Arch. Metall. Mater. **69** (2024), 2, 453-457

DOI: https://doi.org/10.24425/amm.2024.149765

HOAI-HAN NGUYEN[1], THI THU HIEN NGUYEN[1], JONG-KIL KIM[2], YOUNG-SANG CHO[1*]

SYNTHESIS OF SILICA NANOPARTICLES FROM SODIUM SILICATE AND CARBON DIOXIDE AS REACTANTS

In this study, Taylor-vortex reactor was adopted to synthesize silica nanoparticles from sodium silicate solution and carbon dioxide. The outstanding advantages of the reactor have been demonstrated by comparing the synthesis results of silica nanoparticles by Erlenmeyer reactor. The results showed that silica particles synthesized from Taylor-vortex reactor are smaller in size than silica particles synthesized from the Erlenmeyer reactor. SEM images and histogram of particle size distribution obtained from experiments clearly exhibited that the concentration of SiO_2 in the solution, reaction temperature, and rotation speed of the cylinder significantly affected morphology as well as size of the silica particles.

Keywords: silica nanoparticle; sodium silicate solution; CO_2; Taylor-vortex reactor

1. Introduction

Silicon is the second most abundant element in the Earth's crust and it links up with oxygen to form silica, the most common mineral on Earth [1,2]. Over the past decades, synthetic silica nanoparticles (SNPs) have become important ingredients in cosmetics, rubber tires, plastics, electronics, coating, and other applications. Because of its excellent properties such as high specific surface area, high porosity, low density, and good insulation, silica has been widely studied and used in recent years [3-6].

The three main classes of amorphous silica are pyrogenic silica, silica gel, and precipitated silica. Among them, precipitated silica has the greatest commercial significance. In laboratory scale, most of the silica is synthesized from tetraethyl orthosilicate (TEOS) as precursor by traditional sol-gel method [7]. However, TEOS is very expensive, so it costs a lot to synthesize silica particles. On the contrary, sodium silicate is known to be a economic material, because it is made from inexpensive and readily available raw materials. Therefore, utilizing sodium silicate as an alternative material to synthesize silica could be the most promising in the future [8].

In recent years, excessive increase of CO_2 in the atmosphere is considered cause of climate change. Therefore, storage and use of CO_2 is one of the practical environmental protection measures [9]. And carbonation method using CO_2 feedstock in this study can contribute to this effort. The aim of this study is to compare the structure and properties of silica particles generated from the Erlenmeyer reactor and the Taylor-vortex reactor. Structurally, the Erlenmeyer reactor is a commonly used laboratory flask with a conical shape, featuring a narrow neck and a wider base. It relies on manual stirring or shaking to enable the mixing and reactions between the reactants. In contrast, the Taylor-vortex reactor consists of two concentric cylinders, with the inner cylinder rotating while the outer one remains stationary. This configuration creates a shearing effect between the cylinders, leading to enhanced mixing and flow characteristics. Methodologically, the Erlenmeyer reactor utilizes conventional mechanical agitation methods, such as magnetic stirrers or manual shaking, to achieve the desired mixing of the reactants. Conversely, the Taylor-vortex reactor capitalizes on the principle of Taylor vortices, which are generated by the rotation of the inner cylinder. The rotation induces complex flow patterns characterized by axial and azimuthal flow components, thereby facilitating improved mass transfer and reaction kinetics.

The structural and methodological distinctions between the Erlenmeyer and Taylor-Couette reactors are vital for understanding the observed variations in silica particle synthesis. By providing an in-depth description of these disparities, a clearer understanding can be gained as to why silica particles synthesized

[1] TECH UNIVERSITY OF KOREA, DEPARTMENT OF CHEMICAL ENGINEERING AND BIOTECHNOLOGY, 237, SIHEUNG-SI, GYEONGGI-DO 15073, REPUBLIC OF KOREA
[2] BIO NANO KOREA CO. LTD., 237, SIHEUNG-SI, GYEONGGI-DO 15073, REPUBLIC OF KOREA

* Corresponding author: yscho78@tukorea.ac.kr; yscho78@gmail.com

in the Taylor- vortex reactor exhibit superior characteristics, such as smaller and more uniform particle size, compared to those produced in the Erlenmeyer reactor [10,11].

2. Experimental

In this study, sodium silicate solution was purchased from Samchun Chemical and used as a starting material for synthesis of silica nanoparticles. CO_2 gas was procured from Daesung Gases Co., Ltd. as the reactant.

The synthesis process was divided into 2 stages: precipitation of silica nanoparticles and washing of the precipitate by vacuum pump filtration. In this study, precursor of SiO_2 concentrations of 6, 8, and 10% were diluted from the Na_2SiO_3 stock solution. Before starting precipitation reaction, each solution was stirred for 30 minutes to make a homogeneous solution. After 30 minutes, CO_2 was introduced at specified flow rate. The reaction was terminated when the solution turned from transparent to milky white, until pH was recorded from 10 to 10.5. Then, the solution was aerated by letting it stand for 3 hours. In the second stage, the precipitate was washed with sufficient amount of water using a vacuum pump filtration system. pH of the solution before and after washing was recorded as 10.0 to 10.5 and 6.0 to 6.5, respectively. The reaction of sodium silicate solution and CO_2 resulted in precipitated silica nanoparticles and sodium carbonate salt. The salts need to be removed so as not to affect purity and surface area of the silica product. The method of salt washing by vacuum pump system can be considered effective, when it is possible to remove all the salts from the precipitated silica particles. The precipitated silica nanoparticles after washing were allowed to dry at room temperature for 24 hours. The synthesis was performed in the same way in the Erlenmeyer and Taylor-vortex reactor.

Morphologies of the precipitated silica were characterized by field emission scanning electron microscope (SEM, Nova NanoSEM 450, FEI). FT-IR spectra of the samples were measured using an FT-IR spectrometer (Nicolet iS5, Thermo Fisher Scientific co. Ltd). X-ray diffraction (XRD) patterns were recorded with a BRUKER D2 PHASER diffractometer that used CuKα radiation (30 kV, 10 mA, λ = 1.54184 Å) with a scan range of 2θ = 10-80°. Chemical composition of synthesized silica nanoparticles was analyzed using X-ray fluorescence (X-ray fluorescence Analyzer MESA-50, HORIBA Scientific) measurements.

3. Results and discussion

In the carbonation method, CO_2 is used as a reactant. For precipitation, aqueous sodium silicate reacts with CO_2 according to the following reaction, forming silica nanoparticles and sodium carbonate.

$$Na_2SiO_3 + CO_2 + H_2O \rightarrow SiO_2 + Na_2CO_3 + H_2O$$

Process of synthesizing silica nanoparticles from sodium silicate solution by carbonation is shown in Fig. 1. After CO_2 and sodium silicate were reacted, mixture of hydrated silica

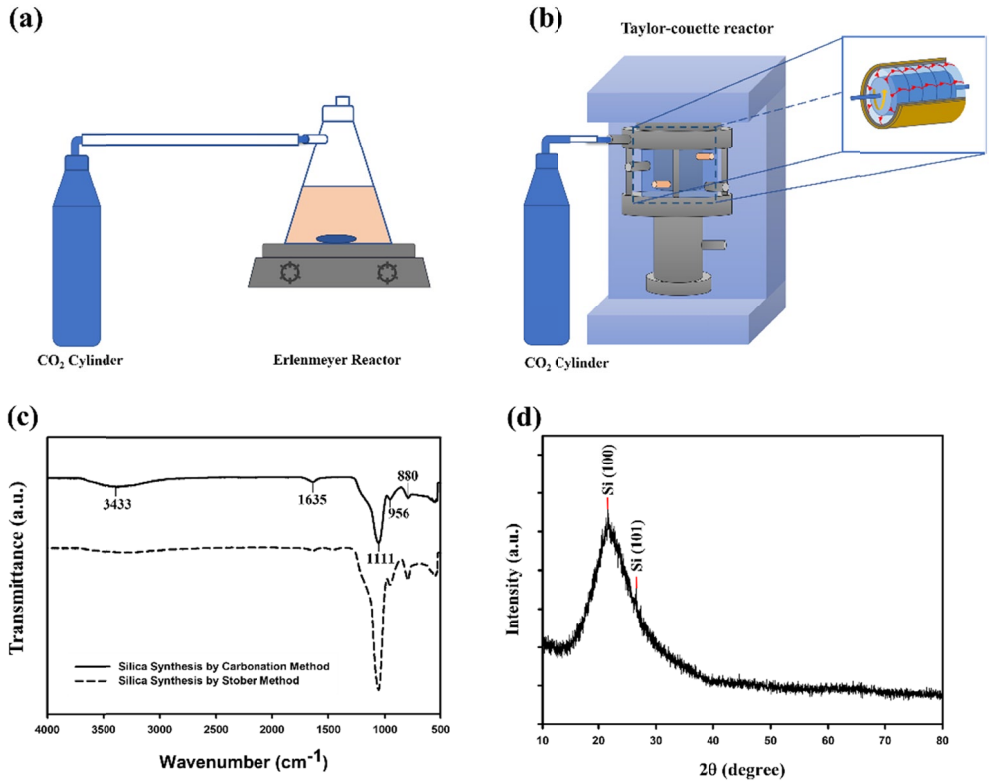

Fig. 1. Synthesis of silica nanoparticles using (a) Erlenmeyer and (b) Taylor-vortex reactor. (c) FT-IR spectrum and (d) XRD analysis result of silica nanoparticles

nanoparticles and NaCl was washed with water using a vacuum filtration system for complete removal of NaCl from the mixture. Resulting samples were naturally dried within 24 hours. Composition of the dried powder was determined as silica by FT-IR spectrum and XRD analysis as presented in Fig. 1(c) and 1(d), respectively. In Fig. 1(c), broad IR band at around 3,300 cm^{-1} is due to the stretching vibration of Si-OH groups of precipitated SiO_2. Bending vibration of OH groups was also observed at around 1,635 cm^{-1}. Asymmetric stretching vibrations of Si-O-Si groups was confirmed by the IR band at 1,000 to 1,200 cm^{-1} [12,13]. The IR spectrum of silica nanoparticles synthesized from carbonation method was also compared with the IR spectrum of silica nanospheres synthesized from the Stober method in Fig. 1(c). The results show that stretching and bending vibrations of Si-OH groups, OH groups, and siloxane bonds (Si–O–Si) of both IR spectrums are the same. Crystallinity of the sample was examined by XRD and presented in Fig. 1(d), which shows that synthesized silica nanoparticles is amorphous with high purity, because no other sharp crystal diffraction peaks were detected [3,9]. XRF analysis was carried out to determine chemical composition of the silica product. XRD analysis result shows that the component is dominated by SiO_2 (96.05%) and a small amount of other impurities, indicating that synthesis of silica nanoparticles by carbonation method resulted in high-purity silica.

To investigate factors affecting shape and size of silica nanoparticles, a series of experiments were performed according to the conditions summarized in TABLE 1. For SEM observation, electron microscope images in Fig. 2 were taken at high magnification (200,000 X) to clearly observe the primary particles. Morphology of silica synthesized from two reactors such as Erlenmeyer and Taylor-vortex using Na_2SiO_3 concentration of 6% (SNPs1, SNPs4 samples) are all dense agglomerates as shown in Fig. 2(a) and 2(d). The morphology of samples synthesized with 8 and 10% of Na_2SiO_3 concentrations (SNPs2, SNPs3, SNPs5, SNPs6 samples) was observed as porous agglomerates as presented in Fig. 2(b), 2(c), 2(e), and 2(f), respectively.

TABLE 1

A detailed description of the silica synthesis experiment

Sample	Experimental conditions				
	Na_2SiO_3 concentration (%)	CO_2 (L/min)	Rotation speed (rpm)	Temperature (°C)	Reactor type
SNPs1	6	10	505	25	Erlenmeyer
SNPs2	8	10	505	25	Erlenmeyer
SNPs3	10	10	505	25	Erlenmeyer
SNPs4	6	10	505	25	Taylor-vortex
SNPs5	8	10	505	25	Taylor-vortex
SNPs6	10	10	505	25	Taylor-vortex
SNPs7	10	10	712.5	25	Taylor-vortex
SNPs8	10	10	920	25	Taylor-vortex
SNPs9	10	10	1127.5	25	Taylor-vortex
SNPs10	10	10	505	40	Taylor-vortex
SNPs11	10	10	505	60	Taylor-vortex
SNPs12	10	10	505	80	Taylor-vortex

Sizes of primary particles of silica nanoparticles were measured and re-presented as particle size distribution histograms shown in the inset. Specifically, Fig. 2(a), 2(b), and 2(c) are the results of size distribution of silica nanoparticles synthesized by

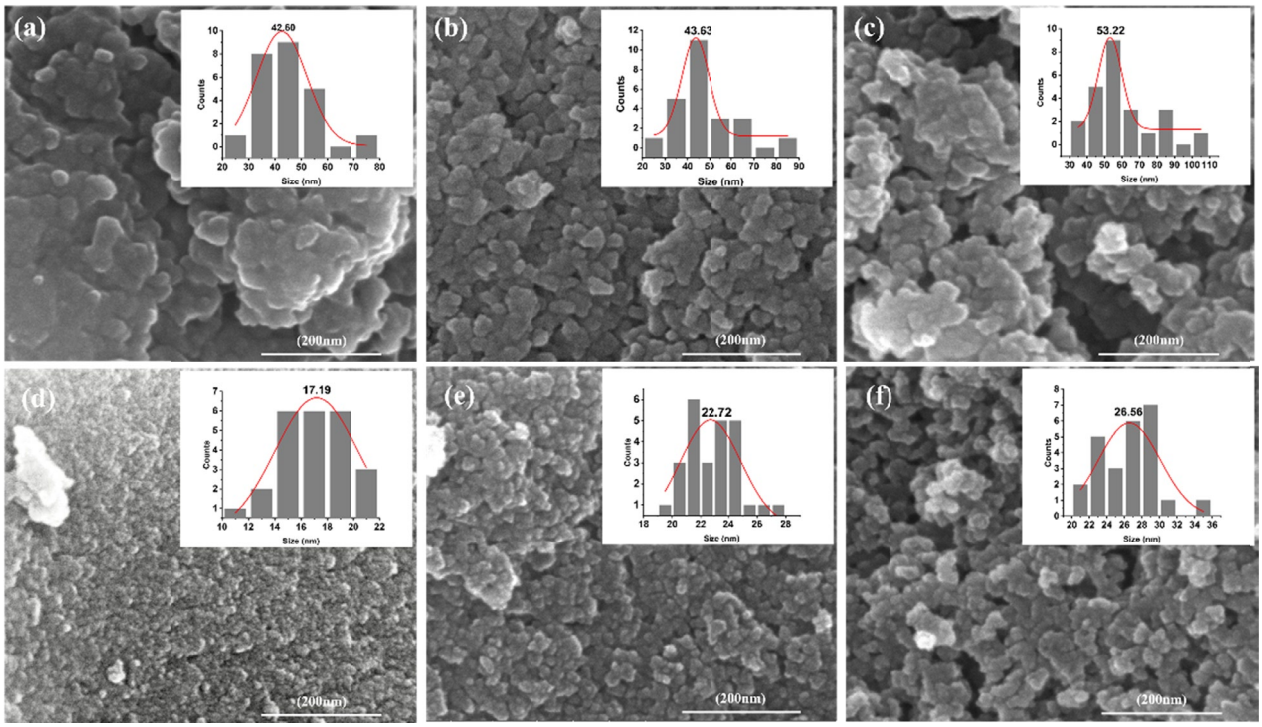

Fig. 2. SEM image and particle size distribution (inset) of silica nanoparticles synthesized by Erlenmeyer reactor with Na_2SiO_3 concentrations of 6% (a), 8% (b), and 10% (c), respectively. SEM image and particle size distribution (inset) of silica nanoparticles synthesized by Taylor-vortex reactor with Na_2SiO_3 concentrations of 6% (d), 8% (e), and 10% (f), respectively

Erlenmeyer reactor with Na_2SiO_3 concentrations of 6% (SNPs1), 8% (SNPs2), and 10% (SNPs3), respectively. The histograms show that the primary particle size range from 25 to 105 nm with average particle size of 42.6, 43.63, and 53.22 nm, respectively. Fig. 2(d), 2(e), and 2(f) are the results of the particle distribution of silica nanoparticles synthesized by Taylor-vortex reactor with Na_2SiO_3 concentrations of 6% (SNPs4), 8% (SNPs5), and 10% (SNPs6), respectively. The results show that primary particles are ranged from 11 to 35 nm with average particle size of 17.19, 22.72, and 26.56 nm, respectively. This result has been charted in Fig. 3(a), and it can be seen that silica nanoparticles synthesized by Taylor-vortex reactor showed homogeneous morphology with primary particle size smaller than the silica particles prepared using Erlenmeyer reactor (less than approximately 1/2 the size).

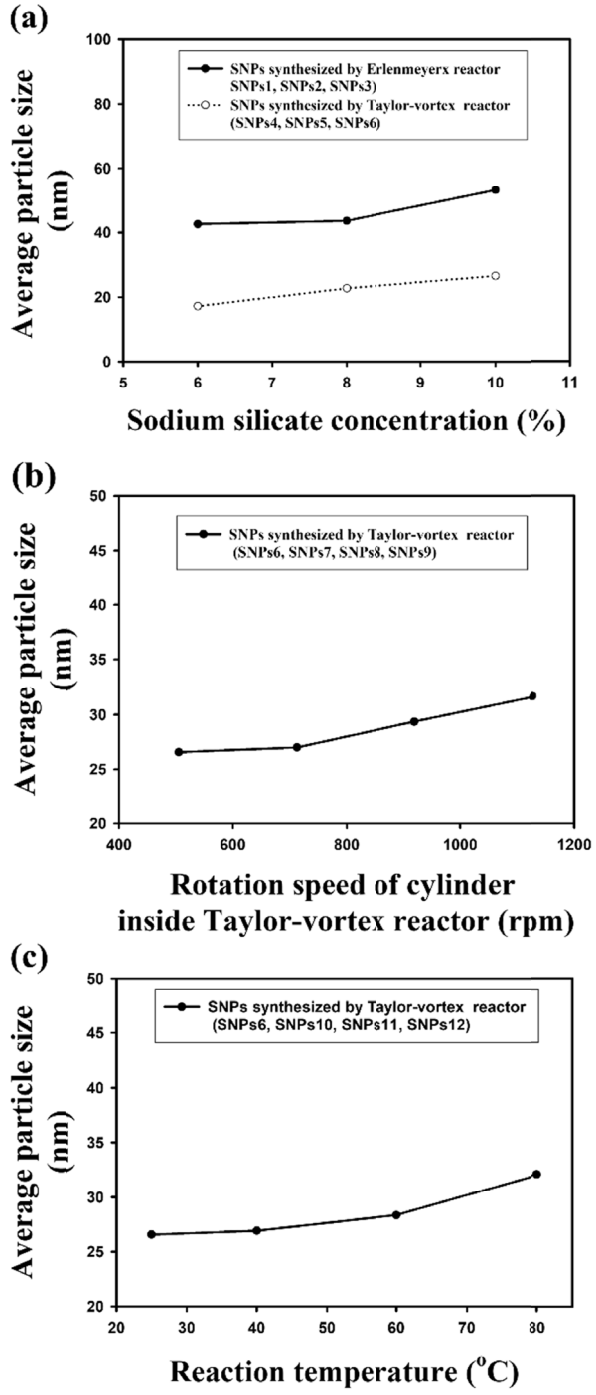

Fig. 3. Effect of (a) Na_2SiO_3 concentration, (b) rotation speed of inner cylinder, and (c) reaction temperature on average size of silica nanoparticle prepared by Taylor-vortex reactor

To test the effect of Na_2SiO_3 concentration on average particle size, Na_2SiO_3 concentration was varied as a range from 6 to 10%, while fixing other reaction conditions. The average particle size of silica particles increased with increasing concentration of Na_2SiO_3, as presented in Fig. 3(a). It can be speculated that high concentration of Na_2SiO_3 promoted rapid growth of the crystal nucleus. At the same time, increasing concentration of Na_2SiO_3 hindered homogeneous dissolution of CO_2 gas, because of increased viscosity of reaction solution. Finally, coagulation of nuclei caused the formation of larger particles. To test effect of rotation speed of inner cylinder of Taylor-vortex reactor, the rotation speed was varied at a range from 505 to 1,127.5 rpm, while fixing other reaction conditions. The average particle size of silica particles increased with increasing rotation speed, shown in Fig. 3(b). The high rotational speed may promoted growth of the crystal nucleus resulting in a larger size of the produced silica [3]. To find effect of reaction temperature on average particle size, synthesis was performed at Na_2SiO_3 concentration of 10% for various reaction temperature at a range from 25 to 80°C, while fixing other factors. According to the results in Fig. 3(c), size of silica nanoparticles increased with increasing reaction temperature. As reaction temperature increased, it promoted growth rate of the nucleus faster than nucleation rate, resulting in larger particle size.

4. Conclusions

Synthesis process of silica nanoparticles using Taylor-vortex reactor was carried out using economic raw materials such as Na_2SiO_3 and CO_2. The results showed that relatively small-sized silica particle (about 17.19-22.72 nm) could be synthesized with Na_2SiO_3 concentration from 6 to 8%, CO_2 flow rate as 10 L/min, reaction temperature of 25°C, and rotation speed of 505 rpm. By using Taylor vortex reactor, Taylor flow promoted ideal mixing of reacting solution to produce silica nanoparticles with uniform shape and size.

Acknowledgments

This research was supported by grant from Ministry of SMEs and Startups (Collabo R&D, S3249683) and the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. RS-2023-00250648).

REFERENCES

[1] D.E. Canfield, E. Kristensen, B. Thamdrup, Aquatic geomicrobiology. Adv. Mar. Biol. **48**, 441-463 (2005).
DOI: https://0.1016/S0065-2881(05)48017-7

[2] D. Savvas, G. Ntatsi, Review: Biostimulant activity of silicon in horticulture. Sci. Hortic. **196**, 66-81 (2015). DOI: https://doi.org/10.1016/j.scienta.2015.09.010

[3] X. Cai, R.Y. Hong, L.S. Wang, X.Y. Wang, H.Z. Li, Y. Zheng, D.G. Wei, Synthesis of silica powders by pressured carbonation. Chem. Eng. J. **151**, 380-386 (2009). DOI: https://doi.org/10.1016/j.cej.2009.03.060

[4] R. Dewatia, Suprihatinb, K. Sumadac, S. Muljani, Precipitated Silica from Sodium Silicate by CO_2 on Fixed Bed Column. Materials Science Forum **966**, 14-18 (2019). DOI: https://doi.org/10.4028/www.scientific.net/MSF.966.14

[5] B. Zhu, W. Wei, G. Ma, Y. Zhuang, J. Liu, L. Song, X. Hu, H. Wang, J. Li, A pressurized carbonation sol–gel process for preparing large pore volume silica and its performance as a flatting agent and an adsorbent. J. Supercrit. Fluids **97**, 1-5 (2015). DOI: https://doi.org/10.1016/j.supflu.2014.11.006

[6] Y. Huang, P. Li, R. Zhao, L. Zhao, J. Liu a, S. Peng, X. Fu, X. Wang, R. Luo, R. Wang, Z. Zhang, Review: Silica nanoparticles: Biomedical applications and toxicity. Biomed. Pharmacother. **151**, 113053 (2022). DOI: https://doi.org/10.1016/j.biopha.2022.113053

[7] W.H. Shin, S. Kim, H.M. Jeong, Synthesis and Characterization of Core-Shell Silica-Phosphor Nanoparticles via Sol-Gel Process. J. Korean Powder Metall. Inst. **25** (1), 12-18 (2018). DOI: https://doi.org/10.4150/KPMI.2018.25.1.12

[8] F. Akhter, A.A. Rao, M.N. Abbasi, S.A. Wahocho, M.A. Mallah, H. Anees-ur-Rehman, Z.A. Chandio, A Comprehensive Review of Synthesis, Applications and Future Prospects for Silica Nanoparticles (SNPs). Silicon **14**, 8295-8310 (2022). DOI: https://doi.org/10.1007/s12633-021-01611-5

[9] Y. Zhang, Z. Zhang, D. Feng, F. Zhang, J. Gao, M. Xie, Y. Zhao, S. Sun, G. Chang, Y. Qin, Effect of microbubbles on preparation of precipitated silica by carbonization: physical-chemical structure, kinetic parameters and mass transfer characteristics. Carbon Capture Science & Technology **1**, 100002 (2021). DOI: https://doi.org/10.1016/j.ccst.2021.100002

[10] T. Ogihara, M. Nomura, Continuous Synthesis of Monodispersed Alumina Particles by the Hydrolysis of Metal Alkoxide Using a Taylor Vortex. KONA Powder and Particle Journal **20**, 231-237 (2002). DOI: https://doi.org/10.14356/kona.2002025

[11] S.A. Altmeyer, Effect of Axial and Radial Flow on the Hydrodynamics in a Taylor Reactor. Fluids **7** (10), 336 (2022). DOI: https://doi.org/10.3390/fluids7100336

[12] S. Musić, N. Filipović-Vinceković, L. Sekovanić, Precipitation of amorphous SiO2 particles and their properties. Braz. J. Chem. Eng. **28** (01), 89-94 (2011). DOI: https://doi.org/10.1590/S0104-66322011000100011

[13] I. Joni, Rukiah, C. Panatarani, Synthesis of silica particles by precipitation method of sodium silicate: Effect of temperature, pH and mixing technique. AIP Conference Proceedings **2219**, 080018 (2020). DOI: https://doi.org/10.1063/5.0003074