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Short communication

무독성 친환경 세정제의 합성 및 평가에 관한 연구

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Synthesis and Evaluation of Ecofriendly Nontoxic Cleaning Agents

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초 록

기존 유기 세정제의 문제점인 인체 독성을 낮추기 위하여 생분해도 및 LD_{50}가 향상된 에테르 및 에스테르 작용기를 동시에 갖는 세정제 4종을 새롭게 합성하였다. 합성한 세정제를 한국기계전기전자시험연구원에서 국가산업표준 방법으로 분석하여 물리적인 성질과 생분해도 및 LD_{50}을 측정하고 세정성 평가를 수행하였다. 물성 측정 결과, 물리화학적 성질이 세정제로서 적합한 것으로 확인되었다. 세정력 평가를 위하여 60 × 40 mm 크기의 스테인리스 강 기판에 절삭유, 방청유, 인발유, 윤활유를 각각 기판에 도포하여 합성한 세정제**(1-4)**에 침적하여 세정력을 평가하였다. 최대 5 min 간 침적하였을 때 절삭유는 96-100%, 방청유에서는 64-72%, 인발유는 59-88%, 윤활유는 72-84% 정도의 높은 세정력을 보였다. 또한 세정제**(1-4)**의 생분해도 99% 이상, LD_{50} 2,000 mg/kg 이상의 값을 보임으로서 인체에 거의 해가 없는 친환경 세정제임을 확인하였다.

Abstract

In order to reduce toxicity on the human body, four new cleaning agents (1-4) containing ester and ether functionalities have been invented. The synthesized cleaning agents's physical properties, biodegradabilities, and LD_{50} values, which were conducted by Korea Testing Certification Institute by using standard method, showed excellent values. A specimen for cleaning ability was prepared by cutting in 60 × 40 mm size of stainless steel plate. The surface of the above specimens was treated with four different kinds of contaminants, such as cutting oil, anti-rust oil, drawing oil, and lubricating oil. Contaminated specimens were then immersed in compounds **(1-4)** for 1 to 5 minutes to dissolve oil in the cleaning agent. The data indicate that all compounds **(1-4)** exhibit good cleaning ability toward four contaminant oils. It is also confirmed that these compounds can be applicable to various industrial cleaning fields as nontoxic and biodegradable cleaning agents because of their excellent biodegradabilities and LD_{50} values.

Keywords: *Cleaning Agent, Biodegradability, Nontoxicity,* LD_{50} *value*

1. Introduction

A number of organic cleaning agents have been used and developed to clean soils from surfaces. A chlorine-based solvent such as, 1,1,2-trichloroethylene (TCE), 1,2-dichloropropane, and methylene chloride has been widely used for its excellent cleaning ability. However, since chlorine-based solvent has high volatility, it is harmful both to human body and environment[1-3]. The hydrocarbon-based cleaning agent has been used as the substitute, but the problems that relate to flammability and drying are being blamed. Flammability is important because many industrial facilities are not equipped to safely handle flammable hydrocarbons. In addition, hydrocarbon containing an aromatic hydrocarbon, such as benzene, toluene, and xylene are being regulated due to its high toxicity on human body and environmental pollution[4,5]. Therefore development of new environmentally acceptable cleaning agent would be highly desirable.

Oxygenated hydrocarbons that are typically used in various industrial cleaning fields are alcohols, ketones, and esters. Among them esters have been extensively used as cleaning agent because of good physical properties and show high biodegradability[6,7]. The biodegradation of ester is impeded by the presence of aliphatic substituents, cyclic structures, aromatic rings, and unsaturated systems in their molecules. Esters with unbranched linear chain are most readily biodegradable.

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Table 1. Physical Properties of Compounds (1-5)

Physical Properties / Comp.	Flash point (℃)	Boiling point (℃)	Kinematic Viscosity (mm^2/s, at 40 ℃)	Viscosity (cP, at 20 ℃)	Specific Gravity (at 15/4 ℃)	Density (g/cm^3)	Surface tension (dyne/cm)	Wetting index[a]
1	67	163	0.853	0.812	0.955	0.953	28.5	41.18
2	70	167	0.860	0.823	0.960	0.957	27.9	41.67
3	72	169	0.857	0.814	0.952	0.950	28.3	41.23
4	75	173	0.861	0.827	0.963	0.961	28.1	41.35
5[b]	57	165	1.193	1.040	0.874	0.872	26.4	31.76
Test Method	KS M ISO 2592 : 2007	KS M 2142 : 2009	KS M 2014 : 2004	KS M 2014 : 2004	KS M ISO 12185 : 2003	KS M ISO 12185 : 2003	KS M ISO 2525 : 2005	-

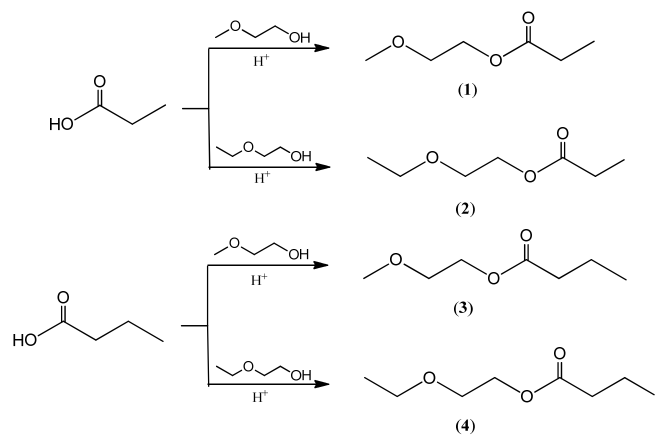
[a] Wetting Index = $\frac{\text{density} \times 1000}{\text{viscosity} \times \text{surface tension}}$

[b] n-pentyl propionate

Table 2. Biodegradability and Acute Oral Toxicity of Compounds (1-5)

Bio. & LD_{50} / Comp.	Biodegradability (%)	Acute Oral Toxicity (LD_{50}) (mg/kg)
1	99.7	2,000 >
2	99.7	2,000 >
3	99.7	2,000 >
4	99.7	2,000 >
5[a]	97.6	2,000 >
Test Method	KS M ISO 7827 : 2008	NIER notice No. 2010-29

[a]n-pentyl propionate



Scheme 1. The synthetic scheme of compounds (1-4).

Currently, the main disadvantage of esters is low polarity. That means the polarity of the whole cleaning agent become low so that the solubility is decreased. On the other hand, ethers have an excellent compatibility with materials having low polarity, i.e., esters. Knowing the chemical structure effect on important polarity property permits us to develop the most effective cleaning agent. Herein we describe a synthesis and evaluation of dual function compounds with ester and ether groups within a molecule which exhibit low toxicity to human body due to their excellent biodegradability and LD_{50} value.

The core structure of the target compounds **(1-4)** is linear ester group which connected to corresponding alcohol chain with ether functional group. The synthesis of target compounds is outlined in Scheme 1. The ester compounds **(1-4)** were synthesized by esterification reaction of propionic and butyric acid with corresponding alcohols in the presence of acid catalysis in moderate yield.

All synthesized ester compounds **(1-4)** were estimated for their possibility of cleaning agent by examining physical properties which were conducted by Korea Testing Certification Institute by using standard methods (Table 1). All compounds have various good physical properties which are almost similar to other cleaner[8,9]. When biodegradability and LD_{50} value of all compounds **(1-4)** were compared with that of simple ester compound, n-pentyl propionate **5**, the data indicated all compounds show as equal biodegradability and low toxicity as **5** (Table 2). This finding suggests that all synthesized compounds **(1-4)** can be a new candidate as environmentally friendly cleaning agent.

2. Experimental

2.1. Materials and Measurements

The reagents used for this study were purchased from Aldrich Chem. Co. All proton nuclear magnetic resonance (NMR) spectra were recorded on a Varian Unity Inova spectrometer at 300 MHz and are reported in parts per million (ppm) on the δ scale relative to chloroform-d_1 (δ 7.24) or tetramethylsilane (δ 0.00). Analytical thin layer chromatography (TLC) was performed with E. Merck pre-coated TLC plates, silica gel 60F-254, layer thickness 0.25 mm.

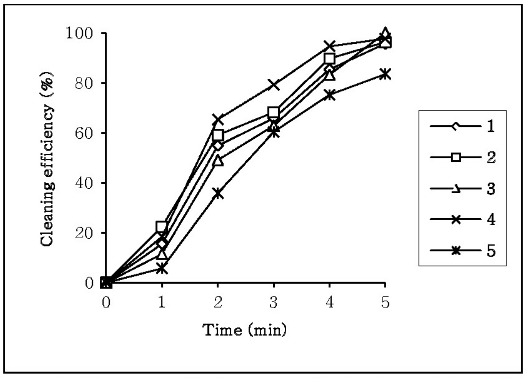


Figure 1. Cleaning efficiency of (1-5) for cutting oil.

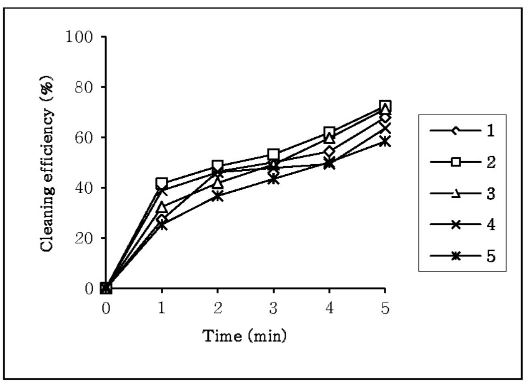


Figure 2. Cleaning efficiency of (1-5) for anti-rust oil.

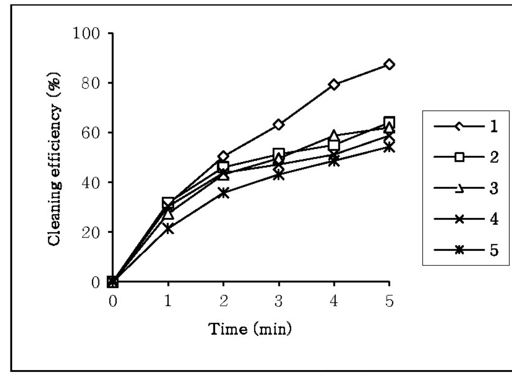


Figure 3. Cleaning efficiency of (1-5) for drawing oil.

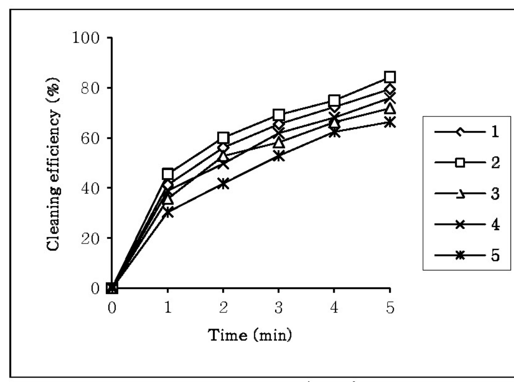


Figure 4. Cleaning efficiency of (1-5) for lubricating oil.

All new compounds **(1–4)** were evaluated for their cleaning efficiency by simple immersion cleaning method. A specimen was prepared by cutting in 60 × 40 mm size of stainless steel plate and weighted. The surface of the above specimens was applied with four kinds of contaminants, such as cutting oil, anti-rust oil, drawing oil, and lubricating oil which were used for various industrial processing. The weight that was added with the specimen was recorded down to four places of decimals. The above specimens were immersed in 100 mL of compounds **(1–4)** for 1 to 5 minutes to dissolve oil in the cleaning agent. After that, the specimens were dried and weights were measured.

2.2. Synthesis

2-Methoxyethyl propionate (1) : To a stirred solution of 2-methoxyethanol (2.0 kg, 26.28 mol) and c-H_2SO_4 (2 g, 0.02 mol) in toluene (300 mL) was added slowly propionic acid (1.5 kg, 20.25 mol) at room temperature. The resulting mixture was heated to remove water for 8 hours by Dean-Stark trap. After cooling to room temperature, 10% aqueous $NaHCO_3$ (4.0 L) was added to the reaction mixture. The organic layer was separated and dried with $MgSO_4$, filtered, and solvent evaporated under reduced pressure. The crude product was purified by vacuum distillation (20 mmHg, 85～90 ℃) to afford 1 (2.53 kg, 78%)[10]; ^{1}H NMR (300 MHz, $CDCl_3$) 1.13 (t, 3H, J = 7.5 Hz), 2.37 (q, 2H, J = 7.5 Hz), 3.37 (s, 3H), 3.57 (t, 2H, J = 4.75 Hz), 4.21 (t, 2H, J = 4.75 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.93, 27.31, 58.83, 63.27, 70.40, 174.41.

2-Ethoxyethyl propionate (2)

(20 mmHg, 88～93 ℃, 80%), ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.09 (t, 3H, J = 7.5 Hz), 1.21 (t, 3H, J = 7.0 Hz), 2.38 (q, 2H, J = 7.5 Hz), 3.47 (q, 2H, J = 7.0 Hz), 3.58 (t, 2H, J = 5.0 Hz), 4.20 (t, 2H, J = 5.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.02, 15.05, 27.42, 63.55, 66.58, 68.35, 174.49.

2-Methoxyethyl butyrate (3)

(20 mmHg, 88～93 ℃, 77%), ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, 3H, J =7.5 Hz), 1.65 (m, 2H), 2.31 (t, 2H, J = 7.4 Hz), 3.37 (s, 3H), 3.58 (t, 2H, J = 5.0 Hz), 4.21 (t, 2H, J = 5.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.51, 18.30, 35.91, 58.83, 63.15, 70.43, 173.54.

2-Ethoxyethyl butyrate (4)

(20 mmHg, 90～95 ℃, 73%), ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, 3H, J = 7.5Hz), 1.21 (t, 3H, J = 7.0 Hz) 1.64 (m, 2H), 2.33 (t, 2H, J = 7.5 Hz), 3.5 (q, 2H, J = 7.0 Hz), 3.6 (t, 2H, J = 5.0 Hz), 4.21 (t, 2H, J = 5.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.58, 15.05, 18.37, 36.03, 63.41, 66.56, 68.36, 173.65.

3. Results and discussion

3.1. Result of Cleaning Test

Four tests were performed on each compound. The amount of oil that was initially adhered on the specimen and the amount oil that was removed by the cleaning agents were calculated and putted on a percentage basis in Figures 1, 2, 3, and 4.

Figures 1, 2, 3, 4 indicate that all compounds **(1−4)** show somewhat low cleaning efficiency for four contaminants in 1-2 minutes dipping. However, gradual increment of dipping time can raise cleaning efficiency. Although the data in Figures 2, and 3 indicate that all compounds exhibit lower cleaning ability toward anti-rust oil, and drawing oil, it is observed that all compounds **(1−4)** are more excellent cleaning agent than simple ester compound, n-pentyl propionate **5**. Accordingly, one might suggest that these compounds **(1−4)** are suitable for new cleaning agents.

3.2. Result of Biodegradability and LD_{50} Test

Data for the biodegradability of the compounds **(1−4)** are given in Table 2. Generally, all synthesized compounds **(1−4)** are highly biodegradable according to commonly accepted standards[11,12]. When biodegradability of all compounds **(1−4)** were compared with that of simple ester compound, n-pentyl propionate **5**, the data indicated all compounds show as equal biodegradability as **5** (Table 2). The biodegradability test showed after 21 days all the tested compound **(1−4)** were biodegraded by over 99%. From this biodegradability studies, it can be said that the synthesized mixed esters with ether function have good potential for use as biodegradable cleaning agents.

In acute toxicity tests, the LD_{50} value in mice was determined. This study aims to investigate the acute oral toxicity and safety of compounds **(1−4)**. The results of acute oral toxicity using ICR mouse showed that LD_{50} of value over 2,000 mg/kg for all compounds examined. Compounds did not show any toxic effects in ICR mice and they are very safe for ICR mice. This finding suggests that all synthesized compounds **(1−4)** can be a new candidate as nontoxic cleaning agents.

4. Conclusion

We have prepared four ester compounds **(1-4)** with ether functional group in moderate yield from propionic, and butyric acid and corresponding alcohols. These compounds can be applicable to various industrial cleaning fields as nontoxic and biodegradable cleaning agent because of their good physical, biodegradable, and nontoxic properties and cleaning abilities for contaminants. The future work including formulation of **(1-4)** with other solvents to find out nontoxic and biodegradable cleaning systems is under investigation in our laboratory.

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