



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

Arrival of era of global environment ideology

Koichi Kitazawa, President, Japan Science and Technology Agency (JST)



The coming era of renewable energy sources will require "geographic averaging" made possible by a network of superconducting cables for power distribution. The principle drawback of renewable energy is that it is intermittent: wind stops blowing, the sun is obscured by clouds, and power generation grinds to a halt. This creates a need to store energy, but "time averaging" that is involved in storing electricity is exceedingly difficult and very expensive.

This whole conundrum could be solved with a globe-girding network of superconducting cables. Such a grid would not only even out the daily differences between night and day and the seasonal differences between winter and summer, it would also eliminate the fluctuations in electrical power resulting from the averaging effect. The capability to develop and deploy this technology is now at hand.

Dr. Yukinori Kuwano, the former general manager of Sanyo Group's R&D Headquarters, was an early advocate of the GENESIS project that would bring power generated by solar cells in the Sahara Desert to Japan via superconducting cables. If solar cells were deployed over 25% of the surface area of the Sahara, it would meet the total energy requirements of the entire world. And if we could combine this kind of "optimum site for generating power" with "geographic averaging," this would be even better still.

Over these past 20 to 30 years I have always felt that increasing nuclear power was the only viable alternative. Now I believe that it would be very desirable if we could shift our emphasis to renewable energy sources by the latter half of the 21st century. We owe it to our children and to our grandchildren to leave them with a secure source of energy that is no more than two to three times the prevailing cost.

We can anticipate in the near future the emergence of a new *era of global environment ideology* centered around greenhouse gas emissions. This ideology will affect the way people live, and will become a key consideration in negotiations between nations. The recent election of Obama in the U.S. has hastened the transition to this new era. Japan too has felt a discernable *Obama effect*, and has quickened the pace of developing renewable energy sources. The European Commission is already investing close to 0.5% of its GDP in renewable energy, and is recommending that 20% of its energy come from renewable sources by the year 2020.

The younger generation in Japan grew up under the influence of animation classics with environmentalist themes such as *Nausicaa of the Valley of the Wind* and *Princess Mononoke*. Not surprisingly polls show that young people are ahead of their elders in regarding the environment as ideological in nature. When the younger generation takes over the reins of power, I bet we'll see a major paradigm shift in all the big electrical power using industries: silicon manufacturing, electrolytic steel production, electrolytic recycling, water electrolysis industry—and last but not least, the chemical industry.

8th GSC Award, METI Award(2008)

Development of new propylene oxide process by cumene recycling

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Abstract

It is very important as convincing measures for the issue of environment / resources to practice green chemistry, synthesizing only an object efficiently without draining byproducts. Propylene oxide (PO) is widely used with production more than 7 million tons per year worldwide as raw materials for urethane. With the development of a high performance epoxidation catalyst, Sumitomo Chemical has succeeded in establishing a novel PO only manufacturing process where cumene is used and recycled as a reaction medium. Our PO cumene process gives higher yields than conventional processes while only producing small amounts of by-products.

Propylene oxide (PO) can be produced by conventional chlorohydrin or hydroperoxide process. Each conventional process has the unsolvable disadvantage, such as producing a large amount of valueless chloride salt or co-producing a huge amount of styrene or isobutene.

Sumitomo Chemical has developed a new PO only production process that does not produce any co-products. Cumene is used and recycled as a reaction medium like "oxygen carrier" through three reaction steps of oxidation, epoxidation and hydrogenation in the process (figure 1).

Most important problem was how to develop a highly active catalyst for the epoxidation using such a large molecule like cumene hydroperoxide with propylene. Microporous Ti-silicate zeolite such as TS-1 is well-known to be a very active epoxidation catalyst by the reaction with hydrogen peroxide, but it showed extremely low activity for the epoxidation with cumene hydroperoxide. The three factors are thought to be important for developing high performance catalyst, (1) to maximize tetrahedral titanium active sites highly dispersed in a silica matrix, (2) to have mesoporous structure (nano space) which a large molecule like cumene hydroperoxide can be easily diffused, and (3) to have sufficient hydrophobic property for high propylene affinity. As a result of challenging catalyst development especially focusing on how to make as many meso pores as possible, we have succeeded in finding and industrializing a high performance Ti-silica epoxidation catalyst, which have a characteristic "mesoporous structure". Figure 2 shows a reaction image with a mesoporous epoxidation catalyst. We think this is a first example of industrialized mesoporous catalyst.

In our process, all reaction steps proceed in especially high yields, and the usage of process energy is very low since all exothermic reaction heat of oxidation, epoxidation and hydrogenation is recovered and effectively utilized. Therefore, we think our PO cumene process is superior in raw material consumption and energy consumption to other processes including the hydrogen peroxide method. We can estimate that the energy saving effect of our new process against a conventional process is equivalent to the carbon dioxide reduction of about 300,000 tons/y, based on a PO 200,000 tons/y plant. Our new PO process is very economical and "green". The first plant using our new technology was built in Japan and started up in 2003, and the second plant at Petro Rabigh in Saudi Arabia is to start up this year.

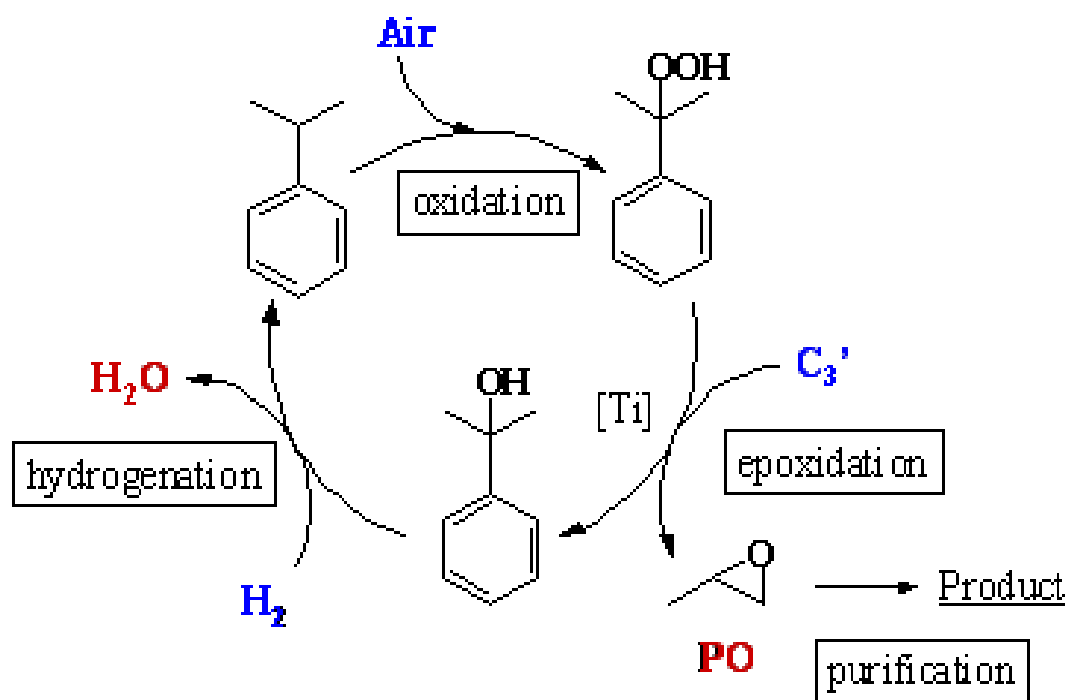


Figure 1. New Sumitomo PO Process

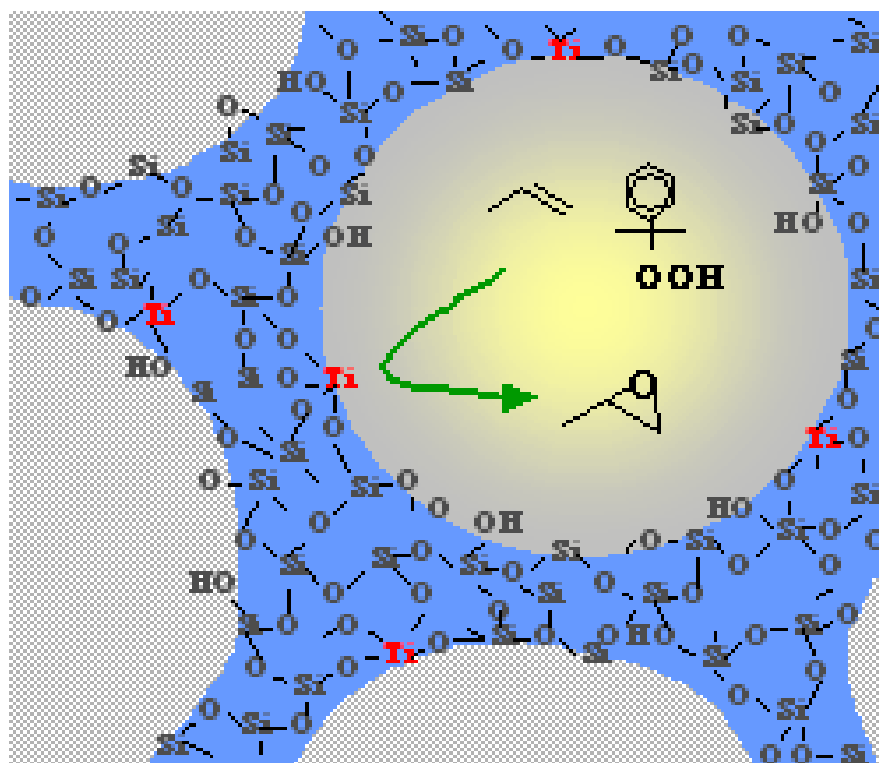


Figure 2. Reaction Image with a Mesoporous Catalyst

8th GSC Award, MEXT Award (2008)

Development of plastic dye-sensitized solar cells by printing technology

Graduate School of Engineering, Toin University of Yokohama,

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Abstract

By combining low-temperature deposition of titanium dioxide (TiO₂) porous films with printing technology, the ability to produce low-cost dye-sensitized solar cells (DSSCs) on plastic substrate is now available. With energy conversion efficiencies up to 7%, these lightweight flexible plastic solar cells are now poised for large scale commercial production and will see extensive application to portable applications. DSSC technology is environmentally friendly because the fabrication processes are extremely energy efficient and the constituent materials can be easily recovered and recycled. An easy-to-assemble dye-sensitized solar cell kit was developed as a learning tool to teach school children about energy and the environment.

1. Fabrication of dye-sensitized solar cells by low-cost chemical processes

Dye-sensitized solar cells (DSSCs) have now reached practical efficiency levels that are high enough to compete with conventional solar cells, and can be fabricated inexpensively in open air conditions. The development of dye-sensitized semiconductors grew out of efforts to increase the sensitivity of photosensitive materials, and photoelectrochemical research has a long history stretching back more than 40 years. Recently, energy conversion efficiencies up to 11% have been achieved using very large sheets of dye-sensitized nanocrystalline porous titanium oxide (TiO₂) film with a surface roughness coefficient of greater than 2000. Dye-sensitized porous TiO₂ films are highly light absorbent, and are thus able to capture diffuse visible light on overcast days outdoors and from artificial light sources indoors very efficiently. As the ubiquitous network society continues to evolve, these lightweight unbreakable and flexible photovoltaic cells show enormous promise for replacing the vast number of batteries that people use in the mobile devices that they carry around. In the deposition of semiconductor nanocrystalline porous TiO₂ film—the heart of the DSSC fabrication process—typically a paste that consists of nano particulate TiO₂ suspended in a resin binder is coated onto a substrate, which is then sintered by firing at a high temperature of 450°C or above. This forms the photovoltaic layer that absorbs or is sensitive to the dye.

Until recently, expensive transparent conductive glass coated tin oxide was used for the substrate, so the substrate alone accounted for close to half the manufacturing cost. If this glass substrate could be replaced by plastic film, this would greatly simplify the fabrication process and also permit continuous roll-to-roll manufacturing such as used to make textiles that would dramatically reduce the production costs.

2. Printable plastic dye-sensitized solar cells

With the goal of producing electrodes for DSSCs using plastic substrate, the authors developed an innovative new type of paste for the porous TiO₂ that is cured by dehydration drying at low temperatures below 150°C and thus doesn't require high-temperature firing. Not including the binder, the paste is a viscous composite that consists of nanocrystalline TiO₂ particles and titanium dioxide aqueous sol as a particle binder that is dispersed in branched alcohol-water. The paste is coated onto the substrate by screen printing, and the nanocrystalline porous film is cured by applying dry heat under 150°C and dehydration-condensation reaction. Using ITO transparent conductor coated PEN (polyethylene naphthalate) for the substrate, Ru complex dye N719 for the sensitizer, and iodine in 3-methoxypropionitrile for the electrolyte, we fabricated dye-sensitized solar cells with an active area of 0.23 cm² that yielded energy conversion efficiencies of 5.9% in strong light (1 sun = 100 mWcm⁻²) and 7% in low light.

Next we developed a prototype practical module that interconnected the solar cells to investigate ways of fabricating grids for energy collection and sealing materials using similar low temperature processing. Using a deformable plastic substrate, we were able to dramatically reduce the thickness of the electrolyte (the amount of electrolyte used) to 1/5 the usual thickness, and because the light filtering effect caused by the coloring of the electrolyte was eliminated, incident light from both sides of the electrode could be effectively used.

Photo 1 shows what the parallel-type large-area prototype module looks like.

Photo 2 shows the large-area prototype plastic integrated modules (0.8 X 2.1 meters) that are made up of 10-cm-square submodules (6-cell arrays, 4.2 V each). The modules were exhibited at the 1st International Photovoltaic Power Generation Expo in 2008 (PV EXPO 2008) and efficiently generated 112 volts of electricity using the diffuse artificial light in the exhibition hall. This printable technology that doesn't involve high-temperature firing makes it possible to fabricate high-performance dye-sensitized solar cells at very low cost. The constituent materials can also be readily reused: the inorganic materials in the electrodes (TiO₂, ITO, and metal) and plastic can be stripped out and recovered by mechanical deformation, and the dye and electrolyte can also be recovered by washing.

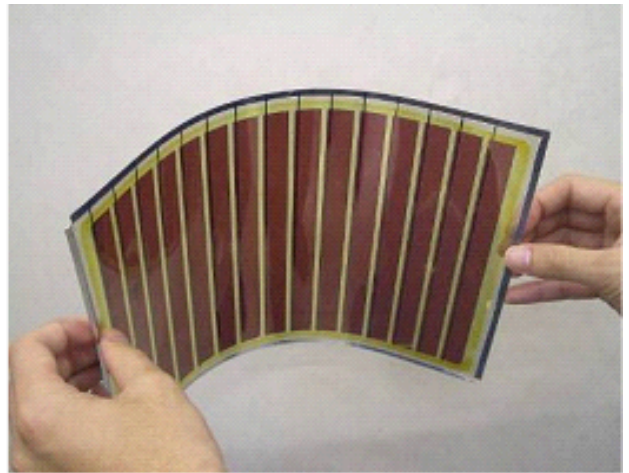


Photo 1: Plastic dye-sensitized solar cell module (A4 size, parallel type, voltage 0.7 V).

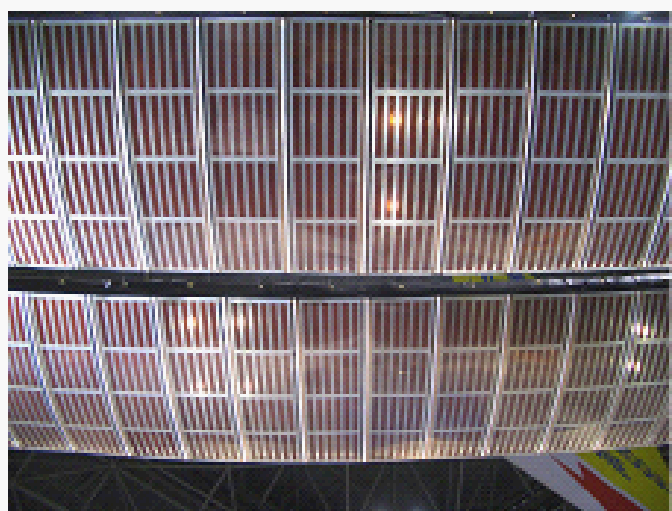
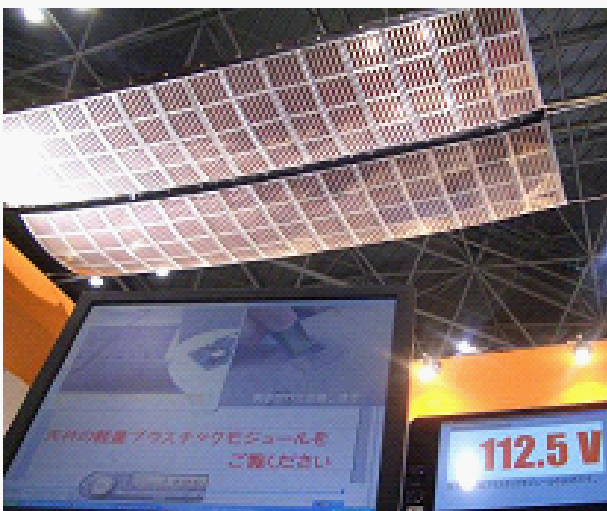


Photo 2: Large-area integrated plastic dye-sensitized solar cell module (0.8 X 2.1 m in size, weighs less than 1 kg/m², and produces 110 V from diffuse indoor lighting).

3. Supporting environment and energy education

Photo 3 shows a DSSC kit developed by Peccell Technologies that can be easily assembled by students without any vacuum or high-temperature processing. In assembling these models, students can experience the entire process from application of the paste to assembly of the energy-producing cell. The solar cell kit can be easily put together from a handful of ordinary components. It has proven to be an effective teaching tool, and has been widely distributed to classrooms around the country.

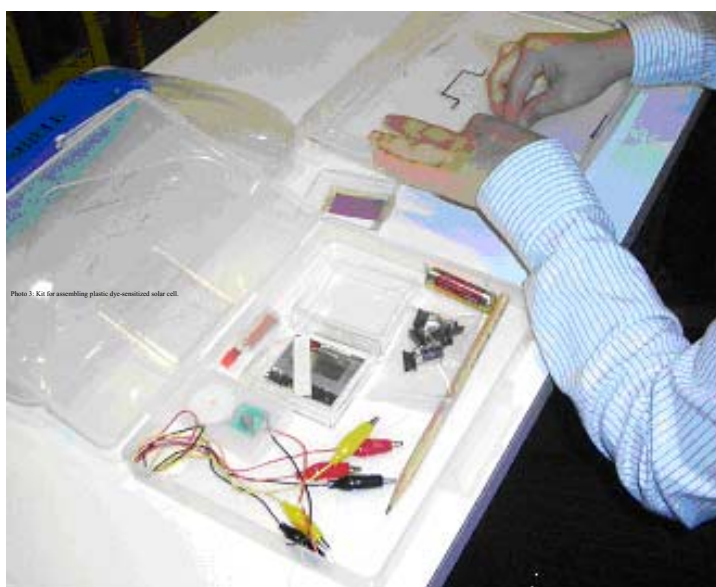
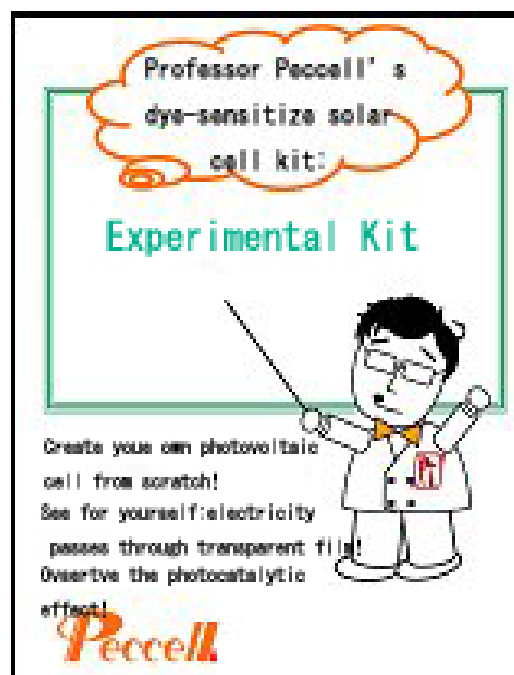


Photo 3: Kit for assembling plastic dye-sensitized solar cell.



Professor Peccell's
dye-sensitized solar
cell kit:

Experimental Kit

Create your own photovoltaic cell from scratch!
See for yourself: electricity passes through transparent film!
Observe the photocatalytic effect!

Peccell

8th GSC Award, ENV Award (2008)

Development and Spread of Energy Saving Technology by Using Drag-reducing Additives

Takashi Saeki, Dept. of Applied Chemistry and Chemical Engineering Yamaguchi University
Keiji Tokuhara, Shunan Region Local Industry Promotion Center Foundation
Toshio Matsumura, ESP Cooperative Society

A new class of energy-saving drag-reducing additives has been developed and deployed that markedly reduces the pumping power for fluid transport in air conditioners and other water closed-loop HVAC equipment. The technology has been adopted at over 120 sites throughout Japan and has been shown to reduce the energy consumption of pumps by 20-50%. It is estimated that if the technology were applied to the HVAC systems in all business buildings throughout Japan, CO₂ emissions could be slashed by as much as 500,000 tons a year. So far the technology has been investigated primarily at the academic level, but wider dissemination of the technology through cooperation between business, universities, and government could bring enormous energy-saving benefits, and contribute to the goals of green sustainable chemistry (GSC).

This initiative was launched as a collaborative project between the Shunan Regional Local Industry Promotion Center and the LSP Cooperative Society (made up of three small-to-medium-sized companies in the Shunan district of Yamaguchi Prefecture) based on starter seed technology developed at Yamaguchi University. Reduction in drag flow compared to a Newtonian fluid is called the *drag-reduction effect*, and it's well known that certain polymer solutions and surfactant aqueous solutions exhibit this effect. Among these, surfactant systems show particular promise for use with closed-loop HVAC systems because they form aggregates of rod-like micelles that suppress flow turbulence, and even when these micelles structures are broken up by the shear force of pumps and other equipment, they are immediately reconstituted.

In the presence of counter-ions (salicylic acid derivative), we found that quaternary ammonium salt cationic surfactants stably exhibited the drag-reduction effect over a wide range of temperatures, and we conducted field trials—the first in Japan—using this compound in HVAC equipment 1994. Based on the results of these trials, we successfully obtained patents for our basic intellectual property pertaining to cationic surfactants exhibiting drag-reducing effects, as well as for the energy-saving use of surfactants to reduce drag in fluid transport.

We developed a drag-reducing additive product called *LSP-01* (see photo in Figure 1) that is tailored for use in air conditioners and other closed-loop HVAC systems. *LSP-01* was an innovative breakthrough water treatment chemical product that saves substantial energy. We followed up with the development of a range of OEM and other similar products based on our basic intellectual property.

We addressed many issues as the drag-reducing technology continued to spread—we developed methods for determining the optimum additive and how to apply and manage the additive for actual equipment systems that are much like black boxes filled with instrumentation, we investigated the effects that surfactants have on the environment, and so on. In the process of dealing with these issues, we developed a substantial body of expertise that has supported further penetration of the technology. By the second half of 2008, equipment using the drag-reducing technology could be found at over 120 sites across Japan including general businesses, retail stores, hospitals, factories, high-rise buildings, theme parks, and airports, and the energy consumed by pumps at these sites was substantially slashed by 20 to 50%. Meanwhile, we have sought to raise awareness about the technology by participating in various

exhibitions and seminars, and taking every opportunity to give presentations about the technology. We are currently working to apply the technology to all kinds of plant equipment and not just HVAC systems, so the drag-reducing technology will be applied to a far greater range of applications in the years ahead. There is also enormous potential for application of this approach to other fluids besides water, so we can expect a lot of research in this area.

Finally, we observed certain characteristic near-wall momentum and heat transfer behavior in flows that calls for further investigation. The behavior is attributed to the effects of uneven transfer phenomena of micelle motion in pipes for drag-reducing flows, and investigation of this phenomenon should lead to new insights regarding the mechanism involved in drag-reducing flows.



Fig.1 Drag-reducing Additives (LSP-01)

8th GSC Award (2008)

Development of high quality material recycling technology for vulcanized rubber

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 FTS Co.Ltd. Y.TANAKA
 TOYOTA Central Laboratory M.Matsushita
 TOYOTA Motor Corporation Y.SUZUKI

This technology is a kind of manufacturing technology to produce the high quality reclaimed rubber while cutting only crosslinking point in cured rubber, which is usually said hard-to-recycle, in short period of time.

The cured rubber is considered as a kind of hard-to-recycle materials, then new recycling technology with better productivity and high quality is highly expected.

Authors have thought the weakest S-S bonds among C-C bonds, C-S bonds and S-S bonds in cured rubber. must be quickly broken when adequate energy is applied. This new technology enables to continuously produce high quality reclaimed rubber with a twin screw extruder, while cutting mainly S-S crosslink by applying suitable energy such as heat, pressure and shear stress. The manufacturing process is more simple and smaller space than those of existing Pan method and the processing time is greatly shrunk by one sixtieth of Pan method. Furthermore, human safety is improved thanks to its automated process.

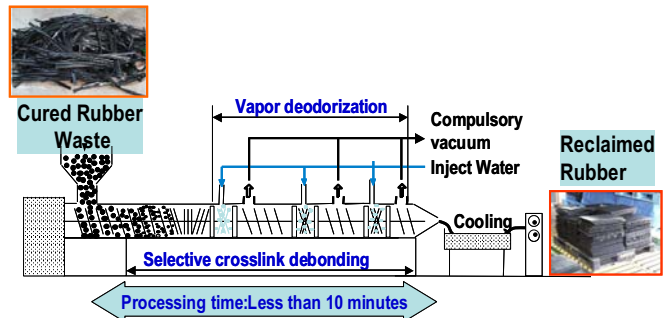


Fig.1 Continuous reclaiming equipment (Twin-screw extruder)

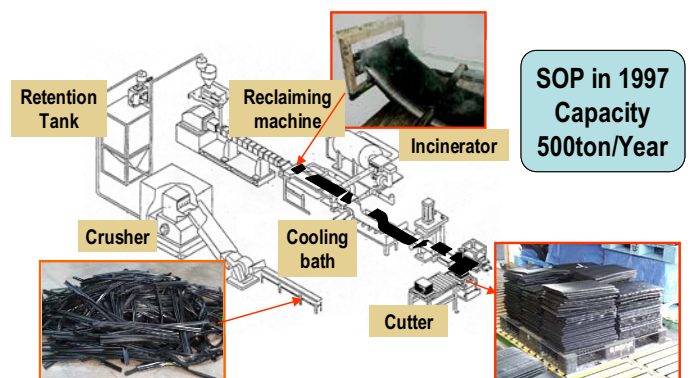


Fig.2 Example of rubber reclaiming process – TOYODA GOSEI

Applying this devulcanization technology, thermo plastic elastomer can also be produced while devulcanizing, dispersing plastic resin and re-vulcanizing the reclaimed rubber dispersed in plastic resin again.

In terms of environmental aspect, land-fill disposal has been reduced by recycling the rubber waste within our manufacturing plant for more than 10 years. Also, this technology has been licensed to other manufacturers including tire manufacturer.

The amount of annual rubber waste exceeds more than 1 million ton. We hope this new technology helps to recycle those waste rubber and to establish resource circulating society.

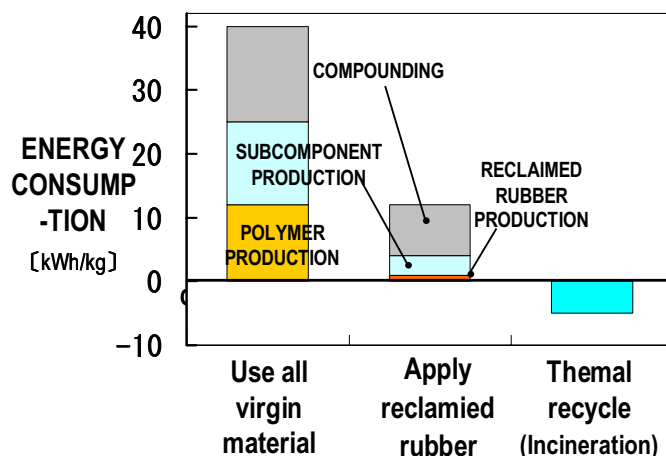


Fig.3 Energy comparison concerning rubber production

8th GSC Award (2008)

Development of Environmental Benign Organic Synthesis based on Advanced Biocatalysis Processes Regulated by a Chemical Method.

Toshiyuki Itoh

Graduate School of Engineering, Tottori University

The use of ionic liquids (ILs) to replace organic or aqueous solvents in biocatalysis processes has recently gained much attention and great progress has been accomplished in this area. Prof. Itoh and his team in Tottori University made a great contribution in this area of Chemistry. (1) They demonstrated an efficient lipase recyclable use system using an ionic liquid solvent system as illustrated in Fig. 1: lipase-catalyzed transesterification of secondary alcohols proceeded smoothly in an ionic liquid and a perfect lipase-recycling system has thus been realized. (2) They discovered that a remarkable activation of a lipase was accomplished by the coating of enzyme protein with alkyl PEG sulfate imidazolium salt (IL1) while maintaining original enantioselectivity: Furthermore they found that (*R*)-pyrrolidine-substituted imidazolium cetyl-PEG10-sulfate (D-ProMe) derived from D-proline worked as a very excellent activating agent of lipase PS. (3) They demonstrated a very rapid transesterification of secondary alcohols in

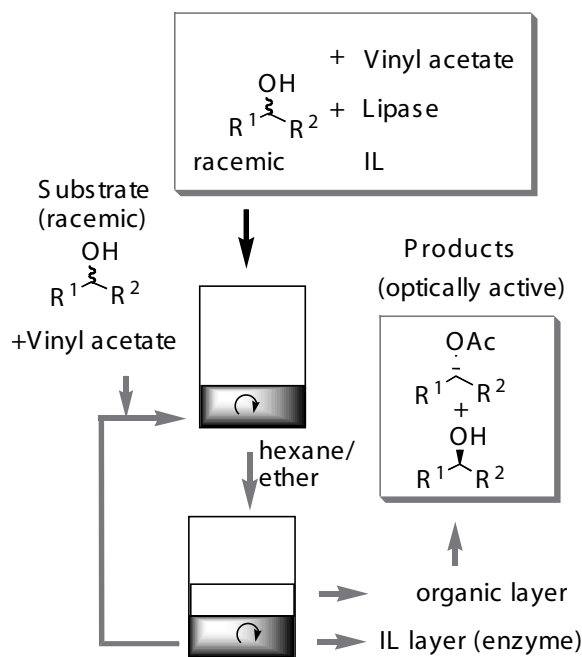


Fig. 1 Enzyme recyclable use system using an ionic liquid as solvent

2-methoxyethyl(tri-*n*-butyl)phosphonium bis(trifluoromethanesulfonyl)amide as solvent using ionic liquid coated enzyme and afforded the first example of a reaction rate superior to that in conventional organic solvent such as diisopropyl ether.

It should be emphasized that ionic liquids can be used repeatedly after simple purification process. Enzymatic reaction processes based on the concept of the Green Sustainable Chemistry have thus been accomplished using ionic liquid as a key reaction medium.

9th Green Sustainable Chemistry Symposium

The 9th GSC Symposium was held on March 9-10, 2009 (Monday and Tuesday) at the Hitotsubashi Memorial Auditorium, National Center of Sciences, Chiyoda-ku, Tokyo. Dedicated to the theme "GSC Practice and Prospects Toward a Sustainable Society," the symposium brought together 320 participants spanning the business, academic, and government communities to hear presentations and discuss the latest research and practices regarding green sustainable chemistry. The symposium including three keynote addresses, nine invited talks, five presentations by GSC award winners, and numerous poster presentations. Awards were then presented for the 5th GSC poster presentations, the 3rd Student Travel Grant Awards, and the 8th GSC awards. This was followed by a reception.

The symposium was kicked off the first day with an opening address by Koji Oe, the GSC Network Chairman. Chairman Oe highlighted the critical role that chemical technology must play in achieving the sustainable society, and called for businesses, universities, and government to mobilize and redouble their support and cooperation for the GSC Network. Chairman Oe was followed by Chisato Kajiyama, the Director of the Japan Student Services Organization (JASSO), who gave a stirring keynote presentation addressed mainly to younger researchers and students on "the role of education in building a sustainable society." The third keynote address was by Satomi Takahashi, the Vice Chairman of the Chemical Society of Japan (and Executive Director of the Kaneka Corporation board) who described an excellent visionary approach entitled "An R&D Strategy based on the viewpoint of attacking a low-oxygen society."

Six guest lecturers gave talks detailing the great importance and place of a fully implemented and robust science program. The first four invited lectures were given on the day one, and the speakers clearly outlined the latest developments in their respective fields. The speakers were Professor Kyoko Nozaki of the Tokyo University Graduate School, Kazuhiko Sato, a senior researcher with the National Institute of Advanced Science and Technology, Professor Akihiko Kudo of the Tokyo University of Science, and Mizuo Maeda, a senior researcher at RIKEN.

The poster session was held in the afternoon in the Central Conference Hall, and some 114 presentations were heard covering a wide range of topics. This year, biomass utilization was added as a new category to the themes that we have addressed in years past: new synthetic methods, catalysts, alternative solvents, processes, resources and energy, biotechnology, biodegradable plastics, green products, recycling, environmental cleanup and restoration, and safety and education. This inclusion of biomass utilization reflects a major new trend. Out of the 114 presentations, 63 sought consideration for a poster prize. Members of the selection committee had a difficult task, but did an excellent job in choosing this year's 6 poster prize winners.

Following the presentation portion of the symposium, the 3rd Student Travel Grant Awards ceremony was held, and 7 students were presented with commendations and cash awards. This was followed by the 5th poster awards ceremony, and the 6 winners received commendations.

Next, the 8th GSC awards ceremony and reception took place at the Josuikan Star Hall. Amid thunderous applause from the crowd of 200, the award winners were called up to the front where GSC Network Chairman Takashi Tatsumi recounted their achievements and they were presented with plaques and certificates from the distinguished guests: Yoshikazu Goto, Director-General of Manufacturing Industries Policy for METI, Takao Kuramochi, Deputy Director-General of the Higher Education Bureau for MEXT, Hirotsugu Kimura, Director of the Environmental Health and Safety Division for MOE, and Koji Oe, GSC Network Chairman. Following the awards ceremony, a reception was held where Chairman Oe gave a welcoming address, Messrs. Goto, Kuramochi, and Kimura made brief speeches, and Makoto Misano, Director of the National Institute of Technology and Evaluation, toasted the winners. A wonderful time was had by all as the attendees mingled and chatted and socialized.

The second day started off with talks by Atsushi Fukuda, Director of the Fine Chemicals Office of Manufacturing Industries Bureau at METI, and Hirotsugu Kimura, Director of the Environmental Health and Safety Division at MOE who laid out the government perspective. This was followed by the remaining two invited lectures in the science program by Professor Tadafumi Adschjiri of the Tohoku University Graduate School and Hideshi Kurihara of Teijin Limited. In the afternoon, we heard talks from the five GSC prizewinners. I hope you will take time to read the summary overviews of the winning papers printed in this issue. In the last session, Professor Buxing Han of the Institute of Chemistry at the Chinese Academy of Sciences gave a presentation, and briefed the assembly on the upcoming 4th International Conference on Green and Sustainable Chemistry (GSC-4) and 2nd Asian-Oceanian Conference on Green and Sustainable Chemistry (AOC-2) that will be held in Beijing in August 2009. This was followed by one last keynote address by Chairman Oe on "GSCN activities to build a sustainable society." Finally, GSC Network Chairman Tatsumi recapped the symposium, highlighted what the participants might expect in years ahead, and closed the meeting with some final remarks.

This symposium was made possible by the generous support of the Asahi Glass Foundation. In addition, assistance was received from 68 groups and organizations. It's gratifying and I really appreciate the fact that our GSC activities are supported by so many good organizations. Finally, I would also express my appreciation to all the speakers, the participants, and the many others whose collective efforts made this symposium possible.