Studies on the evaporation of crude oil and petroleum products:
I. the relationship between evaporation rate and time

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Abstract

The time dependance of evaporation was studied for several crude oils and petroleum oil products. Evaporation was determined by weight loss measured on a balance and recorded constantly on a computer. Examination of the data shows that most oil and petroleum products evaporate at a logarithmic rate with respect to time. This is attributed to the overall logarithmic appearance of many components evaporating at different linear rates. Petroleum products with fewer chemical components, such as diesel fuel, evaporate at a rate which can be best modelled as a square root of time. The particular behaviour is shown to be a result of the number of components evaporating by experimentation with artificial oils consisting of 1 to 15 components. Oils with greater than 7 components evaporating at one time can be modelled with logarithmic equations; those with 3 to 7 components, with square root equations. © 1997 Elsevier Science B.V.

1. Introduction

Evaporation is a very important process for most oil spills. In a few days, light crude oils can be reduced by up to 75% of their initial volume and medium crudes by up to

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40% of their volume [1]. In contrast, heavy or residual oils will only lose about 5% of their volume in the first few days following a spill. Most oil spill behaviour models include evaporation as a process and in the output of the model. Despite the importance of the process, relatively little work has been conducted on the basic physics and chemistry of oil-spill evaporation [2]. The particular difficulty with oil evaporation is that oil is a mixture of hundreds of compounds and this mixture varies from source to

Table 1
Properties of the test liquids

Test liquid	Description	Density g/ml	Viscosity mPa·s at 15°C
Amauligak	A light crude oil from Canada's Beaufort Sea	0.871	14
Avalon	One of the test crude oils from Newfoundland's Hibernia field	0.871	15
ASMB	Alberta Sweet Mixed Blend-a common crude oil in Canada	0.839	9
AV Gas 80	Aviation gasoline with an octane rating of 80	0.715	0.44
Brent	A common British, North Sea oil, sometimes exported to Canada	0.833	6
Bunker C	A heavy residual fuel containing distillation residuals	0.98	48,000
Diesel	Standard automotive/truck diesel fuel	0.809	2
Endicott	Oil from one of the smaller fields on Alaska's north slope	0.915	84
Federated	A light, sweet Alberta crude that forms the primary feed of Edmonton's refineries	0.826	5
FCC Heavy	A light refinery intermediate product, the 'Heavy' refers to the number of times the product is re-cycled	0.908	3
Gasoline	Standard automotive non-leaded gasoline	0.709	0.6
Gullfaks	A common Norwegian oil-sometimes exported to Canada	0.882	13
Issungnak	Oil from the Canadian Beaufort Sea, a very light oil	0.849	4
Komineft	Crude oil from the Russian Komi Republic	0.85	14
Prudhoe Bay	Oil from the largest field on Alaska's north slope	0.905	26
Santa Clara	A heavy crude oil from Southern California	0.92	300
Statfjord	A common Norwegian oil-sometimes exported to Canada	0.834	7
Terra Nova	One of the oils from the Hibernia field off Newfoundland	0.864	17
Benzene	Pure Hydrocarbon-C6	0.879	
Dodecane	Pure Hydrocarbon-C12	0.749	
Undecane	Pure Hydrocarbon-C11	0.742	
p-Xylene	Pure Hydrocarbon-C8	0.861	
Nonane	Pure Hydrocarbon-C9	0.722	
Decane	Pure Hydrocarbon-C10	0.73	
Heptane	Pure Hydrocarbon-C7	0.684	
Octane	Pure Hydrocarbon-C8	0.703	
Decahydron	Decahydronaphthalene-pure hydrocarbon-C10	0.893	
Tridecane	Pure Hydrocarbon-C13	0.755	
Hexadecane	Pure Hydrocarbon-C16	0.773	

source and even over time. Much of the work described in the literature focuses on 'calibrating' equations developed for water evaporation [2]. Furthermore, very little empirical data on oil evaporation is published.

Scientific and quantitative work on water evaporation is decades old [3,4]. The basis for the oil work in the literature is water evaporation. There are several fundamental differences between the evaporation of a pure liquid such as water and that of a multi-component system such as crude oil. Most obviously, the evaporation rate for a single liquid such as water is a constant with respect to time [3,4]. Evaporative loss, by total weight or volume, is not linear with time for crude oils and other multi-component fuel mixtures [5]. This paper addresses the relationship of time and evaporation rate with the nature of the oil being evaporated.

2. Experimental

Evaporation rate was measured by weight loss using an electronic balance. The balance was a Mettler PM4000, capable of measurements to 0.01 ± 0.02 g. The weight was recorded using a computerized system consisting of a Toshiba 3100, a serial cable to the balance and a modified version of the software program, 'Collect' (Labtronics, Richmond, Ontario). Adjustments were made to the program to allow different time multiples for data acquisition. This allowed minimization of data quantity at times after the initial rapid evaporation period. Intervals of data acquisition could be set at multiples such that each time increment had an approximately equal weight loss increment. For example, in one day, using a timing multiplier of 1.1 and an initial interval of 10 s, 75 data points were collected compared to 8640 if regular time intervals of 10 s were used. The procedure yielded data sets which were manageable.

Measurements were typically conducted in the following fashion. A tared petri dish

Table 2
Constituents of the hydrocarbon mixtures

Number of components	Equal mass constituents
1	Heptane
2	Heptane, Octane
3	Heptane, Octane, Nonane
4	Heptane, Octane, Nonane, Decane
5	Heptane, Octane, Nonane, Decane, Undecane
6	Heptane, Octane, Nonane, Decane, Undecane, Hexadecane
7	#6 above and Dodecane
8	#6 above and Dodecane, Tridecane
9	#6 above and Dodecane, Tridecane, Benzene
10	#6 above and Dodecane, Tridecane, Benzene, Toluene
11	#10 above and p-Xylene
12	#10 above and p-Xylene, Ethyl Benzene
13	#10 above and p-Xylene, Ethyl Benzene, Decahydronapthalene
14	#13 above and Propyl Benzene
15	#13 above and Propyl Benzene, Cyclohexane

Table 3
Experiments and best fit equations

Date	Year	Oil type	Total time (h)	Temperature (°C)	R^2 best equation	Best equation
June 21	1993	ASMB	15	21.2	0.991	ln
June 23	1993	ASMB	22	21	0.978	ln
June 24	1993	ASMB	23	21.8	0.97	ln
June 25	1993	ASMB	182	22.6	0.99	ln
July 2	1993	ASMB	15	22.4	0.937	ln
July 3	1993	ASMB	51	21.9	0.975	ln
July 5	1993	ASMB	65	24.4	0.954	ln
July 9	1993	ASMB	25	23.8	0.952	ln
July 16	1993	ASMB	73	21.7	0.96	ln
July 20	1993	ASMB	36	22.8	0.963	ln
Aug. 30	1993	ASMB	18	20.1	0.897	ln
Sept. 1	1993	ASMB	73	20.3	0.886	ln
Sept. 4	1993	ASMB	217	20	0.937	ln
Sept. 13	1993	ASMB	64	22.1	0.981	ln
Sept. 16	1993	ASMB	56	17.8	0.952	ln
Sept. 18	1993	ASMB	47	19.2	0.987	ln
Sept. 20	1993	ASMB	23	18.8	0.988	ln
Sept. 21	1993	ASMB	25	20.1	0.985	ln
Sept. 22	1993	ASMB	71	23.1	0.976	ln
Oct. 15	1993	ASMB	32	18.6	0.977	ln
Oct. 16	1993	ASMB	89	22.9	0.98	ln
Oct. 20	1993	ASMB	76	20.4	0.993	ln
Oct. 23	1993	ASMB	66	20.3	0.986	ln
Oct. 26	1993	ASMB	88	19.1	0.962	ln
Dec. 24	1993	Bunker	99	11.8	0.687	ln
Dec. 28	1993	Gasoline	19	13.4	0.983	ln
Dec. 29a	1993	Gasoline	4	9.1	0.922	ln
Dec. 29b	1993	Gasoline	2	19.5	0.889	ln
Dec. 29c	1993	Bunker	72	19.6	0.875	ln
Jan. 1	1994	Prudhoe 1	49	21.5	0.993	ln
Jan. 3	1994	Prudhoe 2	71	21.3	0.997	ln
Jan. 8	1994	Brent	48	18	0.995	ln
Jan. 10	1994	Brent	27	21.6	0.991	ln
Jan. 12	1994	Brent	67	19.53	0.991	ln
Jan. 15	1994	Brent	74	18.1	0.986	ln
Jan. 18	1994	Endicott	42	20.1	0.972	ln
Jan. 20a	1994	AV Gas 80	3	5.6	0.974	ln
Jan. 20b	1994	AV Gas 80	2	18	0.964	ln
Jan. 20c	1994	Issungnak	47	19	0.947	ln
Jan. 22	1994	Terra Nova	43	18.8	0.971	ln
Jan. 24	1994	Diesel	95	5.6	0.991	sq. rt.
Jan. 28a	1994	Jet 40 Fuel	6	20.8	0.915	ln
Jan. 28b	1994	Prudhoe Bay	190	11.2	0.986	ln
Feb. 5	1994	Santa Clara	48	24.1	0.967	ln
Nov. 13	1994	1-component	6	29	0.999	linear
Nov. 14a	1994	2-component	7	17	0.999	linear
Nov. 14b	1994	4-component	11	23.7	0.995	sq. rt.
Nov. 15a	1994	3-component	5	20	0.988	linear

Table 3 (continued)
Experiments and best fit equations

Date	Year	Oil type	Total time (h)	Temperature (°C)	R^2 best equation	Best equation
Nov. 15b	1994	6-component	49	19	0.948	sq. rt.
Nov. 17	1994	5-component	27	21.2	0.985	sq. rt.
Dec. 10	1994	14-component	21	18.6	0.975	sq. rt.
Dec. 11	1994	13-component	30	19	0.923	sq. rt.
Dec. 12	1994	12-component	25	8	0.984	sq. rt.
Dec. 13	1994	11-component	92	9.2	0.916	sq. rt.
Dec. 17	1994	10-component	50	22.2	0.913	sq. rt.
Dec. 19	1994	9-component	40	18.6	0.954	sq. rt.
Dec. 21	1994	8-component	29	23.4	0.956	sq. rt.
Dec. 22	1994	7-component	25	23	0.968	sq. rt.
Dec. 23	1994	Komineft	121	23.3	0.995	ln
Dec. 28	1994	Federated	142	23.1	0.982	ln
Jan. 3	1995	Federated	95	15	0.985	ln
Jan. 7	1995	Federated	96	15	0.988	ln
Jan. 11	1995	Avalon	70	15	0.96	ln
Jan. 14	1995	Gulfaks	89	15	0.983	ln
Jan. 18	1995	Brent	79	15	0.995	ln
Jan. 21	1995	Amauligak	120	15	0.952	ln
April 14	1995	FCC Heavy	48	24	0.986	sq. rt.

ln = logarithmic, sq. rt. = square root.

of defined size was loaded with a measured amount of oil. At the end of the experiment, the weathered oil was saved for other experiments. 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. The evaporation was conducted directly from the glass surface of the dish. Initial experiments, not reported here, were conducted using a water surface. This added complexity which was found to be unnecessary and could result in errors if the water was exposed to air and evaporated itself. Thus, the glass pans were used directly. The height of the lip of the glass above the oil varied from 1 to 8 mm, depending on the amount of oil in the pan.

Temperatures were measured using a Keithley 871 digital thermometer with a thermocouple supplied by the same firm. Temperatures at the fume hood location, where these experiments were performed, were often close to 20°C. The sensor was placed at 1 cm over the evaporation pan to take readings. Temperatures were taken at the beginning and at the end of a given experimental run.

The fume hood fan was not operated. There were no air velocities over the oil and this was verified with a hot wire anemometer (TSI-Thermo Systems model 1053b, with power supply (TSI model 1051-1), averaging circuit (TSI model 1047) and signal linearlizing circuit (TSI model 1052)). The hot wire sensor (TSI model 1213-60) was angled at 45°. The sensor was placed directly over the floor of the evaporation pan and at the lip level of the evaporation pan. 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.

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 (Microsoft, Redmond, Washington).

Curve fitting was performed using the software program 'TableCurve' (Jandel Scientific, San Raphael, California). The weight% and the absolute weight were always fitted separately and statistics on these parameters recorded separately. This was done to enable subsequent analysis of dimensionless and absolute evaporation. It is important to note that the absolute weight calculation still relates to the weight of the starting substance. The program 'TableCurve' enables the user to fit hundreds of relationships to a set of data and rank the resulting fit in order of regression coefficient (R^2). In this study, the 'common' functions were generally used.

Oils were taken from supplies of the Environment Canada and were acquired from various oil companies for environmental testing (Table 1). Properties of the oils can be found in standard references [6]. Artificial oils consisting of pure hydrocarbons were made by adding equal proportions by weight. Table 2 shows the composition of these artificial oils.

3. Results and discussion

Table 3 lists the experiments performed and the results in terms of the best fit equations. These were calculated using the program 'TableCurve', as noted above. The best fit was done on the basis of the simplest equation fitting with the highest R^2. Obviously, more complex equations, such as those with more parameters, can fit the
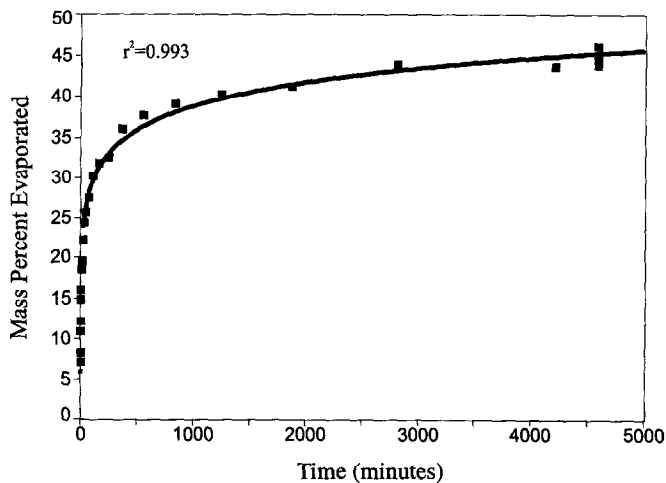

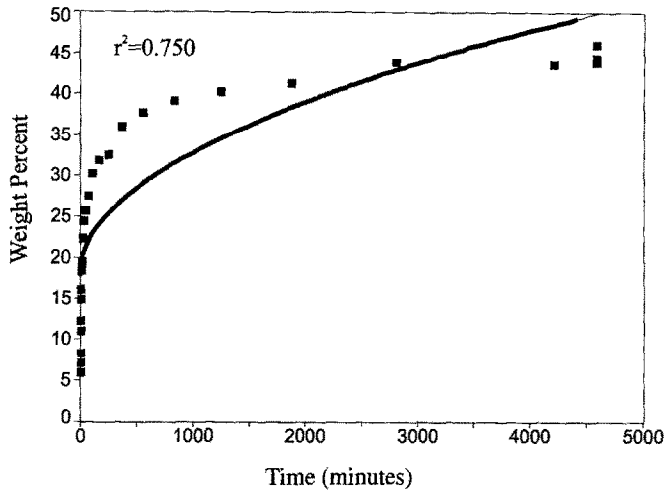Fig. 1. Logarithmic curve fit to ASMB evaporation data.

Fig. 2. Square root curve fit to ASMB evaporation data.

data better, and thus the criteria for best fit also includes the simplest form of an equation. For most oils, logarithmic equations fit best in so far as they are the simplest equations that have only two constants with the highest R^2. Pure substances, including the hydrocarbons and water, evaporate in a linear manner (loss with respect to time) as illustrated by the one-component mixture shown in Table 3. Diesel fuel fits a square root equation best as can be seen in Table 3. Diesel oil is a refinery product with a very narrow 'cut'. The oil has few compounds and probably is dominated by about 4 compounds compared to several dozen for a typical crude oil [6]. Other oils can also
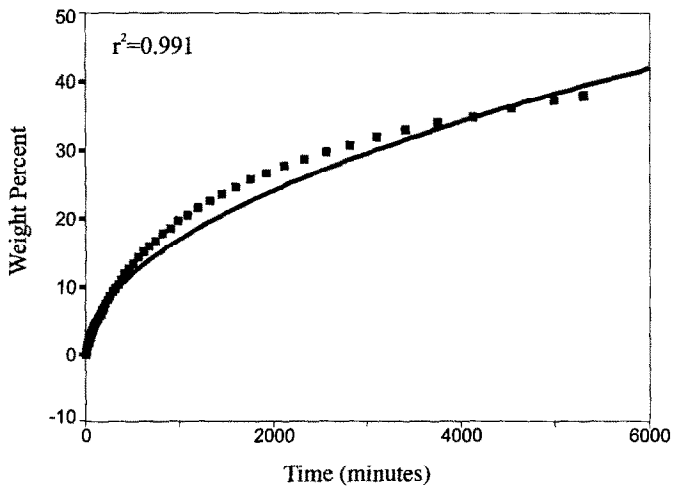

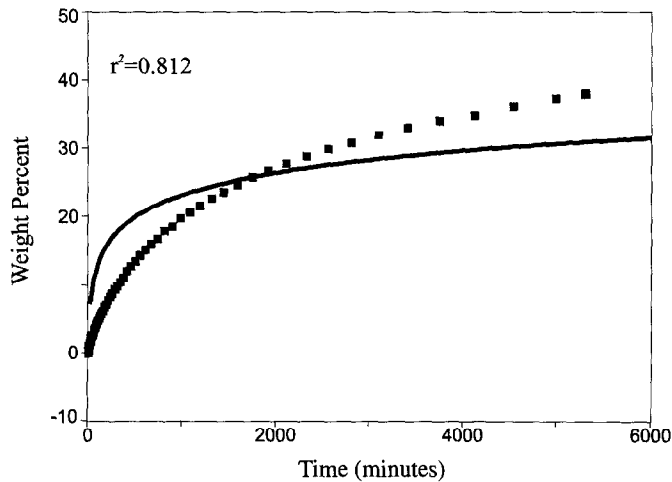Fig. 3. Square root curve fit to diesel evaporation data.

Fig. 4. Logarithmic curve fit to diesel evaporation data.

show this behaviour, e.g., FCC Heavy Cycle or certain Bunker fuels where diesel is an ingredient, as also seen in Table 3. Fig. 1 shows the evaporation behaviour of a typical crude oil, Alberta Sweet Mixed Blend or ASMB, and the curve fit with a logarithmic curve. Fig. 2 shows the same data fit with a square root equation. These figures show that the logarithmic curve fits the data better than the square root one. Fig. 3 shows the evaporation of diesel fuel fit with a square root equation. Fig. 4 shows the same data fit with a logarithmic equation. Figs. 3 and 4 clearly show that diesel fuel evaporates as a square root with time and not the logarithm as do other oils. This is true for the time periods shorter than 1 to 5 days as performed in this set of experiments. Long-term evaporation for these oils may be predicted more accurately with other equations.

Table 4
Power exponents for multiple-component evaporation

Components	Best-fit power factor
1	1
2	0.998
3	0.994
4	0.588
5	0.494
6	0.252
7	0.36
8	0.31
9	0.283
10	0.202
11	0.23
12	0.41
13	0.263
14	0.463

Equation y=a+bexp(-x/c) [Exponential]
r2=0.845   DF Adj r2=0.798   FitStdErr=0.124   Fstat=30.0
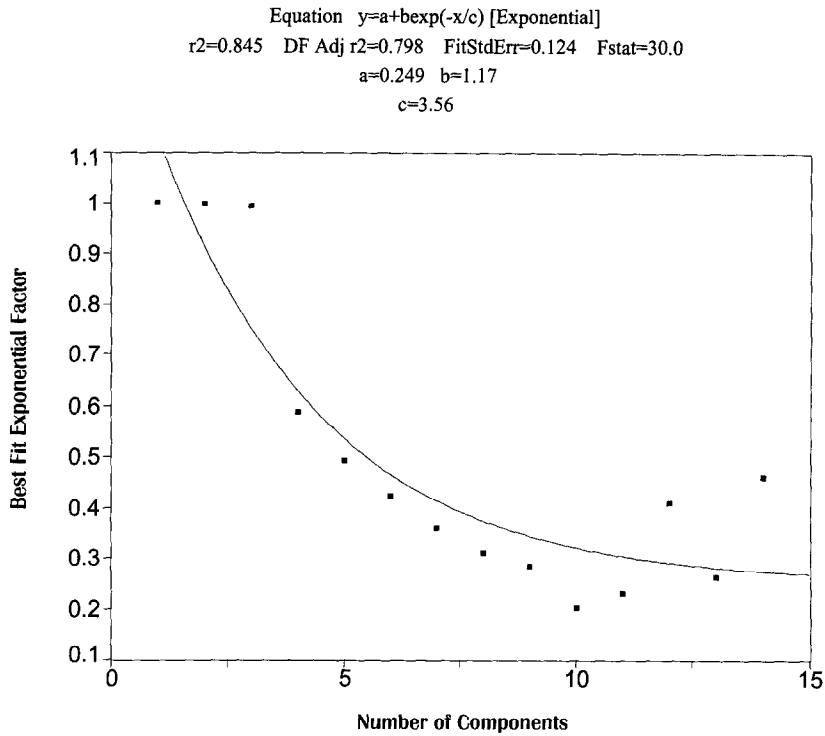a=0.249   b=1.17
c=3.56

Fig. 5. The evaporative behaviour of multi-component liquids.

To test whether the type (or shape) of the curve is a result of the number of components evaporating, a series of experiments was conducted using pure hydrocarbons. Table 2 gives the constituents of the hydrocarbon mixtures. The evaporation data were fitted to the equation $Y = a + bX^e$, where Y is the percent of the artificial component mixture evaporated, a and b are empirical constants, X is the time and e is the power exponent. This was done to measure the best e for each set of data. For example, an exponent of 0.5 is a square root equation. Table 4 shows the number of components and the 'best' power factor for each experimental run. The resulting curve is shown in Fig. 5. As this figure shows, the number of evaporating components can account for the type of equation fit to the data. The component mixture changes composition somewhat as it progresses past 10 components. More volatile components were used to produce the new mixture from 10 to 15 components. The best fit resulted from using a power equation. As can be seen, the number of components evaporating changes the curve type smoothly until the mixture changes to the more volatile components noted. A logarithmic curve is approximately a power factor of 0.35 for the values of time used in this study (10 to 2000 min), thus approximately 7 or more components evaporating are required to yield a logarithmic curve. Fig. 5 indicates also that those oils (such as FCC Heavy Cycle, some Bunker fuels and diesel fuel) which show a square root equation as having the best fit, have approximately 5 components

evaporating. This indicates that the type of curve fit (e.g., logarithmic or square root) is a result of the number of components undergoing evaporation at the same time.

4. Conclusions

Pure compounds evaporate in a linear manner. Most crude oils, consisting of several compounds evaporating at one time, evaporate in a logarithmic manner, that is the loss of mass is approximately logarithmic with time. This behaviour is due to the number of components evaporating at once, each of which has a linear evaporation behaviour. The envelope of these linear rates results in a logarithmic curve.

The study of the nature of the evaporative curve shows that 'best' fit largely depends on the number of components evaporating simultaneously. Mixtures of components between about 5 and 7 components evaporate as a square root with time. Logarithmic equations result when approximately 7 or more components evaporate simultaneously.

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