6	0.0277	499.3	0.08467
419.8	0.0018	1102.2	0.0021	405.5	0.01316	539.7	0.00861
507.8	0.00146	1196.6	0	952.6	0.00773	567.4	0.05005
675.7	0.00104	1325.7	0.013	996.5	0.02033	589.5	0.02432
743.2	0.00073	1406.2	0.0134	1001.6	0.02083	613.6	0.02519
989.1	0.0007	1406.4	0	1225.5	0	625.3	0.04186
1196.7	0.00084	1406.6	0.0125	1250.3	0.00941	637.7	0.04113
1316.3	0.00079	1406.8	0	1274.3	0.00414	637.8	0.04167
1751.8	0.00046	1407.9	0	1304.2	0.0091	686.8	0.05826
2119.5	0.00038	1408.2	0	1317.7	0.00717	711	0.09288
3048.3	0	1409	0.025	1349.3	0	720.9	0

Italics: maximum value.
Line shows last point where evaporation is greater than boundary layer regulation.

increases because of the direct effect of the wind on the balance mechanism. As noted in Section 2, these data were recorded during periodic no-wind breaks. The instantaneous evaporation rates are inherently noisy. To calculate the instantaneous evaporation rate for these runs, 4 data points were averaged during the initial 15 min of the run and 14 data points thereafter. This then yielded smoothed data that is representative of the actual evaporation. At 1 m/s wind, this manipulation was not necessary, because the noise level of the data did not result in negative values. The data used for this portion of the study are given in Table 4, truncated for illustration purposes. The full data set was, however, used to plot the data in the figure below. The maximum evaporation rate measured for each series is shown by the shaded value in Table 4, and the value of time and instantaneous evaporation rate, after which no value is greater than 0.075 g/min, is underlined. This value is of significance because it is the level after which boundary layer regulation is insignificant; it is the evaporation rate of ASMB without wind. For the no-wind situation, the evaporation rate attains the maximum value of 0.075 g/min at 2 min. This is then taken as the boundary-layer-regulated maximum rate. At 1 m/s, the value of 0.075 g/min is not found beyond 6.2 min; for the 1.6-m/s wind, not past 1.5 min; and for the 2.1-m/s wind, not past 4.3 min. Thus, it appears that ASMB oil is only boundary-layer-regulated during the first 6 min of evaporation time. This would be the time during which the primary evaporative loss would come from components more volatile than decane, of which most light oils contain little and heavier oils, even less. In fact, even gasoline. shows similar evaporative behaviour.

The instantaneous evaporation rates are illustrated in Fig. 9, which shows the composite evaporation rates for all four runs with varying winds from 0 to 2.1 m/s.
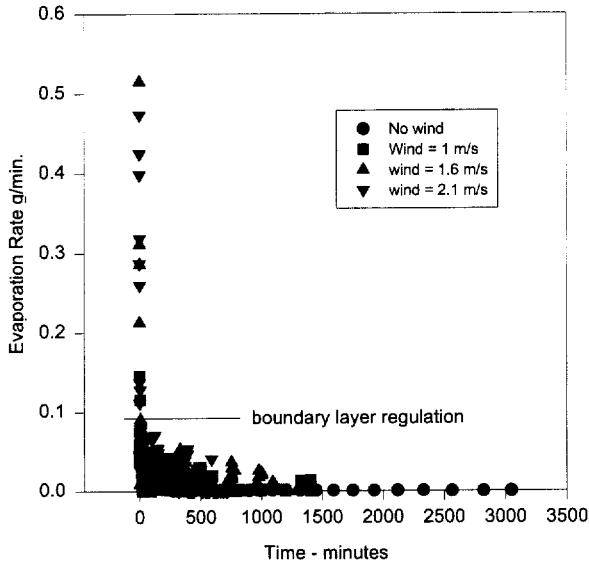

Fig. 9. Plot of ASMB evaporation vs time-variable winds.

Table 5
Saturation concentration of water and hydrocarbons

Substance	Saturation concentration in g/m^3 at 25°C[a]
Water	20
n-pentane	1689
Hexane	564
Cyclohexane	357
Benzene	319
n-heptane	196
Methylcyclohexane	192
Toluene	110
Ethybenzene	40
p-xylene	38
m-xylene	35
o-xylene	29

[a] Values taken from Ullman's Encyclopedia [10].

This shows that all the rates of evaporation are below 0.075 m/s after about 5 min of evaporation.

Another evaluation of evaporation regulation is that of saturation concentration, the maximum concentration soluble in air. Table 5 lists the saturation concentrations of water and several oil components [10]. This table shows that saturation concentration of water is less than that of many common oil components. The saturation concentration of water is about two orders less in magnitude than the saturation concentration of volatile oil components such as pentane. This further explains why oil has a boundary layer limitation higher than that of water.

4. Conclusions

Oil evaporation is not strictly boundary-layer-regulated. The results of the following experimental series have shown the lack of boundary layer regulation.

(1) A study of the evaporation rate of several oils with increasing wind speed shows that the evaporation rate does not change significantly except for the initial step over the 0-level wind. Water, known to be boundary-layer-regulated, does show a significant increase with wind speed, U (U^x, where x varies from 0.5 to 0.78, depending on the turbulence level).

(2) Increasing area does not significantly change the oil evaporation rate. This is directly contrary to the prediction resulting from boundary layer regulation.

(3) The volume or mass of oil evaporating correlates with the evaporation rate. This is a strong indicator of the lack of boundary layer regulation because with water, volume (rather than area) and rate do not correlate.

(4) Evaporation of pure hydrocarbons with and without wind (turbulence) shows that compounds larger than nonane and decane are not boundary-layer-regulated. Most oil and hydrocarbon products consist of compounds larger than these two, and would not be expected to be boundary-layer-regulated.

Even after concluding that boundary layer regulation is not specifically applicable to oil evaporation, this still remains to be explained. The reason is twofold: oil evaporation, especially after an initial time period, is relatively slow compared to the threshold where it is boundary-layer-regulated, and the threshold to boundary layer regulation for oil evaporation is much higher than that for water. These two factors were highlighted three ways:

(a) A comparison of the length of time that oils exceed the boundary layer limit, taken as the maximum evaporation rate in the absence of wind, shows that the length of time during which the evaporation rate in the presence of wind exceeds the boundary layer limit, can be as short as 2 min. This represents a very small fraction of the required time to significantly evaporate oil (in these experiments, typically 2000 to 8000 min). For most of the time, the evaporation is far below the boundary-layer-regulated rate.

(b) A comparison of the maximum rates of evaporation for some oils, gasoline and water, in the absence of wind, shows that some oil rates exceed that for water by as much as an order of magnitude (water = 0.034 g/min, ASMB = 0.075 g/min, and gasoline = 0.34 g/min — all under the specific conditions noted).

(c) The saturation concentration of several hydrocarbons in air reveals that some hydrocarbon saturation concentrations in air can be greater than that of water by as much as 1×10^2.

The fact that oil evaporation is not strictly boundary-layer-regulated implies a simplistic evaporation equation will suffice to describe the process. The following factors do not require consideration: wind velocity, turbulence level, area, thickness and scale size. The factors important to evaporation are time and temperature. The latter is the subject of further experimentation.

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