GSCN News Letter No.33

GSCN was established in 2000 to promote research and development for the Environment and Human Health and Safety, through the innovation of Chemistry .

For the expansion of GSC Network

Tsuneo Moriya,
2009 GSCN Chairman

As globalization progresses, global problems such as the depletion of energy and resources, global warming, disparities in wealth and development between regions of the world, and economic cooperation and integration are becoming increasingly prominent, and are having a major effect on our daily lives. To solve the tremendous amount of global problems and create a sustainable society, summits are being held at the United Nations and between world governments. As citizens of the world, we must also participate in actively addressing the problems.

The Green and Sustainable Chemistry Network (GSCN) seeks to "achieve human and environmental health through chemical technologies and promote activities that contribute to the realization of a sustainable society." It was established as a collaborative organization between industry, government, and academia in 2000. In the ten years since then, we have been developing various activities to evangelize our goals. We hold symposia to spread awareness of GSC, create publications, and establish prizes to encourage outstanding GSC technologies and to promote GSC activities. Thanks to support from the government, the Ministry of Economy, Trade and Industry Prize, the Ministry of Education, Culture, Sports, Science and Technology Prize, and the Ministry of Environment Prize have contributed greatly to the promotion of our activities. Our activities are also not limited to just Japan. We are broadening our activities internationally by partnering with the U.S. Green Chemistry Institute (GCI) and Europe's SusChem. Furthermore, in 2007, we held the first Asia-Oceania conference, and the second conference in 2009.

Again, I want to express deep respect and gratitude to our predecessors who established these activities, and to those who poured energy into its continuance and expansion.

Now, what should we do to continue our activities, and to further expand them? There are many things that we can do and challenges to be met. We must prioritize them, strengthen partnership between industry, government, and academia, and quietly proceed while further obtaining the support of the government.

As a starting point for discussions, the following are my personal opinions.

1. Expand planning organizations

GSCN was inaugurated with ten organizations. Currently it has 25 participating organizations. There are still many organizations with a foundation in chemistry, as well as organizations in different industries that have a keen interest in the development of chemical technologies. I definitely want to reach out to them.

2. Strengthen support to academia

The development of innovative technologies cannot occur without the creative foundations of academia. For example, at JCII we are planning support of budding research. I want them to be considered as ramps to GSC.

3. Strengthen international exchanges

As mentioned earlier, anticipating demands of this era, GSCN actively continues international exchanges. From the geopolitical standpoint of Japan, it is necessary to strengthen ties with Asia-Oceania quantitatively and qualitatively. By combining the further efforts of involved parties, I hope for strong support from the government.

4. Development of human resources

Understanding and recognizing the importance of GSC is becoming widespread for persons involved in chemistry in industry, government, and academia. It is critical to transmit such valuable experience and knowledge to the next generation of chemists and entrust them with the future.

A variety of activities has been voluntarily carried out. However, if one takes a look at the university curriculums on the Internet, one can see that lessons centered on GSC are not held nationwide. I want GSC to be a part of high school education. This is only possible with not just consensus of opinion among members of industry, government, and academia, but with strong guidance and support from the government.

5. Organizational reform

As mentioned earlier, GSCN has been active for ten years, and has grown in terms of both quality and quantity. I predict that the roles that GSCN should carry will become even heavier. I think now is a necessary time to review the organization of GSCN. I look forward to discussions from relevant members.

I have spoken out on various matters, and they may sound quite opinionated. I ask for your indulgence.

I hope that this essay will at least be a little bit helpful to the expansion of GSCN.

Development of Hybrid Materials Based on Plant-derived Polylactic Acid and Natural Rubber for Industrial Uses

Kouhei Shiraishi, Kazuo Sugiyama

Faculty of Engineering, Kinki University

Kunihiko Hashimoto, Toru Yano

Nishikawa Rubber Co., Ltd.

Polymers derived from plants, such as polylactic acid, are called “green polymers” (GP), as they considered “carbon neutral.” Their development and application are being vigorously pursued. The method presented here discusses the development and commercialization of a material using more than 97% of plant matter from natural rubber and polylactic acid, which are representative of GP. The material has outstanding properties of impact strength and heat resistance.

Since the Industrial Revolution, the amount of fossil resources used has grown tremendously, as has the amount of carbon dioxide emitted. This has resulted in a huge impact on the global environment, and the reduction of carbon dioxide gas has become an international challenge.

Polylactic acid, which is derived from non-fossil resources, is representative of biomass plastics that can be obtained at a relatively low price. However, because it is hard and brittle, low in heat resistance and durability, and is easily hydrolyzed, it has weaknesses, such as it cannot be used as a durable component outdoors.

To give properties of heat resistance and impact strength, which are required for industrial components, to poly-L-lactic acid, we sought to create a compound that includes an agent granting flexibility, a nucleating agent of proprietarily developed starch and poly-D-lactic acid, and a compatibilizer. Natural rubber was added for tensile strength and to improve physical properties such as stretching. To improve the properties of hydrolyzability and fire retardancy, the aforementioned agents and a third component was added.

To turn the ingredients into a compound, a twin-screw extruder was used(Figure 1). Each additive was added in the appropriate order to the water-adjusted raw materials, and the compound was produced as pellets for injection molding.

Figure 1 Polymer compound using twin-screw extruder

Compared to polylactic acid itself, the injection molding products obtained from the modified polylactic compound (88% to 98% plant material) has an increased heat resistance of 50°C and 10x greater impact strength. As shown in Figure 2, it has attained use as automobile interior parts.

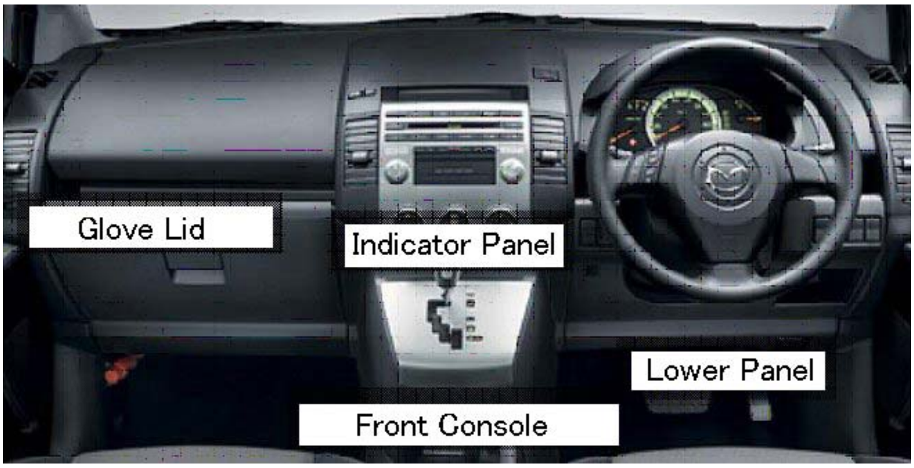

Figure 2 Application for automobile interior parts of developed materials

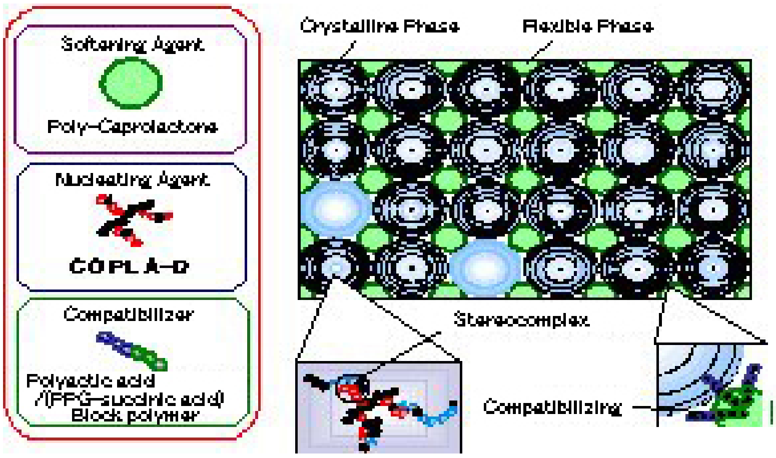

Figure 3 Diagram of conceptual resin structure

As shown in Figure 3, the physical improvements in polylactic acid are due to the bonding of the uniformly distributed polylactic acid crystalline phase and the immiscible flexible phase by the compatibilizer.

To further expand on our research, we used natural rubber as the flexible phase, and combined epoxidized natural rubber, which joins the flexible and rigid phases, and a hydrolysis inhibitor to create a new compound for injection molding that uses more than 97% plant material. This compound can be used as industrial components.

To create a recycling-based society, we seek to develop a material that is 100% plant-based and accelerate the expansion of its applications.

Green Biocatalysis in Supercritical Carbon Dioxide

Tomoko Matsuda Department of Bioengineering, Graduate School of Bioscience and Biotechnology, Tokyo Institute of Technology

Biocatalysis in supercritical CO_2 has been an important technology to develop green chemistry since both CO_2 and enzyme are environmentally friendly materials. The use of CO_2 for biotransformation makes reactions efficient and simplifies work-up procedures. So far, the most of the reports concerns lipase-catalyzed reaction, and optically active compounds have been synthesized. Recently, the carboxylation reaction using CO_2 as a substrate and solvent as well as asymmetric reduction in CO_2 have been reported.

The development of utilization methods of abundantly existing CO_2 has been an important subject to investigate. In nature, enzymatic reactions using CO_2 produce necessary materials as shown in Fig. 1. Similarly, organic synthesis to make useful compounds for mankind such as pharmaceuticals etc. using enzyme and CO_2 has been a successful method to build sustainable society. Especially, CO_2 in supercritical state is useful and valuable to utilize CO_2 effectively.

Advantages of using supercritical CO_2 as a solvent for enzymatic reaction instead of aqueous media or organic solvents is as follows. 1) CO_2 can be easily separated from products just by reducing pressure. 2) CO_2 is a safe material, so there are a few problems for a trace amount of solvent existing in products. 3) Supercritical CO_2 has high diffusibility like gas, so rate of diffusion limited reaction can be accelerated. 4) Hydrophobic compounds can be dissolved into supercritical CO_2 as in hydrophobic organic solvents. 5) Density of CO_2 in supercritical CO_2 is high, so reaction using CO_2 as a substrate is easier to develop. 6) Density of CO_2 can be change largely and continuously by manipulating pressure and/or temperature to control solvent property to be suitable for reactions.

As a system for biocatalysis, flow system (Fig. 2) is the most efficient to make the reaction vessel to be as small as possible. (Vessel should be small because of the high pressure of supercritical CO_2.) Substrate and CO_2 are sent to the reaction vessel packed with enzyme, and then they flow into back-pressure regulator, where the pressure is reduced to atmospheric to separate CO_2 from products. Organic solvents are not used at all. Actually with the system, optically pure alcohols were obtained using lipase. As shown in Fig 3 (a), 3 days' operation resulted in a quantitative transformation of (R/S)-1-phenylethanol (221 g) to (S)-alcohol with 99% ee and (R)-acetate with 99% ee using 1.73 g of the immobilized enzyme. Similarly, the aliphatic alcohols, 2-undecanol and 1-tetralol, were kinetically resolved with the lipase to give a mixture of optically active (R)-esters and unreacted (S)-alcohols.

In conclusion, lipase catalyzed reaction in supercritical CO_2 using flow system is described in details. Other kinds lipase catalyzed reactions such as one-pot reaction of reduction of ketone using a chemical catalyst and lipase catalyzed kinetic as well as dynamic kinetic resolution have been reported, recently. As well, the use of other kinds of enzymes has been reported as shown in Fig 3 (b,c). Furthermore, polymer synthesis/recycling and food processing have been also actively investigated using supercritical biotransformation technology. Study for biocatalysis in supercritical CO_2 has just begun due to the strong concern with the natural environment. With more investigations, it will be developed to be suitable for green industrial applications.

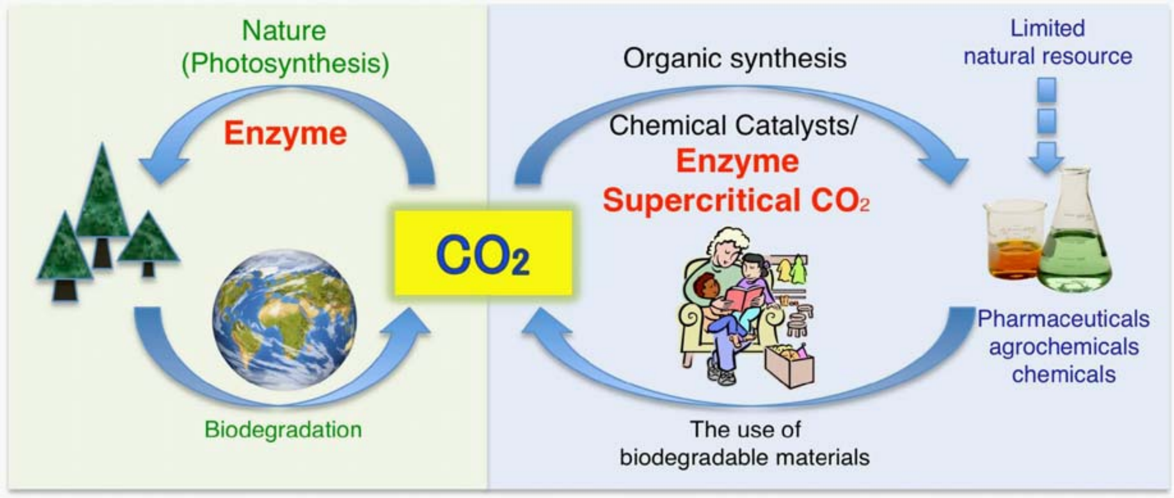

Fig. 1 Photosynthesis in nature using CO_2 catalyzed by enzyme vs. organic synthesis catalyzed by enzyme using CO_2 as substrate and/or solvent.

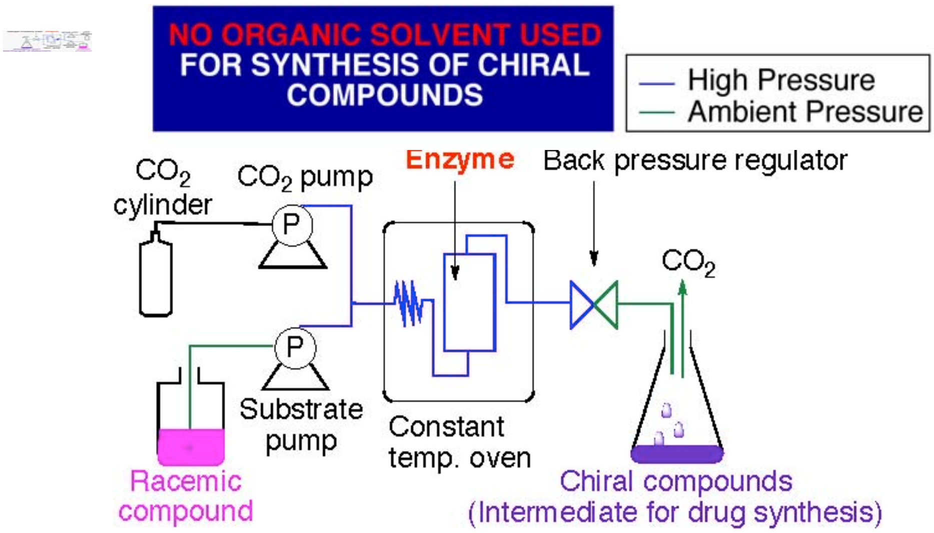

Fig. 2 Lipase catalyzed chiral synthesis using flow supercritical CO_2 reaction system

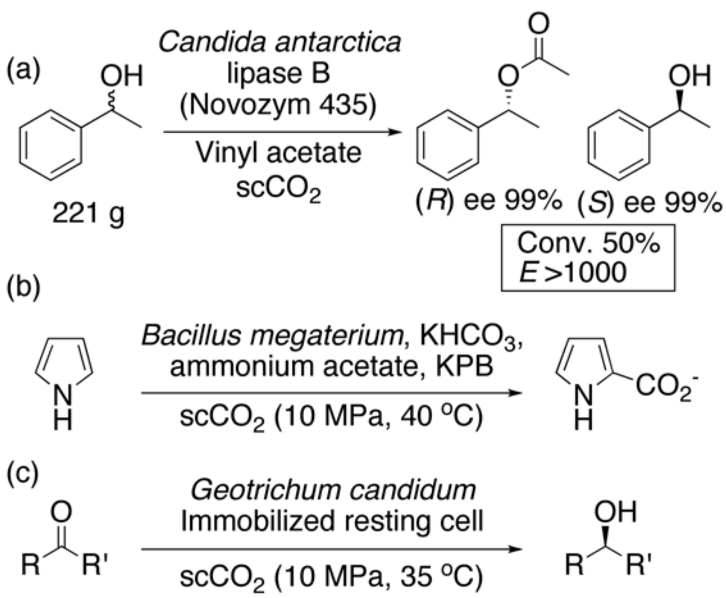

Fig. 3 Examples for enzymatic reactions using supercritical CO_2

Joint Conference of the 4th International Conference on Green and Sustainable Chemistry (GSC-4) & the 2nd Asian-Oceanian Conference on Green and Sustainable Chemistry (AOC-2)

Tsutomu Takahata,

Technological Strategy & Planning Division

Japan Chemical Innovation Institute

The 4th International GSC Conference (GSC-4) and the 2nd Asian-Oceanian GSC Conference (AOC-2) were held jointly in Beijing from August 20 to 24, 2009 (organizing committee chairman: Professor Buxing Han, the Chinese Academy of Sciences). The conferences were a success, drawing about 400 participants from inside and outside China. One could sense the widening of GSC activities to the regions of Asia and Oceania.

Since its establishment, the GSC Network has worked to expand its activities to the regions of Asia and Oceania. After agreement from China, South Korea, Malaysia, Australia, and Taiwan, the Asia-Oceania Network (AON) was launched. The conferences in China this year are significant in that the GSC conference and the GSC Asia-Oceania Conference were held for the first time in Asia (besides Japan). (The first GSC conference was held in 2003 in Tokyo; GSC-2 was held in 2005 in the U.S.; and GSC-3 was held in 2007 in the Netherlands. The first GSC Asia-Oceania conference was first held in 2007 in Tokyo.) As part of GSCN's activities, it organizes speeches by GSC award recipients, implements the Student Travel Grant Awards, and participates in the conferences.

Jiuhua Resort and Convention Center, site of GSC-4 and AOC-2

The conferences were held at the Jiuhua Resort and Convention Center, located 30 km north of central Beijing. The conferences were a rousing excess, drawing about 400 participants.

During the sessions, there were ten keynote lectures, 36 invited lectures, and 48 lectures by general participants, for a total 94 oral presentations.

From Japan, the keynote lecturer was professor Takashi Tatsumi of the Tokyo Institute of Technology. The invited speakers were professors Tadafumi Adschiri of Tohoku University, Motonobu Goto of Kumamoto University, Masatake Haruta of Tokyo Metropolitan University, Shu Kobayashi of the University of Tokyo, and Kazuhiko Hiyoshi of the Japan Chemical Innovation Institute. Of the general lectures, the lecture "Attract Students' Interest in Chemistry through Green & Sustainable Chemistry" by Kazuko Ogino, professor emerita of Tohoku University, especially drew the participants' interest. Professor Ogino demonstrated GSC through small experiments, which drew smiles from the participants.

The poster session was held on August 22 in the afternoon. There were 177 presentations, including seven by the 2008 Student Travel Grant Award winners from Japan, one by 2006 GSC prize winner Kazuki Goto of Toray Industries, and one by 2006 GSC prize winner Yuji Akao of Citizen Electronics. Discussions took place in a congenial atmosphere.

The Best Poster Prize was given to 12 outstanding young presenters, and the Green Chemistry Prize was given to five presenters. Of the 17 total awards, Japanese students won seven, demonstrating the high quality of GSC research in Japan.

Of the Student Travel Grant Award recipients, Taisuke Banno (Keio University), Nobuko Ohba (Tokyo Institute of Technology), and Maki Ohashi (Osaka Prefecture University) won the Best Poster Prize. Sayoko Shironita (Osaka University) and Kenichiro Koshika (Waseda University) won the Green Chemistry Prize. Besides the Student Travel Grant Award recipients, Kaichiro Kuwano (Tokyo Metropolitan University) and Yasuaki Matsuo (Tohoku University) also won the Best Poster Prize.

The success of this year's conferences demonstrated that GSC's philosophy is taking root in the Asian-Oceanian region. Young researchers who participated also made new acquaintances with overseas colleagues, which promises to widen GSC's activities in the future.

The next GSC international conference (GSC-5) will be held in June 2011 in the U.S. The next Asia-Oceania Conference (AOC-3) will be held in fall 2011 in Australia.

Recipients of the Best Poster Prize and Green Chemistry Prize

The delegation to the conferences were supported by a grant from the Commemorative Organization for the Japan World Expo '70.

Commemorative photo of the conference participants (taken August 21, 2009)

Comment about Participation in GSC-4/AOC-2

Kenichiro Koshika
Graduate School of Advanced Science and Engineering
Waseda University

I created an organic secondary battery consisting of polymers together with positive/negative electrodes, and made a presentation of its charge/discharge properties and suitability to green chemistry. Despite the fact that my presentation was in an area of energy devices that is not yet a major field in GSC, many participants showed interest, and I received much helpful advice. Also, during the oral presentation session, I was able to listen to researchers who are doing world-class research in green chemistry. This was a valuable experience for me. I hope to use the experience from the Beijing conference to polish my research in the future.

Maki Ohashi
Graduate School of Engineering
Osaka Prefecture University

The GSC conference was an extremely significant event for me. I was able to directly listen to lectures given by top scientists in the world on topics from the basic philosophy of GSC to research findings. I am thankful to be given the wonderful chance to broaden my vision by being in contact with an extraordinarily wide range of research fields at once, not only in my field of organic photochemistry, but in all fields of chemistry and also in biology and education. I received questions from researchers from a variety of fields on the poster presentation of my research, and I was able to re-evaluate my research from the standpoint of GSC. I am thankful to receive the GSC Poster Prize. I intend to apply my experience from this conference to my future research.

Nobuko Ohba
Graduate School of Engineering
Tokyo Institute of Technology

At this year’s conference, I was able to listen to the newest research announcements in GSC and deepen my knowledge. There were many speeches on the current state and challenges facing GSC, and it made me consider deeply what positions we should take in chemistry with regards to GSC. I was also able to exchange comments with many researchers at my poster presentation. I am thankful to receive extremely meaningful comments that differed from the usual viewpoints, and felt the value of attending such a large-scale conference. I intend to make use of this experience, and contribute to the further development of GSC.

Sayoko Shironita
Graduate School of Engineering
Osaka University

Thank you for allowing me to participate in GSC-4/AOC-2, and for allowing me to present my poster on "Preparation of noble metal nanoparticle using photo-assisted deposition on single-site photocatalyst." Furthermore, I am deeply honored to receive the Green Chemistry Poster Prize. At the conference, I was able to have discussions about the leading edge of green chemistry with researchers from different countries prominent in their fields. In the future, I wish to make GSC a basis of my research into material design, and make advancements in the development of catalysts to ~~address~~ solve the environment and energy problem.

Satoshi Suganuma
Materials and Structures Laboratory
Tokyo Institute of Technology

I sincerely thank the GSCN, whose support allowed me to attend the 4th GSC International Conference. At the conference, I gave a presentation on cellulose hydrolytic reaction using solid carbon-based acid. Carbon-based solid acids can hydrolyze cellulose, and its catalytic activity is comparable to that of sulfuric acid. This reaction system is useful as a hydrolytic reaction system utilizing solid acid, which has a low environmental load. From discussions at the conference about the reaction mechanics and catalyst structure, I was able to reconsider my research anew. I hope to make use of the knowledge I obtained in Beijing and contribute to the development of chemical technologies to realize a recycling society.

Shinji Suzuki
Graduate School and School of Engineering
Nagoya University

I was able to learn about the range wide of approaches to GSC (Green and Sustainable Chemistry) at the GSC-4 conference, held in Beijing. Because GSC spans many different research areas, I was able to learn a variety of information that transcends my own field. It was stimulating. I was also blessed with the opportunity to give an oral presentation, which was an incredibly valuable experience. Making use of the knowledge and experience I obtained from the conference, I will aim for simple and green developments and strive for GSC-oriented research activities.

Taisuke Banno
Graduate School of Science and Technology
Keio University

At the GSC international conference, I was blessed with the opportunity to present a poster on the creation of surfactants that has excellent biodegradability and can be chemically recycled. I received many helpful suggestions from researchers from a variety of fields. I was also able to listen to wide-ranging research achievements of GSC, and deepen my understanding of GSC. I recognized the importance of obtaining knowledge and information that transcends my own field. I will strive to apply what I experienced at this conference to my research and develop next-generation surfactants that are friendly to the environment to contribute however I can to society.