Orthogonal Study of Biodegradation of Lubricating Oil Accelerated by Lauroyl Glycine

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Abstract

Different contents of lauroyl glycine were incorporated into HVI 350 mineral lubricating oil and the biodegradabilities of the formulated oils were evaluated on a biodegradation tester. Thereafter, the interaction affections of four influencing factors, viz. lubricating oil content, lauroyl glycine, microbe nutriments and oxygen supply, on biodegradation of HVI 350 lubricating oil in soils were studied based on a L9(3^4) orthogonal array test. The results indicated that lauroyl glycine obviously promoted biodegradation of HVI 350 lubricating oil, especially at the lauroyl glycine contents of about 1.0~1.5%. Of the four influencing factors, the effect of lauroyl glycine on biodegradation of HVI 350 lubricating oil in soils proved to be the most significant in various biodegradation durations, demonstrating that lauroyl glycine markedly contributed to the biodegradation of the lubricating oil.

Keywords: Lauroyl glycine, Mineral oil, Biodegradation, Orthogonal test

1. Introduction

It has been known that environmental pollution caused by petroleum-based lubricants is severe due to their inherent toxicity and non-biodegradable nature (W. J. Bartz, 1998) (F. Haus, G. Jean, G. A. Junter, 2001). During the last decades, the increased public attention and the awareness of protection of the environment have stimulated the development of lubricants that show more or less compatibility with the environment, and environmental compliance of lubricants has become a topic of interested research (S. Boyde, 2002) (S. Z. Erhan and S. Asadauskas, 2000) (G. Rebeccal and M. Rogere, 1998). The ecologically responsive technology and lubricant design seek to meet both performance and environmental needs, to harmonize the technical performance and the ecological requirements. The key issue in formulating biodegradable lubricants is the choice of reliable base oils and suitable performance additives. Nowadays, many base fluids such as vegetable oils and synthetic esters have found practical applications in the formulation of biodegradable lubricants because of their excellent biodegradability and non-toxicity (S. J. Randles and M. Wright, 1992) (A. Willing, 2001). On the other hand, the development of alternatives to conventional lubricant additives such as zinc dialkyldithiophosphate (ZDDP) has also been a subject of significant interest, mainly due to environmental concerns arising from S, P and metal atoms of the additives (S. H. Roby, 1995). As we know, petroleum-based lubricants, which consist predominantly of hydrocarbons and subsidiarily of additives which are often environmentally hazardous, are for many reasons still dominating the lubricant market of today and will presumably continue to play their important roles in the future lubrication applications. Even though choice of mineral base oils in biodegradable lubricant formulations has as far never been recommended, improvement of their environmental safety such as better biodegradability is indeed indispensable, from both technical and environmental points of view. A question thus occurs: can the biodegradability of unreadily biodegradable lubricants be enhanced, by formulating so-called 'biodegradation accelerants'?

The answer is yes! It has been known that biodegradability is not an exact property or characteristic of a substance, but is also a system's concept, i.e. a system with its conditions determines whether or not a substance within it is biodegraded. Studies have shown that many compounds such as phosphorous and nitrogenous ones, are highly effective in promoting hydrocarbons to biodegrade, and have been successfully employed in the bio-remediation of petroleum polluted areas such as water and soil (M. Molnar and L. Leitgib, 2005) (T. Sobisch and H. Niebelschutz, 2000). A study has also shown that some phosphorous and nitrogenous compounds are effective in enhancing biodegradability of mineral lubricating oils (B. S. Chen and J. H. Fang, 2008).

Many amino acids have been known to be readily biodegradable and low eco-toxic, and have been described as being environmentally friendly. In addition, many amino acids are also known to be nutriments for microbes and, if incorporated into an unreadily biodegradable lubricant, are expected to be capable of promoting microbial production and increasing microbial populations, thus improving biodegradability of the lubricant. In the present paper, the effect of lauroyl glycine on biodegradability of a mineral lubricating oil was preliminarily reported.

2. Experiments

2.1 Materials

HVI 350 lubricating oil: A well refined petroleum-based paraffinic lubricating base oil whose kinematic viscosity at 40℃ is 98.16 mm^2/s.

Lauroyl glycine: A readily biodegradable amino acid prepared by the authors, with molecular formula being $CH_3(CH_2)_{10}CONHCH_2COOH$.

Oleic acid: A chemically purified, readily biodegradable unsaturated acid, used as a reference substance in the biodegradation test.

Soil specimen: Obtained from under the earth's surface of about 15 centimeters and screened out with a sizer 1 mm in pore diameter.

2.2 Biodegradation Test

For evaluating the effect of lauroyl glycine on biodegradability of HVI 350 lubricating oil, different weight percentage of lauroyl glycine, viz. 0.2%, 0.5%, 1.0%, 1.5%, 2.0% and 2.5%, were incorporated into the lubricating oil. The biodegradabilities of neat oil and the formulated oils were evaluated on a fast biodegradability tester created by the authors, the detailed principle and operation processes of which were particularly expatiated in the reference (J. H. Fang and B. S. Chen, 2004). In short, determination of biodegradability of a lubricant by this method is conducted by parallel biodegradation reactions of the lubricant and the reference substance oleic acid. After 8 days of biodegradation under formulated conditions, the accumulated amount of carbon dioxide produced by the tested lubricant and oleic acid were measured, respectively. Biodegradability Index (BDI), a comparative parameter of the percentage ratio of the amount of CO_2 created by individual tested lubricant to that created by oleic acid, was introduced to evaluate the biodegradability of the lubricant. The higher the BDI values, the better the biodegradability for different lubricants. The method proves to be well correlated with the prevailing biodegradation test method of CEC-L-33-A-94. Fig. 1 shows the schematic diagram of our method.

2.3 Orthogonal Test

For further valuating the significance of lauroyl glycine in promoting biodegradation of lubricating oil, the biodegradabilities of neat oil and the formulated oils in soils under different biodegradation conditions were studied and analyzed based on the orthogonal test. An $L9(3^4)$ orthogonal array that has 4 factors, 3 levels with 9 runs was designed. In the present study, the four factors that were considered to be important in influencing biodegradability of lubricating oil were lubricating oil content (factor A), lauroyl glycine (factor B), microbial nutriment (factor C) and oxygen supply (factor D), respectively. The three levels for each factor in the present test were set as shown in Table 1.

The biodegradability of HVI 350 lubricating oil in soils was then tested based on the $L9(3^4)$ orthogonal array and the specific influencing factors and levels shown in Table 1. Before biodegradability testing, the specific amount of oil, lauroyl glycine and microbial nutriments was well blended with 500g of the soil specimens for each run. The formulated soils were then ready for biodegradation test and were labeled numerically. The biodegradation tests of the nine runs were conducted simultaneously at room temperatures. After certain biodegradation durations, e.g. 5 days, 10 days, 20 days, 40 days and 60 days, the total residual concentrations of the tested oil in soils for each run were determined and the biodegradability of the oil was calculated by the equation given bellow:

$$\varepsilon_t = \frac{S_0 - S_t}{S_0} \times 100\%$$

Where ε_t is the biodegradability of oil after *t* days of biodegradation; S_0 is the initial concentrations of oil in soil (mg·g^{-1}); S_t is the residual concentrations of oil in soil after *t* days of biodegradation (mg·g^{-1}). The detailed procedures for determining residual oil concentrations after *t* days of biodegradation are as follows:

10 grams of oil-containing soil samples were taken out and put into an Erlenmeyer flask with stopper. Then, 50 mL of chloroform ($CHCl_3$) as an extracting agent were added into the soil with mild stirring and the flask was then allowed to stand overnight. Thereafter, the flask was heated in a water bath of 50~55℃ for about 1hour, and the extractant was then pump-filtered into an accurately weighed beaker. The soil residue was further extracted with 25 mL of $CHCl_3$ twice following the likewise procedures and the extractant were filtered into the beaker along with the others. After extraction, the beaker was heated in a water bath of 50~55℃ in a ventilating hood to remove $CHCl_3$, and then dried in an oven of 60~75℃ for 4 hours. After cooling to room temperatures, the beaker was again accurately weighed. The weight increase of the beaker was consequently the amount of the total residual oil in the soil. Therefore, S_t, the residual concentrations of oil in soil after *t* days of biodegradation, was obtained by dividing the amount of the residual oil with the amount of the soil samples.

3. Results and Discussions

3.1 Effect of lauroyl glycine on Biodegradability of Lubricating Oil

Shown in Fig. 2 are biodegradabilities of neat HVI 350 lubricating oil and the oils doped with different contents of lauroyl glycine obtained from the fast biodegradability testing.

It can be found from Fig. 2 that incorporation of lauroyl glycine into HVI 350 mineral lubricating oil, at whatever contents, obviously enhanced biodegradability of the lubricating oil, especially at the lauroyl glycine contents of about 1.0~1.5%. This indicated that lauroyl glycine acted as a biodegradation accelerant likely due to its effect as a microbial nutriment thus promoting microbe production. The mechanisms for lauroyl glycine to enhance biodegradation of a mineral lubricating oil need further investigations.

3.2 Biodegradability of Lubricating Oil in Soil

Fig.3 shows the biodegradabilities of lubricating oils in soils after 5 days, 10 days, 20 days, 40 days and 60 days for the 9 runs of biodegradation tests based on the L9(3^4) orthogonal array and the specific influencing factors and levels, respectively.

It can be seen from Fig. 3 that the biodegradability of lubricating oil in each run increased with increasing test durations, although the increases of biodegradability after the same durations differed for different runs. This indicated that the four influencing factors, viz. oil content, lauroyl glycine, microbial nutriment and oxygen supply, and their interactions were important in biodegradation of a lubricating oil.

3.3 Analysis of Orthogonal Tests

Shown in Table 2 are biodegradabilities of HVI 350 lubricating oil after 5 days of biodegradation durations and the statistical results based on the L9(3^4) orthogonal array and the specific influencing factors and levels.

In table 2, the Roman numerals Ⅰ, Ⅱ and Ⅲ are the summations of biodegradabilities corresponding to level 1, level 2 and level 3 for each factor, respectively. Furthermore, k_1, k_2 and k_3 are the averages of Ⅰ, Ⅱ and Ⅲ for each factor correspondingly respectively, while R is the extreme difference of the maximum and the minimum of k_1, k_2 and k_3 for each factor, reflecting the significance of a factor in influencing the biodegradability of the lubricating oil. The greater the values of R for a factor, the more significant it is in influencing the biodegradability. Take factor A for example, Ⅰ = 6.53+16.52+15.49=38.54, Ⅱ= 9.96+12.36+13.62=35.94, Ⅲ= 9.76+11.57+10.69=32.02. k_1 = 38.54/3=12.85, k_2 = 35.94/3 = 11.98, k_3 = 32.02/3 = 10.67, while R = 12.85-10.67=2.17.

From table 2 we can see that the extreme differences for factors A, B, C and D rank in the order of B>D>A>C, indicating that lauroyl glycine was the most prominent factor in accelerating biodegradation of HVI 350 lubricating oil in soil in the initial 5-day biodegradation durations, although oxygen supply (factor D) was also very significant compared with lubricating oil content (factor A) and microbial nutriment (factor C).

Based on the L9(3^4) orthogonal array and the specific influencing factors and levels, the biodegradabilities of HVI 350 lubricating oil in soils after 10 days, 20 days, 40 days and 60 days of biodegradation durations were also determined and the orthogonal test results (see Fig. 3) analyzed in the way likewise described above, respectively. Fig. 4 shows the statistical results of the extreme differences, R, for factors A, B, C and D, at the end of each specific duration.

It can be observed clearly from Fig.4 that the extreme difference for factor B increases with increasing test durations and is always much greater than those for factors A, C and D. This indicates that lauroyl glycine was remarkably significantly in and thus markedly contributed to the promotion of biodegradation of the lubricating oil in the whole test durations of 60 days, especially in the initial 20 days. Otherwise, it can also be seen from Fig.4 that in the whole test durations of 60 days, the magnitudes of the extreme differences for factors A, C and D vary obviously and irregularly, demonstrating that the influences of factors A, C and D on biodegradation of the lubricating oil differed in the different periods of test durations.

4. Conclusions

From above investigations, the following conclusions can be drawn:

Lauroyl glycine, when incorporated in appropriate amount into an unreadily biodegradable lubricating oil such as HVI 350 mineral oil, obviously enhanced biodegradability of the lubricating oil. The effect of lauroyl glycine on biodegradation of HVI 350 lubricating oil in soil was remarkable compared with the effects of lubricating oil content, microbial nutriment and oxygen supply. Lauroyl glycine played a very positive and significant role in the biodegradation of the lubricating oil.

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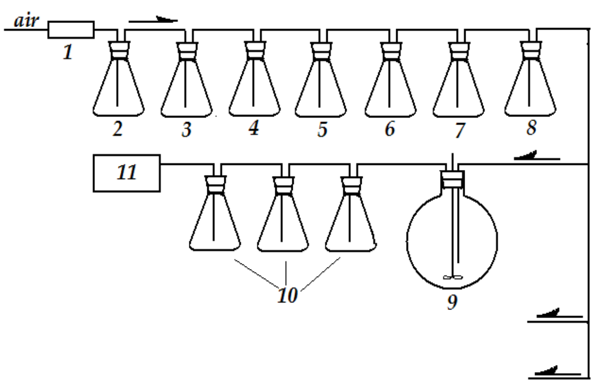
Table 1. The influencing factors and their levels for orthogonal test

Level	Influencing factor			
	A	B	C	D
1	1.0	0.0	without additional nutriment	under natural ventilation
2	5.0	0.5	9(urea) and 2.5($NH_3H_2PO_4$)	pumping air into soil (15 mL/ min.)
3	10.0	1.0	18(urea) and 5($NH_3H_2PO_4$)	adding H_2O_2 into soil each day

A- mass percentage of oil in soil; B-mass percentage of lauroyl glycine in oil; C-mass percentage of nutriments in oil; D-oxygen supply, the mass ratio of H_2O_2 to soil was 0.5 to 100 for level 3.

Table 2. Orthogonal results of biodegradability of HVI 350 after 5 days of biodegradation

Run number	A	B	C	D	ε_t (%)
1	1	1	1	1	6.53
2	1	2	2	2	16.52
3	1	3	3	3	15.49
4	2	1	2	3	9.96
5	2	2	3	1	12.36
6	2	3	1	2	13.62
7	3	1	3	2	9.76
8	3	2	1	3	11.57
9	3	3	2	1	10.69
I	38.54	26.25	31.72	29.58	
II	35.94	40.45	37.17	39.90	
III	32.02	39.80	37.61	37.02	
k_1	12.85	8.75	10.57	9.86	
k_2	11.98	13.48	12.39	13.30	
k_3	10.67	13.27	12.54	12.34	
R	2.17	4.73	1.96	3.44	



1—air flowmeter; 2—buffer ; 3,4,5,6—CO_2 degasser; 7—CO_2 examiner; 8—buffer; 9—bioreactor; 10—CO_2 absorber; 11—titrator

Figure 1. The schematic diagram of biodegradation test

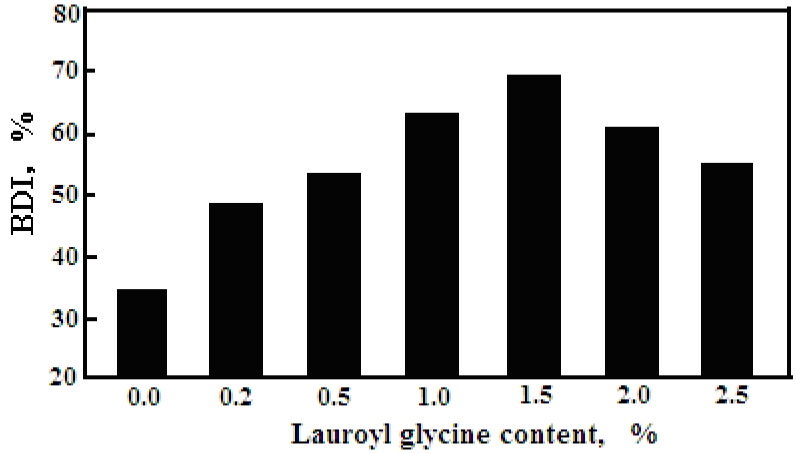


Figure 2. Biodegradation Index of lubricating oil versus lauroyl glycine contents

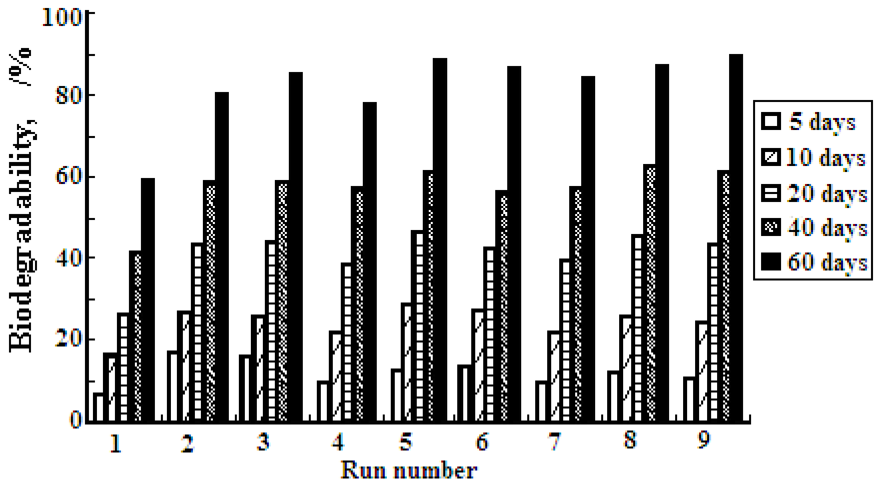


Figure 3. Biodegradability of lubricating oil versus run numbers

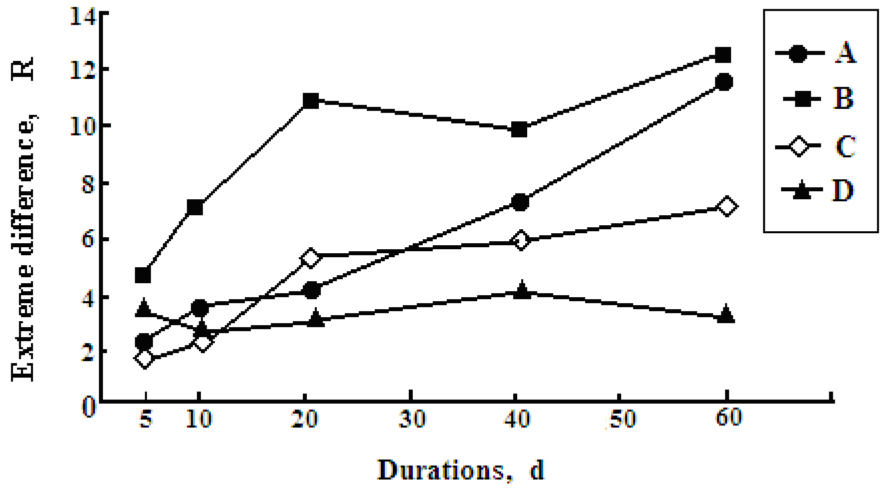


Figure 4. The extreme differences for the influencing factors in various biodegradation durations