

# Development of a new process using combustion technology

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## Abstract

Flame spray pyrolysis technology makes use of the high chemical activity of a flame. A metal salt aqueous solution is used as the material to be treated and is atomized into a furnace by high pressure spraying. The solvent in the sprayed minute liquid droplets evaporates, pyrolysis occurs, and then solid particles are generated. We focused on the spray pyrolysis method for preparation of  $\text{LiMn}_2\text{O}_4$  for use as the positive poles of lithium-ion secondary batteries. We utilized a gas combustion system as the heat source that is characterized by the fact that its operation costs can be much less than that of conventional electric heating systems. On the other hand, in-flame treatment technology uses the high-temperature environment within a flame. In this method, the material to be treated, fine metal and ceramic powders, is introduced directly into an oxygen flame to be melted. The technology related to in-flame melting of silica, which has already been established, is a typical example of this type of technology, which is based on the principle that a material is melted within a flame and spheroidized as a result of its surface tension. Use of a fine powder as the material to be treated enables wide application of this technology.

Key words: powder, flame system, spray pyrolysis, lithium-ion battery, spheroidizing, silica

## 1. Introduction

The rapid progress of high technology demands that materials have new and diverse features. Powders are deeply involved in the creation of materials that have new features. In particular, technologies related to production of powders that have desirable properties and for production of materials through sophisticated control of these powders are considered to be key technologies in present day material development. Furthermore, in the field of ceramics especially, development of material particle refinement technologies has led to nanotechnology becoming the cornerstone of material development.

In our research and development, we do not use combustion technology, a flame, as a conventional heat source, but instead directly apply the combustion energy of the flame to drying, pyrolysis, solid-phase reaction and melting of the material to be treated in order to apply this energy to production technologies related to development of new materials.

The advantages of directly applying a flame to powder production are as follows:

- 1) The production costs when directly applying combustion energy to the powder production process can be reduced compared with that when electric energy, such as plasma, is used.
- 2) Productivity can be improved by instantaneous treatment.
- 3) High melting point materials can be melted.
- 4) Processing that involves chemical reactions, such as pyrolysis and solid-phase reactions, can be carried out.
- 5) Treatment is performed continuously, and the material to be treated is processed in a floating state, that is, in a non-contact state, whereby incorporation of impurity can be prevented.

This paper provides a general outline of the equipments and powder properties related to development of facilities for production of the positive poles of lithium-ion secondary batteries using flame spray pyrolysis technology as the built up process (a method for congregating molecules or ions using chemical reactions and adjusting fine powder). It also provides a general outline of the facilities required for spheroidizing silica using in-flame treatment technology as an upgraded technology of the break down process (a method for pulverizing solid lumps and adjusting fine powder).

## 2. Flame spray pyrolysis technology

-- the positive poles of lithium-ion secondary batteries --

### 2-1. Background

Compared with conventional lead and nickel-hydrogen batteries, lithium-ion secondary batteries can be of higher capacity and more highly miniaturized. These batteries are mainly used in mobile devices, such as cell phones and PCs. Research on enhancing the features and outputs of batteries is being actively conducted to produce batteries that are larger and mountable on automobiles and such. Furthermore, in recent years, improvement of the performance of positive pole powders has led to an increase in the importance of development of low-cost mass production technologies. We focused on the spray pyrolysis method, which is a liquid phase method, and adopted the gas combustion system as its heat source, the operation of which can cost much less than that of an electric heating system.

## 2.2 Principles

A material solution of lithium-manganate is sprayed into a high-temperature field. The solvent in the liquid evaporates in the high-temperature environment at the treatment temperature or more, and the target substance reacts with the gas in the environment and pyrolytically decomposes, producing solid particles (FIG. 1). In conventional spray pyrolysis in the laboratory, supersonic spraying is frequently used as the solution spray method, and the heating system used is frequently an external electric heating system that uses an easy-to-handle ceramic muffle. However, since the flow rate capability of the supersonic oscillator is approximately  $0.2 \text{ dm}^3/\text{h}$ , supersonic spraying is not suited for large-capacity spraying in an industrial scale. Furthermore, the operation costs of the electric heating system are greater, and the uniformity of the temperature distribution cannot keep when a large reaction vessel is used for production. This may result in occurrence of ununiformity in the material temperature history. On the other hand, the present system utilizes a two-fluid nozzle in a furnace to spray a large amount of solution, a flame is introduced directly, and the combustion reaction heat is directly applied to drying and pyrolysis in order to improve production capability.

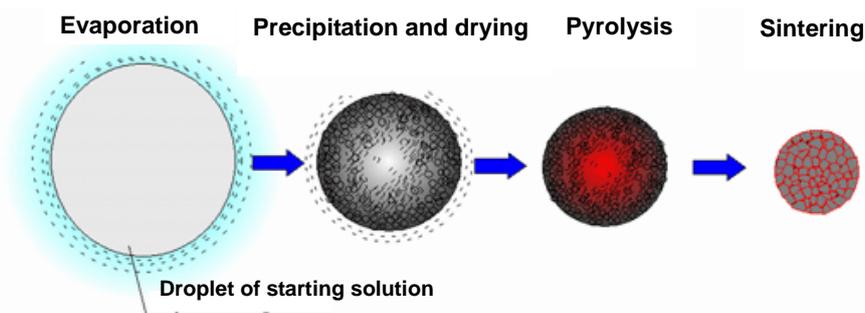


FIG. 1 Principles of the spray pyrolysis method

## 2-3. Test equipment

FIG. 2 is a general view showing the test equipment used in the present research, and FIG. 3 is a photo showing a cross section of the interior of the furnace. This equipment is consisted of a material atomizer, burners, a furnace body, a collector, and a suction fan. The material to be treated is dissolved in a solution, and this solution is atomized into particles using the material atomizer (two-fluid nozzle). The particles are introduced into the furnace, which is heated using the burner flame, in such a manner that they are instantaneously occurred to drying, pyrolysis, and solid-phase reaction in order to obtain powder. The combustion gas generated in the furnace is separated from the powder using the collector (bag filter) and is discharged out of the system.

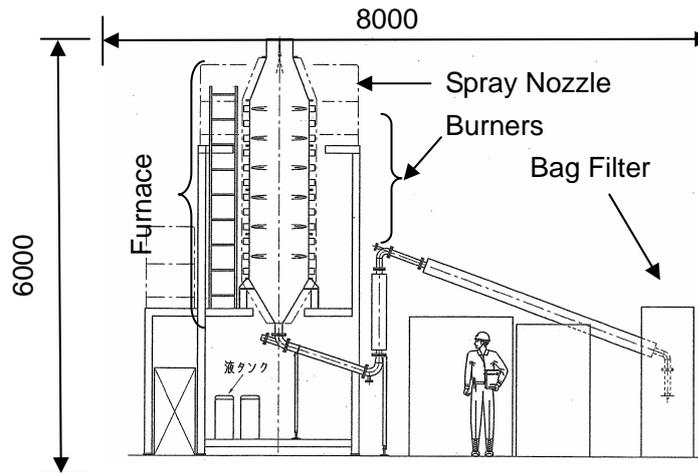


FIG. 2 General view of the test equipment

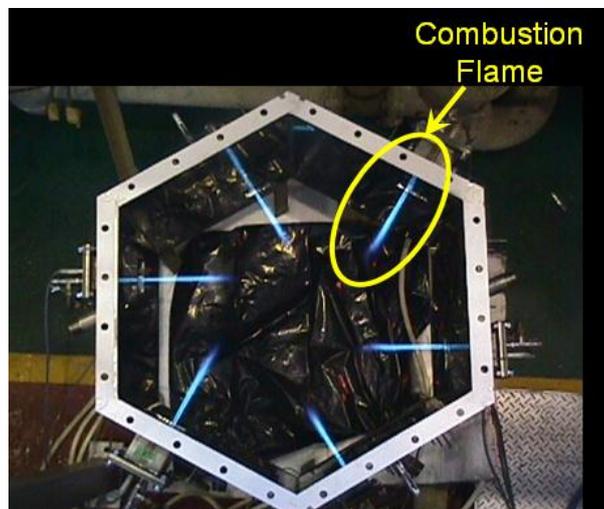


FIG. 3 Photo of a cross section of the interior of the furnace (taken from the top of the furnace)

#### 2-4. Test conditions

The various test conditions, such as the combustion conditions, are described below.

- 1 ) Combustion gas: propane ( $H_L = 91.3 \text{ MJ/m}^3\text{N}$ )
- 2 ) Combustion support gas: air
- 3 ) Combustion capacity: 45 kW
- 4 ) Material solution to be treated:  $\text{LiNO}_3 + \text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  ( $1.0 \text{ mol/dm}^3$ )
- 5 ) Material solution spray rate:  $4 \text{ dm}^3/\text{hr}$
- 6 ) Furnace temperature: Max. 850K

The powder produced by this equipment was analyzed as described below.

- 1) Crystal structure analysis using an X-ray diffractometer (XRD Shimadzu XRD-6100)
- 2) Shape recognition using an electron microscope (SEM Hitachi S-2400)

The average particle diameters of 100 randomly selected particles were visually measured using SEM photos.

## 2-5. Results and discussion

FIG. 4 shows the XRD patterns of  $\text{LiMn}_2\text{O}_4$  produced using (a) the present method (two-fluid nozzle spraying + flame system) and (b) the conventional method (supersonic spraying + external electric heating system). Based on the obtained results, no significant differences were observed between the two methods. The pyrolysis temperature set for the external heating system was approximately 1050K. We were able to obtain similar powder at approximately 750K using the present system. We believe this was because the amount of heat necessary for drying and pyrolysis was applied instantaneously when the sprayed solution passed near the localized flame (at 1250K or more) within the furnace.

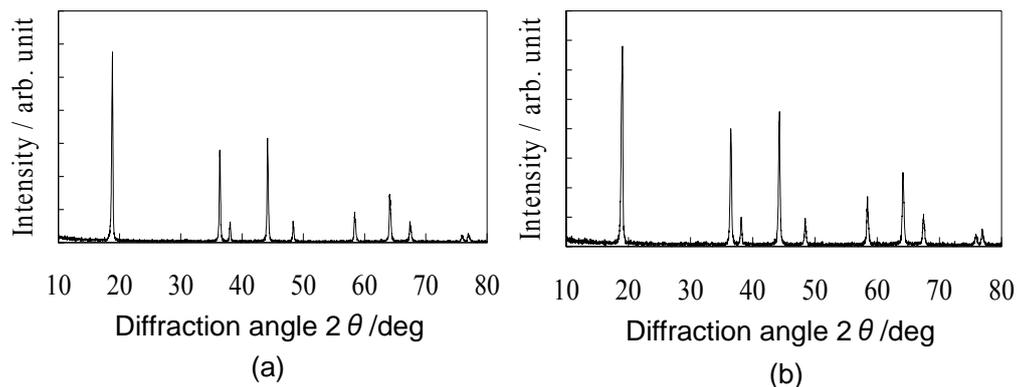


FIG. 4 XRD patterns of  $\text{LiMn}_2\text{O}_4$  at  
(a) The present method (two-fluid nozzle spraying + flame system)  
(b) The conventional method (supersonic spraying + external electric heating system)

FIG. 5 shows SEM photos of the  $\text{LiMn}_2\text{O}_4$  produced using this equipment. Based on the obtained results, the  $\text{LiMn}_2\text{O}_4$  was monodispersed and spherical and had an average particle diameter of approximately  $6 \mu\text{m}$ . Furthermore, the obtained fine powder was made up of secondary particles that were consisted of nano-sized cohesive primary particles.

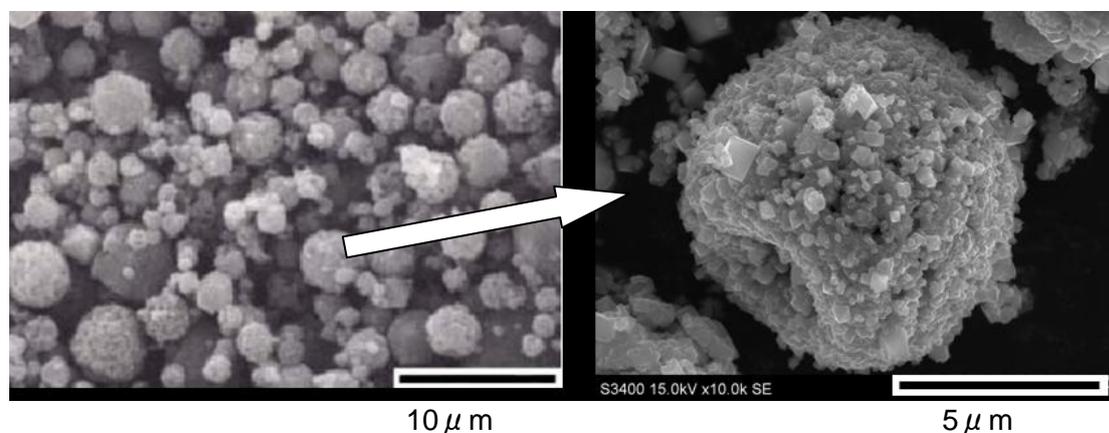


FIG. 5 SEM photos of  $\text{LiMn}_2\text{O}_4$

FIG. 6 shows the results obtained when lithium-ion batteries were produced and their discharge cycle performances were examined; the positive poles of the batteries were made from powder produced using (a) the present method (two-fluid nozzle spraying + flame method) or (b) the conventional method (solid reaction method). Based on the obtained results, increasing the discharge load (from 0.2C to 5C) resulted in improvement of the discharge maintaining ratio from 60% to 87% for the present method in comparison with that for the conventional production method. We believe that this was because lithium separation from and insertion into the electrolyte were simplified as a result of the larger specific surface area of the powder produced using the present method compared with that of the powder produced using the conventional method and that this resulted in lower internal resistance. This means that the powder produced using the present method is suitable for use as the battery materials for automobiles and such, which require quick charge/discharge performances and which are subject to large load fluctuations.

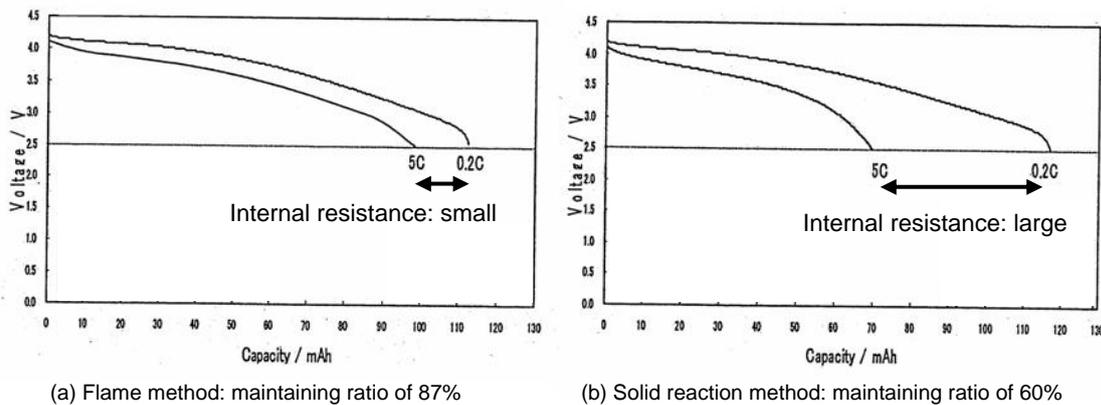


FIG. 6 Discharge cycle performances of  $\text{LiMn}_2\text{O}_4$  at  
 (a) The present method (two-fluid nozzle spraying + flame method)  
 (b) The conventional method (solid reaction method)

### 3. In-flame treatment technology -- spheroidizing of ceramic powder --

#### 3-1. Background

There are various uses for fine ceramics at present, and use as sealant fillers for semiconductors, one of these uses, is important. Due to rapid development of the semiconductor industry in recent years, the importance of sealant fillers and the demands for improved features are continuously increasing. One of these features is shape, and the sphere is the predominant shape at present. This is because spheroidizing improves fluidity and filling density. Although the plasma and

granulation methods are known methods of production, these methods are high in cost, and therefore the predominant method at present uses flame fusion.

### 3-2. Principles

The principle of the present process is that when pulverized powder is introduced into a high-temperature flame, the temperature of each particle reaches its melting point or more; this results in the particle melting, liquefying and becoming spherical in shape as a result of the surface tension of the particle itself. The time taken until each particle reaches its melting point can be approximated by the following expression (1).

$$\tau_m \doteq 0.84 \frac{C \rho D^2}{\lambda} \ln \left( \frac{T_f - T_0}{T_f - T_m} \right) \dots\dots \text{Expression (1)}$$

$\tau_m$	: time to reach the melting temperature
C	: specific heat of the particle
$\rho$	: density of the particle
D	: diameter of the particle
$\lambda$	: heat conductivity of the particle
$T_f$	: temperature of the flame
$T_0$	: original temperature of the particle
$T_m$	: melting temperature of the particle

As described above, since the in-flame residence time of the material cannot be controlled as desired during in-flame treatment, the time to reach the particle melting point indicated in the above expression is very important. Although the main parameters in the expression are the properties of each particle, it is understood according to the above expression that the parameter most affecting the time to reach the melting point is particle diameter. FIG. 7 shows the relationship between the particle diameter and the time to reach the melting point for silica and alumina when the flame temperature is 2500K. As clearly shown in this figure, the larger the particle diameter, the longer the particle takes to melt. However, since the flame length and volume are limited, attention must be paid to the diameters of primary particles in the present process.

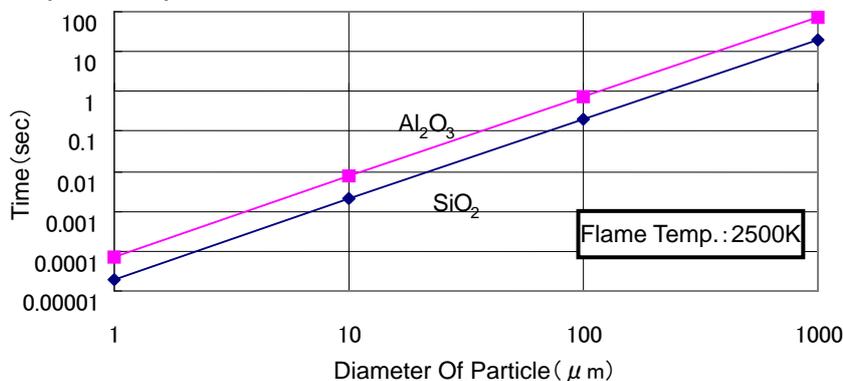


FIG. 7 Relationship between particle diameter and time to reach the melting temperature

### 3-3. Test equipment

FIG. 8 is a general view showing the test equipment that was used in the present research, and FIG. 9 is a photo showing a full view. This equipment is consisted of a material feeder, burner, furnace body, collector, and suction fan. The pulverized material powder is fed from the material feeder (table feeder) to the burner and then introduced from the tip of the burner nozzle into a high-temperature flame produced by oxygen combustion. The powder passes through a melting zone that is surrounded by a refractory material, which is used to reduce the amount of heat radiated by the flame produced by oxygen combustion. It then passes through a cooling zone that has a water-cooling jacket structure and that is used to cool the high-temperature gas and powder to be treated. The powder is then collected using the collector (bag filter). Furthermore, the combustion gas generated in the furnace is separated from the powder using the collector (bag filter) and then discharged out of the system.

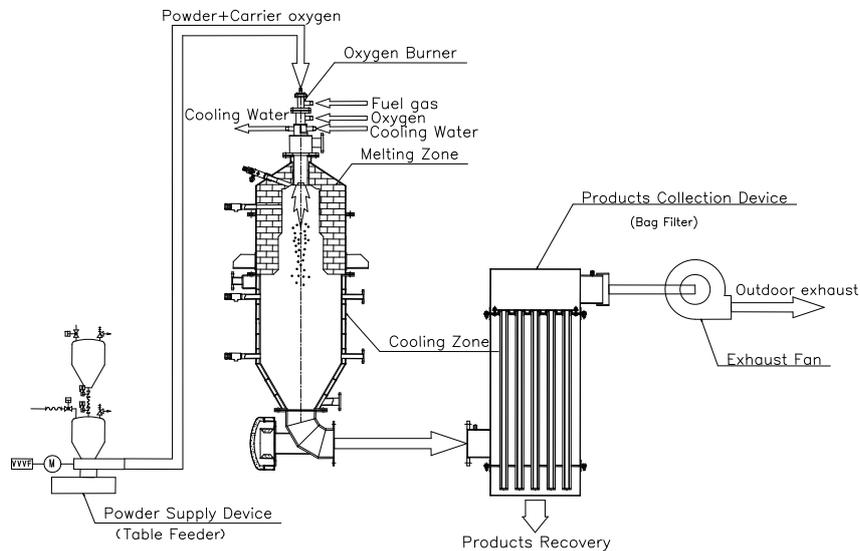


FIG. 8 General view of the test equipment



FIG. 9 Full view of the test equipment

### 3-4. Test conditions

The various test conditions, such as the combustion conditions, are described below.

- 1) Combustion gas: natural gas ( $H_L = 40.6 \text{ MJ/m}^3\text{N}$ )
- 2) Combustion support gas: pure oxygen
- 3) Combustion capacity: 110 kW
- 4) Powder material to be treated: silica (average particle diameter:  $5 \mu\text{m}$ ,  $10 \mu\text{m}$ ,  $17 \mu\text{m}$ )
- 5) Supply rate of powder material: 10 kg/hr
- 6) Furnace temperature: 1550K (melting zone)

The powder was also analyzed before and after spheroidizing treatment as described below.

- 1) Its shape was checked using an optical microscope (Leica DMLM).
- 2) The average particle diameter and particle size distribution were measured using a particle size distribution analyzer (Shimadzu SALD-3000J).
- 3) The angle of repose was measured using a powder tester (Hosokawa Micron PT-R).

The spheroidizing ratios of 100 randomly selected particles were visually measured using optical microscope photos.

### 3-5. Results and discussion

FIGS. 10 and 11 show optical microscope photos of the powder material and the powder spheroidized using this equipment, respectively. Based on these photos, it is evident that the pulverized shape of the material particles became nearly spherical in shape after the spheroidizing treatment.

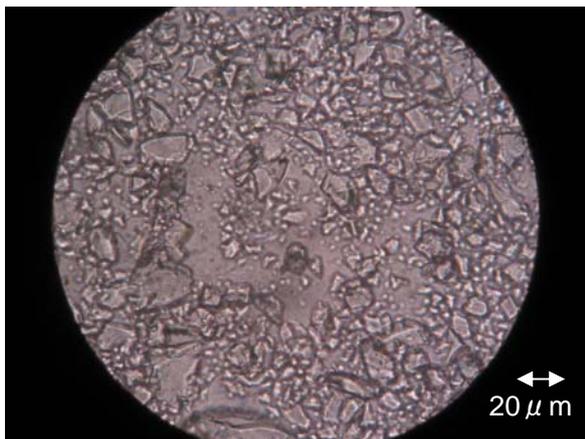


FIG. 10 Optical microscope photo of the powder material (Sample No. 2[Silica], magnification: 1000)

FIG. 11 Optical microscope photo of the spheroidized powder (Sample No. 2[Silica], magnification: 1000)

TABLE 1 shows the results of analysis before and after the spheroidizing treatment, and FIG. 12 shows the measurement results for the typical particle size distribution. The average particle diameter of the powder obtained after the

treatment tended to be slightly larger than that of the powder material. This phenomenon was most notably observed when the particle diameter of the material was small. We believe that this was because the particles melted in a cohesived state as a result of the fact that particles cohere more easily when their material particle diameter is smaller; this results in formation of large spheroidized particles. Moreover, based on the results for the angles of repose before and after the treatment, we were able to determine that the spheroidizing treatment using this equipment significantly improved fluidity.

TABLE 1 Results of analysis before and after the spheroidizing treatment

		Sample 1		Sample 2		Sample 3	
		Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment
Average particle diameter	$\mu\text{m}$	4.7	9.8	8.5	11.2	17.7	16.7
Spheroidizing ratio	%	—	98.0	—	99.7	—	99.5
Angle of repose	$^{\circ}$	43.7	43.5	50.1	38.9	52.2	30.2

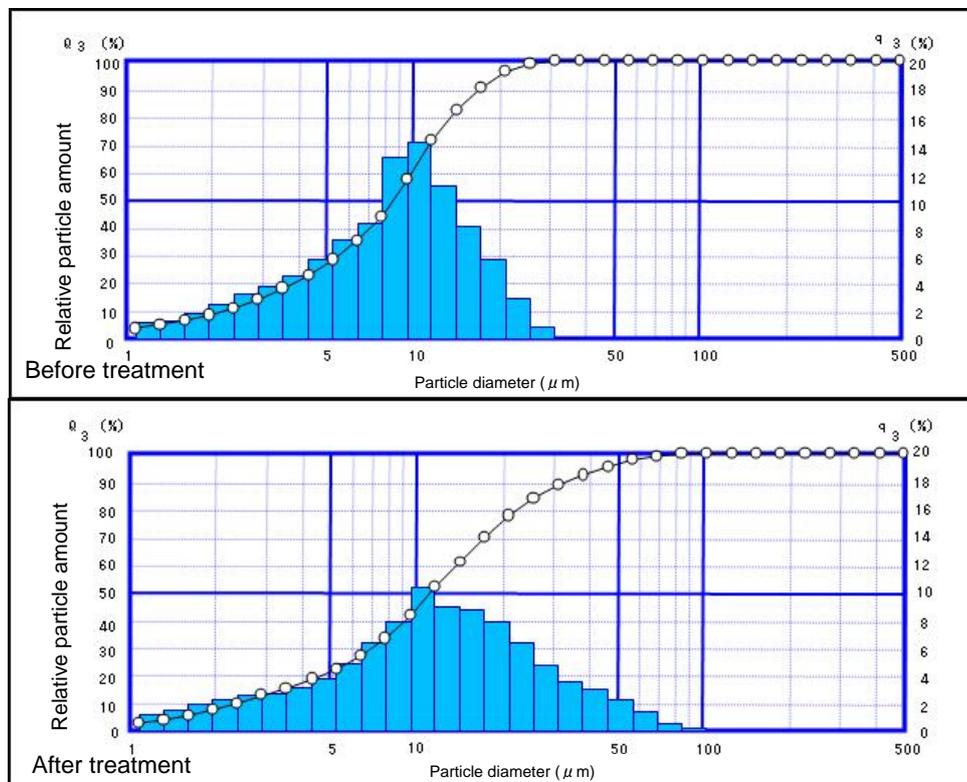


FIG. 12 Measurement results for particle size distribution before and after the spheroidizing treatment (Sample No. 2[Silica])

#### 4. Conclusion

The present report describes the activity taking place at our company with respect to flame spray pyrolysis and in-flame treatment technologies, which make use of combustion technology. Powders and particles are utilized in various fields, and the requirements for performance and the features of these materials are widening in scope and becoming more precise. Although various methods for producing these materials are being researched and developed extensively, there are various problems for these methods in application to actual industrial situations. With some of these types of activities, there are frequently problems with industrialization even when they have been established in terms of their process. In the two processes described herein, the combustion technology was not used as a mere "heat source" but was instead used such that the flame functioned more actively for the material to be treated. This means that the present method can be applied to fields in which conventional methods cannot be applied, and the present method has the potential for application to various fields of powder production. Establishment of the present technology makes it possible to continuously and efficiently produce sophisticatedly controlled powders. We believe that it is important to accumulate a diverse range of data through further development and to flexibly meet the advancing needs of the market in the future.

#### 5. References

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