pISSN 1229-3008 eISSN 2287-6251
Progress in Superconductivity and Cryogenics
Vol.18, No.1, (2016), pp.14~18 http://dx.doi.org/10.9714/psac.2016.18.1.014

Study of the separation method of structural isomer using Magneto-Archimedes method

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(Received 12 February 2016; revised or reviewed 20 March 2016; accepted 21 March 2016)

Abstract

Organic compounds have a problem that the separation of structural isomer in the preparation process requires high energy consumption. This study proposes a new separation method of structural isomer using Magneto- Archimedes method. Firstly, the levitation height of 1, 6-DDA and 1, 10-DDA was respectively calculated by simulation of the forces acting on the particles under magnetic field, and it was indicated that they could be separated by the difference of levitation height. To confirm the phenomenon experimentally, white powders of 1, 6-DDA and 1, 10-DDA were formed into pellets, and were soaked in manganese chloride solution. Then the solution was put on the center of the cryostat of HTS bulk magnet (maximum magnetic flux density is 3T). As a result, it was confirmed that the separation of structural isomer by difference of levitation height could be possible.

Keywords : Magnetic Separation, Magneto-Archimedes method, Recycle

1. INTRODUCTION

There are at least over 90 million kinds of organic compounds, and are fundamental for our daily life. Some organic compounds are used for industrial ingredients like petrochemical products, whereas others are used for articles for daily use like fabrics, cosmetics and drug medicines. Especially, most of the drug medicines are the organic compound.

In general, the synthetic processes of organic compounds consist of multiple processes to obtain a final objective substance. For example, there is a method to obtain the objective substance by transforming the starting materials and reactant to a reactive intermediate, and then to react it with other starting material after the removal of by-product. There is also a method to extract only a necessary ingredient from the natural products. The objective or natural products are basically not pure including impurities, so the process of separating structural isomer is important to obtain the objective substance. The chemical separation methods mainly used for industry are extraction, recrystallization and distillation. However, these methods have the problems of long reaction time for separation, or the difficulty of separation depending on the conditions such as boiling temperature or solubility.

Moreover, it is also the problem that the chemical separation generally needs large device and high energy consumption. It is said that energy consumption by chemical industry accounts for about 40 % in energy consumption of Japanese industry [1]. Moreover, 40% of the total energy consumption derived from the process of separation by distillation [2]. In addition, the amount of carbon dioxide emission by chemical industry accounts for about 6% in that of whole Japan. Even in the whole manufacturing industry, it accounts for 18% which is next to the steel industry [3]. Based on above the background, the energy reduction for separation of organic compounds is necessary to reduce environmental burdens.

In this study, a new separation method of structural isomer was examined instead of extraction or distillation. The separation method using external magnetic force is one of physical method which can separate substances with lower energy.

2. MAGNETIC SEPARATION

Magnetic separation which can separate the substances utilizing the difference of magnetic properties is categorized into 3 techniques; high gradient magnetic separation (HGMS), open gradient magnetic separation (OGMS) and magnetic Archimedes. OGMS is the suitable separation method to separate ferromagnetic substances, and HGMS is suitable for paramagnetic substances with a relatively large magnetic susceptibility around 10^{-4} in addition to ferromagnetic substances. Magneto-Archimedes is suitable for separation of diamagnetic and paramagnetic substances which have relatively small magnetic susceptibility. The application scope of each method is summed up Fig. 1.

The separation objects used in this study are the structural isomers of organic compounds. Both objects are diamagnetic substances which have small magnetic susceptibility. Most of organic compounds including structural isomer excluding radicals are diamagnetic

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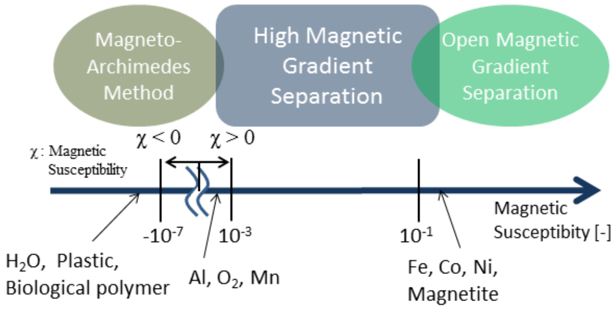


Fig. 1. The applicable scopes of each magnetic separation method depending on magnetic susceptibility.

substance with about $-10^{-5} \sim -10^{-6}$ of magnetic susceptibility [4, 5]. Thus, we adopted Magneto-Archimedes method which is the most suitable for diamagnetic substances.

3. THEORY OF MAGNETO-ARCHIMEDES METHOD

Archimedes principal is one of a physical law about the force acting on the substance that the buoyancy force is equal to the weight of fluid displaced by the substance which acts in the upward direction. In other words, it can be said that the medium with large relative density gives large buoyancy force to the substance. Magneto-Archimedes method is a principle that the buoyancy force which acting on the substance is raises by increasing the apparent weight of the medium by the magnetic force.

Both the organic structural isomers used in this study are the diamagnetic substance, and the buoyancy force in the liquid medium under the magnetic force is used. In case of using paramagnetic medium, the apparent weight of the medium becomes larger because it is drugged by the magnetic force, when setting a magnet under the medium. Thus, the levitation of diamagnetic substances is possible because the buoyancy force acting on the substance becomes larger. For example, the forces acting on the diamagnetic substance in paramagnetic medium under the magnetic field are shown in Fig. 2. Upward vertical direction is set to a positive direction of the z-axis. A magnet is set under the medium. The magnetic field is in positive direction of the z-axis, which means that the magnetic field increases in the vertically downward direction. In this case, the gravity and magnetic force are respectively acting on medium and particles. In addition, the buoyancy force, which is a resultant of the gravity and the magnetic force acting on the medium, acts on the particle. Based on this, the levitation is easy because are acting on particles not only gravity and magnetic force but also buoyancy force. The magnetic susceptibility of diamagnetic substances as small as about $-10^{-5} \sim -10^{-6}$, so repulsion force generated by the magnet is small. In case of the separation under dry condition, the magnetic field as large as 40 T in maximum magnetic flux density is needed to levitate diamagnetic substance under the paramagnetic gas atmosphere such as oxygen which is a paramagnetic gas medium with relatively large magnetic susceptibility.

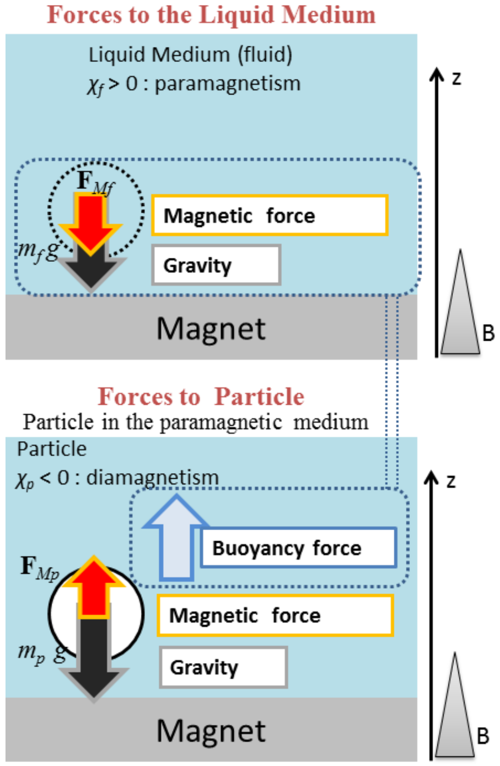


Fig. 2. The relation between the forces acting on particles and the medium.

Therefore, magnetic separation under wet condition was adopted using a liquid medium.

Based on this theory, a condition which particles are levitated by Magneto-Archimedes method is calculated. Here, subscript p and f represent the particle and the fluid. Firstly, F_{fz}' acting on the medium, which is the counteracting force of F_{fz} acting on the particles, was calculated. F_{fz}' is the resultant force of gravity $m_f g$ and magnetic force F_{Mfz} which acts to downward direction, and shown as follows;

$$F_{fz}' = -F_{Mfz} - m_f g \quad (1)$$

F_{fz} acting on the particles is with the same magnitude of force as shown in equation (2) but opposite direction against F_{fz} acting on the medium.

$$F_{fz} = -F_{fz}' \quad (2)$$

Therefore, the force "F_{pz}" acting on the particles is shown below by the gravity "$m_p g$", the buoyancy force "F_{fz}" and the magnetic force "F_{Mpz}" acting on the particles.

$$F_{pz} = F_{fz} + F_{Mpz} - m_p g \quad (3)$$

Thus, formula (3) is rearranged by formula (1) and (2) as below.

$$F_{pz} = -F_{fz}' + \left(F_{Mpz} - m_p g\right)$$

$$= \left(F_{Mpz} + F_{Mfz}\right) + \left(-m_p g + m_f g\right) \tag{4}$$

Here, the potential energy of magnetization per unit volume in vacuum by magnetic field is thought for calculating magnetic force. E_m can be represented as below with the magnetic permeability in vacuum μ_0, the magnetization per unit volume **m** and the external magnetic field **H**.

$$E_m = -\mu_0 \mathbf{m} \cdot \mathbf{H} \tag{5}$$

Therefore, the magnetic force per unit volume $\mathbf{F_m}$ acting on the substance is represented as below.

$$\mathbf{F_m} = -\nabla \cdot E_m \tag{6}$$

The magnetization per unit volume **m** is represented with the magnetic susceptibility χ.

$$\mathbf{m} = \chi \mathbf{H} \tag{7}$$

From formula (5) to (7), the magnetization per unit volume can be represented below.

$$\mathbf{F_m} = \mu_0 \chi \mathbf{H} \nabla \cdot \mathbf{H} \tag{8}$$

The relation between the magnetic flux density **B** and the external magnetic field **H** is represented below with the magnetic permeability μ_0 in vacuum when the magnetic field area is in vacuum.

$$\mathbf{B} = \mu_0 \mathbf{H} \tag{9}$$

Thus, the formula (8) is rearranged as follows.

$$\mathbf{F_m} = \frac{\chi}{\mu_0} \mathbf{B} \nabla \cdot \mathbf{B} \tag{10}$$

Here, V is the volume of magnetic substance. When $\mathbf{F_m}$ is represented by one-dimensional notation for z-axis, it is expressed as follows.

$$F_{Mz} = V \frac{\chi}{\mu_0} B_z \frac{\partial B_z}{\partial z} \tag{11}$$

Then, the formula (4) is represented as the formula (12).

$$F_{pz} = \left[\left(\frac{V\chi_p}{\mu_0} + \frac{V\chi_f}{\mu_0}\right) B_z \frac{\partial B_z}{\partial z} + \left(-m_p g + m_f g\right)\right]$$
$$= V\left[\left(\frac{\left(\chi_f + \chi_p\right)}{\mu_0}\right) B_z \frac{\partial B_z}{\partial z} + \left(\rho_f - \rho_p\right) g\right] \tag{12}$$

Here, ρ_p is as the density of particle, ρ_f is the density of fluid, χ_p is the magnetic susceptibility of particle and χ_f is the magnetic susceptibility of fluid. Particles are levitated when the external force F_{pz} acting on the particles is positive, which can be represented as formula (13).

$$\left[\left(\frac{\left(\chi_f + \chi_p\right)}{\mu_0}\right) B_z \frac{\partial B_z}{\partial z} + \left(\rho_f - \rho_p\right) g\right] > 0 \quad \left(\chi_p < 0\right) \tag{13}$$

From this formula, separation condition of structural isomer was estimated by calculation, and then verified by the experiment.

4. THE ESTIMATE OF THE LEVITATION HEIGHT BY CALCULATION

In this study, 1, 6-DDA (1, 6-Decanedicarboxylic Acid, $C_{12}H_{22}O_4$) and 1, 10-DDA (1, 10-Decanedicarboxylic Acid, $C_{12}H_{22}O_4$) shown in Fig. 3 were used as the separation object for examining the separation method of structural isomer with Magneto-Archimedes method. Here, 10 wt.% manganese chloride solution was used as the medium. This is paramagnetic substance which has more than 10-5 magnetic susceptibility, and has the density is smaller than that of separation target [6]. 1, 6-DDA has been used for electrolytic solution of capacitors etc., whereas 1, 10-DDA has been used for hot-melt adhesive etc.. The density, magnetic susceptibility and boiling point of these substances were summarized in Table 1. From the Table, it is understood that the separation of these isomers is difficult by recrystallization or distillation, because the difference between density and boiling point of 1, 6-DDA and 1, 10-DDA is small.

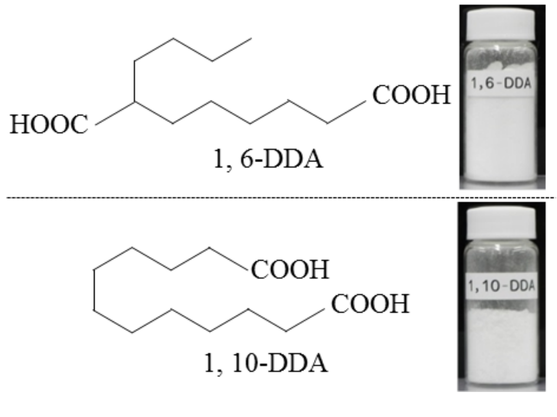


Fig. 3. The structural formulas of 1, 6-DDA and 1, 10-DDA.

TABLE 1
THE DENSITY, THE MAGNETIC SUSCEPTIBILITY AND THE BOILING POINT OF 1, 6-DDA, 1, 10-DDA AND MANGANESE CHLORIDE SOLUTION.

	Density (g/cm^3)	Magnetic susceptibility(-)	Boiling Point (℃)
1,6-DDA	1.12	-8.04×10^{-6}	397
1,10-DDA	1.17	-8.89×10^{-6}	410
10wt.% $MnCl_2$	1.08	1.85×10^{-4}	—

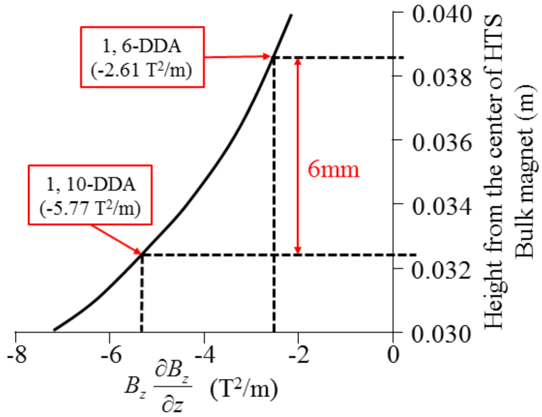


Fig. 4. The relation between the height from the cryostat surface of HTS bulk magnet and magnetic field product of vertical direction.

In order to conduct the Magneto-Archimedes separation, the levitation height was estimated by calculation. From formula (13), the levitation height is a point that the total force which acts on the particles becomes zero. That is $F_{pz} = 0$.

$$F_{pz} = \left[\left(\frac{(\chi_f + \chi_p)}{\mu_0} \right) B_z \frac{\partial B_z}{\partial z} + (\rho_f - \rho_p) g \right] = 0 \quad (\chi_p < 0) \tag{14}$$

More specifically, formula (14) can be transformed as below.

$$B_z \frac{\partial B_z}{\partial z} = \frac{\rho_p - \rho_f}{\chi_p + \chi_f} \mu_0 g \quad (\chi_p < 0) \tag{15}$$

From the formula and the value of the magnetic susceptibility and the density in Table 1, the vertical magnetic field product at the levitation position is respectively -2.61[T^2/m] for 1, 6-DDA and -5.77[T^2/m] for 1, 10-DDA. The difference of levitation height for the isomers is expected to be about 6 mm from these values. Fig. 4 shows the relation between the height from the cryostat surface of HTS bulk magnet and magnetic field product of vertical direction derived from magnetic field analysis. From these estimation, the separation possibility of 1, 6-DDA and 1, 10-DDA was suggested.

5. EXPERIMENTAL METHODOLOGY

Based on above the calculation, we tried to separate actual isomers by Magneto-Archimedes method. White powders of 1, 6-DDA and 1, 10-DDA were formed into pellets by tablet molding equipment. The pellets were put into a glass vessel filled by 10 wt. % manganese chloride aqueous solution. The levitation height of each pellet was measured by putting the glass vessel on the center of the cryostat of HTS bulk magnet. The surface maximum magnetic flux density of the cryostat of HTS bulk magnet

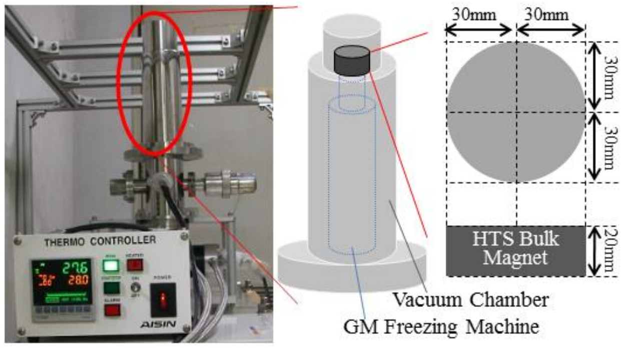
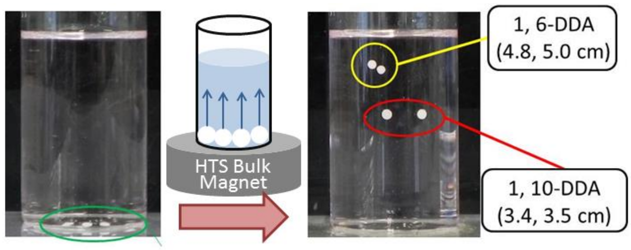


Fig. 5. The condition of the HTS bulk magnet.



4 pellets of 1, 6-DDA and 1, 10-DDA (3 mm in diameter)

Fig. 6. The appearance of separation of structural isomers with Magneto-Archimedes method.

(GdBaCuO, Nippon Steel Corporation, 60 mm φ × 20 mm) used for this study is 3.2 T. The bulk was made by using melting method by mixing 10 wt% Ag_2O, 0.5 wt% Pt and superconductor ($GdBa_2Cu_3O_{7-\delta}$ (Gd123): Gd_2BaCuO_5=1:0.4 (Gd211) = 1:0.4). HTS bulk magnet has non-uniform magnetic field distribution which was characterized by a steep magnetic gradient. Using a magnetic force of the vertical component of the HTS bulk magnet, the pellet was separated by levitation force.

6. RESULTS AND DISCUSSIONS

The result is shown in Fig. 6. It was confirmed that both 1, 6-DDA and 1, 10-DDA in the medium, which were at the bottom of glass vessel, were floated by applying the magnetic field. Moreover, it was confirmed that the levitation height is different between 1, 6-DDA and 1, 10-DDA. It was confirmed that the buoyancy force by Magneto-Archimedes effect acts on both the structural isomers and its magnitude is different. However, the calculation result showed that the difference of levitation height between 1, 6-DDA and 1, 10-DDA was 6 mm, whereas actual difference in height was about 15 mm. The levitation height of 1, 6-DDA was higher than that of the calculation result. The reason is considered that the error caused by the actual and calculated magnetic field product was relatively large, because the absolute value of magnetic field product was as small as 10 T^2/m at the levitation position.

7. CONCLUSION

In this study, separation of structural isomer by Magneto-Archimedes method was examined. As a result, we succeeded to separate structural isomers, 1,6-DDA and 1,10-DDA, by the difference of levitation height. In view of practicality, it is necessary to separate the mixture of fine powder particles. Powdered materials have a problem that tends to aggregate in the solution. It is necessary to eliminate the aggregation to separate the powdered mixture. Currently, we are examining to resolve the aggregation by pH adjustment of the medium and controlling the surface charge of the powder. In future, we would like to expand the applicable scope of Magneto-Archimedes method to powder or other structural isomers.

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