

Establishment of compact processes

— Integration of high-pressure micro-engineering and supercritical fluid —

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In order to realize sustainable development, it is anticipated that industrial structure, social and technical systems based on large-scale production at concentrated sites must be changed in the near future. Establishment of highly controllable compact processes with high-speed reaction is desired to realize distributed production with multi-purpose low-volume production. Integration of high-pressure microengineering and supercritical fluid has received considerable attention as a core technology for compact processes. To realize the technology, basic developments for high-pressure microengineering such as rapid heat exchange and precise temperature control were firstly needed, and then process developments on basic engineering followed. As applications of compact processes, organic synthesis under supercritical water is discussed, and inorganic synthesis and an innovative coating process using supercritical carbon dioxide are also described.

Keywords : Low-volume production at distributed sites, compact process, micro-reactor, supercritical fluid, rapid heat exchange

1 Background and objective of the research

The large-scale production at concentrated sites that forms the core of the chemical industry has significantly raised the modern living standard, and brought great wealth in the latter half of the 20th century. By using this method, the product cost was decreased dramatically, and excellent products became reasonably available to many people. In general, the production cost is said to increase approximately at the power of 0.6 of the production volume. According to this rule of scale-up, the production cost for 1,000 yen/kg will become 10 yen/kg at a production scale 100,000 times greater ($10^{5 \times 0.6} \div 10^5 = 10^{-2}$). The dramatic economic impact of the large-scale production at concentrated sites lead to the expansion (scaling up) of production scale in various fields. However, this system assumes the one-directional use of a large amount of fossil resources, it is extremely difficult to create a material cycling system since it is difficult to balance the recovery and reuse. On the flip side to mass-production, there were the issues of mass consumption (depletion) of fossil resource, immense energy consumption due to the global transportation of fossil resource, and generation of substantial wastewater and waste products. These are inducing various environmental problems such as global warming and organic pollutant contamination.

In order to realize sustainable development, it is anticipated that industrial structure, social and technical systems based on large-scale production at concentrated sites dependent on fossil resources must be changed in the near future. Specifically, it is essential to create a safe, flexible, and efficient process with low environmental load, where cycling of resource and energy can be done easily, and the use of

recyclable resources such as the biomass should be set at the core. This means the realization of distributed production with multi-purpose low-volume production. To achieve this, establishment of highly controllable compact processes with high-speed reaction is desired. The compact process here means a safe, flexible, and efficient process with low environmental load, where the cycling of resource and energy can be done easily. It also must have high-speed and highly controllable performance, enabling low-volume production at distributed sites.

The microreactor is gaining attention as the core technology of the low-volume distributed production due to its compactness and the precise controllability of its reaction field^[1]. In general, it is a device for conducting chemical reaction in a microspace of width from a few μm to a few hundred μm . It is categorized into the microreactor, micromixer, and micro heat exchanger according to its purpose and function. The microreactor has large surface area per unit volume (specific surface area), and therefore has extremely high heat exchange efficiency, and allows rapid temperature operation (heating and cooling) and precise temperature control. The large specific surface area of the reactor means that the reaction occurs at the interface efficiently. Also, since the micro flow channel has short diffusion distance, mixing by molecular diffusion occurs rapidly, and high-speed and efficient mixing takes place. These characteristics fulfill the conditions (high speed and high controllability) required in the compact process. However, the conventional microreactor is composed largely of materials that can be processed easily such as silicon, glass, and plastic, and cannot be used in high-temperature and/or high-pressure conditions, where the property of the

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microreactor can be taken advantage of more efficiently. Currently, the technology for a microreactor that can withstand high-temperature or high-pressure has not been established.

On the other hand, the supercritical fluid is defined as a fluid above its critical point (endpoint of saturated vapor pressure curve), and is called the fourth fluid that does not belong to the three phases of substance: solid, liquid, or gas. However, it is not very special, but is a non-condensable fluid that does not liquify even when compressed to high density. The density of the supercritical fluid can be changed continuously and at great range from gas to liquid equivalent by changing the temperature and pressure, and the transport properties such as viscosity and diffusion coefficient, and solvent properties such as dielectric constant and ion product greatly change accordingly^{[2][3]}. Particularly, the dielectric constant of the supercritical water, which is a state over its critical point (374 °C, 22 MPa), is like an organic solvent, and is considered to be the only stable reaction solvent at high temperature. Also, the ion product can be increased to 10^{-10} , and the supercritical water is expected to take the role of acid or base catalyst. Such properties imply the application of the supercritical water in high-speed chemical reaction, and the technology using supercritical water is expected to become the core technology of the low-volume distributed production.

2 Integration of the microreactor and supercritical water

Until about 2002, the common knowledge was that in the chemical process using supercritical water or high-temperature and high-pressure water, the decomposition of organic compounds (by hydrolysis and pyrolysis) was possible, while synthesis was not^[4]. In fact, although the acid and base properties, which were not present in regular water, were observed in the supercritical water from physicochemical or spectroscopic studies, the results always produced none or very low yield of the target substance when organic synthesis experiments under supercritical water

Table 1 Synthesis of ϵ -caprolactam using supercritical water (experiment result)

The yield was low in the batch reaction, but high yield was achieved in the continuous microreaction. Difference due to reaction time (including heating time) was significant.

Apparatus	Reaction temperature (°C)	Reaction pressure (MPa)	Reaction time (sec)	Yield (%)
Batch reaction	400	40	180	1.9
Continuous microreaction	400	40	0.625	83.0

condition were conducted using the batch reaction device^{[5]-[7]}. From these results, the use of supercritical water in organic synthesis was thought to be extremely difficult, and the research for the application of supercritical water fell into stagnation (the valley of death) for a while. Research funds declined and we had no alternative but to continue to conduct reactions by self fabricating a lab-scale flow reactor using old pumps for liquid chromatography and used-up high-pressure tubes. Suddenly, we found that the yield increased. When we observed closely, we understood that the reason that the target product could not be obtained before was because the breakdown and side reactions of the raw material or the target product occurred in the heating range (cooling range) if long heating (or cooling) time was taken to achieve the reaction temperature, even though the reaction time at the reaction temperature was controlled carefully. From this moment, our research moved forward rapidly^[8]. Figure 1 shows the conceptual diagram of the importance of the rapid heat exchange in this reaction. The example of the reaction that prologued the organic synthesis under supercritical water condition will be described below.

The synthesis of ϵ -caprolactam, a material for nylon, is conventionally done by the Beckmann rearrangement reaction of cyclohexanone oxime using concentrated sulfuric acid as an acid catalyst. However, in this synthesis, the concentrated sulfuric acid must be neutralized by ammonia, which generates large amount of ammonium sulfate, and its disposal is a major environmental and economic issue. We suggested a method of Beckmann rearrangement reaction using the acid catalyst property of the supercritical water^{[5][8]}. The result of the

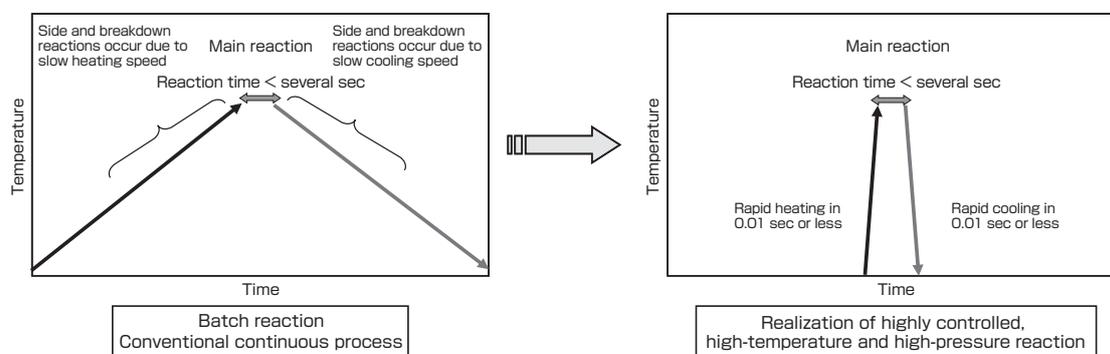


Fig. 1 Points in the development of organic synthesis using supercritical water (need of rapid heat exchange)

Since the supercritical water has high reactivity, side reactions and breakdown reactions occur and inhibit the main reaction if too much time is spent on heating or cooling. Rapid introduction and withdrawal from the reaction field is necessary.

experiment is shown in Table 1. The reaction conditions were the same at 400 °C and 40 MPa, but the yield was a few % in the batch process, while the yield increased dramatically to 80 % or more in the continuous microreaction. This difference was due to the reaction time (here, it is the time required to increase from room temperature to reaction temperature + retention time at reaction temperature). In the batch process, the heating speed was very slow, and cyclohexanone oxime was broken down to cyclohexanone in the heating process. In contrast, since the heating was done by mixing the supercritical water directly with the raw material in the continuous microreaction, the reaction temperature could be reached in an extremely short time, the Beckmann rearrangement became the predominant reaction, and the ϵ -caprolactam was synthesized at high yield. This showed that the effect could be achieved by combining the microreaction field and supercritical water, and would have not been achieved by each alone. This was a result of the integration of supercritical water and microreaction field in the organic synthesis reaction. Several experimental investigations were done on the ranges for high-temperature and high-pressure water below the critical point, in addition to supercritical water, and the possibilities of organic synthesis using water became realistic. The issues after this included the efficient realization of rapid introduction of raw material into the reaction field (rapid heating) and the rapid withdrawal of the product from the reaction field (rapid cooling).

3 Establishment of the high-temperature high-pressure microdevice and high-pressure microengineering

To achieve the rapid heat exchange (rapid heating and rapid cooling) discussed in the previous chapter, it was necessary to develop the direct heat exchange method employed for the ϵ -caprolactam synthesis or an extremely highly efficient indirect heat exchange method. In the direct heat exchange, heating to the target temperature is achieved by the direct mixing of the raw material at ordinary temperature and supercritical water, and cooling to the necessary temperature (where the reaction stops) is done by directly mixing the cooling water with the high-temperature and high-pressure reactants. The necessary temperature and mass flow of the supercritical water and the cooling water are determined by the heat balance calculation. The rate of heat exchange in the direct heat exchange is dependent on the performance of the mixer since it is determined by how the material and the supercritical water, or the high-temperature and high-pressure reactant and the cooling water are mixed to reach the equilibrium temperature. Therefore, the direct heat exchange method results in the development of the high-pressure micromixer capable of rapid mixing. On the other hand, to what extent rapid heat exchange is possible in the indirect heat exchange method will be explained later based on the heat transfer concept.

3.1 High-pressure micromixer (direct heat exchange method)

When the high-pressure micromixer is used as the heat exchange device for the supercritical water reaction, the turbulent condition with high Reynolds number can be readily applied since the supercritical water has 1/10 or smaller of viscosity coefficient compared to the ordinary temperature values, and high flow rate can be applied. In the micro device operation under the ordinary pressure condition, the flow rate must be kept low since the pressure drop cannot be large because of the reactor material (glass or plastic). However in the high-pressure micro device operation, high flow rate condition is possible since there is relatively greater allowance for pressure drop that occurs in the mixer. Therefore, the high-pressure micromixer employs the mixing method based on forced turbulence, and has different mixing method compared to the conventional micromixer where the dispersal is controlled by the laminar condition. The mixer structures include: the commercially available T-shaped mixer; swirl mixer that actively utilizes the swirl flow; and the central collision mixer where the two fluids collide in the mixing chamber. As examples of T-shaped mixers, Fig. 2 shows the standard type SS-100-3 (STD TEE) and low dead volume type SS-1F0-3GC (LDV TEE) of the Swagelok Company. Compared to the internal flow channel diameter of 1.3 mm of the STD TEE, the internal channel diameter of the LDV TEE is only 300 μm , and good mixing result based on large Reynolds number (turbulence effect) has been reported^[9].

The CFD (computational fluid dynamics) simulation results of the two types of mixers are shown in Fig. 3 as the comparison and evaluation of the mixing performance. The calculation conditions were: pressure was constant at 30 MPa; supercritical water was supplied at 463 °C, 33 g/min; raw material at 15 °C, 12 g/min; and the temperature after mixing was 400 °C. The property data of water at 30 MPa were used for the calculations. The Reynolds numbers of the STD (inside diameter of 1.3 mm) and LDV (inside diameter of 0.3 mm) at these conditions were 16,700 and 72,500, respectively. In Fig. 3, in the STD,

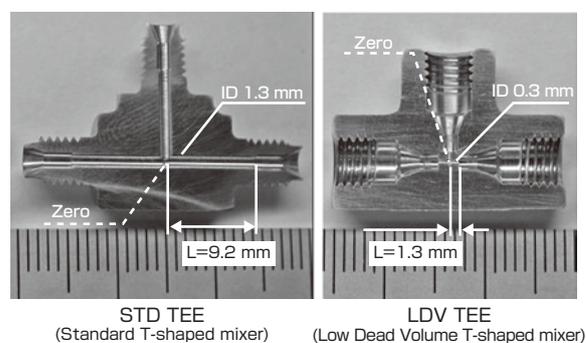


Fig. 2 T-shaped mixers (STD, LDV)

The commercially available 1/16 inch T-shaped mixer (left is the standard type, and right is the micro type of inside diameter 0.3 mm mixing flow channel).

the low-temperature fluid that flows in from the bottom part is mixed with the supercritical water that flows from the left, a temperature transition zone is formed at the bottom of the flow channel, and a temperature gradient forms within the flow channel. On the other hand, in the LDV, the homogeneous temperature fluid is formed in the micro flow channel with inside diameter of 300 μm and length of 1.3 mm, and quick fluid mixing is achieved. Figure 4 shows the plot of the maximum and minimum temperatures in the vertical cross sections from the center of the mixer to the downstream direction of the mixed fluid. It can be seen from the figure that the temperature difference is shown at the mixer exit in the STD (9.2 mm from the mixing point), while the temperature is homogenized rapidly at the mixer exit that is only 1.3 mm from the mixing point in the LDV. Estimating the average heating rate in the flow channel, the STD is 31,000 $^{\circ}\text{C}/\text{s}$ while LDV is 270,000 $^{\circ}\text{C}/\text{s}$, and there is a 9 times difference. The difference in the heating rate, or the mixing rate, indicates that it is possible to precisely control the delicate synthesis reaction in which side reactions may occur.

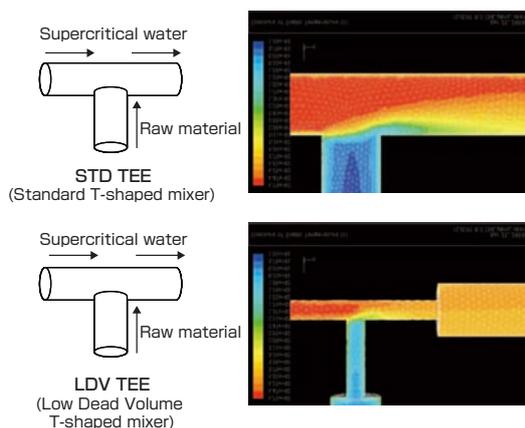


Fig. 3 Result of the CFD simulation of fluid mixing using the T-shaped mixer (temperature contour diagram)

In the STD TEE, the temperature was not even at the exit (length 9.2 mm from mixing point) of the mixer, while in the LDV TEE, mixing was almost entirely even at the exit (length 1.3 mm from mixing point) of the micro flow channel.

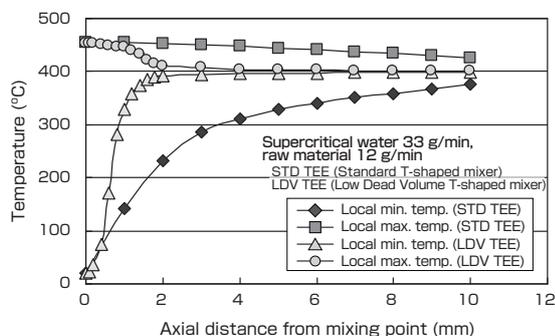


Fig. 4 Temperature profile of fluid after mixing

The temperature did not converge in the STD TEE, while it rapidly evened out in the LDV TEE.

Figure 5 shows the photograph of the micro swirl mixer that we developed and the result of the CFD simulations^[10]. The raw material at ordinary temperature is supplied from the left, and supercritical water divided into two is supplied at 60° angle from the central axis. Further, the supercritical water is connected eccentrically and mutually from the center of the mixer, and the swirl flow can be generated by the divided supercritical water at the center of the mixer. The raw material is given the inertial force in the circumferential direction as well as the axial direction by the swirl flow, and it is considered to enhance the mixing performance. In the T-shaped mixer, a vortex is formed at the bend as the fluid makes a right angle turn. Since this vortex region may cause accumulation, the increase of unexpected retention time is a concern. On the other hand, in the micro swirl mixer, the accumulation region does not form in the center of the mixer since the mixed fluid is rotating and flowing out at all times. The central collision mixer shown in Fig. 6 is composed of the raw material supply channel with a needle that moves up and down in the upper part (the raw material is introduced through the thin film channel along the exterior surface of the needle) and the fluid mixing chamber with several supercritical water streams in the bottom part (central collision area), and is capable of realizing quick mixing and heating^[11]. The raw material is not affected by the heat transfer from the supercritical water (due to the cooling effects by the cooling medium in the inner tube of the needle, the radiation effect by the air cooling fin, and the heat transfer limitations by a small metal seal ring), and is introduced into

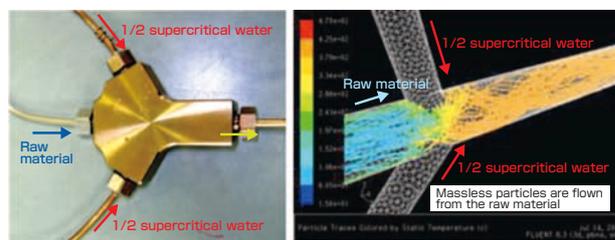


Fig. 5 Photograph of the micro swirl mixer and the result of the CFD simulation (flow line of raw material)

The supercritical water is mixed with the raw material by forming a swirl flow by dividing the supercritical water. The structure prevents the generation of vortex of the T-shaped mixing.

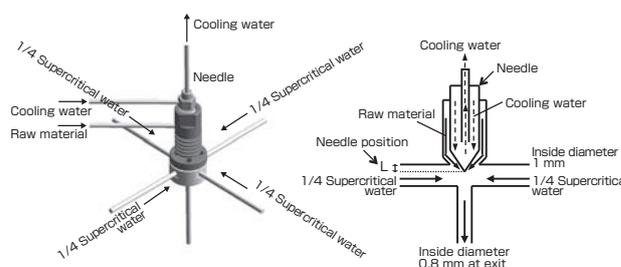


Fig. 6 Central collision mixer

The supercritical water is divided into four, and the raw material is introduced from the top into the central collision section. The needle is inserted from the top to allow adjustment of the mixing state.

the mixing field at almost the ordinary temperature without preheating. In this mixer, the needle length can be changed continuously in the fluid mixing section to control the mixing performance.

3.2 High-pressure micro heat exchanger (indirect heat exchange method)

The heat exchanger in the supercritical water reaction operation plays the role of a heater to achieve rapid temperature increase to reaction temperature, and as a cooler for rapid cooling to temperature range where the reaction stops. The high-pressure micro heat exchanger will basically use a high-pressure microtube from the perspective of pressure resistant design, and the inside of the tube will be used as the microspace. As mentioned earlier, since some degree of pressure drop is allowed in the supercritical water process, the mass flow can be set high. Therefore, the inside of the microtube will be in a severely turbulent condition (high Reynolds number), and extremely high values can be expected for the inside heat-transfer coefficient of the tube (heat receiving side, low temperature side). The issue will

be how high the outside heat-transfer coefficient of the tube (heat giving side, high-temperature side) can be attained. In a general supercritical water manufacturing equipment, the convection and radiation heat transfers from the electric nichrome wire furnace are used as heating source. However, the outside heat-transfer coefficient of the tube, which is the rate at which the heat from the red-hot nichrome wire furnace transfers to the outer surface of the microtube, is extremely small, and that limits the overall rate of heat transfer (overall heat-transfer coefficient).

We proposed a heating method for the high-pressure microheater where the joule heating is done by passing electricity through the microtube itself^[12]. If this method can be employed, the outside heat-transfer coefficient of the tube can be considered apparently infinite, and the heat transfer can be determined by the metal heat transfer resistance and the inside heat-transfer coefficient of the tube. There are two methods to electrify the microtube: electromagnetic induction and direct energization method. In the electromagnetic induction method, it is necessary to install the induction coil on the exterior and is limiting in terms of downsizing, and therefore we selected the direct energization method. Figure 7 shows the schematic diagram of the high-pressure microheater using the direct energization method (tube dimensions: inside diameter of 0.25 mm, outside diameter of 1.6 mm, length of 200 mm), and Fig. 8 shows the evaluation results. The heat transfer property improved as the flow of supplied pure water increased, and this is because the inside heat-transfer coefficient of the tube increases due to the flow increase. The overall heat-transfer coefficient was maximum 10,000 W/m²·°C and the heat efficiency was 95 % or higher, and an extremely efficient heating was realized. Converting this into the rate of temperature increase, it will be maximum 150,000 °C/s. This shows that the water can be heated to critical temperature or above in a few milliseconds, and is a result that matches the temperature increase time by the direct mixing of supercritical water.

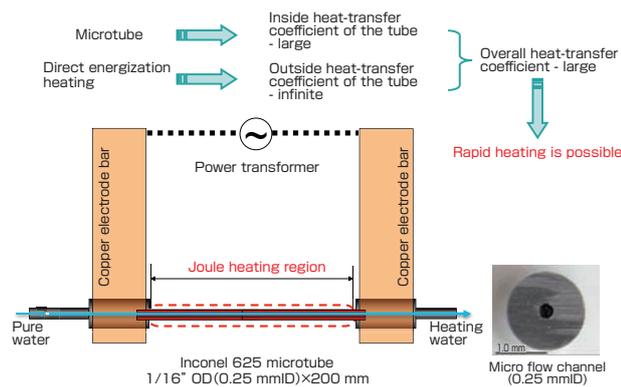


Fig. 7 Schematic diagram of the high-pressure microheater by direct energization heating

By using direct energization heating, the overall heat-transfer coefficient becomes extremely high.

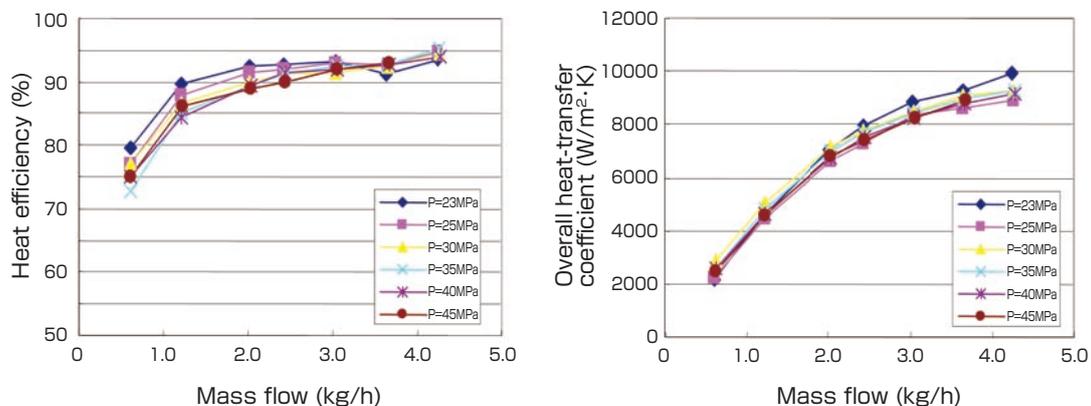


Fig. 8 Result of the evaluation of high-pressure microheater

Extremely efficient heating was achieved with maximum heat efficiency of 95 % and overall heat-transfer coefficient 10,000 W/m²·K.

The description of the high-pressure microcooler will be omitted in this paper, but the high-pressure microcooler can be constructed easily by installing a cooling jacket outside the microtube. In the cooler, the outside heat-transfer coefficient of the tube can be raised by increasing the flow of cooling water. Also, during cooling, the temperature difference can be set larger than in heating, and therefore it is not difficult to achieve relatively large rate of heat transfer.

3.3 Numbering up strategy and the establishment of high-pressure microengineering

As an issue in realizing the microreactor, how to achieve the throughput increase is the major point. In the conventional chemical engineering, this is dealt by scaling up (such as increasing the size of the reaction container). In the microreactor, of course, such scaling up cannot be done because we want to utilize the advantage of being micro. Therefore, the parallelization approach (numbering up)

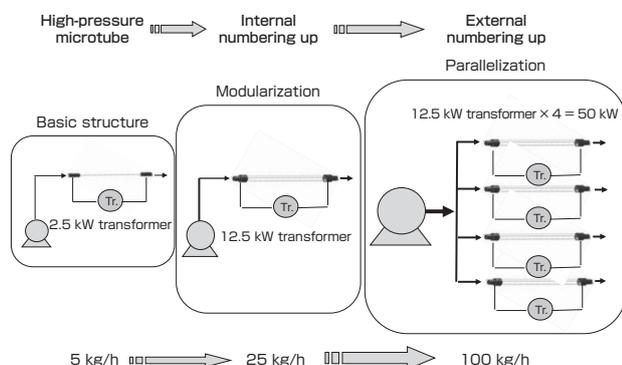


Fig. 9 Numbering up strategy

Throughput increase is accomplished by modularization of the basic structure and the parallelization of the module.

is selected. However, an ordinary microreactor has small throughput per basic structure, and in many cases a realistic parallel number cannot be obtained. In contrast, since the high-pressure microreactor allows pressure drop to some degree, it has the advantage of raising the flow amount per basic structure. The high-pressure microheater described above can process maximum of 5 kg/h per microtube (inside diameter of 0.25 mm, outside diameter of 1.6 mm, length of 200 mm). Maintaining this high-pressure structure, the basic structure can be modularized (5 microtubes/module), and by parallelization of the module (4 modules/device), numbering up to 100 kg/h becomes possible. The concept of numbering up is shown in Fig. 9, and the photograph of the prototype numbering-up equipment is shown in Fig. 10. In this equipment, heating is done by direct energization method (12.5 kW/module × 4 modules), and cooling is done by circulating the cooling water in the jacket installed outside each module. As a result, we confirmed that the heat exchange performance

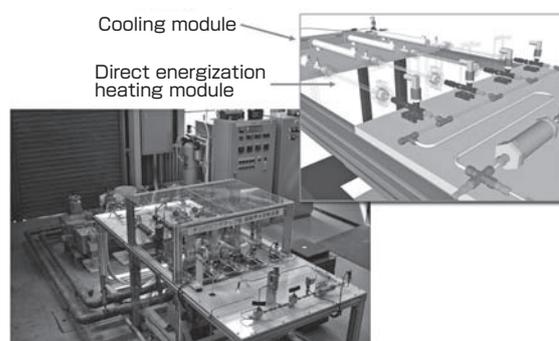


Fig. 10 100 kg/h class microreactor plant (parallel operation of four-module system)

The throughput was successfully increased while maintaining the heat exchange performance in single direct energization heating device.

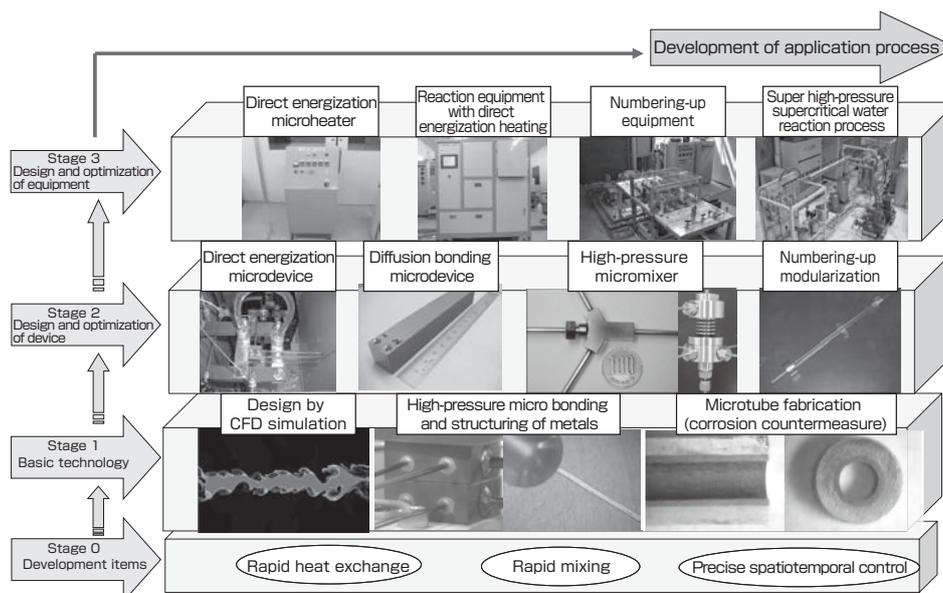


Fig. 11 Establishment of the high-pressure microengineering

From establishment of basic technology, configuration design and optimization of device and equipment, to the development of the application process.

was comparable to the basic structure, and verified that the exchange amount of heat equivalent to the substance production of several hundred tons/year could be carried out rapidly and stably through the compact process that could be installed in about 1 m × 2 m space. Comparing the capacity of the high-pressure microheater by direct energization heating used here with the conventional electric furnace heating method, the heat efficiency is estimated to be about 2 times, and the overall heat-transfer coefficient is 100 times or more. Since the difference of heat efficiency is directly related to the energy requirement, the energy cost will be one-half. Moreover, the difference of heat-transfer coefficient is thought to be almost proportional to the required heat transfer area, or the total length of the heating tube, and the heating tube will be 1/100 or less in length. As mentioned above, with 100 kg/h production capacity, the high-pressure microheater must have the total length of heating tube of 4 m (200 mm × 5 tubes/module × 4 modules/device = 4,000 mm), but the electric furnace heating method will require 400 m or more and the facility will grow large.

Figure 11 summarizes the processes of high-pressure microengineering including the items discussed above. Stage 0 (foundation) means the clarification of technical issues such as rapid heat exchange toward the integration of the microreactor technology and the supercritical fluid technology. To solve the issues, starting from the establishment of basic technologies such as micro structuring and micro bonding (Stage 1), moving on to configuration design and optimization of the high-pressure device such as mixers, and the various high-pressure equipments (Stage 2-3), we are working our way toward the developments for process applications.

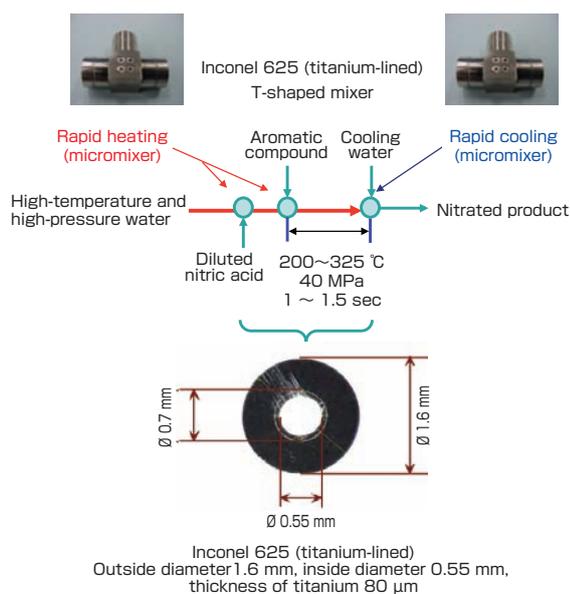


Fig. 12 Outline of non-catalyzed nitration apparatus under high-temperature high-pressure water

Inconel tubes and joints lined with titanium in the interior are used after introduction of nitric acid up to rapid cooling.

4 Establishment of the compact process through high-pressure microengineering

4.1 Organic synthesis process using supercritical water

The organic synthetic process using supercritical water and high-pressure and high-temperature water overturned the common knowledge that the supercritical water was inappropriate media as a organic synthesis field, as in the Beckmann rearrangement explained earlier, by realizing the rapid heating and cooling in the order of millisecond to microsecond by microengineering technology^[8]. As another example, we describe the nitration of the aromatic derivatives. The most frequently used nitration in industry is the method using nitric-sulfuric acid, or the so called mixed acid. However, this production method has been used from the early 20th century without any change in methodology. The serial problems of the disposal of sulfuric acid waste as well as safety still remain, and the development of a new nitration technology with decreased waste has been awaited. To overcome the problems, we developed the new nitration without mixed acid by using the high-pressure and high-temperature microengineering technology, to generate nitronium ion or radical from diluted nitric acid in the high-pressure and high-temperature water. Even though the strong acids including nitric acid in high-pressure and high-temperature water create very corrosive conditions, we newly developed some microdevices, such as microtubes and joints made of titanium-lined inconel 625 and succeeded to operate these strong acids in high-temperature and high-pressure conditions using these devices. Using the high-pressure and high-temperature resistant titanium-lined devices, we conducted the nitration of aromatics, such as naphthalene, with nitric acid. The conceptual diagram of the apparatus is shown in Fig. 12, and the results are shown in Fig. 13. The reaction condition was 40 MPa and 200~325 °C. The nitration of naphthalene proceeded at 225 °C or above, and 91 % of the maximum yield of nitronaphthalene (1-nitronaphthalene 85 % and 2-nitronaphthalene 6 %) was achieved at 250 °C within only 1.3 sec reaction time. It was also found that hardly any highly explosive dinitronaphthalene and trinitronaphthalene were produced.

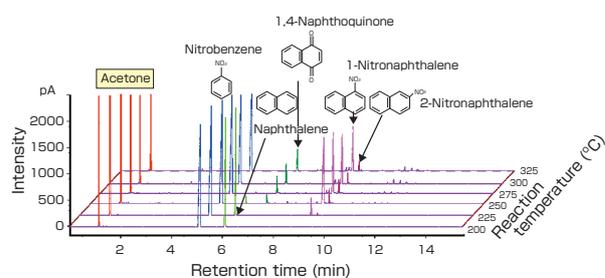


Fig. 13 Result of nitration experiment of naphthalene

Nitration progressed at 225 °C or over, and maximum yield of 91 % was achieved at 250 °C.

We further developed a process for conducting safer nitration using highly active acetyl nitrate as a nitration agent under the high-pressure conditions in microreactor for the precise reaction control of reaction time, reaction temperature and reaction point. In this method, the acetyl nitrate was generated instantly in the micromixer by exothermic reaction with acetic anhydride and nitric acid, while the mixing temperature was maintained at desired temperature of $40\text{ }^{\circ}\text{C} \pm 0.2\text{ }^{\circ}\text{C}$. The nitration of phenol was achieved of the yield of 96 % with the selectivity of almost 100 % at reaction temperature of $40\text{ }^{\circ}\text{C}$ and the reaction time of 1.8 sec. Since the reaction was conducted at low temperature of $40\text{ }^{\circ}\text{C}$, corrosion of reaction system hardly occurred and as the unreacted acetyl nitrate in reaction residue easily hydrolyzed in water after the reaction, we can safely and easily handle these reactions outside of the system. This reaction system can realize efficient low temperature nitration in high-pressure condition, and can be applied to the various aromatic compounds having substituent groups, particularly for the nitration using medical and agrochemical intermediates. We also realized ultrafast and highly efficient organic reaction in water for piancol rearrangement, Claisen rearrangement, and esterification by our reaction methodology with precise control by rapid heating, and rapid cooling in high-pressure and high-temperature micromixer^{[13]-[15]}. At present, we further achieved the high yield, high selectivity synthesis of useful compounds from sugars derived from biomass, such as 5-hydroxymethylfurfural for which physiological activity such as blood pressure decrease has been reported^[16].

4.2 Metal oxide fine particle synthesis process using supercritical water

The supercritical hydrothermal synthesis is a method for obtaining fine nano-level particles by reducing the solubility of the metal oxides produced in the hydrolysis and dehydration reactions by heating the metal salt water solution rapidly to a supercritical state^{[17][18]}. In the subcritical condition ($200\text{--}300\text{ }^{\circ}\text{C}$), the reaction rate of the hydrothermal synthesis is low, the dielectric constant of water is high at about 30, and the produced crystals tend to grow large. On the other hand, in the supercritical condition (representative condition is $400\text{ }^{\circ}\text{C}$, 30 MPa), the reaction rate increases, the dielectric constant falls to a single digit, and the produced crystals do not grow. Therefore, the point of this method is how to increase the temperature rapidly to supercritical condition, and this rapid heating can be realized by the direct mixing of the metal salt water solution and the supercritical water. Figure 14 shows the particle size distribution of the product obtained by using different mixers for the synthesis of boehmite by supercritical hydrothermal synthesis using aluminum nitrate as raw material. The mixers used were 1/16 inch STD TEE described above, swirl mixer, and central collision mixer (adjustable needle of fluid channel space is applied). The reaction condition was $400\text{ }^{\circ}\text{C}$, 30 MPa, and 2 sec. From the figure, both the swirl mixer and the central

collision mixer produced microscopic particles and showed narrow distribution compared to the standard T-shaped mixer (STD TEE: flow channel diameter 1.3 mm). In the central collision mixer, the fluid mixing performance is higher when the needle position is $L = 1\text{ mm}$ (see Fig. 6) with narrower flow channel clearance, and as a result, fine particles were synthesized by rapid mixing. The efficacy of this technology was shown in the synthesis of compound oxides as well as single oxides, and is expected to be applied in various usages such as fluorescent substances, ferromagnetic substances, transparent electrodes, cell electrode materials, and catalysts.

4.3 Innovative painting process by supercritical carbon dioxide

The total amount of volatile organic compounds (VOC) emitted from all industries in Japan is about 1.5 million tons (FY 2000), of which 33 % or 500,000 tons is the emission from the paint industry. The paint industry is the largest VOC emitter among all industries. The VOC is a cause substance of photochemical oxidants and suspended particulate matter, and their reduction is demanded immediately. We aimed to develop a painting method to significantly reduce the VOC emission by changing the thinner solvent (major VOC material) used abundantly in spray coating of conventional organic solvent paints, with extremely small amount of carbon dioxide, while maintaining the finish quality equivalent to the one achieved by organic solvent paints. The basic principle of this technology was developed as a new painting process^[19] principally by the Union Carbide Corporation of the U.S.A., but in this process conventional static mixer was mainly used for mixing paint and carbon dioxide based on the fluid multi-stage segmentation theory, and quick mixing was difficult. For this reason, the paint

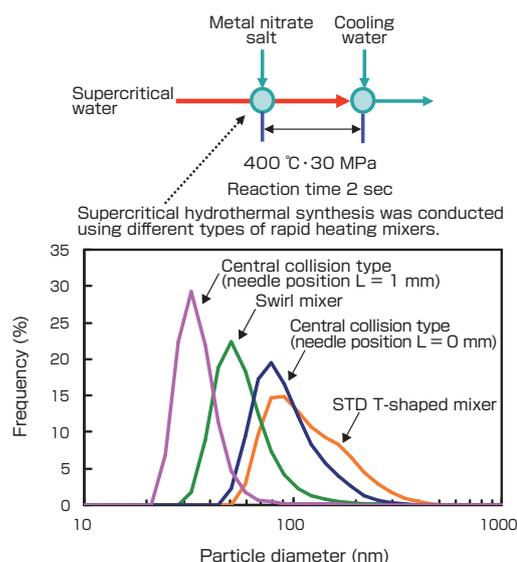


Fig. 14 Particle size distribution of the fine particles from Boehmite synthesis by the micromixer

Large difference in the particle size distribution can be seen depending on the type of the high-pressure micromixer (difference in quick mixing property).

that could be used was limited due to the problem of line clogging. In contrast, the carbon dioxide painting process that we developed uses the high-pressure micromixer based on the turbulence mixing theory, and enables extremely fast mixing and allows stable painting regardless of the type of paint. The conceptual flow diagram of the carbon dioxide painting technology is shown in Fig. 15. The paint and carbon dioxide are mixed instantly in the mixer, and the carbon dioxide dissolves completely in the paint. As a result, the viscosity decreases and spraying is enabled. The mixer was a version of the central collision micromixer modified for painting, and it was originally developed to realize the rapid heat exchange in the supercritical water reaction. As a result of evaluation by a third party of the painted sample using this method (mixer condition: 40 °C, 10 MPa), it was confirmed that the paint film quality was of practical level^[20]. Therefore, the VOC from the thinner solvent can be basically reduced, and seen from the amount of thinner solvent used currently (several hundred-thousand tons per year), the effect of reduction is thought to be significant.

5 Summary and future development

The organic and inorganic synthesis reactions using high-temperature and high-pressure water have the potential of greatly changing the conventional process of the large-scale production at concentrated sites. In this reaction field, an efficient and ideal substance synthesis is possible through rapid and precise temperature, pressure, and spatiotemporal control. As a result, fine chemical synthesis and creation of high value-added substance by natural product conversion in addition to bulk chemical synthesis is strongly expected.

For example, the ϵ -caprolactam that was described as the prologue in the organic synthesis using supercritical water is produced at about 100,000-ton scale per year per factory. It consumes the same amount of sulfuric acid and about half of ammonia, and discards about 1.5 times the amount of ammonium nitrate as waste product. If this is done as low-

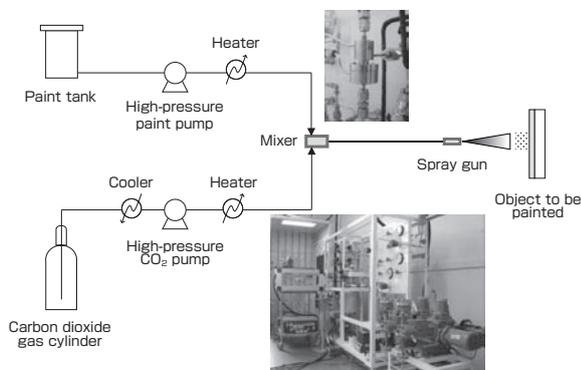


Fig. 15 Schematic diagram of carbon dioxide painting technology

Central collision type micromixer developed for painting was employed as the mixer.

volume distributed production using the supercritical water organic synthesis of 10,000-ton scale per year, production is possible without using sulfuric acid or ammonia. Though further advancement in high-pressure microengineering is necessary to increase the processing amount at a basic unit (structure), to achieve this, a compact process of 10,000-ton scale per year can be realized.

On the other hand, the quick diffusion of carbon dioxide painting is demanded as the key technology for reducing VOC. The objective of this technology is not simply to reduce VOC, but also to save energy by reducing the energy for the drying process etc, and can be considered as the key technology in reducing carbon dioxide. The atomization using carbon dioxide can also be applied to wide ranging areas such as the technologies for painting, printing, adhesion, and application (film coating) of functional films, as well as particle technologies for drugs, polymers, and functional substances.

The establishment of high-pressure microengineering to realize the integration of the microreactor technology and the supercritical fluid technology will help to realize the low-volume distributed production (compact process) and contribute greatly to a sustainable society.

References

- [1] K. Mae: Advanced chemical processing using microspace, *Chem. Eng. Sci.*, 62, 4842-4851 (2007).
- [2] H. Weingärtner and E. U. Franck: Supercritical water a solvent, *Angew. Chem. Int. Ed.*, 44, 2672-2692 (2005).
- [3] W. L. Marshall and E. U. Franck: Ion product of water substance, 0–1000 °C, 1–10,000 bars new international formulation and its background, *J. Phys. Chem. Ref. Data*, 10, 295-304 (1981).
- [4] P. G. Jessop, W. Leitner eds.: *Chemical Synthesis Using Supercritical Fluids*, WILEY-VCH, Weinheim (1999).
- [5] O. Sato, Y. Ikushima and T. Yokoyama: Noncatalytic Beckmann rearrangement of cyclohexanone-oxime in supercritical water, *J. Org. Chem.*, 63, 9100-9102 (1998).
- [6] Y. Ikushima, H. Hatakeda, O. Sato, T. Yokoyama and M. Arai: Acceleration of synthetic organic reactions using supercritical water, Noncatalytic Beckmann and pinacol rearrangements, *J. Am. Chem. Soc.*, 122, 1908-1918 (2000).
- [7] Y. Ikushima, K. Hatakeda, O. Sato, T. Yokoyama and M. Arai: Structure and base catalysis of supercritical water in the noncatalytic benzaldehyde disproportionation using water at high temperatures and pressures, *Angew. Chem. Int. Ed.*, 40, 210-213 (2001).
- [8] Y. Ikushima, K. Hatakeda, M. Sato, O. Sato and M. Arai: Innovation in a chemical reaction process using a supercritical water microreaction system: environmentally friendly production of ϵ -caprolactam, *Chem. Commun.*, 2208-2209 (2002).
- [9] S. -I. Kawasaki, Y. Wakashima, A. Suzuki, Y. Hakuta and K. Arai: Continuous hydrothermal synthesis of nano particles using T-shape micromixer, *Proc. 11th Euro. Meet. Supercrit. Fluids*, (Barcelona) P_PR_36 (2008).
- [10] Y. Wakashima, A. Suzuki, S. -I. Kawasaki, K. Matsui and Y. Hakuta: Development of a new swirling micromixer for

continuous hydrothermal synthesis of nano-size particles, *J. Chem. Eng. Japan*, 40 (8), 622-629 (2007).

- [11] K. Mae, A. Suzuki, T. Maki, Y. Hakuta, H. Sato and K. Arai: A new micromixer with needle adjustment for instant mixing and heating under high pressure and high temperature, *J. Chem. Eng. Japan*, 40 (12), 1101-1107 (2007).
- [12] Y. Wakashima, K. Hatakeda, S. -I. Kawasaki and A. Suzuki: Performance evaluation of a high pressure microtube as a high-speed heating device for supercritical state generation, *J. Chem. Eng. Japan*, 41 (2), 76-83 (2008).
- [13] M. Sato, N. Otabe, T. Tuji, K. Matsushima, H. Kawanami, M. Chatterjee, T. Yokoyama, Y. Ikushima and T. M. Suzuki: Highly-selective and high-speed Claisen rearrangement induced with subcritical water microreaction in the absence of catalyst, *Green Chem.*, 11, 763-766 (2009).
- [14] M. Sato, K. Matsushima, H. Kawanami and Y. Ikushima: A highly selective, high-speed, and hydrolysis-free O-acylation in subcritical water in the absence of a catalyst, *Angew. Chem., Int. Ed.*, 46, 6284-6288 (2007).
- [15] H. Kawanami, K. Matsushima, M. Sato and Y. Ikushima: Rapid and highly selective copper-free Sonogashira coupling in high-pressure, high-temperature water in a microfluidic system, *Angew. Chem., Int. Ed.*, 46, 5129-5132 (2007).
- [16] AIST Press Release: Anka na to kara seiri kassei busshitsu HMF o jinsoku ni seizo - ko'on ko'atsu maikuro riakuta ni yori jistugen (Quick manufacture of physiologically active substance HMF from low-priced sugar – Realized by high-temperature high-pressure microreactor), April 20, 2009 (in Japanese) http://www.aist.go.jp/aist_j/press_release/pr2009/pr20090420/pr20090420.html
- [17] T. Adschiri, K. Kanazawa and K. Arai: Rapid and continuous hydrothermal crystallization of metal oxide particles in supercritical water, *J. Am. Ceram. Soc.*, 75, 1019-1022 (1992).
- [18] T. Adschiri, K. Kanazawa and K. Arai: Rapid and continuous hydrothermal synthesis of boehmite particles in subcritical and supercritical water, *J. Am. Ceram. Soc.*, 75, 2615-1618 (1992).
- [19] C. S. Lee, K. L. Hoy and M. D. Donohue: Supercritical fluid as diluting agent in the liquid mist application of coating (Kotingu no ekитай funmu tofu ni okeru kishakuzai toshiteno chorinkaisei ryutai), Japanese Unexamined Patent Application Publication No. 1989-258770 (Japanese Patent 1927328), application date January 5, 1988 (1988) (in Japanese).
- [20] A. Suzuki, S. Kawasaki, T. Aizawa, M. Ono, Y. Hayasaka, K. Yukishita, N. Hayasaka, H. Sato, T. Chiyokubo and A. Nakatsuka: Koatsu maikuro kongoki o mochiita nisanka tanso toso gijutsu no kaihatsu (Development of carbon dioxide painting technology using high-pressure micromixer), *Toso Kogaku (Journal of the Japan Coating Technology Association)*, 44 (7), 230-237 (2009) (in Japanese).

engineering, and currently aims to establish a new process from the perspective of concert of supercritical technology and micro technology. In this paper, was involved in all aspects, but was particularly in charge of the establishment of high-pressure microengineering and the development of innovative painting device.

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Completed the doctorate program at the Department of Chemistry, Graduate School of Science, Tohoku University in March 1997. Doctor (Science). Worked as an assistant at the Faculty of Science and Engineering, Kinki University, and joined AIST in April 2001. Studied the chemistry of carbon dioxide and water under high-pressure and high-temperature conditions from the standpoint of organic synthesis and organic reaction. Won the Minister of Economy, Trade and Industry Award of the 4th Green Sustainable Chemistry Award (2005). In this paper, was in charge of the establishment of the compact process using high-pressure microengineering and the organic synthetic process using high-pressure and high-temperature water.



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Completed the master's program at the Department of Mechanical Engineering, Graduate School of Science and Engineering, Kagoshima University in March 1996. Joined a water treatment engineering company in April 1996, and engaged in research for the practical application of supercritical water oxidation (SCWO) process for the complete decomposition of persistent hazardous waste (such as polychlorinated biphenyl and dioxin). Completed the doctorate program for Environmental Chemistry and Ecoengineering at the Graduate School of Environmental Studies, Tohoku University in March 2006. Doctor (Environmental Studies). Joined AIST in April 2006, and engages in engineering research for the technology of using supercritical water and supercritical carbon dioxide. Particularly specializes in the development of the micromixer, and studies the metal oxide fine particle synthesis by supercritical hydrothermal process as the core research for fluid mixing devices. In this paper, was in charge of the development of the micromixer and the development of the metal oxide fine particle synthesis using supercritical water.



Kiyotaka Hatakeda

Completed the doctorate program at the Graduate School of Environmental Studies, Tohoku University in March 2005. Doctor (Environmental Studies). Joined the National Industrial Arts Research Institute in 1966. Worked at the Government Industrial Research Institute, Tohoku, Tohoku National Industrial Research Institute, and then at AIST. Experimentally clarified the synthesis of ϵ -caprolactam that initiated the research of organic synthesis using supercritical water. In this paper, was essentially in charge of the continuous synthetic system of the nitro compounds under high-pressure and high-temperature water conditions.



Authors

Akira Suzuki

Completed the master's program at the Department of Chemical Engineering, Graduate School of Engineering, Tokyo Institute of Technology in March 1978. Doctor of Engineering in 1990 (Tokyo Institute of Technology). Joined a water treatment engineering company in April 1978. Engaged in the research and development for supercritical water oxidation process and succeeded in its practical application for the first time in the world. Joined AIST in April 2003. Has been working on R&D mainly for supercritical fluid



Discussions with Reviewers

1 Overall

Comment (Koh Harada, AIST Tohoku)

Please explain why you used both words of “integration” and “concert” in the subtitle.

Answer (Akira Suzuki)

The subtitle “Integration and concert of high-pressure microengineering and supercritical fluid”, expresses the point that these integrations are not merely “1+1=2”, but the property of supercritical fluid may become 3 or 4 or anything by using microengineering. Recently, in the world of chemistry, the phrase, “concerted reaction field”, comes into use. The word “integration” does contain the element that it is more than simply getting together, and therefore to enhance the reader’s understanding, I deleted “concert”, and the subtitle shall be “Integration of high-pressure microengineering and supercritical fluid”.

Comment (Yoshiro Owadano, Research Coordinator, AIST)

For non-specialist readers, I think you should write clearly to which category the compact process described in this paper belongs:

- 1) Makes possible the synthesis that was conventionally impossible
- 2) Achieves lower environmental load or higher yield compared to the conventional method

If 2) is the case, please indicate as much as possible, what the volume of production (possibility) or rate of energy saving is in quantitative terms, or what are the figures set as the goal. For example, I think you should describe a more specific future image, such as what manufacturing method and in which industry this will be used in the sections, “Numbering up strategy” and “Future development”.

Answer (Akira Suzuki)

The compact process described in this paper is a high-speed, highly controllable process to convert the bulk chemicals that were produced conventionally by large-scale concentrated production to low-volume distributed production for producing the necessary amount at the necessary place. Therefore, it is not a process for synthesizing products that were conventionally impossible, but is a process that has low environmental load and realizes high yield compared to the conventional processes. In this paper, two reactions (Beckmann rearrangement and nitration) are given as examples of organic synthesis. While both reactions conventionally use concentrated sulfuric acid as the acid catalyst, in the compact process, high-temperature and high-pressure water plays the role of concentrated sulfuric acid, and it is now possible to establish a process that uses no catalyst (no sulfuric acid → low environmental load) and has high speed (microreaction → high yield).

To clarify the above discussion, we described the superiority of the micro heat exchange compared to the conventional technology in the “Numbering up strategy”. We described the possibility of increasing the production volume using the example of ϵ -caprolactam synthesis in the “Future development”.

Comment (Koh Harada)

I think that the phrase “compact process” used in this paper has a narrower meaning that is used specifically in the chemical

industry, compared to the general usage. Please define what is the “compact process” for non-specialist readers.

Answer (Akira Suzuki)

In the text, we added: “The compact process here means a safe, flexible, and efficient process with low environmental load, where the cycling of resource and energy can be done easily. It also is high-speed and has highly controllable performance, and enables low-volume distributed production”.

2 Balance in establishing a circulating system

Question (Koh Harada)

In the discussion of “1 Background and objective of the research”, you state the “balance or recovery and reuse” are important. Is this a requirement to establish the circulating system?

Answer (Akira Suzuki)

In the large-scale concentrated production method, the amount handled is extremely high. Although reuse in other processes or at other plants may be done through the recovery of the byproduct or recycling of waste products produced in certain processes, I don’t think they provided realistic solutions due to the balance of supply and demand and the problem of transportation. The establishment of the circulating system was difficult in the large-scale concentrated production method.

3 Comparison with conventional method

Question (Koh Harada)

You would be better to mention about a comparison of your method with the conventional method at the beginning of the discussion of “2 Integration and concert of microreactor and supercritical water”.

Answer (Akira Suzuki)

The caprolactam synthesis by Beckmann rearrangement using concentrated sulfuric acid is a high-yield process of 98 %. On the other hand, the yield by high-temperature and high-pressure water described in Table 1 is 83 %, and is inferior in terms of numbers, but is superior in the fact that it does not use concentrated sulfuric acid at all. Here, to emphasize that the yield can be dramatically increased using supercritical water alone by precisely controlling the reaction time, we intentionally did not mention the yield of the conventional method.

4 Advantage of electromagnetic induction

Question (Koh Harada)

In “3.2 High-pressure micro heat exchanger”, what is the advantage of the electromagnetic induction method? It was written that it was not employed due to its size, but in what case would it be more advantageous?

Answer (Akira Suzuki)

Compared to direct energization application, the advantage of the electromagnetic induction may be that there is no need to take measures against electric leaks, and the heating intensity can be changed by how the induction coil is wound. Which is better is a case-by-case consideration, but I think for a microdevice, direct energization application is better because it does not require the induction coil.