Technologies for Green Processes

**Research and Development on Green and Sustainable Chemistry**
The five major programs

Research programs in green and sustainable chemistry (GSC) may be divided into five main categories: raw materials, reaction processes, end products, recycling, and waste processing. There has been a global shift in raw materials from current technologies based on petroleum towards biomass conversion and other renewable resources. We are seeking a way how we should proceed research on biomass in Asia as well as in Japan. As for end products, there is a growing demand for new chemical products and materials which are friendly towards it is especially important that R&D be performed in conjunction with industries. Concerning reaction processes, innovations need mid- and long-range R&D covering a wide range of research from basic to applied. AIST accordingly regards this as a high-priority work and plays a leading role in R&D in Japan. Reaction processes include the three main component technologies of catalysts, separation membranes, and non-organic solvents, and AIST has many years of accumulated technological experience in these areas.

**Innovations in Reaction Processes for Saving Energies and Resources, and Poison-free Materials**

(1) Halogen-free, energy and resource saving selective oxidation processes

To produce functional chemical products from petroleum, namely, or hydrocarbons, it is necessary to selectively add oxygen, and this oxidation reaction processes occupy the second largest market in chemical industry after polymer synthesis. At the present time, however, the major industrial processes consist of multi-stage reactions using halogen or costly organic peroxides. It would be desirable if we could develop processes which enable us to selectively synthesize desired organic oxygenate compounds (e.g., unsaturated alcohols, aldehydes, epoxides) using hydrogen peroxide (where the only by-product would be water) or, ultimately, using only molecular oxygen.

One example of such a process is shown in Figure 1, which illustrates an attempt to synthesize adipic acid, which is used to make nylon-6,6, using hydrogen peroxide. The current method of producing adipic acid is to react cyclohexanone and cyclohexanol with nitric acid, but this produces nitrous oxide as a byproduct. While this nitrous oxide could be used as an oxidizing agent, in actual practice it is often transformed into N2 through decomposition. At AIST, we have discovered a new sodium tungstate catalyst for the synthesis of adipic acid in a simple route shown at the bottom of Figure 1.

![Fig. 1 New route for the synthesis of adipic acid (row material for nylon –6,6)](image1)

![Fig. 2 Palladium membrane reactor and its application to direct phenol synthesis](image2)

![Fig. 3 (above) Synthesis of ε-caprolactum with microreaction system utilizing supercritical water](image3)

![Fig. 3 (below) Environmentally-friendly material recycling system utilizing supercritical water –nylon 6 synthesis](image4)
(2) Energy-saving separation and concentration techniques using separation membranes

In the chemical industry, it is said that over 50 percent of all energy consumed is used in separation and concentration processes, but if separation membranes were applicable to these processes it would lead to remarkable reduction in energy consumption. Moreover, the ion chamber equipped with separation membranes can overcome the limitations of chemical equilibria (e.g., in dehydrogenation reactions), leading to increased conversion and selectivity. An example of this has recently been presented by AIST, where we have succeeded in direct synthesis of phenols from benzene in a single-stage reaction by sending dissociated hydrogen atoms through a palladium membrane and controlling the reactivity of oxygen molecules reacting with the benzene. (See Figure 2.)

(3) Simplified synthesis reactions using supercritical fluids

In order to innovate reaction processes, changing solvents in which reactions take place is one effective mean of doing so. Interest has also grown in methods where carbon dioxide or water is used in a supercritical state, because supercritical fluids impose environmental burden than organic solvents less vapor pressures of which at room temperature are relatively high and the vapor is often toxic. An example can be seen in the synthesis of ε-caprolactum, which is used to make nylon-6. Reaction can be completed in a short time within a second with an ε-caprolactum selectivity of 99% if a supercritical water micro-reaction system is used. This method eliminates the need for acid catalysts and the recovery and reuse of solvents and is therefore a very interesting environmentally-friendly method for the synthesis of a raw compound for making nylon. (See Figure 3.)

Green and Sustainable Chemistry Network

Green and sustainable chemistry, which means a type of chemistry friendly to both people and the environment and capable of supporting a sustainable society, would represent a major innovation in production in chemical industry, and work directed towards making GSC a reality is being performed all around the world. This work has begun since the United Nations Conference on Environment and Development in Rio de Janeiro in 1992 (i.e., in accordance with Chapter 19 on the management of chemicals in Agenda 21), with this work being performed by Organization for Economic Co-operation and Development. At the Risk Assessment Steering Group’s Venice Workshop on Sustainable Chemistry held in October 1998, an agreement was reached which stated that the participants recognized that green and sustainable chemistry would contribute to the improvement and advancement of environmental management programs and that governments, industries, and academia in all nations should initiate programs to make GSC a reality and strive to promote GSC. Under a restructuring of the OECD which took place in June 1999, work on GSC began to be performed by an organization placed directly underneath the OECD joint meeting (i.e., meeting of representatives of member nations of the OECD).

In response to these global developments and in recognition of the fact that an organization ought to be formed in Japan, Green and Sustainable Chemicals Network (GSCN) was established in March 2000 under the direction of what was then Chemicals Office of Ministry of International Trade and Industry to make GSC a reality in Japan. Including what was then National Institute of Materials and Chemical Research, a total of ten organizations participated in GSCN: three academic associations (The Society of Chemical Engineers, Japan, The Society of Polymer Science, Japan and The Chemical Society of Japan), Japan Association for International Chemical Information, The Association for Progress of New Chemistry, Japan Chemical Industry Association, Japan Chemical Innovation Institute, Chemical Evaluation and Research Institute, and Japan Bioindustry Association. National Institute of Advanced Industrial Science and Technology (i.e., AIST) has continued to serve as a member of GSCN since it was reestablished as an independent administrative institution.

Serving as a main member of the GSCN

The main activities of the GSCN are divided into two types: domestic activities and international activities related to the OECD. Just as it is stated in Chapter 19 on the management of chemicals in Agenda 21, the initiating force behind the green and sustainable chemistry movement, in recognition of the importance of education and providing the public with information in order to gain the understanding of the people about GSC activities, in domestic activities GSCN has devoted a great deal of effort to public information and education activities. Of course work is also being done to promote the performance of research directed towards making GSC a reality. In September 2002 we published Initiative GSC21: Challenge of Chemical Technology, a document which set forth general guidelines concerning the future of GSC research.

Presently, the main activities of GSCN consist of (i) the organizing of annual GSC symposium, and (ii) granting GSC awards. The first international conference on green and sustainable chemistry, GSC Tokyo 2003, was held in March 2003 at Waseda University with 760 participants including 120 participants from twenty nations not including Japan, and the conference proved a huge success. AIST has helped to support the international conference by serving as members on the action committees for the conference, and amongst the research presentations, 22 of the 129 presentations consisted of presentations of research performed at AIST, thus resulting in a substantial contribution to the success of the conference. As for the GSC awards, three minister’s awards (i.e., the Ministry of Economy, Trade and Industry Minister’s Award, the Ministry of Education, Culture, Science, Sports and Technology Minister’s Award) have been granted since 2002, and Dr. Akira Sekiya of AIST’s Research Center for Developing Fluorinated Greenhouse Gas Alternatives was given the honor of sharing the MoE Minister’s Award with the Zeon Corporation.

GSCN is currently composed of five working groups including GSCN Operating Committee. AIST researchers serve as members on all of the GSCN’s working groups and committees, and AIST itself serves as one of the main organizations working towards the realization of green and sustainable chemistry. Finally, it should be noted that over 20 organizations are now the members of the GSCN.