

The Biodegradation Characteristics of the Mixtures of Bunker-A, B Oils with Dispersants in the Seawater

Joong-Soo BAEK, Gwang-Su KIM* and Eun-il CHO

Department of Environmental Engineering, Pukyong National University, Pusan 608-737, Korea

*Faculty of Maritime Transportation System, Mokpo National Maritime University, Mokpo 530-729, Korea

The biodegradation experiment, the TOD analysis and the element analysis for dispersant, Bunker-A oil and Bunker-B oil were conducted to study the biodegradation characteristics of a mixture of Bunker-A oil with dispersant and a mixture of Bunker-B oil with dispersant in the seawater. The results of biodegradation experiment showed 1 mg of dispersant to be equivalent to 0.26 mg of BOD₅ and to 0.60 mg of BOD₂₀ in the natural seawater. The results of TOD analysis showed each 1 mg of dispersant, Bunker-A oil and Bunker-B oil to be equivalent to 2.37 mg, 2.94 mg and 2.74 mg of TOD, respectively. The results of element analysis showed carbon, hydrogen, nitrogen and phosphorus contents of dispersant to be 82.1%, 13.8%, 1.8% and 2.2%, respectively. Carbon and hydrogen contents of Bunker-A oil were found to be 73.3% and 13.5%, respectively, and carbon, hydrogen and nitrogen contents of Bunker-B oil to be 80.4%, 12.3% and 0.7%, respectively. Accordingly, the detection of nitrogen and phosphorus in dispersant shows that dispersants should be used with caution in coastal waters, with relation to eutrophication. The biodegradability of dispersant expressed as the ratio of BOD₅/TOD was found to be 11.0%. As the mix ratios of dispersant to Bunker-A oil (3 mg/l) and a mixture of Bunker-B oil (3 mg/l) were changed from 1 : 10 to 5 : 10, the biodegradabilities of a mixture of Bunker-A oil with dispersant and Bunker-B oil with dispersant increased from 2.1% to 7.2% and from 1.0% to 4.4%, respectively. Accordingly, the dispersant belongs to the organic matter group of middle-biodegradability while mixtures in the mix ratio range of 1 : 10~5 : 10 belong to the organic matter group of low-biodegradability. The deoxygenation rate constant (K_1) and ultimate biochemical oxygen demand (L_0) obtained from the biodegradation experiment and Thomas slope method were found to be 0.125/day and 2.487 mg/l for dispersant (4 mg/l), respectively. K_1 and L_0 were found to be 0.079~0.131/day and 0.318~2.052 mg/l for a mixture of Bunker-A oil with dispersant and to be 0.106~0.371/day and 0.262~1.106 mg/l for a mixture of Bunker-B oil with dispersant, respectively, having 1 : 10~5 : 10 mix ratios of dispersant to Bunker-A oil and Bunker-B oil. The ultimate biochemical oxygen demands of the mixtures increased as the mix ratio of dispersant to Bunker-A, B oils changed from 1 : 10 to 5 : 10. This suggests that the more dispersants are applied to the sea for the cleanup of Bunker-A oil or Bunker-B oil, the more decreases the dissolved oxygen level in the seawater.

Key words : dispersant, Bunker-A oil, Bunker-B oil, biodegradability, deoxygenation rate constant, ultimate biochemical oxygen demand

Introduction

When massive oil spills occur close to shore, sufficient time is not available for a variety of processes including evaporation, solution formation, spreading on the surface, emulsification, oxidation, uptake by living organisms, and adsorption by bottom sediments to affect the total amount of oil involved (Stocker and Seager, 1976). Clean-up operations should be performed as soon as possible before spilled oil damages or approaches ashore. Generally, the containment and the recovery of spilled oil are preferred, but in some ins-

tan ces it may be necessary to use dispersants, burning, or other alternative response technologies. According to the guidelines developed by International Maritime Organization, a national oil spill contingency plan should state which clean-up techniques should be used and in what circumstances (IMO, 1995). It was pointed out that in Korea, the clean-up operations tend to depend on the use of dispersants in case of the massive oil spills or the urgent response to oil pollution (KNMPA, 1987). For recent instances in Korea, 289kℓ of dispersants were applied for combating 1,228 tons of Bunker-C oil spill in Kwangyang Bay

caused by the collision of the tanker barge No.5 Keumdong with M/V Bijisan in 1993, 655kℓ of dispersants were used to deal with 700~800 tons of Bunker-C oil spill off Yeosu caused by the wreck of the tanker Sea Prince in 1995, and 60 tons of dispersants were consumed for response to oil spill caused by the founder of the tanker No.1 Yuil laden with 2,870 tons of Bunker-C oils off Pusan in 1995 (Cho and Mok, 1995). Dispersants, known by a variety of names such as emulsifiers, detergents, degreasers and oil spill removers, are chemical agents which alter the physical behavior of oil on the sea surface. The primary components of a dispersant are a surfactant, a solvent, and stabilizers. The net effect of the dispersant is to lower the surface tension of the oil to the point where it will break up and disperse in the water in the form of tiny droplets. The use of dispersants increases the surface area of an oil slick and distributes the oil droplets into a large volume of water. These two effects enhance the natural degradation of oil by microorganisms. The chemical dispersants themselves do not destroy any oil. Dispersed oil will degrade much more rapidly than oil in a surface slick and in some circumstances it will present less of a threat to the environment. Evaluation of the results of their use in the past indicates that dispersants should be used with caution. The environmental gains resulting from an increase in the rate of biodegradation may be offset by the toxicity of the dispersants themselves and dispersed oil readily made available to organisms in the water body. This condition was evident when dispersants were first used, which brought considerable controversy as to the acceptability of dispersants in combating oil pollution. Through a continuous process of experimentation and research, dispersants which are more effective and less toxic are now being manufactured. Bronchart et al. (1985) developed a new dispersant that contains nitrogen and phosphorus for enhancing microbial oil degradation. Scientific studies and governmental reports around the world are coming to the view that dispersants, in strict defined ci-

rcumstances, are a viable option for response to oil pollution incidents (IMO, 1988). Dispersants in use today are of two main types: Hydrocarbon or conventional dispersants are based on hydrocarbon solvents and contain between 15% and 25% surfactant. They are intended for neat application to oil, with typical dose rates between 1:1 and 1:3 (dispersant:oil). Concentrate or self-mix dispersants have alcohol or glycol solvents and usually contain a higher concentration of surfactant components. These products should preferably be applied neat but can be diluted with sea water before spraying, with typical dose rate between 1:5 and 1:30 (neat dispersant:oil). Both concentrates diluted with sea water and hydrocarbon-based dispersants require thorough mixing with the oil after application to produce a satisfactory dispersion (ITOPF, 1986). The use of dispersants should be determined by a comparison of potential damages to the marine environment from both treated and untreated oil with consideration of both long-term and short-term effects (IMO, 1988). Dewling et al. (1971) emphasized that the biodegradability of dispersant must be taken into account and must stand alongside toxicity when making a decision regarding the use of dispersant for oil spill cleanup, and from the standpoint of water quality, there must be concern for the rate of degradation and the ultimate oxygen demand of the dispersant and/or dispersant-oil mixture. Due to the severe oxygen requirement for the degradation process, the degradation of the dispersant and/or dispersant-oil mixture might cause additional damage to marine life by depleting the oxygen (Stocker and Seager, 1976). Kim et al. (1993a; 1993b) made a study of the biodegradability of dispersants and dispersant/Bunker-C oil mixtures, and its relation with the dissolved oxygen consumption in the seawater. However, there has not been any study regarding the biodegradation of Bunker-A oil and Bunker-B oil treated with dispersant in the seawater.

Accordingly, in order to research the biodegradation characteristics of a mixture of Bunker-A oil with

dispersant and a mixture of Bunker-B oil with dispersant in the seawater, the biodegradation experiment, the TOD analysis and the element analysis for dispersant, Bunker-A oil and Bunker-B oil were performed.

Materials and Methods

1. Materials

1) Dispersant

The dispersant for experiment passed the test and was approved to be fit for the standard of dispersant efficiency (KMPA, 1979; Korean Industrial Standards, 1984) by Korea Maritime and Port Authority.

2) Bunker-A oil and Bunker-B oil

The properties of Bunker-A oil and Bunker-B oil used in experiment are shown in Table 1.

3) Natural seawater

The natural seawater used in experiment was sampled off the coast of Choongmu, Korea in Aug., 1994, immediately transferred to the laboratory and analyzed. The properties of natural seawater are given in Table 2.

2. Methods

1) Determination of biodegradation

Prior to experiment, natural seawater was filtered through 50~60 μ m mesh net. Dispersant samples of

which concentration was 4.0 mg/l in natural seawater were used to determine the biodegradation of dispersant. The mixture samples of Bunker-A oil and Bunker-B oil with dispersant with mix ratios of 10 : 1, 10 : 2, 10 : 3 and 10 : 5, respectively. The biochemical oxygen demand (BOD) for the determination of biodegradation was obtained by determining dissolved oxygen in each sample which was stored with blank sample of natural seawater at 20°C in incubator for 20 days.

2) TOD analysis

Total oxygen demand analyzer (IONICS Model 225) was used for the TOD analysis of dispersant, Bunker-A oil, and Bunker-B oil.

Potassium biphthalate (C₆H₄(COOK)COOH) and glucose (C₆H₁₂O₆) stock solution were used for calibration and verification, respectively.

3) Element analysis

CHN Corder (Yanagimoto Model MT-2) was used for the element analysis of samples.

In order to analyze the phosphorus content of dispersant, 10mg/l of dispersant sample was digested in the boiling water for an hour and was determined by Ascorbic acid method.

4) Estimation of biodegradability

The biodegradability was expressed as the ratio of BOD₅ to TOD or BOD₅/TOD (Inoue, 1972).

Table 1. Properties of Bunker-A and Bunker-B oil used in experiment

	Specific gravity	Kinematic viscosity (50°C, Cst)	Pouring point (°C)	Flash point (°C)	Sulfur content (%)	Water content (%)
Bunker-A oil	0.8917	13.2	-8.0	65.0	1.96	0.10
Bunker-B oil	0.9286	32.0	-6.0	75.0	2.55	0.20

Table 2. Properties of natural seawater used in experiment

Items	Values	Items	Values
Temp. (°C)	25.0	NH ₄ ⁺ - N (μ g-at/l)	0.64
pH	8.1	PO ₄ ³⁻ - P (μ g-at/l)	0.17
Salinity(‰)	31.35	TSS (mg/l)	3.45
NO ₂ ⁻ - N (μ g-at/l)	0.06	VSS (mg/l)	1.72
NO ₃ ⁻ - N (μ g-at/l)	3.43	COD (mg/l)	1.91

Table 3. Biochemical oxygen demand of dispersant (4.0 mg-dispersant/l) in mg/l and in mg-O₂/mg-dispersant

Day (t)	BOD (mg/l)	BOD (mg-O ₂ /mg-dispersant)
1	0.41	0.103
2	0.60	0.150
3	0.76	0.190
4	0.92	0.230
5	1.04	0.260
6	1.16	0.290
7	1.24	0.310
20	2.40	0.600

5) Deoxygenation rate constant (K_1) and ultimate biochemical oxygen demand (L_0)

The deoxygenation rate constant and the ultimate biochemical oxygen demand were calculated using Thomas slope method (Thomas, 1950).

Results and Discussion

1. Biochemical oxygen demand (BOD)

1) Biodegradability by microorganisms in natural seawater

A mixture of 150 mg glucose/l and 150 mg glutamic acid/l was used as a standard check solution and its BOD was found to be 205.0 mg/l, which was very similar to 198 ± 30.5 ppm shown in *Standard Method* (APHA-AWWA-WPCF, 1989) and to 220 ± 10 ppm presented by Takemoto et al. (1978).

2) BOD of dispersant

The BOD values of 4.0 mg-dispersant/l for 20 days were shown in Table 3 and Fig. 1, and were converted to the unit of mg-O₂/mg-dispersant and shown in Table 3 as well. The BOD₅ and BOD₂₀ of dispersant were 0.260mg-O₂/mg-dispersant and 0.600 mg-O₂/mg-dispersant, respectively, and were found to be lower than the respective values of 0.410 mg-O₂/mg-dispersant and 0.799 mg-O₂/mg-dispersant presented by Dewling et al. (1971) and 0.595 mg-O₂/mg-dispersant and 0.855 mg-O₂/mg-dispersant by Kim et al. (1993). These differences might be mainly due to the

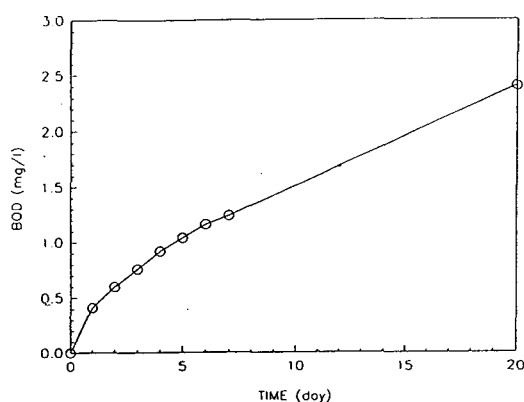


Fig. 1. BOD curves of dispersant (4 mg/l).

different characteristics of natural seawater, the different microorganisms and the different components of dispersant. The values of BOD showed the dispersant to be an oxygen demanding waste in the seawater.

3) BOD of the mixtures of Bunker-A, B oils with dispersant

The BOD values of mixtures with mix ratios of 10 : 1, 10 : 2, 10 : 3 and 10 : 5 for 20 days were shown in Table 4.

The BOD values of mixtures of Bunker-A oil with dispersant were much higher than those of mixtures of Bunker-B oil with dispersant. As mix ratios of dispersant to Bunker-A and B oils (3 mg/l) changed from 1 : 10 to 5 : 10, BOD of mixtures increased. This suggests that the more dispersant is applied to the constant quantity of Bunker-A, B oils on the sea for oil spill clean-up, the more increases the BOD of

The Biodegradation Characteristics of the Mixtures of Bunker-A, B Oils with Dispersants in the Seawater

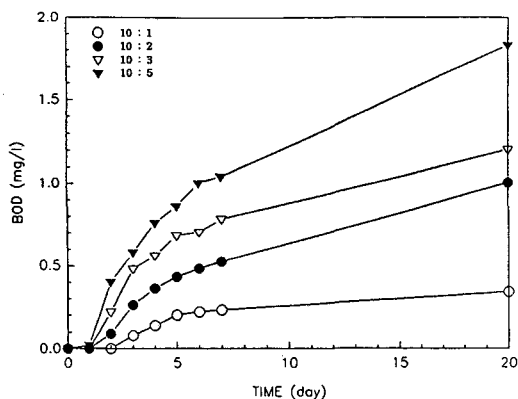


Fig. 2. BOD curves of mixtures of Bunker-A oil with dispersant in the ratios of 10 : 1 ~ 10 : 5.

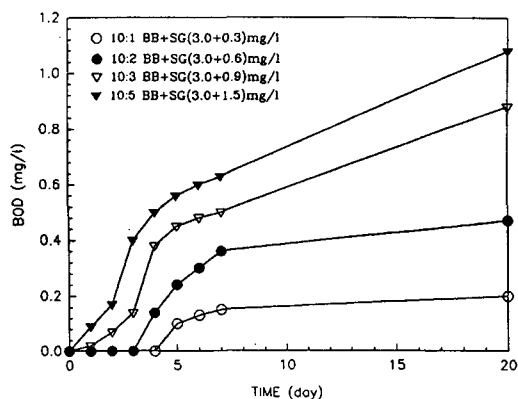


Fig. 3. BOD curves of mixtures of Bunker-B oil with dispersant in the ratios of 10 : 1 ~ 10 : 5.

mixtures or the more can the level of dissolved oxygen decrease in the seawater. The reason is that the BOD value of mixtures is derived from the combination of BOD for dispersant and BOD for Bunker-A, B oils (Gatellier et al., 1973). Because of the toxicity of Bunker-A oil to microorganisms in the seawater as shown in Fig. 2, the biodegradation of a mixture of Bunker-A oil with dispersant was found to delay and to start on the third day in case of 10 : 1, on the second day in cases of 10 : 2 and 10 : 3, and on the first day in case of 10 : 5. Because of the toxicity of Bunker-B oil to microorganisms in the seawater as shown in Fig. 3, the biodegradation of a mixture of Bunker-B oil with dispersant was found to delay and to

start on the fifth day in case of 10 : 1, on the fourth day in case of 10 : 2, and on the first day in cases of 10 : 3 and 10 : 5. The toxicity of a mixture of Bunker-B with dispersant was found to be higher than that of a mixture of Bunker-A oil with dispersant. The toxicities of mixtures of Bunker-A, B oils with dispersant were found to be mitigated, as mix ratios changing from 10 : 1 to 10 : 5.

2. Total oxygen demand (TOD)

The results of TOD analysis for glucose, dispersant, a mixture of Bunker-A oil with dispersant and a mixture of Bunker-B oil with dispersant were given in Table 5.

Table 4. Biochemical oxygen demands of mixtures of Bunker-A, B oils with dispersant in mg/l

Day (t)	Bunker-A with dispersant				Bunker-B with dispersant			
	10 : 1	10 : 2	10 : 3	10 : 5	10 : 1	10 : 2	10 : 3	10 : 5
	(3.0+0.3) mg/l	(3.0+0.6) mg/l	(3.0+0.9) mg/l	(3.0+1.5) mg/l	(3.0+0.3) mg/l	(3.0+0.6) mg/l	(3.0+0.9) mg/l	(3.0+1.5) mg/l
1	0.00	0.00	0.00	0.02	0.00	0.00	0.02	0.09
2	0.00	0.09	0.22	0.40	0.00	0.00	0.07	0.17
3	0.08	0.26	0.48	0.58	0.00	0.00	0.14	0.40
4	0.14	0.36	0.56	0.76	0.00	0.14	0.38	0.50
5	0.20	0.43	0.68	0.89	0.10	0.24	0.45	0.56
6	0.22	0.48	0.70	1.00	0.13	0.30	0.48	0.60
7	0.23	0.52	0.78	1.04	0.15	0.36	0.50	0.63
20	0.34	1.00	1.20	1.83	0.20	0.47	0.88	1.08

Table 5. Total oxygen demands of glucose, dispersant and mixtures of Bunker-A, B oil with dispersant

Glucose 100 mg/l	Dispersant 100 mg/l	Bunker-A with dispersant		Bunker-B with dispersant	
		(100+100) mg/l	(100+50) mg/l	(100+100) mg/l	(100+50) mg/l
107.1	237.0	531.0	412.5	542.0	432.5

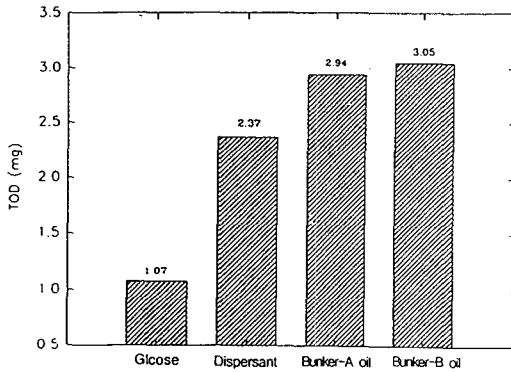


Fig. 4. TOD values per each 1 mg of glucose, dispersant, Bunker-A oil and Bunker-B oil.

The mean TOD values of Bunker-A oil and Bunker-B oil were obtained from the calculation which subtracted the mean TOD value of dispersant from those of a mixture of Bunker-A with dispersant and a mixture of Bunker-B with dispersant, respectively, and the TOD values for each 100 mg/l of Bunker-A oil and Bunker-B oil were found to be 294.0 mg/l and 305.0 mg/l, respectively.

TOD values for each 1 mg of glucose, dispersant, Bunker-A oil and Bunker-B oil were shown in Fig. 4 for comparison with each other. TOD value for 1 mg of dispersant was equivalent to 2.37 mg found to be a little lower than 2.80 mg obtained by Kim et al. Those for each 1 mg of Bunker-A oil and Bunker-B oil were also found to be 2.94 mg and 3.05 mg,

respectively, and to be a little lower than 3.16 mg for 1 mg of Bunker-C oil obtained by Kim et al. (1993b) and 3~4 mg of oxygen which was required for the complete oxidation of 1 mg of petroleum hydrocarbon to CO₂ and H₂O (ZoBell, 1969; Gatellier et al., 1973).

The ThOD (Theoretical oxygen demand) value for 1 mg of glucose was calculated from the formula (C₆H₁₂O₆) and found to be 1.067 mg, and comparing with 1.071 mg of TOD, the relative error of glucose between ThOD and TOD was found to be 0.37%. Therefore, it was possible to suppose that TOD agreed with ThOD for all samples.

3. Element analysis

Dispersant was composed of C (82.08%), H (13.02%), N (1.82%) and P (2.20%), Bunker-A oil of C (73.30%) and H (13.47%), and Bunker-B oil of C (80.37%), H (12.31%) and N (0.68%) as shown in Table 6. It is interesting that in the same name of dispersant, nitrogen (N) and phosphorus (P) are detected at this time, while those elements were not found in the result by Kim et al. (1993a). It infers that a new dispersant that contains nitrogen and phosphorus has been developed for enhancing microbial oil degradation. Accordingly, the detection of N and P in dispersant shows that dispersants should be used with caution in coastal waters, with relation to eutrophication. Nitrogen was not detected in Bunker-A oil, while being detected in Bunker-B oil.

Table 6. Element analysis of dispersant, Bunker -A oil and Bunker-B oil

Element	dispersant	Bunker-A oil	Bunker-B oil
C	82.08 %	73.30 %	80.37 %
H	13.02 %	13.47 %	12.31 %
N	1.82 %	ND	0.68 %
P	2.20 %	-	-

Table 7. Biodegradabilities (%) of dispersant, mixtures of Bunker-A oil with dispersant and mixtures of Bunker-B oil with dispersant

Dispersant	Mixture of Bunker-A oil				Mixture of Bunker-B oil			
	10 : 1	10 : 2	10 : 3	10 : 5	10 : 1	10 : 2	10 : 3	10 : 5
10.97	2.10	4.20	6.21	7.19	1.01	2.27	3.99	4.41

4. Biodegradability

The biodegradabilities for dispersant, a mixture of Bunker-A oil with dispersant, and a mixture of Bunker-B oil with dispersant in natural seawater expressed as BOD₅/TOD were presented in Table. 7.

The biodegradability of dispersant was 10.97%, and dispersant belonged barely to the organic matter group of middle-biodegradability according to the classification of organic matters defined by Inoue (1972), who investigated biochemical degradabilities of various organic matters using the BOD values and classified organic matters into three groups, or a group of high-biodegradability in case of the value of BOD₅/ThOD being more than 40%, another group of middle-biodegradability in case of 10~40% and the other group of low-biodegradability in case of less than 10%. In biodegradability, dispersant was found to be similar to methylethylketone of which the biodegradability (BOD₅/ThOD) was reported to be 13% by Okasawa (1970).

The biodegradabilities of mixtures of Bunker-A oil with dispersant and mixtures of Bunker-B oil with dispersant with mix ratios of 10 : 1~10 : 5 were similar to those of aniline being 3% (Okasawa, 1970), cellulose being 7% (Okasawa, 1970), urea and benzene being less than 7% (Kim and Park, 1982). Generally speaking, the mixtures of Bunker-A, B oils with dispersant with 10 : 1~10 : 5 mix ratios were found to belong to an organic matter group of low-biodegradability.

The biodegradabilities of a mixture of Bunker-A oil with dispersant and a mixture of Bunker-B oil with dispersant increased from 2.10% to 7.19% and from 1.01% to 4.41%, respectively, as the mix ratio changed from 10 : 1 to 10 : 5. The reason is that the more dispersant is added to Bunker-A oil or Bunker-B oil, the more are the oil droplets dispersed into

seawater by dispersant, the more are the surface areas of oil droplets increased and the easier are the oil droplets degraded by microorganisms (Canevari, 1969; Tarzwell, 1969; Brown, 1987).

5. Deoxygenation rate constant (K₁) and ultimate biochemical oxygen demand (L₀)

In order to obtain the deoxygenation rate constants and ultimate biochemical oxygen demands of dispersant, a mixture of Bunker-A oil with dispersant and a mixture of Bunker-B oil with dispersant, based on the BOD values with time excluding degradation delay period due to toxicity, the regression lines for Thomas slope method were given in Fig. 5, Fig. 6, and Fig. 7, and the results were presented in Table 8.

0.125/day of K₁ and 2.487 mg/l of L₀ for dispersant (4 mg/l) were a little lower than K₁ and L₀ obtained by Kim et al. (1993a), respectively, and the calculated L₀ was found to be a little higher than 2.40 mg/l of BOD₂₀ as shown in table 3.

K₁ and L₀ for mixtures of Bunker-A oil with dispersant and mixtures of Bunker-B oil with dispersant

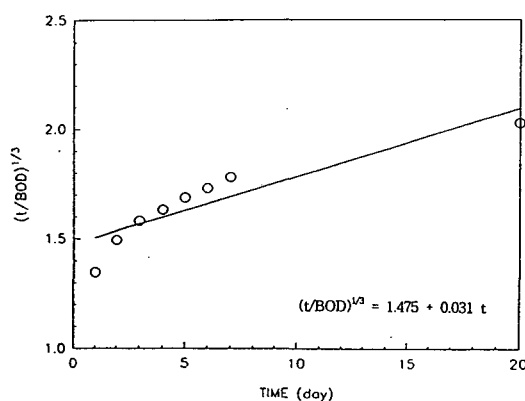


Fig. 5. Plots of (t/BOD)^{1/3} versus time (day) to determine K₁ and L₀ of dispersant (4 mg/l).

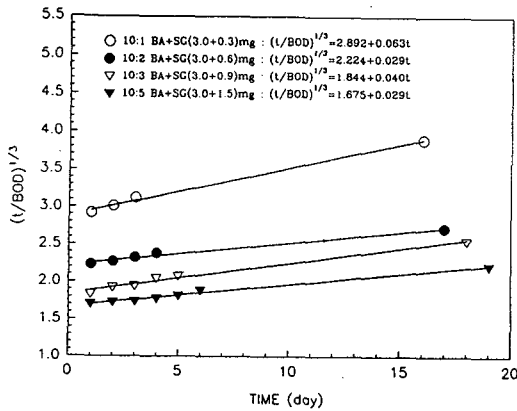


Fig. 6. Plots of $(t/BOD)^{1/3}$ versus time (day) to determine K_1 and L_0 of mixtures of Bunker-A oil with dispersant with mix ratios of 10 : 1~10 : 5.

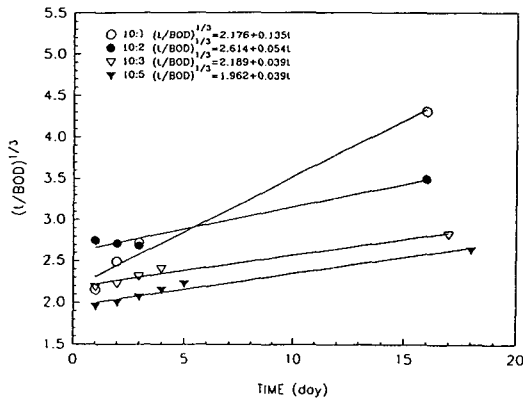


Fig. 7. Plots of $(t/BOD)^{1/3}$ versus time (day) to determine K_1 and L_0 of mixtures of Bunker-B oil with dispersant with mix ratios of 10 : 1~10 : 5.

with mix ratios of 10 : 1~10 : 5 were 0.079~0.130/day and 0.318~2.052 mg/l, and 0.106~0.371/day and 0.262~1.106 mg/l, respectively. The ultimate biochemical oxygen demands for mixtures of Bunker-A oil with dispersant and mixtures of Bunker-B oil with dispersant increased with mix ratios changing from 10 : 1 to 10 : 5. This means that the more dispersant is applied to Bunker-A oil or Bunker-B oil spilled on the sea, the more is dissolved oxygen consumed in the seawater (Dewling et al., 1971).

Summary and Conclusion

1 mg of dispersant was found to be equivalent to 0.26 mg of BOD_5 and to 0.60 mg of BOD_{20} in the natural seawater. Each 1 mg of dispersant, Bunker-A oil and Bunker-B oil were equivalent to 2.37 mg, 2.94 mg and 2.74 mg of TOD, respectively. Carbon, hydrogen, nitrogen and phosphorus contents of dispersant were 82.1%, 13.8%, 1.8% and 2.2%, respectively. Carbon and hydrogen contents of Bunker-A oil were found to be 73.3% and 13.5%, respectively, and carbon, hydrogen and nitrogen contents of Bunker-B oil to be 80.4%, 12.3% and 0.7%, respectively. Accordingly, the detection of N and P in the dispersant shows that the dispersants should be used with caution in coastal waters, with relation to eutrophication.

The biodegradability of dispersant shown as the

Table 8. Deoxygenation rate constants (K_1 , day^{-1}), ultimate biochemical oxygen demands (L_0 , mg/l), correlation coefficients (r), intercepts (a) and regression coefficients (b) of dispersant and mixtures of Bunker-A, B oils with dispersant

Dispersant	Mixture of Bunker-A with dispersant				Mixture of Bunker-B with dispersant			
	10 : 1 (3.0+0.3)	10 : 2 (3.0+0.6)	10 : 3 (3.0+0.9)	10 : 5 (3.0+1.2)	10 : 1 (3.0+0.3)	10 : 2 (3.0+0.6)	10 : 3 (3.0+0.9)	10 : 5 (3.0+1.2)
mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
K_1	0.125	0.130	0.079	0.131	0.371	0.124	0.106	0.120
L_0	2.487	0.318	1.152	1.221	2.052	0.262	0.451	1.106
r	0.911	0.998	0.992	0.992	0.994	0.992	0.983	0.986
a	1.458	2.892	2.224	1.844	1.675	2.176	2.614	2.189
b	0.031	0.063	0.029	0.040	0.029	0.135	0.054	0.039

ratio of BOD₅/TOD was found to be 11.0%. As mix ratios of dispersant to Bunker-A oil (3 mg/l) and Bunker-B oil (3 mg/l) changed from 1 : 10 to 5 : 10, respectively, biodegradabilities of a mixture of Bunker-A oil with dispersant and a mixture of Bunker-B oil with dispersant increased from 2.1% to 7.2% and from 1.01% to 4.4%, respectively. Accordingly, dispersant belongs to the organic matter group of middle-biodegradability, while mixtures of Bunker-A, B oils with dispersant in the mix ratio range of 10 : 1~10 : 5 belong to that of low-biodegradability.

The deoxygenation rate constant (K_1) and ultimate biochemical oxygen demand (L_0) were found to be 0.125/day and 2.487 mg/l for dispersant (4 mg/l), respectively. K_1 and L_0 were found to be 0.079~0.131/day and 0.318~2.052 mg/l for a mixture of Bunker-A oil (3 mg/l) with dispersant and to be 0.106~0.371/day and 0.262~1.106 mg/l for a mixture of Bunker-B oil (3 mg/l) with dispersant, respectively, with 1 : 10~5 : 10 mix ratios of dispersant to Bunker-A oil and Bunker-B oil. The ultimate biochemical oxygen demands of mixtures increased as a mix ratios of dispersant to Bunker-A, B oils changing from 1 : 10 to 5 : 10. This means that the more dispersants are applied to the sea for the cleanup of Bunker-A oil or Bunker-B oil, the more decreases the dissolved oxygen level in the seawater.

References

- APHA-AWWA-WPCF. 1989. Standard methods for the examination of water and wastewater. 17th Ed. Washington, USA. pp. 5-2~5-10.
- Bronchart, R.D.E. 1985. A new approach in enhanced biodegradation of spilled oil : Development of an oil dispersant containing oleophilic nutrients. Proc. Oil Spill Conf., 453~470.
- Brown, L.R. 1987. Oil-degrading microorganisms. Chemical Engineering Progress, 35~40.
- Canevari, G.P. 1969. General dispersant theory. Proceedings of joint conference on prevention and control of oil spills, API/FWCPA, USA., 171~177.
- Cho, D.O. and Mok, J.Y. 1995. A study on the plan for the acceptance of OPRC convention. KMI, 52~57 (in Korean).
- Dewling, R.T., J.S. Dorler and G.D. Pence. 1971. Dispersant use vs water quality. Proceedings of joint conference on prevention and control of oil spills, API/EPA/USCG, USA., 271~277.
- Gatellier, C.R., J.L. Oudin, P. Fusey, J.C. Lacaze and M.L. Priou. 1973. Experimental ecosystems to measure fate of oil spills dispersed by surface active products. Proceedings of joint conference on prevention and control of oil spills, API/EPA/USCG, USA., 497~504.
- IMO. 1988. Manual on oil pollution, Section IV Combating oil spills, London, pp. 124.
- IMO. 1995. Manual on oil pollution, Section II Contingency planning, London, pp. 18.
- Inoue, J. 1972. The chemical structures and biodegradability of various organic matters. Journal of water and waste, 14 (12). 142~166 (in Japanese).
- ITOPF. 1986. Response to marine oil spills. London, pp. III-4.
- Kim, G.S., C.K. Park and S.J. You. 1993a. Study on the biodegradability of dispersants and dispersant/Bunker-C oil mixtures and the dissolved Oxygen consumption in the seawater (II) : The biodegradability of dispersants and the dissolved oxygen consumption in the seawater. Bull. Korean Fish. Soc. 26 (5), 493~501 (in Korean).
- Kim, G.S., C.K. Park and J.G. Kim. 1993b. Study on the biodegradability of dispersants and dispersant/Bunker-C oil mixtures and the dissolved Oxygen consumption in the seawater (II) : The biodegradability of dispersants/Bunker-C oil mixtures and the dissolved oxygen consumption in the seawater. Bull. Korean Fish. Soc. 26

- (5), 493~501.
- Kim, S.J. and C.K. Park. 1982. A study on the correlation among BOD, COD, TOD and TOC values for food-processing wastewaters. *J. of Kor. Soc. Env. Eng.* 4 (1), 8~21 (in Korean).
- KNMPA. 1987. A study on the composition change of oil spill dispersant. *Experimental & Research Report*, 3, 92~116 (in Korean).
- Korean Industrial Standards. 1984. KSM-2800.
- Korea Maritime and Port Authority. 1979. Notice of KMPA - No.217.
- Okasawa. W. 1970. The biodegradability of various organic matters. a collection of research papers of the 6th forum for the study of sanitary engineering, Japan. 1 (in Japanese).
- Stoker, H.S. and S.L. Seager. 1976. *Environmental Chemistry-air and water pollution*. Scott, Foresman and Co., USA. 180. pp.
- Thomas, H.A. 1950. Graphical determination of BOD curve constants. *Water and Sewage Works*, 97, 123. pp.
- Takemoto. S, E. Mitani, C. Matsushita, S. Tabuki, Y. Kuge and S. Asado. 1978. Study of BOD test for industrial wastes containing sea water. *Journal of Environmental Pollution Control*, 14 (9). 77~85 (in Japanese).
- ZoBell, C.E. 1969. Microbial modification of crude oil in the sea. *Proceedings of joint conference on prevention and control of oil spills*, API/FW-CPA, USA., 317~326.

Received October 7, 1996

Accepted November 7, 1996