SPILL TECHNOLOGY

NEWSLETTER

ISSN 0381-4459

VOLUME 18 (4) October-December 1993

AN INTRODUCTION TO OIL SPILL BEHAVIOUR, CHEMISTRY, AND MATHEMATICAL MODELLING

Merv F. Fingas
Emergencies Science Division
Environmental Technology
Centre
Environment Canada
Ottawa, Ontario, Canada

Introduction

The fate and behaviour of oil spills at sea is important in that the behaviour of a given spill is often unique from other spills in the same area. Spill behaviour also dictates the effects that the oil will have on marine life or the shoreline. The precise fate of an oil spill depends on the type of oil spilled and the sea and weather conditions.

The behaviour of oil spills is dominated by the chemistry or composition of oil which can be simplified by measuring the

group components of saturates, aromatics, asphaltenes, and resins. The most important behavioural aspect of oil spills is their evaporation, which generally causes the largest changes in mass balance after a spill and influences other behavioural parameters. Emulsification, which depends on oil composition, is the second most important aspect. Oils that emulsify undergo a rapid increase in viscosity, typically 1000 times, and nearly cease spreading and evaporating. Resins and asphaltenes in the oil stabilize water in the emulsion; whereas, aromatics dissolve the asphaltenes and thus delay

emulsification. Some oils can loose sufficient aromatics by evaporation so that they begin to emulsify. Natural dispersion is the third-most important behaviour displayed by spilled oils. The saturate component of oils disperses in highly turbulent situations. Asphaltenes, however, are a deterrent to natural dispersion.

The behavioural aspects of oil spills are generally poorly-studied and poorly modelled. Most data are empirically-derived with a generous portion of assumptions thrown in. Evaporation, however, is probably the best

The behaviour of oils depends on their chemical composition. This article is a brief introduction as to how oils behave under different conditions.



understood and modelled behaviour, emulsification is well understood but poor models for this exist. Natural dispersion is poorly understood and very poorly modelled. To improve spill modelling, fundamental physical and chemical studies are needed to understand oil spill behaviour.

Chemistry

The chemistry of crude and refined oils defines their behaviour at sea. Crude and refined oils are composed of many, in some cases, hundreds, of different compounds, each with their own behaviour and properties. The combination of these compounds can be modelled from a number of different perspectives: as a combination of selected typical compounds, as a single compound, or each oil may be viewed as a unique substance. All of these points of view have disadvantages in modelling. If an oil is viewed as a combination of a few marker compounds, some of the behavioural aspects are not accounted for - e.g., asphaltenes and their role in water-in-oil emulsification. Taking the oil as a single compound removes many of it's behavioural characteristics and, therefore, is not useful for spill modelling if behaviour is an important factor. Taking an oil as a unique combination complicates spill modelling in that it is difficult to

add new oils. The importance of understanding the composition and overall behaviour of a specific oil cannot be over-emphasized.

Crude oils (and refined products in most cases) are a mixture of many compounds (Neumann et al., 1981, Kinghorn, 1983), but most crude oil consists of saturates or alkanes. Alkanes are the desirable end-product of a crude oil because the C₈ to C₁₈* fraction is directly used as gasoline and diesel fuel, the greatest use for crude oil. Larger alkane compounds (>C24) are known as waxes and may be treated by petroleum companies to convert them into smaller compounds. The chemistry and behaviour of alkenes are similar to the alkanes, except that they contain one or more double bonds, and are less desirable as a source for fuel. They may, however, be treated in refineries and converted to alkanes.

Aromatics are cyclic compounds containing double bonds that are conjugated or that are spaced two-apart and in rings, all of which allows for special stability. Large aromatic compounds, known as polycyclic aromatic hydrocarbons (PAHs), exist in crude oils and are a frequent environmental concern resulting from combustion sources. Cycloalkanes or naphthenes, are another class of petroleum compounds similar to the

aromatics except that they contain no double bonds. There is also a class known as the naphthenoaromatic compounds that contains both aromatic and naphthenic rings. The class of compounds known as resins or polars are compounds of the other classes having heteroatoms or molecule(s) such as sulphur, oxygen, or nitrogen. These compounds are characterized by their polarity and are partially soluble in water and oil. This entire class of compounds is only characterized by a precipitation method, so in fact, many dozens of compounds are typically included in this class. Asphaltenes are similar compounds, but are much larger in molecular size. The basic structure of some asphaltenes is that of a naphthenic backbone with some side chains bearing polar heteroatoms such as sulphur, oxygen, and nitrogen. Some asphaltenes are partially water-soluble as well. Asphaltenes are an especially amorphous group and much effort can be expended to identify the structure of even one asphaltene compound in an oil (Ravey et al., 1988). Many other classes of compounds exist, but do not influence the behaviour of oil to a large extent. Examples of such classes include: mercaptans - smaller sulphur-containing compounds; metal-containing compounds; steroids; and even biologically-derived compounds.

^{*} C_x is the carbon number (the number of carbons present in the compound)

A number of oil properties are important to the understanding of oils and their behaviour (McCain, 1990). The most important is viscosity or resistance to flow. Technically defined, viscosity is the shear resistance (force) divided by the shear rate (velocity). The viscosity of an oil defines its spreading rate and is related in some way to most behavioural aspects.

Density is the weight of specific volume of oil and in terms of behaviour defines how an oil will float in water. Density is strongly correlated to viscosity for most oils. American Petroleum Institute (API) gravity is a different way of stating density (API° = 141.5/d -131.5).

Water content is an important measurement for oils that have emulsified or formed water-in-oil emulsions. This is an indication of the expansion of spill volume resulting from water incorporation and to a lesser degree of the stability of the resulting emulsion. Water content is unimportant for oils that have not emulsified.

Surface and interfacial tension are often cited as being important factors. The interfacial tension is the energy difference between the oil layer and air or water, which is not as important as some might stress, since it cannot be used in isolation to predict any behavioural aspects of the oil, and varies little between oils.

Pour point is the temperature below which the oil ceases to pour as a fluid. Pour point is a difficult measurement and is subject to variance. Pour point is not a precise physical measurement with a multi-component oil such as crude and many of the distilled products.

The variance of these properties with temperature has been the subject of many studies (McCain, 1990). The change in a given property is generally a function of the logarithm of the temperature in Kelvin. The properties of oil, therefore, do not change drastically with temperature.

Many of the relationships that have been developed for chemical property analysis are based on the assumption of a single component behaving as an ideal gas. These assumptions are sometimes acceptable for a crude oil and under other conditions they are not.

The chemical contents of oils are important in determining the behaviour of oil spills. Oil can be categorized into four groups: saturates, aromatics, resins or polars, and asphaltenes. An oil can be divided into it's constituents using precipitation methods. The saturates or alkanes constitute the backbone of the commercial desire for oil. Studies show that saturates are largely dispersed chemically or naturally in water and that this behaviour can be correlated with saturate content (Fingas et al.,

1992: 1993a;b). These studies also show a negative correlation of natural dispersability with increasing aromatic, asphaltenic, and resinic content. Larger saturates, or waxes (alkanes with chain lengths greater than C₂₄) at concentrations greater than about 3% in oils, begin to affect properties such as viscosity. adhesion, and weathering. Resins and asphaltenes stabilize water-in-oil emulsions (Bobra, 1990; 1991; Fingas et al., 1993d). The larger the resin and asphaltenic content, the more viscous the oil and the less it spreads. Saturate content has also been related to biodegradability in the same way as natural dispersion.

To determine the long-term fate and behaviour of oil, it is necessary to have data on its saturate, aromatic, resinic, and asphaltenic fractions. Determination of chemical composition by analytical methods such as gas chromatography is difficult, however, because of the many components and their similarity. One useful parameter to know is the total amount of BTEX (Benzene, Toluene, Ethyl benzene, and Xylenes). This fraction is largely evaporated soon after a spill, but it is also the fraction that is responsible for the short-term aquatic toxicity of the oil. A number of biomarkers in the oil such as the steranes and hopanes, are useful to measure when performing studies such as biodegradation or identification. These components have variable susceptibility to evaporation and

biodegradation, some of them being completely resilient, and thus serving as a marker of the degree of degradation or evaporation.

Behaviour of Oil in the Environment

The behaviour of oil in the environment is largely dictated by its chemical composition. The behaviour of oil might be best summarized by examining several specific groups of oils. Fuels such as gasoline or diesel fuel are most influenced by evaporation in the environment. Gasoline in warm climates will be 90% evaporated on water within about one day and in about two days in cold climates. Both gasoline and diesel fuel will disperse naturally to a large degree in turbulent waters. Diesel fuel will evaporate to about 70% (percentage lost) in 2 days on warm water and in 4 days on very cold water. A light crude oil will evaporate to about 50% in 2 days and will disperse naturally (depending very much on saturate content) in turbulent seas. A medium crude oil will evaporate to about 30% in 2 days. After evaporation, water-in-oil emulsions may form, depending on asphaltene, resin, and aromatic content. Medium crudes rarely disperse naturally to any great extent. A heavy crude will evaporate by about 15% and will almost never disperse naturally. Heavier crudes usually have a large percentage of asphaltenes and

resins and will, after some evaporation, often form water-in-oil emulsions. Residual oils, such as Bunker C, will only lose about 4% of their volume to evaporation after two days. Bunker C may have a higher volume of asphaltenes and a lower content of aromatics and thus can, therefore, form emulsions. Bunker C will not disperse naturally to any extent because it has little saturate content.

Evaporation is the most important behavioural aspect of oil and is responsible for the largest mass balance change in oils except for those rare times when oils disperse naturally. Evaporation is generally necessary before emulsification occurs and is a competing process to natural dispersion. If emulsification (the second most important behavioural aspect) occurs, the spill dynamics and behaviour of the oil are changed to a large degree. The viscosity of the resulting product is 1000 times the starting viscosity, the spilled product is now five times the volume of the starting spill volume, and spreading and evaporation nearly cease. Natural dispersion (the third factor) is an important phenomenon. Where a high-saturate oil is spilled in a turbulent sea, the oil can be dispersed into the water column in the form of small droplets (e.g., the BRAER spill in the Shetlands). Other oils will disperse to little degree. Dissolution is a fourth behavioural phenomenon,

although never greater than 1% of the oil, it is important for the toxicity of the oil to aquatic life. Finally there are other phenomena, such as photooxidation, sinking, and biodegradation which are less important in terms of the oils overall mass balance.

Evaporation- is the most important change that most oil spills undergo and many spill models incorporate evaporation as a component of their prediction. In the few days following a spill, light crudes can lose up to 75% of their volume and medium crudes up to 40%. Heavy or residual oils, however, will only lose about 10% of their volume.

Although the process of evaporation of crude oils is understood, the application of evaporation equations in spill models is sometimes difficult. This relates to the input data required to make many of the equations operative. There are only three relatively well-used schemes used in models. The most common is that of evaporative exposure (Stiver and Mackay, 1984). Difficulties with the implementation of this model result from lack of input data. The basic model implementation requires a constant mass transfer coefficient and a vapour pressure for each oil. These are not routinely measured for oil and must be estimated using other techniques. The second most commonly used method is that of applying fractionated cut data. The distillation curves are

readily available. These methods are applied by using the distillation curves to estimate parameters for the Stiver and Mackay equations or as a direct technique by themselves. The third method is to assume a loss rate which is estimated from the oil properties data and presume that the oil moves linearly or logarithmically to that endpoint.

Most of the evaporative work is based on the extensive studies on the evaporation of water (Brutsaert, 1982; Jones, 1992). In fact, the empirical portions of the equations from this work are still used. There are several fundamental differences between the evaporation of a pure liquid such as water and for a multi-component system such as crude oil. First, the evaporation rate for a single liquid such as water is a constant with respect to time. Evaporative loss - by total weight or volume - for crude oils and other multi-component fuel mixtures is logarithmic with respect to time because of the depletion of more volatile components, that are exponentially depleted with time. The second major difference between water and oil evaporation is the effect of atmospheric conditions. Water evaporation is strongly dependent on wind speed and relative humidity. Air can only hold a certain volume of water. The air does not contain a high level of benzene and other components and the saturation level of these in air is often well above concentrations that can be achieved from an evaporating

slick. The full understanding of how wind affects oil slick evaporation has not yet been achieved.

Mackay and Matsugu (1973) approached the problem by adopting the classical water evaporation and new experimental work. The water evaporation equation was corrected for hydrocarbons using the evaporation rate of cumene. It was noted that the difference in constants was related to the enthalpy differences between water and 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.

Mackay and Matsugu noted that for hydrocarbon mixtures the evaporation process is more complex, being dependent on the liquid diffusion characteristics, a liquid phase resistance being present. Experimental data on gasoline evaporation were compared with computed rates. The computed rates showed fair agreement and confirm the presence of a liquid phase mass transfer resistance.

The most frequently used work in spill modelling is that of Stiver and Mackay (1984). The work is based on some of the earlier work by Mackay and Matsugu, but significant additions have been made. [Additional information is given in a thesis by Stiver (1984)].

Payne and co-workers (1984a;b;c;d; 1988; and 1991) developed an oil spill model using the pseudo-component approach. This approach has been used in other studies and typifies much of the current work on spill modelling of evaporation. Reed (1989) reports on the development of an evaporation equation using the familiar Mackay and Matsugu (1973) approach to estimate the mass transfer coefficient.

In conclusion, many models exist incorporating evaporative equations using one of three approaches: the Mackay and Matsugu (1973); the use of distillation cut data to simulate each fraction; and the Stiver and Mackay (1984) approach. The equations developed by Mackay and co-workers can be implemented in various ways. Often the difference in models is the manner in which the models are applied. Bobra (1992b) conducted laboratory studies on the evaporation of crude oils. The evaporation curves for several crude oils and petroleum products were measured under several different environmental conditions. These data were compared to the equations developed by Stiver and Mackay (1984) and Stiver et al. (1989). This comparison shows that the Stiver and Mackay equation predicts the evaporation of most oils relatively well until time exceeds about 8 hours, after which it over-predicts the evaporation that occurs. The 'overshoot' can be as much as two orders of magnitude in terms

of evaporative exposure, at the 24-hour mark. This represents a difference of about 8% in mass lost by evaporation. This is especially true for very light oils. The Stiver and Mackay equation also under-predicts or over-predicts the evaporation of oils in the initial phases; however, this is not a serious concern. Bobra noted that most oil evaporation follows a logarithmic curve with time. The comparison by Brown and Nicholson (1991) shows that for the heavy and mixed oils the Mackay and Matsugu approach was better than the distillation cut approach: however, the mass transfer coefficient required adjustment.

Actual evaporation data exist that have been gathered from laboratories (e.g., Bobra, 1992c; Fingas, 1993). These data are known to be relatively accurate and are the type that were used to develop earlier models. Another, perhaps more accurate means, to model oil spill evaporation is to use these data directly.

Emulsification- is the process of the formation of water-in-oil emulsions often called "chocolate mousse" or "mousse" among oil spill workers. These emulsions change the properties and characteristics of oil spills to a very large degree. Stable emulsions contain between 50% and 80% water thus expanding the volume of spilled material from two to five times the original. The density of the resulting emulsion can be as

great as 1.03 g/mL compared to an initial density as low as 0.80 g/mL. Most significantly, the viscosity of the oil changes from a few hundred centistokes (cSt) to about 100 000 cSt, a typical increase of 1000. A liquid product changes to become a heavy, semi-solid material. Emulsification is thought to be the second most important behavioural characteristic of oil after evaporation. Emulsification has a very large effect on the behaviour of oil spills at sea. As a result of emulsification. evaporation slows by orders-of-magnitude, spreading slows by similar rates, and the oil rides lower in the water column, showing different drag with respect to the wind. Emulsification also has significant effects on other spill aspects; spill countermeasures are quite different for emulsions. Emulsions are difficult to recover

The literature shows that there is basic understanding of the formation of water-in-oil emulsions. However, there is less information on the kinetics of formation at sea and other modelling data. Emulsion formation results from the surfactant-like behaviour of polar and asphaltene compounds. These compounds are similar and behave like surfactants when they are not in solution. When there are insufficient amounts of aromatic components to solubilize the asphaltenes and polars, these precipitate and are available to stabilize water droplets in the oil mass. The

mechanically, to treat, or to burn.

minimum mass percentage of either asphaltenes or resins required to stabilize an emulsion is about 3%. Emulsions begin to form with these chemical conditions and when there is sufficient sea energy. This sea energy is not measurable and the relative amount required is not known in terms of emulsion onset. Literature indicates that the relative energy required to form emulsion varies, but is not high. The rate of emulsion formation was investigated in some laboratory studies and found to be first-order with time. This can be approximated with a logarithmic (or exponential) curve.

Little work on modelling of emulsion formation has been done. Most models that incorporate the phenomenon use the Mackay *et al.* (1980) and Mackay (1980) estimation technique, or a variation of this.

Mackay proposed a differential equation for the formation of emulsions, but suggested that this equation not be used since it can only be solved for $k_2 = 0$ or a very large number. This corresponds to a very stable or unstable emulsion. A simpler equation was proposed as well and is used in most models where emulsification is incorporated. Because the equation predicts that most oils will form emulsions rapidly given a high wind speed, most users have adjusted the equation by changing constants or the form slightly. Similarly, Mackay and Zagorski (1982a;b) proposed two additional relationships to

predict the formation of emulsions on the sea. Kirstein and Redding (1988) used a variation of the Mackay equation to predict emulsification. Reed *et al.* (1989) used the Mackay equations in series of models and adjusted the constants to be more in line with field observations.

All of these studies were based on the Mackay equations which were developed before extensive work on emulsion physics took place and none have been well correlated to either laboratory or field results. The literature would suggest that both the tendency and the formation of emulsions could be predicted with a degree of accuracy using empirical data (Fingas et al., 1993d; Friberg, 1991; Aveyard et al., 1991; Schramm, 1992; Sjöblom et al., 1992). The formation of emulsions is known to occur when the asphaltenic and resin fraction combined is greater than 3% and the amount of the BTEX (benzene, toluene, ethylbenzene, and xylene) is less than this amount. Since evaporation on the sea rapidly removes the BTEX component, predication of formation could be approximated by predicted evaporative loss and the weight fraction of the asphaltenes and resins. When the latter rises over 3% and there is sufficient sea energy, an emulsion will form. There is insufficient empirical or theoretical information to predict the requirement for energy. Observations in the literature suggest that the energy requirement is variable, but that

some oils will form emulsions at apparently low sea energies, others at higher turbulent levels.

Emulsion formation is quite rapid and in the laboratory occurs fully - at moderate energies - in 3 to 10 hours. The rate is shown to be first order with respect to time so an exponential function could be used to estimate formation rate. A simplified approximation is that emulsions form immediately given the correct oil composition and minimum energy.

The effect of emulsion formation on other modelling parameters is great (Fingas *et al.*, 1993c). The viscosity rises two to three orders-of-magnitude, the spreading rate decreases by a similar value, and evaporation nearly ceases.

Natural Dispersion- is the movement of droplets, 1 to 50 um in size, into the water. This is without the addition of chemical dispersing agents or chemical dispersion. Natural dispersion is sometimes grouped with the temporary transport of very large droplets (>50 μm) and dissolution. This is often termed entrainment (Spaulding, 1988). To characterize this phenomenon, empirical equations were developed by Delvigne and Sweeney (1988) using a wave tank. The difficulties with this type of approach are that the predictions of entrainment are typically excessive (often 50% is predicted to go into the water column versus an actual

percentage far less than 1%). All three phenomena of dispersion, macro-droplet transfer, and dissolution are grouped into one process, and finally the process is hinged to the amount of "whitecaps" present on the ocean. The presence of whitecaps is known to be a poor indicator of sea energy and dispersion is known to occur without the presence of any whitecaps (Delvigne, 1993).

Studies into the natural dispersion of oil have shown that dispersion only occurs with the saturate fraction of oil and that the presence of significant amounts of asphaltenes retards this process (Fingas et al., 1992; 1993 a:b). The amount of dispersion increases with increasing turbulent energy, a parameter which is very difficult to measure. In the studies conducted by Fingas and co-workers the natural dispersion increased linearly with increasing revolutions of the test vessels.

In the future, it will be possible to use the new data available in the literature to construct a model of oil spill dispersion alone. The composition factors are known (saturate content versus asphaltene content). The relationship between energy and dispersion has been extensively measured in the laboratory and the relationship to the field can be estimated using historical spill observations. Sea measurements that might be meaningful in terms of energy include wave height, wave steepness, and sea state. In the

future, the laboratory energy measurements will be, no doubt, extended to the field, giving a full empirical correlation.

Dissolution- accounts for only a small portion of oil loss but is still considered to be a very important behaviour parameter because the soluble components of oil - particularly the smaller aromatic compounds, are toxic to aquatic species. Modelling interest in dissolution is directed to predicting the concentrations of dissolved components in the water column. Most models in existence do not separate the dissolution component. The entrainment model is sometimes used, but fails to distinguish between dispersion and dissolution.

Bobra and Tennyson (1989) studied the dissolution behaviour of oils and concluded that only a small portion of oils are truly soluble in water. The solubility varies from 1 ppm to about 100 ppm. The oil-to-water ratio is important in the measurement of total solubility. At sea this is expected to be a large ratio and thus the total solubility is low. The solubility for a fuel can be as great as 100 ppm and that for Bunker C less than 1 ppm. This represents very low loss rates for the fuel and for modelling purposes is not significant or relevant. The process of solubilization appears to be very rapid and based on laboratory data would be complete after about 15 minutes of contact with water.

Modelling can be accomplished by using the empirical data from Bobra (1992a). These data give a concentration of hydrocarbons, individually and in groups, for a specified ratio of water volume under the slick. These data could be used directly to predict the source strength of the dissolved components.

Photooxidation, Sinking, and **Biodegradation**- Photooxidation is the transformation of some chemical components of the oil into polar components through the addition of oxygen. This essentially increases the resinic components and to a lesser degree, asphaltenic components of the oil. It is important only in that as photooxidation increases so too does the potential for emulsion formation. Bobra and Tennyson (1989) studied a number of oils and found that oils vary widely in their susceptibility to photooxidation. Some oils photooxidize to a great extent, others do not, measurably. There is a significant knowledge gap in being able to predict the degree of photooxidation and the extent that this would influence emulsification.

Sinking of oil can be divided into two phenomena, sedimentation of oil droplets and sinking *en masse*. The latter can be further divided into over-washing by water and simple sinking. All phenomena are not well understood in terms of prediction capability in models. None of these phenomena are consistent behaviours in spills around the world and therefore they were

not completely studied. Sinking en masse has been studied by a number of workers (e.g., Ross Environmental Research Ltd., 1987). Sedimentation has been studied, but the results have varied from a significant effect (40% sedimented) to no effect. Sedimentation is difficult to assess (Mackay and Hossain, 1980).

Biodegradation is a very slow process that changes the behaviour and fate of oil spills to only a very small degree (Atlas and Bartha, 1992). For this reason, few modellers include these phenomena in their models.

Summary and Conclusions

The chemistry of crude oils dominates their behaviour at sea. Crude oil consists of hundreds of compounds, many with different properties and characteristics. These can be divided into several bulk groups with typical behavioural characteristics: saturates, aromatics, resins, and asphaltenes. The saturates are the predominant group in most crude oils and are the most subject to dispersion and evaporation. The larger saturates or waxes can cause behaviour anomalies if they are present in large quantities (>3%). Aromatics are best considered as two groups, small and large. The small aromatics have significant water solubility, but evaporate from spilled crude oil very rapidly. The larger aromatics do not show either behaviour to a great extent. The

resins and asphaltenes show the same properties to some degree. Asphaltenes can be viewed as large resins. Both groups do not appreciably evaporate, disperse, or degrade. Both groups stabilize water-in-oil emulsions when they are present in large quantity (>3%). The multiplicity of oil composition implies that many of the properties of pure substances such as boiling point or melting point, are not relevant. This makes it difficult to characterize an oil and its behaviour. Furthermore, many of the assumptions made in chemistry such as ideal gas and liquid behaviour do not apply to oil. Physical equations developed for oil are often inaccurate for this reason.

The most important behaviour of oil in terms of modelling spills is evaporation. Light crude oils can lose up to 50% of their weight and volume in two days. The evaporation of oil is exponential with time. Significant number of modelling equations are available, but so is empirical data.

The second most important behaviour aspect of oil is the formation of water-in-oil emulsions. The formation of emulsions is due to the surfactant-like action of the polar and asphaltene components of oil. The polars and asphaltenes are stabilized in many crude oils by the aromatic compounds. If aromatic compounds are not abundant or are lost through evaporation the resins and asphaltenes can precipitate and stabilize water-in-oil droplets. A

relatively large amount of energy may be required to form these emulsions after the chemical conditions are correct. Model equations for emulsion formation largely follow the work developed before extensive laboratory and field work on physics of emulsion formation. New equations do not exist, but simple relationships using the known physics might be used to improve the accuracy of prediction.

Natural dispersion of oil is the next most important factor. Oils which contain few asphaltenes and resins and contain significant fractions of smaller saturates will disperse naturally given high sea energies. Modelling equations for this factor do not correspond to laboratory experiments. A related factor, dissolution, is not as important in terms of mass balance but is important in terms of toxicity to the environment. Laboratory work shows that the dissolution of oils can be predicted and measured, but no models incorporate dissolution as a separate term from dispersion.

There are several lesser chemical and behaviour aspects of oil, these include photooxidation, sinking, and biodegradation.

References

Atlas, R.M. and R. Bartha, "Hydrocarbon Biodegradation and Oil Spill Bioremediation", *Advances in Microbial Ecology,* 12: 285 - 238, Plenum Press, NY (1992).

Aveyard, R., B.P. Binks, P.D.I. Fletcher, X.Ye, and J.R. Lu, "The Resolution of Emulsions, Including Crude Oil Emulsions in Relation to HLB Behaviour", in: *Emulsions - A Fundamental and Practical Approach*, Johan Sjöblom (ed.), Kluwer Academic Publishers, Dordrecht, Netherlands, pp. 97 - 110 (1991).

Bobra, M. and E.J. Tennyson, "Photooxidation of Petroleum", in: *Proceedings of the Twelfth Arctic Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ont., pp. 129 - 147 (1989).

Bobra, M.A., "A Study of the Formation of Water-in-Oil Emulsions", in: *Proceedings of the Thirteenth Annual Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ont., pp. 87 - 117 (1990).

Bobra, M.A., "Water-in-Oil Emulsification: A Physicochemical Study", in: Proceedings of the International Oil Spill Conference, American Petroleum Institute, Washington, D.C., pp. 483 - 488 (1991).

Bobra, M.A., "Solubility Behaviour of Petroleum Oils in Water", Manuscript Report, EE 130, Environment Canada, Ottawa, Ont. (1992a).

Bobra, M.A., "A Study of Water-in-Oil Emulsification", Manuscript Report, EE-132, Environment Canada, Ottawa, Ont. (1992b). Bobra, M.A., "Evaporation of Oil", Manuscript Report, EE-131, Environment Canada, Ottawa, Ont. (1992c).

Brutsaert, W., Evaporation into the Atmosphere, Reidel Publishing Company, Dordrecht, Holland, 299 p. (1982).

Delvigne, G.A.L. and C.E. Sweeney, "Natural Dispersion of Oil", *Oil and Chemical Pollution, 4*:281 - 310 (1988).

Delvigne, G.A.L., "Natural Dispersion of Oil by Different Sources of Turbulence", in: *Proceedings of the 1993 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 415 - 419 (1993).

Fingas, M.F., D.A. Kyle, and E.J. Tennyson, "Physical and Chemical Studies on Oil Spill Dispersants: Effectiveness Variation with Energy", in: *Proceedings of the Fifteenth Arctic Marine Oilspill Technical Seminar*, Environment Canada, Ottawa, Ont., pp. 135 - 142 (1992).

Fingas, M.F., unpublished data on the evaporation of crude oils (1993).

Fingas, M.F., D.A. Kyle, J.B. Holmes, and E.J. Tennyson, "The Effectiveness of Dispersants; Variation with Energy", in: *Proceedings of the* 1993 International Oil Spill Conference, American Petroleum Institute, Washington, D.C., pp. 567 - 572 (1993a).

Fingas, M.F., D.A. Kyle, and E. Tennyson, "Physical and Chemical Studies on Dispersants: The Effect of Dispersant Amount and Energy", in: Proceedings of the Sixteenth Arctic and Marine Oil Spill Program Technical Seminar, Environment Canada, Ottawa, Ont., pp. 861 - 876 (1993b).

Fingas, M.F., B. Fieldhouse, M.A. Bobra, and E.J. Tennyson, "The Physics and Chemistry of Emulsions", in: *Proceedings of the Workshop on Emulsions*, Marine Spill Response Corporation, Washington, D.C., 11 p. (1993c).

Fingas, M.F., B. Fieldhouse, M.A. Bobra, and E.J. Tennyson, "The Physics and Chemistry of Emulsions", in: *Proceedings of the Workshop on Emulsions*, Marine Spill Response Corporation, Washington, D.C., 11 p. (1993d).

Friberg, S., Emulsion Stability, in Emulsions - A Fundamental and Practical Approach, Johan Sjöblom (ed.), Kluwer Academic Publishers, Dordrecht, Netherlands, pp. 1 - 24 (1991).

Jones, F.E., Evaporation of Water, Lewis Publishers, Chelsea, MI, 188 p. (1992).

Kinghorn, R.R.F., An Introduction to the Physics and Chemistry of Petroleum, John Wiley and Sons, NY, 420 p. (1983). Kirstein, B.E. and R.T. Redding,
"Ocean-Ice Oil-Weathering
Computer Program User's
Manual", Outer Continental Shelf
Environmental Assessment
Program, Vol. 59, U.S.
Department of Commerce,
National Oceanic and
Atmospheric Administration and
U.S. Department of the Interior,
Washington D.C. (1988).

Mackay, D. and R.S. Matsugu, "Evaporation Rates of Liquid Hydrocarbon Spills on Land and Water", Canadian Journal Chemical Engineering, 51: 434 - 439, Canadian Society for Chemical Engineering, Ottawa, Ont. (1973).

Mackay, D., "A Mathematical Model of Oil Spill Behaviour", Manuscript Report No. EE-7, Environment Canada, Ottawa, Ont. (1980).

Mackay, D., I.A. Buist, R. Mascarenhas, and S. Paterson, "Oil Spill Processes and Models", Manuscript Report No. EE-8, Environment Canada, Ottawa, Ont. (1980a).

Mackay, D. and K. Hossain,
"Studies of Oil Sedimentation",
in: Proceedings of the Third
Arctic Marine Oil Spill Program
Technical Seminar, Environment
Canada, Ottawa, Ont.,
pp. 120 - 127 (1980).

Mackay, D. and W. Zagorski, "Studies of Water-in-Oil Emulsions", Manuscript Report, EE-34, Environment Canada, Ottawa, Ont., 93 p. (1982a). Mackay, D. and W. Zagorski,
"Water-in-Oil Emulsions: A
Stability Hypothesis", in:
Proceedings of the Fifth Annual
Arctic Marine Oilspill Program
Technical Seminar, Environment
Canada, Ottawa, Ont.,
pp. 61 - 74 (1982b).

McCain, W.D., *The Properties of Petroleum Fluids*, PennWell Books, Tulsa, OK, 548 p. (1990).

Neumann, H-J., B. Pczynska-Lahme, and D. Severin, *Composition and Properties of Petroleum*, Halsted Press, NY, 137 p. (1981).

Payne, J.R., G.D. McNabb, Jr., B.E. Kirstein, R. Redding, J.L. Lambach, C.R. Phillips, L.E. Hachmeister, and S. Martin, "Development of a Predictive Model for the Weathering of Oil in the Presence of Sea Ice", Outer Continental Shelf Environmental Assessment Program, Contract No. 83-ABC-00062, NOAA/Ocean Assessments Division, Anchorage, AK (1984a).

Payne, J.R., B.E. Kirstein, G.D. McNabb, Jr., J.L. Lambach, R. Redding, R.E. Jordan, W. Hom, C. de Oliveira, G.S. Smith, D.M. Baxter, and R. Gaegel, "Multivariate Analysis of Petroleum Weathering in the Marine Environment - Subarctic", U.S. Department of Commerce, National Oceanic and Atmospheric Administration, OCSEAP, Vol. 21 (1984b).

Payne, J.R. and G.D. McNabb, Jr., "Weathering of Petroleum in

the Marine Environment", *Marine Technology Society Journal*, 18: 24 - 42, Washington, D.C. (1984c).

Payne, J.R., B.E. Kirstein,
G.D. McNabb, Jr., J.L. Lambach,
R. Redding, R.E. Jordan,
W. Hom, C. de Oliveira,
G.S. Smith, D.M. Baxter, and
R. Gaegel, "Multivariate Analysis
of Petroleum Weathering in the
Marine Environment - Subarctic",
U.S. Department of Commerce,
National Oceanic and
Atmospheric Administration,
OCSEAP, Vol. 22 (1984d).

Payne, J.R., G.D. McNabb, Jr., L.E. Hachmeister, B.E. Kirstein, J.R. Clayton, Jr., C.R. Phillips, R.T. Redding, C.L. Clary, G.S. Smith, and G.H. Farmer, "Development of a Predictive Model for the Weathering of Oil in the Presence of Sea Ice", Outer Continental Shelf Environmental Assessment Program, Vol. 59, National Oceanic and Atmospheric Service, AK (1988).

Payne, J.M., J.R. Clayton Jr., G.D. McNabb Jr., and B.E. Kirstein, "Exxon Valdez Oil Weathering Fate and Behaviour: Model Predictions and Field Observations", 1991 Oil Spill Conference, American Petroleum Institute, Washington, D.C., pp. 641 - 654 (1991).

Ravey, J.C., G. Ducouret, and D. Espinot, "Asphaltene Macrostructure by Small Angle Neutron Scattering", *Fuel*, *67*: 137 - 143 (1988).

Reed, M., "The Physical Fates Component of the Natural Resource Damage Assessment Model System", *Oil and Chemical Pollution*, 5:99 - 123 (1989).

Reed, M., E. Gundlach, and T. Kana, "A Coastal Zone Oil Spill Model: Development and Sensitivity Studies", *Oil and Chemical Pollution*, 5:411 - 449 (1989).

Ross (S.L.) Environmental Research Ltd., "The Transient Submergence of Oil Spills: Tank Tests and Modelling", Manuscript Report, EE-96, Environment Canada, Ottawa, Ont. (1987).

Schramm, L.L., "Petroleum Emulsions - Basic Principles", in: *Emulsions: Fundamentals and Applications in The Petroleum Industry*, Laurier L. Schramm, (ed.), American Chemical Society, Washington, D.C., pp. 1 - 49 (1992).

Sjöblom, J., L. Mingyuan, A.A. Christy, and T. Gu, "Water-in-Crude-Oil Emulsions from the Norwegian Continental Shelf: 7, Interfacial Pressure and Emulsion Stability", *Colloids and Surfaces*, 66: 55 - 62 (1992).

Spaulding, M.L., "A State-of-the-Art Review of Oil Spill Trajectory and Fate Modelling", *Oil and Chemical Pollution, 4:* 39 - 55 (1988).

Stiver, W. and D. Mackay, "Evaporation Rate of Spills of Hydrocarbons and Petroleum Mixtures", *Environmental* Science and Technology, 18:834 - 840 (1984).

Stiver, W., "Weathering Properties of Crude Oils when Spilled on Water", Master of Applied Science Thesis, Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ont. pp. 4 - 7, 110 - 126 & 132 - 137 (1984). Stiver, W., W.Y. Shiu, and D. Mackay, "Evaporation Times and Rates of Specific Hydrocarbons in Oil Spills", Environmental Science and Technology, 23:101 - 105 (1989).

The Spill Technology Newsletter was started with modest intentions in 1976 to provide a forum for the exchange of information on spill countermeasures and other related matters. We now have more than 2000 subscribers in over 40 countries.

To broaden the scope of this newsletter, and to provide more information on industry and foreign activities in the field of spill control and prevention, readers are encouraged to submit articles on their work and views in this area.

Mr. M.F. Fingas
Technical Editor
Environmental Emergencies
Science Division
Technology Development Directorate
Environmental Protection Service
Environment Canada
Ottawa, Ontario
K1A 0H3

Phone: (613) 990-7297

Environmental Protection
Publications
Technology Development Directorate
Environmental Protection Service
Environment Canada
Ottawa, Ontario
K1A 0H3
Phone: (810) 052 5021 or

Phone: (819) 953-5921 or (819) 953-5750