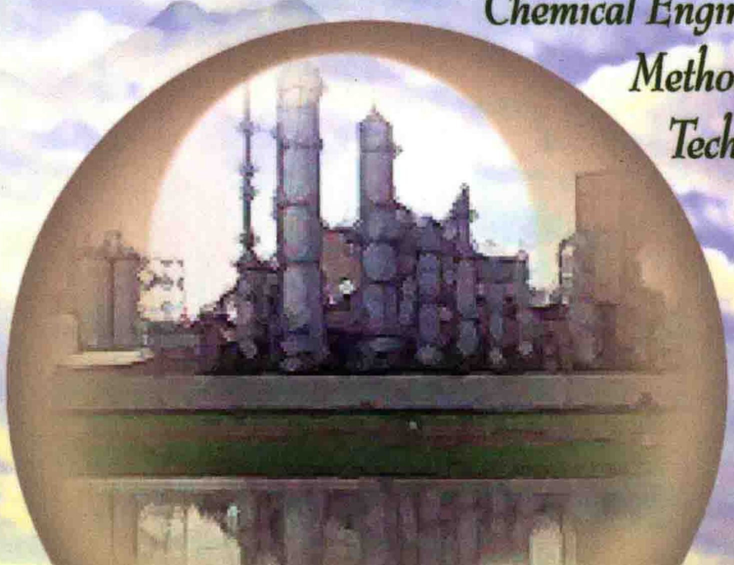
Non-Phosgene Polycarbonate from CO_2

Industrialization of Green Chemical Process

Chemical Engineering Methods and Technology



Shinsuke Fukuoka

NOVA

CHEMICAL ENGINEERING METHODS AND TECHNOLOGY

NON-PHOSGENE POLYCARBONATE FROM CO_2

INDUSTRIALIZATION OF GREEN CHEMICAL PROCESS

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ABSTRACT

Society has expected to the Chemical Industries to industrialize the innovative chemical processes for producing important products, which processes are environmentally friendly and yet useful for utilizing CO_2. Now, such an excellent chemical process is revealed.

The world's first non-phosgene process for producing an aromatic polycarbonate (PC) using CO_2 as a starting material has succeeded in development and industrialization by Asahi Kasei Corporation, Japan. The new process is not only environmentally friendly but also economically superior to the current processes. Furthermore, the plants under commercial operations, in which this process is used, have fixed CO_2 into the polymer in the largest quantities.

All polycarbonate (PC) in the world had been produced using CO as a starting material until the new process was industrialized in 2002; among them, more than about 90% of polycarbonate (PC) had been produced by so-called phosgene process.

The phosgene process must use not only highly toxic and corrosive phosgene ($COCl_2$) made from CO and Cl_2, but also large quantities of solvents, water and methylene chloride CH_2Cl_2 which is suspected to be a carcinogen. Furthermore, the phosgene process must execute the disposal treatment of large quantities of wastewater to remove the contaminated organic materials before discharge from the factory.

The Asahi Kasei Non-Phosgene Polycarbonate Process enables high-yield production of the two products, high-quality polycarbonate (PC) having excellent properties and high-purity monoethylene glycol (MEG), starting from ethylene oxide (EO), CO_2 and bisphenol-A, without waste and wastewater.

The Asahi Kasei Process not only overcomes the drawbacks of the current processes but also achieves resource-conservation and energy-conservation. Furthermore, the reduction of CO_2 emission (1,730 tons/10,000 tons of polycarbonate production) is also achieved, because the products have fixed the all CO_2 used chemically in the products as the main chain components. That is, CO_2 is chemically divided to CO part and O part, the CO part composes the carbonate group of the polycarbonate (PC), and O part composes the one OH group of monoethylene glycol (MEG).

The first commercial plant (65,000 tons/year) constructed by Chimei-Asahi Corporation in Taiwan has been successfully operating since June 2002, and the capacity has been increased to 150,000 tons/year since 2006.

The adoption of the process is rapidly expanding in the world. Following the success of Chimei-Asahi Corporation, three plants (each 65,000 tons/year) constructed under licensing

of Asahi Kasei have been successfully operated since 2008, respectively. Furthermore, the biggest plant (260,000 tons/year) in Saudi Arabia has started in 2011.

The success of *Industrialization* of the Green and Sustainable Chemical Process, Asahi Kasei's innovative non-phosgene polycarbonate process from CO_2, is a typical example, which makes *Economic, Environmental and Health Impacts* on the society and humanity.

In addition to the non-phosgene PC process from CO_2, an outline of the chemical fixation of CO_2 in the polymer, which is useful for reduction of CO_2 emission, and non-phosgene MDI process, are also described. The latter two also just fit the theme *Economic, Environmental and Health Impacts* and fit the mission that the society and humanity expect from the chemical industry.

PREFACE

Society and humanity have expected the Chemical Industries to industrialize the innovative chemical processes for producing useful, convenient and indispensable products or materials, which processes are environmentally friendly or utilize CO_2 as a raw material and recycle CO_2 into useful products.

Concerning the subject for preservation or improvement of the global environment, society and humanity have expected that chemistry, chemical engineering and chemical industry would have been playing the important roles as before, because they have been solving many important environmental problems up to this time in response to the requirements from the society and humanity. Many chemical processes have been converted to more environmentally friendly and more economical processes after their many years' endeavors.

In spite of many of their endeavors, however, some processes have remained without changing for many years owing to the difficulties in overcoming the hard technological barriers. For example, the processes using toxic phosgene, which is one of the chemical weapons, are such remained chemical processes.

An aromatic polycarbonate (PC), which is one the important and indispensable materials in our daily life, is the most consuming engineering plastic, about 3.5 million tons per year in the world for the use of mobile phones, smart phones, CDs, DVDs, car parts, cameras, personal computers, etc. Until recently, the production of all polycarbonate (PC) has used CO as a starting material. Furthermore, more than about 90% of them has been produced by so-called "phosgene process" using phosgene ($COCl_2$) manufactured from CO and Cl_2.

However, the "phosgene process" for producing polycarbonate (PC) has several environmental problems based on the use of highly toxic phosgene and the use of large quantities of chlorinated solvent such as CH_2Cl_2, and the use of large quantities of water. Therefore, the actualization of an environmentally friendly and economical process, that is, green process or green sustainable process for producing polycarbonate (PC), has been longed for many years.

On the other hand, carbon dioxide (CO_2), one of the greenhouse gases, is widely recognized to be a main material causing the global warming (Climate Crisis), and the reduction of the emission into the environment is required all over the world.

Naturally, the content of CO_2 in the atmosphere had been well balanced, because the emitted CO_2 into the atmosphere by the activities of living things had been fixed by several natural functions. However, it is said that the increase of CO_2 by the large quantity of fossil fuel consumption since the Industrial Revolution has broken the balance.

The amount of the carbon resources being used as chemical raw materials is little compared with the amount of the carbon resources being used as fuels for automobiles and thermal power generations where a large quantity of CO_2 are exhausted. However, the absolute quantity for the chemical use is not so little. The chemical industries have been contributing to society and humanity by offering useful and convenient materials or products, including the products useful for energy-saving or resources-saving. Therefore, it is the best chance for the researchers and technologists belonging to the chemical industries to fulfill their important missions for solving the urgent subject of society and humanity.

For the chemists and chemical engineers, chemical fixation of CO_2 is one of the most important and familiar trials to reduce the emission of CO_2. A lot of research and developments for the chemical fixation of CO_2 have been reported; however, the industrialized process is a few except for the urea production from CO_2 and NH_3.

Now, the innovative process for producing polycarbonate (PC), which enables satisfying both requirements for solving the remaining environmental problems and for reduction of CO_2 emission by the chemical fixation, has been revealed. Namely, a novel non-phosgene process for polycarbonate (PC) production using CO_2 as a raw material developed by Asahi Kasei Corporation, Japan has been successfully industrialized.

The main purpose of this book is to describe about the non-phosgene Asahi Kasei Process for producing polycarbonate (PC) from CO_2. The other purpose is to describe the outline of chemical fixation of CO_2 in the polymers and about the non-phosgene isocyanate process developed by us.

ACKNOWLEDGMENTS

The success of the development and industrialization of the non-phosgene polycarbonate process using CO_2 as a raw material is owed to many endeavors of several persons in Asahi Kasei Group (Asahi Kasei Corp. Asahi Kasei Chemicals Corp., and Asahi Kasei Engineering Co., all in Japan), Chimei-Asahi Corp. in Taiwan (formerly a Joint Venture of Asahi Kasei and Chi Mei; now a subsidiary of Chi Mei Corp.) and Chi Mei Group (Chi Mei Corp. and Poly Chemical Engineering Co., both in Taiwan). The author expresses his grateful acknowledgement to all members who have put their hearts into the development and industrialization of our new process and have led to success.

Especially, the author would like to express his hearty thanks to the late Mr. Masashi Kohno (the first general manager of the Petrochemical Research Laboratory), Dr. Masazumi Chono, Dr. Isaburo Fukawa, Mr. Hiroshige Okamoto, Dr. Tsuneaki Tanabe, Dr. Haruyuki Yoneda, the late Dr. Kyosuke Komiya, Mr. Tomonari Watanabe, Mr. Masahiro Tojo, the late Dr. Hiroshi Hachiya, Mr. Muneaki Aminaka, Mr. Kazumi Hasegawa, Dr. Yoro Sasaki, Mr. Ryoji Deguchi, Mr. Yoshihumi Kawakami, Mr. Shin-ya Kawazoe, Mr. Seiji Shimizu, Mr. Toshiharu Hama, Mr. Kazuhiro Oonishi, Mr. Kazuo Tomoyasu, Mr. Masataka Nishi, Mr. Koji Takeuchi, Mr. Hironobu Yamauchi, Mr. Tatsumi Araki, Mr. Yuko Matsuda, Dr. Akira Miyamoto, Mr. Kazuharu Yasuda, Mr. Kazuhiro Shibuya, Mr. Nobutsugu Nanba, Mr. Tokuichi Hisamatsu, Mr. Tetsuo Hamada, and the late Mr. Tetsuro Dozono for their endeavors in R & D, to Mr. Hideaki Obana, Mr. Kunio Kohga, Mr. Mamoru Kawamura, Mr. Kunihiko Wada, Mr. Akio Yamaguchi, Mr. Risuke Ikeo, Mr. Yutaka Kuwabara, Mr. Manabu Ooishi, Mr. Fumio Kotani, Mr. Koji Miura, Mr. Mamoru Yoshihuku, Mr. Yukio Karuno, Mr. Tetsuro Yakuwa, and Mr. Masato Kanno for their endeavors in Engineering, and to Mr. Hiroshi Susumago, Mr. Tsutomu Katsumata, Dr. Kazuhiko Matsuzaki, Dr. Shigeo Tsuyama, Mr. Shigenori Konno, Mr. Shinji Nakagawa, Mr. Takashi Adachi, Mr. Rikio Fujiwara, Mr. Shinji Takagi, Mr. Masatoshi Yoshitake, Mr. Yoshihiko Ninagawa, Mr. Ken Someya, and Mr. Hironori Miyaji for their endeavors in Industrialization, and to Mr. Mikio Suzuki, Mr. Hisatsugu Wakamatsu, Mr. Tomio Ozawa, Mr. Hideaki Okubo, Mr. Hideharu Yamaki, Dr. Koshiro Yokota, Mr. Hisao Ito, Mr. Jun-ichi Sugimoto, Mr. Hitoshi Ohta, Mr. Saburo Takatsuka, Mr. Kenji Akatsuka, and Mr. Hiroya Fujita for their endeavors in Licensing and Technology Transfer, and Mr. Seizaburo Watanabe, Mr. Shuji Kanazawa, Mr. Masami Komiyama, Mr. Syunsuke Mutoh, and Mr. Michio Kasahara for their endeavors in Intellectual Properties. The author deeply regrets the premature deaths of Dr. Kyosuke Komiya from disease (December, 2010) and Dr. Hiroshi Hachiya from disease (July, 2011);

they were splendid leaders in R & D and Industrialization of this innovative polycarbonate process.

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Finally, the author would like to express his thanks to Asahi Chemical Industries Co., Ltd. and Asahi Kasei Corporation for supports in his R & D for many years.

ABOUT THE AUTHOR

Dr. Shinsuke Fukuoka was born in Osaka Prefecture, Japan in 1943. He received his B.S. degree in 1966, from Osaka University and his Doctoral degree of Engineering in 1971, from Osaka University under the supervision of late Professor Shigeru Tsutsumi. He joined Asahi Chemical Industries Co., Ltd. (Japan; now Asahi Kasei Corporation) in 1971. He was engaged in the R & D of aromatic polyamides and spinning thereof and a plastic optical fiber in the Fiber Development Laboratory from 1971 to 1978. From 1977, he by himself had started the thorough investigation of the prior arts and the basic research for developing a non-phosgene process of polycarbonate. He transferred to the Petrochemical Research Laboratory in 1979, since then, he had led the R & D of the non-phosgene processes for producing polycarbonate (PC) or isocyanates (MDI, HDI) until 2000.

He acted as the general manager of Chemistry & Chemical Process Laboratory from 1992 to1995. Then, he acted as the general manager of the project for developing the non-phosgene polycarbonate (PC) process from 1995 to 2000. The object of the project was to establish the technology enabling the industrialization in a foreign country at the pilot stage. He led the project to success. As a result, the world's first non-phosgene polycarbonate (PC) process using CO_2 as a raw material has been industrialized since 2002. Now, four companies in the world have been operating their plants under licensing from Asahi Kasei Corporation and have succeeded in the polycarbonate (PC) business as the newcomers. Furthermore, the fifth company has started to operate his plant in 2011.

The Emperor of Japan gave him "Medal with Purple Ribbon" for his contribution to the development of science and technology for many years in 2008. He also received "The Commendation for Science and Technology by the Japan Minister of Education, Culture, Sports and Science and Technology, Prize for Science and Technology, Development Category" in 2007.

He is also a recipient of many awards, for example, "Green and Sustainable Chemistry Award 2002" (Japan's Minister of Economy, Trade and Industry Award) (GSC Network), "35-th Japan Chemical Industry Association Award in 2003," "Nikkei Global Environment Technology Award in 2004" (Nihon Keizai Shinbun, Inc.), "The Chemical Society of Japan Award for Technical Development for 2004," "Japan Patent Office Commissioner Award for Invention Encouragement" (2005), "The Okochi Memorial Grand Technology Prize 2005" (Okochi Memorial Foundation) and "The Award of the Society of Polymer Science, Japan" (2006), "The Minister of Education, Culture, Sports and Science and Technology Award for Invention Encouragement" (2007), and "ICIS Innovation Awards 2007, Best Process Awards."

He is the author and coauthor of *ca.* 40 original papers, reviews and books, and *ca.* 850 patents.

He was a Technical Advisor, New Business Development, Asahi Kasei Corporation from 2006 to 2009, and a Senior Consultant, Technology licensing Department, Asahi Kasei Chemicals Corporation from 2004 to 2009.

Now, he is a Professional Engineer Japan (Chemistry), and an Advisor of The Noguchi Institute, Japan.

CONTENTS

Chapter 1

INTRODUCTION: SOCIETY AND CHEMICAL INDUSTRY

1.1. MISSION OF CHEMICAL INDUSTRIES

The important mission of the chemical industries is to offer the useful and convenient materials or products to society and humanity at reasonable prices for their values.

Using raw materials, such as naphtha, natural gases, coals, air, water, and sodium chloride, the chemical industries have been offering the intermediate materials or primary products to the other chemical or related industries.

Such intermediate materials or primary products are, for example, all kinds of gases (hydrogen, oxygen, nitrogen, inert gases, etc.), all kinds of basic inorganic compounds (chlorine, sodium hydroxide, soda ash, hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid, etc.), ethylene, propylene, butadiene, benzene, toluene, all kinds of monomers (styrene, acrylonitrile, acrylic acid or esters, methyl methacrylates, vinyl chloride, etc.), all kinds of organic solvents, alcohols, aldehydes, organic acids, organic esters, chemical fertilizers, dyes, detergents, surfactants, insecticides, pesticides, agricultural chemicals, inks, paints, all kinds of polymers or plastics (commodity plastics such as polyethylene, polypropylene, polystyrene, PET, polyvinyl chloride, polymethylmethacrylate, polyacrylonitrile, ABS; engineering plastics such as polycarbonates, polyamides, PBT, polyacetals; specific polymers such as fluoropolymers, silicones; thermosetting resins such as unsaturated polyester resins, urea resins, etc.), synthetic fibers, synthetic rubbers, etc.

Furthermore, the chemical industries have been offering the materials or products to the many other industries relating our daily lives directly, such as clothing or fabrics and shoes industries (fibers, man-made leathers, rubbers, polyurethanes, etc.), food industries (films, casings, plastic bottles, etc.), living or housing industries (plastics, paints, fabrics, insulating foams, etc.), medicinal or medical industries (medicines, man-made kidneys, plastics tubes, sheets, films, etc.) electric or electronic industries (plastics, silicon wafers, photo resists, etc.), automobile and the related industries (rubbers, plastics, fabrics, etc.).

Thus, the chemical industries have played important roles for making our lives more plentiful, safer, more convenient, more comfortable and by offering the useful materials or products.

Almost all chemical industries in the world have been continuously endeavored to accomplish the above important mission for many years.

Another important mission of the chemical industries is to solve the subjects concerning the local environment or the global environment using their excellent chemical technologies.

1.2. Environmental Ploblems and Chemical Industries

Society and humanity would have continuously expected chemistry, chemical engineering and chemical industry to play important roles in solving the subject for preservation or improvement of the local and global environment as before, because they have solved many important environmental problems up to this time in response to the requirements using chemical technologies.

Concerning the chemical processes, chemical industries have converted many chemical processes to more environmentally friendly processes after their endeavors for many years by development and industrialization.

For example, chemical industries have changed the acetaldehyde production process from the hydration of acetylene using a mercury catalyst to the catalytic ethylene oxidation (Wacker Process). The reason of the process conversion was that the discharged wastewater of the chemical plants containing mercury compounds into the sea or the river caused a miserable disease (the Minamata Disease) to many people, who ate the fish and shellfish in the Minamata Bay or Agano River in Japan (Water Pollution).

This water pollution, which caused the miserable and pitiable effects to the society and humanity, accelerated the process conversion from the process using mercury to the non-mercury process. Further, chemical industries have changed most of brine (sodium chloride solution) electrolysis processes for producing NaOH and Cl_2 (chloroalkali process) from the mercury cell process or the diaphragm cell process, which uses permeable diaphragm made of asbestos fibers, to the membrane cell process using the ion exchange membrane.

In Japan, chemical industries have changed all of the mercury cell electrolysis processes to the membrane cell processes or to the diaphragm processes until 1986; furthermore, the entire diaphragm processes changed to the membrane cell processes, which are more effective in the electronic power consumption until 1999. Unfortunately, however, some of the mercury cell processes and the diaphragm cell processes have remained without the process conversion in the world.

The other typical example that is used to explain how the chemical technologies played important roles for solving the subject for preservation or improvement of the global environment is the endeavors to prevent Air Pollution.

For the nitrogen oxides (NOx) and sulfur oxide (SOx) of the fixed emission sources such as power stations and industrial facilities, the effective catalytic de-NOx (de-nitrification) processes and de-SOx processes have been developed and operated in the world.

Furthermore, the combined technologies of chemical and automobile industries have converted the hydrocarbons, CO, and NOx, which are emitted from mobile emission sources such as automobiles, to less harmful gases for prevention of air pollution by the catalytic conversion of the exhaust gases of automobiles. This is also one of the excellent chemical processes.