

[002]九州大学グローバルCOEプログラム新炭素資源 学ニューズレター

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G-COE PROGRAM KYUSHU UNIVERSITY

NOVEL CARBON RESOURCE SCIENCES

NEWSLETTER

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M E S S A G E

Professor Emeritus of Kyushu University
Member of National, Public, and Private Universities CONSORTIUM-FUKUOKA
Research Professor of Research Institute for East Asia Environments, Kyushu University



Wataru Koterayama

I visited Asian countries as a member of several projects of Kyushu University and took a close look at energy and environmental situation in these countries. With their rapid economic growth, Asian countries are suffered from severe environmental pollution caused by plants, power plants and transportations, with higher speed and larger scale than any other pollution that human beings have ever experienced in its history. The pollution in these areas is making much impact not only on Asian developing countries but also on developed countries such as Japan and South Korea, and also on any other countries all over the world.

But at the same time, the economic growth in Asian region is bringing to an end the global economic depression followed by the breakdown of American subprime loans. It has become increasingly recognized that economic benefits and environmental problems brought about by Asian countries are two sides of the same coin.

Japan has placed the overcoming of environmental problems as the top-priority issue in the process of its earlier economic growth, achieved a successful outcome to an extent, and developed environmental technology up to the top level in the world. But the process of economic growth has also done much harm to the people, as was shown in Minamata and Yokkaichi. If we leave the current situation in Asia uncontrolled, the damage will inevitably spread globally. Japan is directly influenced through westerlies in the atmosphere and through Kuroshio and Tsushima Current in the ocean. Kyushu area is especially suffered from urban ozone formation and from the damage to the fisheries industry caused by heavy infestations of Echizen jelly fish.

International environmental problem is a reverse side of economic growth, and easily become a political problem. International cooperation is not easy to achieve, as is typically shown in the conflict between developed and developing countries concerning emission control of greenhouse gases. The key to solve such a problem is accumulation of scientific knowledge, as is shown in the historical example of cross-border air pollution in North European countries caused by Germany and Great Britain.

Kyushu University locates closest to Asia as a research-oriented university, and has much number of brilliant researchers in the field of energy and environment. The university has established Research Institute for East Asia Environments to promote advanced efforts to approach the environmental problems in East Asia in FY 2008, and became a main member of National, Public, and Private Universities CONSORTIUM-FUKUOKA dealing with energy and environment, which is organized by Fukuoka Institute of Technology, Kyushu University, Seinan Gakuin University and Fukuoka Women's University. Northern Kyushu area in which the university locates has historically been a center of coal industry and heavy manufacturing industry, and has played the most advanced part in overcoming associated environmental problems.

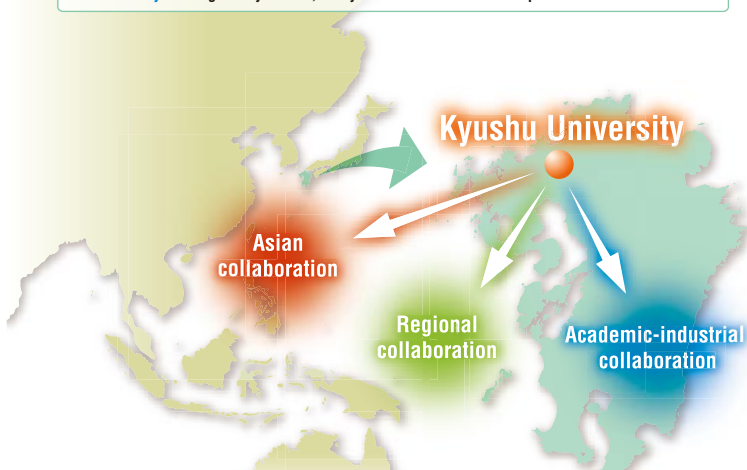
It may be no exaggeration to say that the Global COE Program "Novel Carbon Resource Sciences" was set up inevitably and has a very historical mission in such circumstances. It is strongly required for the Program to function as the center of network by grouping excellent researchers together and to bring up high-potential human resources.

Summary of G-COE Program "NOVEL CARBON RESOURCE SCIENCES"

The Global COE program, Novel Carbon Resource Sciences (NCRS) was established by joint work of Kyushu University and Fukuoka Women's University in FY 2008. Our COE program, which consists of 8 major courses in the 2 universities, aims at establishing a new field of science for efficient use of carbon resources in view of global environmental sustainability, and education of young researchers in such a field. Carbon resources such as oil and coal are vital for human life not only as energy resources but also as chemical raw materials. The crude oil price dropped dramatically to one third of its record high price from summer in 2008 due to a worldwide financial crisis triggered by bankruptcy of Lehman Brothers Holdings Inc., and then the price is gradually rising again. This reflects that there continuously exist fundamental issues including competition for resources or its depletion among developing countries as they are experiencing dramatic economic development. While oil is deeply involved in material civilization, coal is widely distributed in the world and its reserve is relatively huge. So it has been used as an energy resource in thermal power plants. However, inadvertent use of low-quality coal produces air pollutant such as nitrogen oxide and sulfur oxide, resulting in cross-border pollution and also produces massive emissions of carbon dioxide which is ascribed as the cause of global warming. As these problems are becoming familiar, the world is trying to find out its solution. How can we produce energy effectively with environmentally-friendly and well-balanced approach? While various countermeasures are being explored in the world, our COE is striving to solve the problem with the objective of creating environmentally-friendly society for the next generation. To do that, we are promoting development of science technology for efficient use of carbon resources and materials derived from carbon resources to realize a

low-energy society, and education of young researchers who are capable of considering a future strategy and tackling practical problems through advanced research.

Kyushu University = rich history of leading coal research, future plans for an "Energy campus"
Northern Kyushu = gateway to Asia, many fossil-resource related experimental facilities



NOVEL CARBON RESOURCE SCIENCES

20th century

More indiscriminate consumption of fossil resources

21st century

More sustainable utilization of fossil resources

■ Cooperation with local community and Asian countries

The center takes full advantage of Kyushu University's location in Northern Kyushu, a gateway to Asia. We will be actively engaging in bidirectional exchanges of research and education among universities, institutes in China, Korea, Indonesia, India and Australia,

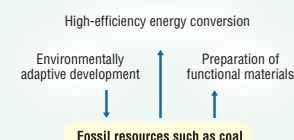
collaborating internationally on education with Fukuoka Women's University. Also, we will be sharing intelligence with people in region through public lecture and partly promoting nationwide, international joint research between industry and academia.

■ Development and integration of two research fields

This COE pursues: in carbon resource utilization field, smart use of carbon resources such as coal that is extremely effective energy use and energy-saving material, device and system derives carbon resources. At the same time, to figure out environmental change and find a solution mutually by economic, science and engineering in carbon resource environment field. This COE aims at establishing new integrated research field 'Novel Carbon Research Sciences'.

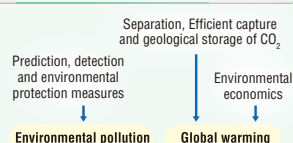
Carbon Resource Utilization

- a) Basic research in the environmentally benign development of fossil resources such as coal and high-efficiency energy conversion technologies (Clean Coal Technology)
- b) Basic research in the manufacturing of functional materials from fossil resources such as coal
- c) Upgrading technology for low-quality coal



Carbon Resource Environment

- a) Basic research in the prevention of environmental pollution
- b) Basic research in global warming and its prevention



**NOVEL
CARBON RESOURCE
SCIENCES**

Recruitment of Doctoral students, Postdoctoral Researchers

This COE calls for Doctoral Students, Postdoctoral Researchers domestically / abroad.

For details:

URL: <http://ncrs.cm.kyushu-u.ac.jp>

G-COE Program Researcher Map

Program members
Carbon resource utilization cluster

Program members
Carbon resource environment cluster

Program collaborators

Collaborative member

Energy Utilization of Coal and Other Fossil Fuels: Development of Environmentally Efficient Technology

Coal upgrading and gasification, Energy conversion

NEDO

"Innovative zero emission coal gasification electric power project"

Tsuyoshi Hirajima

Advanced processing of carbon resources; Biomass utilization

Isao Mochida

Coal gasification; Carbon materials, Carbon nanofibers

Seong-Ho Yoon

Carbon nanofibers; Reaction engineering of carbon materials

Yasutake Teraoka

Functional inorganic materials; Environmental catalytic chemistry

Jun Fukai

Thermal analysis of coal conversion; Energy saving utilization of carbon fibers

Katsuki Kusakabe

Inorganic separation membrane; Separation of environmental pollutant

Jun-ichiro Hayashi

Sustainable carbon cycle chemistry; Coproduction

Central Research Institute of Electric Power Industry, Other Universities
Ehime Univ., etc.

Koyo Norinaga

Chemical reaction engineering for carbonaceous resource conversion; Detailed simulation of chemically reacting flows

▶ P21

Advanced Technological Development for Low Energy Consuming Society

Basic chemistry

Katsuhiko Tomooka

Organic synthetic chemistry; Efficient oxidation reaction

Minoru Nishida

Transmission electron microscopy; Structure control in crystalline materials

Haruo Honjo

nonlinear physics; fractal physics

Seigi Mizuno

Structural analysis of solid surfaces; Graphite films on vicinal SiC

Yoshiaki Takahashi

Polymer chemistry; Analysis and control of soft matters

Environmental material development

Hideo Nagashima

Environmentally benign chemistry; Efficient metal complex catalysts

Seong-Ho Yoon

Carbon nanofibers; Reaction engineering of carbon materials

Advanced electronic material development

Shiyoshi Yokoyama

Device applications of carbon resources; Polymer photonic materials

Hiroki Ago

Carbon electronics; Synthesis and applications of carbon nanotubes and graphene films

Katsuhiko Fujita

Organic photovoltaic cells; Organic EL device

Ministry of Economy, Trade and Industry "Advanced Education for Effective Utilization of Fossil Resources"

Kyushu society for low-carbon system

Kyushu University

G-COE, NEDO, JST, JST-MOST

Kyushu Electric Power Co., Inc.

Lignite utilization technology, nuclear power

Kyushu Bureau of Economy, Trade and Industry

Local Businesses, Other Universities

Kyushu Institute of Technology, Saga University, Kumamoto University, etc.

Energy material development

Michitaka Ohtaki

Thermoelectric device; Heat energy recovery

Shigeto Okada

Energy active materials and storage technology for next generation rechargeable lithium battery

Green process development

Shigeru Koyama

Heat energy conversion system; Heat transfer characteristics of CO₂

Yoshio Iwai

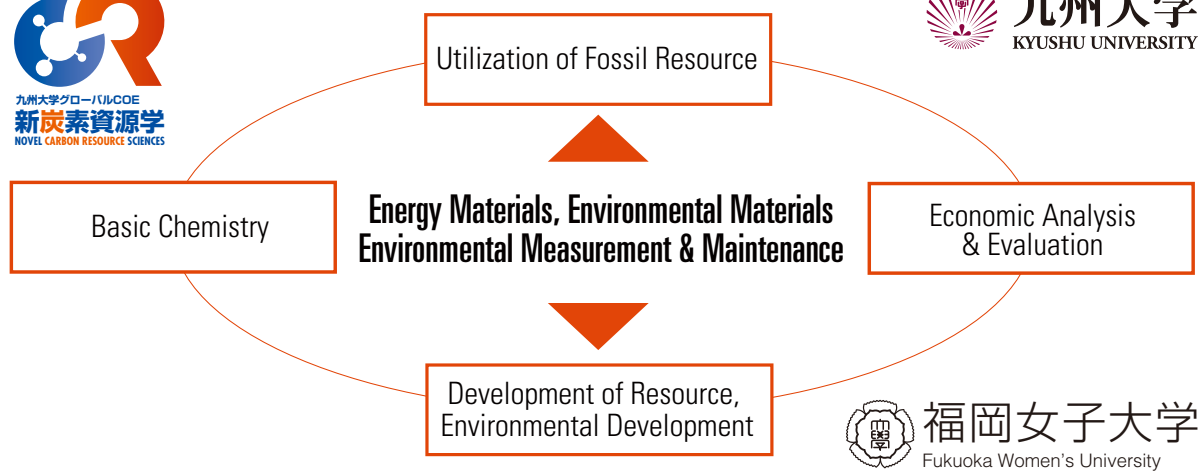
Separation technology; Supercritical fluid technology

Toshihisa Kajiwara

Polymer processing; Computer simulation

Yoshifumi Tsuge

Large scale process management; Process support system



Technology for Fossil Resource Development of Coal and Other Fuels

Technology for resource development below the earth

Tsuyoshi Hirajima

Advanced processing of carbon resources; Biomass utilization

Kikuo Matsui

Environmental restoration associated with resource development; Coal mining development and environmental issues

Hideki Shimada

Low Impact Mining; Coal Ash Utilization

Technology for resource development in the ocean

Masahiko Nakamura

Marine-viewing vehicle; Positional controls of marine constructions

Yusaku Kyojuka

Utilization of ocean energies; Simulation of marine environments

Changhong Hu

Sea keeping performance of a ship in actual seas; Simulation of ships

Technology for Fossil Resource Utilization of Coal and Other Fuels

Basic chemistry

Akira Harata

Ultrasensitive environmental analysis; Laser spectroscopic analysis

Economic analysis

Toshiyuki Fujita

Environmental economics; Analyses of global environmental issues

Separation, removal of pollution

Yasutake Teraoka

Functional inorganic materials; Environmental catalytic chemistry

Masaki Minemoto

Analysis of flow and transport phenomena; Upgrade of various types of plants

Environmental measurement

► P5

Itsushi Uno

Numerical simulation of transborder air pollution; Aerial environmental modelling in Asia

Toshihiko Takemura

Global scale simulation of aerosol

Kazuhide Ito

Chemical pollution of life environments; Indoor and environmental chemistry

Tetsuo Hayashi

Analysis of urban thermal environment; Prediction of energy consumption in residential buildings

Tadakatsu Ohnaka

Physiological and psychological features and life environment; Research on thermo-environment and aero-environment condition

Chang-Jin Ma

Global scale air pollution; Properties of Asian dust storm particles

Environmental restoration technology

Koichiro Watanabe

Geoscience database; Environmental impact by resources development

► P6

Ryuichi Itoi

Development of geothermal energy; Development of fossil fuel resource

Keiko Sasaki

Remediation of groundwaters and soils; Reactive materials for environmental remediation

CO₂ Capture and storage (CCS)

Kyuro Sasaki

CO₂Storage; CO₂-ECBM; CO₂-EOR

Economic analysis

Nobuhiro Horii

Economic development and coal industry; China's coal and power industry

Functional devices and materials for environmental concerns

► P10

Norio Miura

Sensors for environmental concerns; Electrochemical devices

Kengo Simanoe

Design of gas sensors; Development of high performance electrocatalyst

Asian Dust Transported One Full Circuit Around the Globe

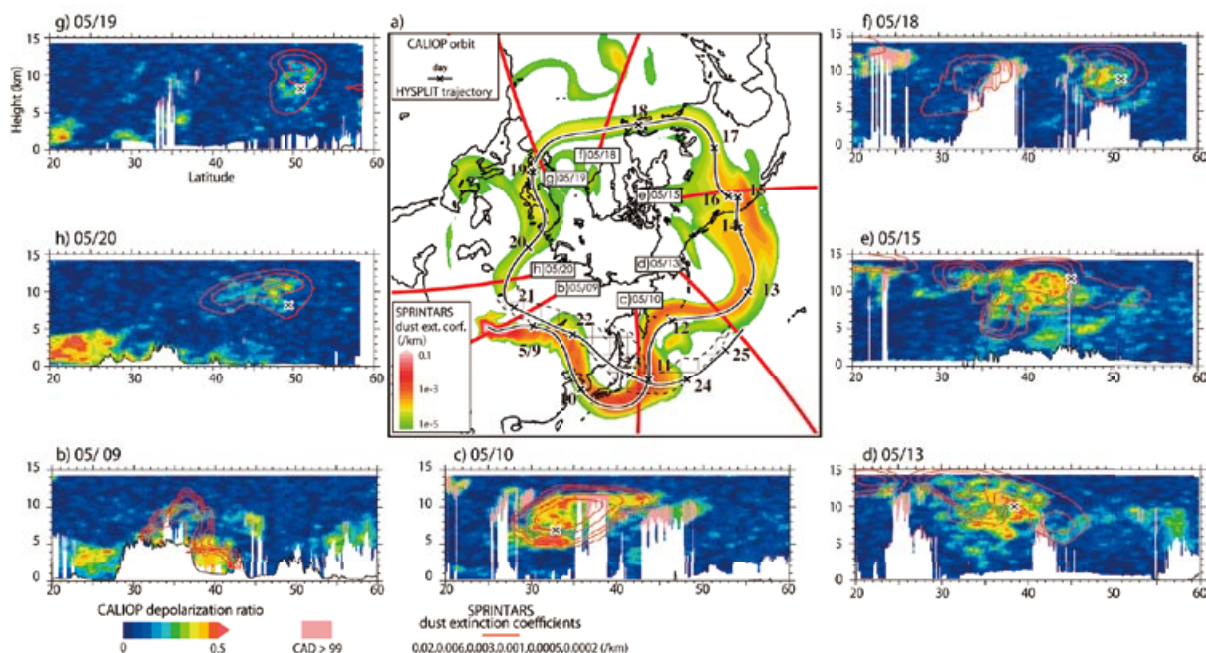
Itsushi Uno

Research Institute for Applied Mechanics, Kyushu University

The transport of mineral dust is well known to occur usually within the lower troposphere. Long-range transport of Asian dust has occasionally been observed on a trans-Pacific scale, and, in a few cases, Asian dust has been detected in the ice and snow cores in Greenland and French Alpine. Here, we present findings from a comprehensive study of an extensive dust storm occurring in China's Taklimakan Desert during May 8-9, 2007. We found the dust-veiled cloud was transported in the upper troposphere more than one full circuit around the globe. This extraordinarily long-range transport was tracked by the recently launched CALIOP space-lidar and confirmed by our model simulations. The dust transport took approximately 13 days. Upon reaching the northwestern Pacific after one circuit, the dust descended to the lower troposphere caused by the subsidence of a high-pressure system, indicating the possibility that Asian dust can supply mineral nutrients to open oceans far from the source region. During the transport, the dust appears to have interacted with cirrus clouds, suggesting that the Asian dust can impact the global radiation budget via indirect effects.

For details, please see original article in "Nature Geoscience".

I. Uno, K. Eguchi, K. Yumimoto, T. Takemura, A. Shimizu, M. Uematsu, Z. Liu, Z. Wang, Y. Hara & N. Sugimoto, Asian dust transported one full circuit around the globe, *Nature Geoscience*, Vol.2, No. 8, DOI:10.1038/NGEO0583, 2009.



CALIPSO orbit path (bold line), HYSPLIT dust trajectories (white-black thick line) and SPRINTARS simulated dust extinction coefficient (tone) along the HYSPLIT trajectory. Number indicates the date of May 2007; (b) – (h) the latitude-height cross-section of CALIOP observed depolarization (tone) and SPRINTARS dust extinction coefficient (contours). X denotes the position of HYSPLIT trajectory crossing at each section.

Introduction of Hi-LINK Project

Ryuichi Itoi

Faculty of Engineering, Kyushu University

Hi-LINK stands for international technical project named as “Project for Improving Higher Education Institutions through University-Industry-Community Links in Gadjah Mada University” and was conducted in Indonesia who is a member of ASEAN countries. Universities in Indonesia have been requested by their government to encourage contribution to society through transfer of intellectual achievement while fulfilling fundamental functions such as education and research. At the same time, the government have shifted main national universities to be autonomous for enhancing their self-sustainability and also requested universities to promote University-Industry-Community (UIC) linkage and collaborations.

UIC collaboration activities, however, have been widely and actively conducted by faculty members at their individual level, but organizational functions to form UIC collaboration have not yet been well developed. Furthermore, there is still room for those members to improve their research capabilities for collaboration activities such as joint research. Then, the Government of Indonesia requested Japanese Government who has plenty experiences with their national universities to make them autonomous as well as developing organization that handle, initiate and form UI collaborations. With this background, Japan International Cooperation Agency (JICA) formed a Technical Cooperation Program to which Kyushu University made organizational approach and submitted a project proposal which was successfully awarded.

The project was started June 2006 and finished March 2009. This three years project was conducted by Kyushu University(KU) with IC Net Inc. and Gadjah Mada University(UGM) with financial supports by both governments. The main purpose of the project is to 1) enhance UIC collaboration functions in UGM, and 2) strengthen research capabilities of faculty members in the field of engineering. The first phase of the project was conducted at UGM, and then the outputs made in the first phase would be transferred to other universities in Indonesia. Gadjah Mada University locates in Yogyakarta City, known as one of the traditional and old city in Central Java. The university was founded in 1949 as the first university in Indonesia, and consists of 18 faculties with more than 50,000 students, acting as one of the representative university in Indonesia.

Geological Engineering Department of UGM has been playing a host university in the field of earth resources and geology in ASEAN University Network/ the Southeast Asia Engineering Education Development Network (AUN/SEED-Net) Project that started 1996 with financial support of JICA. UGM has developed international course and accepts master course students from ASEAN countries

such as Vietnam, Cambodia and Myanmar. At the same time, Department of Earth Resources Engineering, KU acts as representative of Japanese university supporting UGM. Faculty members and graduate students of our department often visited UGM for conducting field works together with UGM faculty members and students as well as giving special lectures at UGM. We have developed a reliable and tight human network through these activities. If we can develop and extend this kind of mutual and practical relationship among other departments in our faculty, it can be a favorable opportunity for KU who has strategy to strengthen relationship with Asian countries. Furthermore, this project may trigger to initiate new scheme of international collaboration among KU, UGM, private sectors and local governments.

Faculty of Engineering, UGM, consists of 8 department; Architecture, Civil, Mechanical and Industrial Engineering, Electricity, Chemical Engineering, Geological Engineering, Engineering Physics, Geodesy. The number of faculty and students as of 2007 are 367 faculty members, 4,464 for undergraduate student, 1167 for master student. The number of PhD student is small so that their actual number does not appear in annual report of the faculty. Project team members are in charge of supervising each department and they were nominated from Graduate School of Engineering, Information Science and Electrical Engineering, and Human-Environment Studies (Fig.1). Members of Intellectual Property Management Center KU (IMAQ) also joined the team for UIC collaboration. Furthermore, enthusiastic supports by International Affairs Department,



Fig. 1 Member of the project team at the branch office of Kyushu University in the Department of Geological Engineering, Faculty of Engineering, Gadjah Mada University.

Administrative Office of Faculty of Engineering were also made.

Most faculty members in UGM as well as other universities in Indonesia earned their advanced academic degree, PhD in particular, in overseas universities. The number of faculty is also large who earned their PhD degree in universities in Japan. They found out physical environment such as research facilities and instruments are of poor quality when they came back to home university after their completion of PhD program in overseas universities and research fund they can get is also small. The large workload on "education" is also a problem. However, young faculty members of thirties and forties make an effort to enhance their academic capacity as well as improve their position in both domestic and international academic societies.

The project prepared research fund of 8 to 9 million Japanese Yen each year for supporting collaborative research with industry and local community and governments. Additional fund from KU, 2 million Yen per year, was provided from the second year. These funds supported 10 to 14 research projects each year. Many research projects are related to local industry. Examples of researches are shown in pictures such as development of waste water treatment technology using bagasse (Fig.2), utilization of bamboo as construction material (Fig.3), dissemination of biogas digester to rural area, and development soil improvement material using zeolite. Our professors supervised researchers and made discussion when they made regular visit to UGM. When they submitted their paper on their research output and accepted for presentation at international conferences, budgets were also allocated to them to cover their trip and registration fee. Attending international conference and making discussion over their output with other researchers from overseas can advance their incentives for continuing their research activities. I understand well their attendance at international conferences depends on availability of budget support.



Fig. 2 Dr. Agus Prasetya of Chemical Engineering Department stands by his experimental apparatus for research on waste water treatment using bagasse.

When professors of the project visited UGM, they gave special lectures on their respective field. This was also a good opportunity to have interview with faculty members who plan to apply for post graduate program, in particular for PhD program. Thus, we accepted more than 10 exchange students to our PhD programs in KU and all of them succeeded in getting official or private scholarship. Prof. Hirajima, one of GCOE member, is supervising three PhD students from Indonesia, and they focus their research related to carbon resources such as biomass, low quality coal, and coal fly ash. Furthermore, international university-university-industry collaborations were also made for feasibility study on biomass resources in Indonesia, waste water treatment system using bagasse, and development of soil and road improvement material using coal fly ash. On the basis of human network between KU and UGM that we developed during the project, Prof. Hirajima's group submitted a research proposal to JST-JICA program on Science and Technology Research Partnership of Sustainable Development.

Economies of ASEAN countries such as Singapore and Thailand have been seriously affected by the financial crisis started September in 2007. Under this serious economic condition, domestic demand in Indonesia remains stable and active and their GDP steadily increase. Energy demand in Indonesia also increases year by year. Indonesia exports large amount of natural gas and coal to Japan that occupies about 20 % of our total consumption for each fuels. Thus, we have to actively collaborate with Indonesia for mutual interests in the field of effective utilization technology of carbon resources as well as human capacity development with enthusiastic supports of private sector and university.



Fig. 3 Two stories local house under construction. Bamboo is used as construction material that is research output by Prof. Munawar group of Civil Engineering Department.

Research Project on the Development and the Mechanism of Low-carbon society in Asian major cities

Mami Shinozaki

The Research and Education Center of Carbon Resources, Kyushu University

1. The background of research

It is thought with the economic growth of Asian countries including China and India, and progress of urbanization that CO₂ discharge of the Asia urban areas will increase from now on. In order for many Asia cities not to be restrained by energy quantity-dependent society in the future, it is necessary to choose the course of low carbon type economic development. However, it is difficult for poverty, adaptation of pollution and a climatic change, etc. to have the various subjects in connection with sustainable development in the Asia developing country, and to implement a measure aiming only at construction of a low carbon society.

Therefore, after being based on the feature of the area or cities, it is important for deployment of the low carbon type which is based on the needs of the field.

The research on the promotion of an individual low carbon measure is still insufficient. It is needed for the research of the effective deployment mechanism as a bottom-up process low carbon type development measure in the public welfare section with which the local governments, such as home and small and medium-sized enterprises.

2. Purpose of research

In order to promote the low carbon type development measure, is taken up focusing on the public welfare section of the Asia developing country. The Purpose of Research is showing the measure of effective low carbon type social construction in Asia.



Fig. 1 The meeting in Chongqing University

3. Outline of research

Project outline for FY 2009 is as follows,

- Consider issues and activities of LCS (Low Carbon Society)
- Sort out Asian cities based on the development stage and patterns of LCS
- Select of the target cities, areas, sites, and companies
- Collect the information and the data about LCS
- Survey and interview with major stakeholders and local government etc.
- Evaluate each activities and demonstrate good practices and the effective mechanisms

4. Composition of research

This work was supported by the global Environment Research Fund, the Ministry of Environment from FY (Fiscal Year) 2009 to FY2011.

This research is promoted by four researchers of Kyushu University and other universities.

(A) First year enforcement situation

The city for investigation is selected to Liaoning province Dalian and direct control city Chongqing in China. The field survey is carried out as joint research of Dalian University Of Technology and Chongqing University.

It is arranging for the work' shop as part of a report of the joint research.

In addition, in Thailand' Bangkok capital and Vietnam' Ho Chi Minh City, we start to investigate for the following fiscal year.



Fig. 2 Dalian University of Technology's researchers



Fig. 3 The environmental symbiosis house in DALIAN

(B) The outline of each subject

Research of this study consists of six themes as follows.

B-1. Interrelation between development and LCS

(Researcher: Professor Shiro HORI)

- Survey factors influencing energy consumption, LCS, such as weather, income, urbanization, energy accessibility, and other energy related factors.
- Analysis the interrelationship between development stage and LSC.

B-2. Incentive and institutional framework

(Researcher: all researchers)

- List up the incentives and an institutional framework to facilitate LCS in major cities
- Evaluate the effect of each incentives including financial support (subsidiary), economic benefit(energy saving), social benefit (living improvement), and benefit for business activities which is a company reputation
- Study the interaction of LCS and city development plan



Fig. 4 Waste: The situation of a garbage place

B-3. Residence

(Researcher: Professor Tetsuo HAYASHI)

- Considering climate circumstance in respective cities, select several sites to investigate. And collect basic data such as building plan, energy data, purpose of building etc.
- Evaluate the effect of methods and technologies (heat insulators, heat accumulation, energy use improvement, and replacement of electronic equipment)
- Propose more effective method in respective site and cities

B-4. House-hold

(Researcher: Associate Professor Kayoko KONDO)

- Considering different life style in urban and rural area, conduct survey the living activities in household
- Study factors toward energy saving life style, including purchase of house appliances, automobile use, light, cooking, house heating, waste treatment, and other energy consumption activities
- Demonstrate incentives and practices to change lifestyle

B-5. SMEs (small and medium-sized enterprises)

(Researcher: Associate Professor Toshiyuki FUJITA)

- List up energy saving technology and framework(regulation, tax, emission trading, voluntary agreement, rating, labeling, ESCO)
- Interview with local government officials to find out regulations and institutions to encourage SMEs to promote environment friendly actions
- Survey on SMEs activities and demonstrate the factors to promote energy saving actions

B-6. Other measures

(The University of Kitakyushu Seiichi ICHIKAWA)

Survey on LCS activities, institutions in waste treatment and water pollution control.

Micro Review

Development of Solid-State Electrochemical Gas Sensors Aiming at On-board Diagnosis and Environmental Monitoring

Norio Miura

Art, Science and Technology Center for Cooperative Research, Kyushu University

Among various analytical methods developed for detection of environmental pollutants, electrochemical solid-state gas sensors have received great attention due to their advantages such as high sensitivity, high selectivity, rapid response and portability. Over the years, we have developed a large number of high-performance solid-state gas sensors using various sensing electrode (SE) materials. One of the important approaches is the use of yttria-stabilized zirconia (YSZ)-based gas sensors employing oxide-SEs under various detection modes. Several experimental parameters such as operating temperature, thickness and morphology of SE have been optimized to achieve highly desirable sensing characteristics. The obtained sensors showed excellent performances with a great scope for application in on-board and environmental monitoring. This micro review provides an overview of the mixed-potential-type, amperometric and impedancemetric gas sensors recently developed by our group for detection of environmental pollutants.

1. Introduction

With recent increasing global awareness towards environmental issues, the aggravation of atmospheric environment in urban area caused by environmental pollutants, such as nitrogen oxide (NO_x) and hydrocarbon (HCs), emitted from automobiles and industrial processes is more and more serious. The strict emission controls are implemented globally, and the regulations will be increasingly strict (Figure 1). For example, the Euro VI, the next European emission regulation (which will be in effective in 2014), will strictly limit the diesel car's emission of NO_x, HCs and CO to a very low level of 0.06, 0.1, 1.0 g/km, respectively¹⁾. In order to achieve this, there is a need to improve the fuel efficiency as well as reduce drastically the amount of gas emission from vehicles. This requires not only the development of new catalytic converters but also highly sensitive gas sensors that monitor and diagnose the level of different pollutants for appropriate operation of those catalysts²⁾. There is also a high demand for the development of the highly sensitive gas sensors to monitor air polluting gases, in order to

replace the expensive and large analytical instruments, such as GC-MS and chemiluminescent gas-analyzer.

Among various types of exhaust sensors proposed and examined so far, the sensors using yttria-stabilized zirconia (YSZ) are considered to be the most practical. This is based on the records of the use of YSZ for over 30 years for oxygen (air-fuel-ratio) sensors to optimally control the conversion efficiency of three-way catalyst for gasoline-powered vehicles³⁾. Approximately 120 million of the air-fuel-ratio sensors are annually produced around the world, and they have been excellent in high-temperature property, sensing performance, and chemical and mechanical stability. This type of sensors makes up oxygen concentration cell with a Pt electrode on both sides of a YSZ tube. Its sensing signal is the equilibrium electromotive force (emf) based on Nernst's equation caused by the ratio of each partial pressure of oxygen between the two electrode sides. In comparison to these usual equilibrium-potential type sensors, the typical examples of the new zirconia-based gas sensor are a) the amperometric NO_x sensor⁴⁾ which employs the oxygen pump current caused by the electrochemical reduction of NO as a sensing signal, and b) the mixed-potential type NO_x sensor which will be discussed later⁵⁾.

Table 1 presents the summary of the zirconia-based gas sensors that have been reported by our group so far⁶⁻⁴⁴⁾. These gas sensors use a tubular or flat YSZ as the base material and mainly use metal oxide as a sensing electrode (SE) material. We have classified them into mixed-potential-type, amperometric, and impedancemetric gas sensors, depending on the sensing signal used. Table 1 indicates that the choice of SE materials strongly affects the type of gases and the concentration to be tested and suggests the importance of the appropriate choice of SE materials. Even if the same SE materials are used, the response characteristics vary depending heavily on the particle diameter, porosity and thickness. They also vary depending on the operation condition (in particular, operating temperature and operating method). Examination of these factors also leads to clarification of the sensing mechanism. Table 1 also indicates several

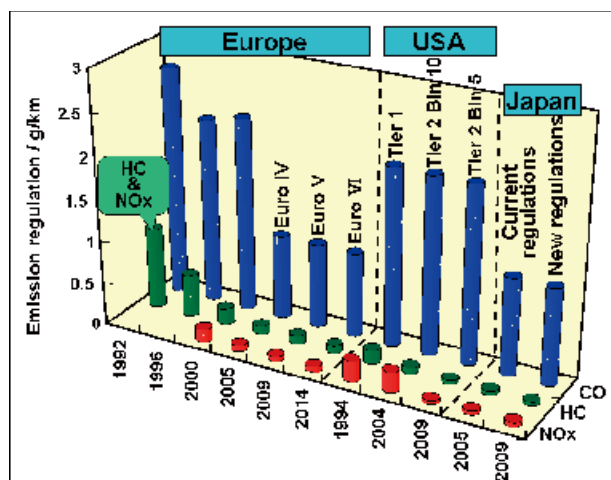


Fig. 1 Global trend of automobile gas emission control.

examples that adequately selecting the factors, such as the types of the sensing materials, their microstructure and operation condition, would result in the excellent sensing characteristics.

In this paper, we will introduce our recent representative results of the above mentioned three types of zirconia-based gas sensors from the viewpoint of on-board diagnosis and environmental monitoring.

Table 1 Our recent reports regarding various types of zirconia-based gas sensor

SE	Gas	Conc. (ppm)	Temp (°C)	Year
Mixed-Potential-Type				
CdMn ₂ O ₄	NO _x	5-4000	500-600	1996
CdCr ₂ O ₄	NO _x	20-600	500-600	1997
CdO/SnO ₂	CO	20-4000	600	1998
CdO	HCs	50-800	600	2000
WO ₃	NO _x	5-200	500-700	2000
NiCr ₂ O ₄	NO _x	25-436	550-650	2001
ZnCr ₂ O ₄	NO _x	50-436	600-700	2002
ZnFe ₂ O ₄	NO _x	50-436	600-700	2002
Cr ₂ O ₃	NO _x	10-200	600	2003
ZnO	NO _x	40-450	600-700	2004
NiO	NO _x	10-400	700-900	2005
Cr ₂ O ₃	NO _x	50-400	700	2006
NiO+Rh	NO _x	5-100	800	2006
NiO+WO ₃	NO _x	1-100	800	2007
NiO+Au	NO _x	50-400	600-800	2007
In ₂ O ₃	HCs	0.01-0.2	450	2007
In ₂ O ₃	HCs	50-800	790	2008
ZnCr ₂ O ₄	HCs	10-400	550	2008
NiO/Au	NH ₃	10-100	800	2008
Nano-Au	HCs	50-400	550	2009
Ni _{1-x} CoxO	NO _x	10-400	800	2009
Amperometric				
CdCr ₂ O ₄	NO _x	20-600	500-600	1998
ZnO+Pt	HCs	10-800	600	2007
Impedancemetric				
ZnCr ₂ O ₄	NO _x	50-400	600-700	2002
In ₂ O ₃	H ₂ O	70-30000	500-900	2004
ZnO+Pt	HCs	10-800	600	2006
ZnO	HCs	0.05-0.8	600	2007
ZnO/SnO ₂	HCs	0.05-0.8	600	2007

2. Mixed-Potential-Type Gas Sensor

The mixed-potential type gas sensors do not use the equilibrium electromotive force based on Nernst's equation as a sensing signal. Instead, as shown in Fig. 2, it uses mixed potential (steady-state potential) as the sensing signal. This mixed potential is generated by the following two electrochemical reactions when they proceed concurrently in the opposite direction at the interface between electrode and solid electrolyte; (1)

electrochemical reaction of the target gas (e.g. cathodic reaction of NO₂) and (2) electrochemical reaction of oxygen (e.g. anodic reaction of oxide ion). Furthermore, when target gas and oxygen penetrate the SE layer, both gases are involved in (3) gas-phase reaction (e.g. NO₂ decomposition to NO and O₂). Because of this, the amount (i.e. concentration) of target gas will be largely affected by the catalytic activity of SE material for the gas-phase reaction. Therefore, in order to obtain highly sensitive and highly selective mixed-potential response, there is a need to control the balance of three catalytic activities for two opposing electrochemical reactions at the interface and the gas-phase reaction.

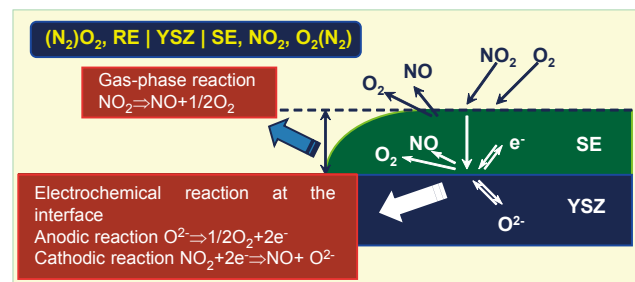


Fig. 2 Sensing model for NO_x detection.

2.1 High-temperature NO_x sensor using NiO-SE

The temperature of car engine sometimes reaches up to 900°C when cars are running at high speed. Therefore, the exhaust sensor requires high heat resistance. However, with the mixed-potential-type NO_x sensor, when the operation temperature reaches over 600°C, the sensitivity drastically drops in most of the cases. Recently, when we conducted a systematic search for the SE materials from the perspective of high temperature operation, we found that the use of NiO as SE could result in fairly high NO₂ sensitivity at the high temperature of 850°C (Figure 3(a))^{15, 16}. We also found that the NO₂ sensitivity could be improved when 3 wt.% Rh or 10 wt.% WO₃ was added to NiO^{21, 22}. Figure 3(b) represents the concentration dependency of the NO₂ sensitivity when pure NiO, NiO (+ 3 wt.% Rh) and NiO(+ 10 wt.% WO₃) were used as SE. In each case, the sensitivity varies linearly with the logarithm of the NO₂ concentration and the addition of the second component leads to the significant improvement in NO₂ sensitivity. When adding WO₃, it was even possible to detect the low NO₂ concentration of 1 ppm. Taking into consideration the fact that the material cost is approximately 1/100 of Rh, this is more practical.

We then examined the effect of the particle size of SE material as well as the thickness of SE on the sensor responses^{14, 17}. First, we changed the sintering temperature of SE in the range of 1100 - 1400°C and controlled the average particle size of NiO between 0.5 μm and 2 μm. Figure 4(a) shows the response transients to 200 ppm NO₂ at different sintering temperatures¹⁴. This indicates that the particle size of NiO increases with increasing sintering temperature and then the response becomes slightly slower and the electromotive force value becomes larger. We believe this is because the expansion of the particle

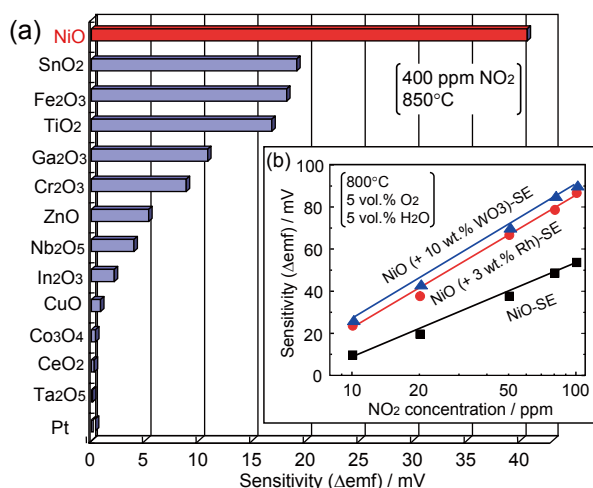


Fig. 3 (a) Comparison of NO_2 sensitivity of mixed-potential-type YSZ sensor using various metal-oxide SEs, (b) dependence of sensitivity on NO_2 concentration for the sensor using NiO-SE.

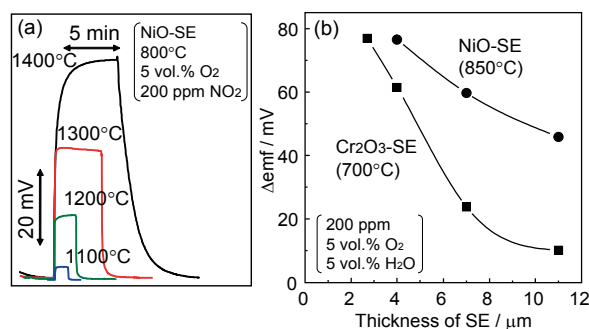


Fig. 4 (a) Response transients to NO_2 for the mixed-potential-type YSZ sensor using NiO-SE formed at various sintering temperature, (b) dependence of NO_2 sensitivity on the thickness of NiO-SE or Cr_2O_3 -SE.

size reduces the catalyst activity of gas-phase reaction of NO_2 and increases the amount of NO_2 that reaches the electrode interface. On the other hand, it seems that the response/recovery speed decreases as the three-phase boundary area, where electrode reaction takes place, is reduced. When taking into account the sensitivity and the response speed, the optimum sintering temperature seems to be 1300°C. Figure 4(b) presents the dependence of the sensitivity to 200 ppm NO_2 on the thickness of the NiO- or Cr_2O_3 -SE layer¹⁷⁾. This shows that the thinner the thickness is, the higher the sensitivity becomes. We believe that this is caused by the decrease in catalytic activity of gas-phase NO_2 decomposition as the thickness becomes thinner. The above results show that the proper control of the catalyst activity of gas-phase reaction as well as the electrode activity by changing the microstructure or thickness of SE will enable to improve the sensing characteristics of mixed-potential type gas sensors.

2.2 Hydrocarbon sensors for monitoring automobile exhaust and atmospheric environment

Automobile exhausts usually contain not only NO_x but also a lot of HCs. We therefore examined various zinc-based oxides as SE material for the mixed-potential type YSZ-based sensor, aiming to accomplish selective detection of HC. As a result, the sensor attached with ZnCr_2O_4 -SE was found to respond selectively to HCs (except for CH_4) at 550°C and showed hardly any responses to the other gases such as CO , NO_x and H_2 . When we measured the sensitivities to nine kinds of HCs, the sensitivity was approximately proportional to the carbon number of HC, and it was not affected by the bonding nature between C and H (saturated or unsaturated HC). These findings indicate the possibility of measuring total hydrocarbon concentration of HCs in exhaust gas.

It is also possible to detect HC at extremely low concentrations of ppb level by the use of the mixed-potential-type YSZ-based sensor by selecting both of the appropriate SE material and the optimum operation temperature. Currently, a gas chromatograph with a flame-ionization detector (GC-FID) and a gas chromatograph mass spectrometer (GC-MS) are used to monitor HCs in an atmospheric environment. These analytical instruments, however, have shortcomings including being large, expensive, and unable to measure in real time.

Because of this, development of an affordable and small hydrocarbon sensor is strongly required. We have found that it is possible to detect even very low concentration of 10 ppb C_3H_6 by employing In_2O_3 -SE operating at 450°C, which is the relatively low operation temperature for YSZ-based sensors^{35,40)}. Figure 5 shows (a) the response transients of this sensor against 10-200 ppb C_3H_6 and (b) the sensitivity dependency on the C_3H_6 concentration. The 90% response time was approximately 3 minutes, which

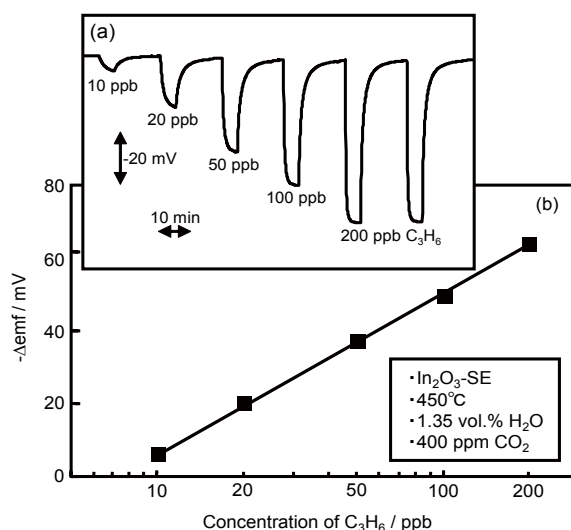


Fig. 5 (a) Response transients to the extremely low concentrations of C_3H_6 and (b) C_3H_6 concentration dependence of the sensitivity for the mixed-potential-type YSZ-based sensor attached with In_2O_3 -SE.

is acceptable for atmospheric environment monitoring. The sensitivity showed a nearly linear relationship with the logarithm of C_3H_6 concentration, and the sensitivity of 20 mV was observed for even very low concentration of 20 ppb C_3H_6 . Such a relatively high gas sensitivity to several tens ppb level has never been reported so far by using mixed-potential-type YSZ-based sensors. Very lately, we also found that optimization of the SE materials and the operation condition makes it possible to detect VOCs (e.g., toluene) highly sensitively and selectively. These results suggest that the mixed-potential-type gas sensor has high potential to be practically applied to atmospheric environment monitoring.

2.3 Application of nano-sized materials to SE

We also examined the possibility of large improvement in the sensing characteristics by using nano-sized SE materials for the mixed-potential-type sensors. First, the sensing characteristics were examined when the thickness of SE was reduced to nano-size^{18,19}. The thin SE layers were fabricated by sputtering of Ni target on the surface of YSZ plate, followed by oxidation to NiO by heat treatment. The thickness of NiO-SE was controlled in the range of 60 to 180 nm by changing the sputtering time. Figure 6(a) shows the comparison of the sensitivities of NiO-SEs with different thicknesses for detection of various concentrations of NO_2 at 800°C. The sensitivity increased with decreasing thickness for any NO_2 concentrations. As shown in Fig. 6(b), the sensitivity was increased more than threefold by reducing operation temperature of the sensor from 800°C to 600°C. However, the selectivity to NO_2 was poor, because the cross sensitivities to various reducing gases were rather high. We then fabricated the laminated electrodes by sputtering Au thin layer of about 60 nm on the NiO layer and examined their sensing characteristics to various gases. As a result, it was found that the Au layer worked as a gas-phase oxidation catalyst of the reducing gases, resulting in a dramatic improvement in the selectivity of NO_2 ^{34,38}.

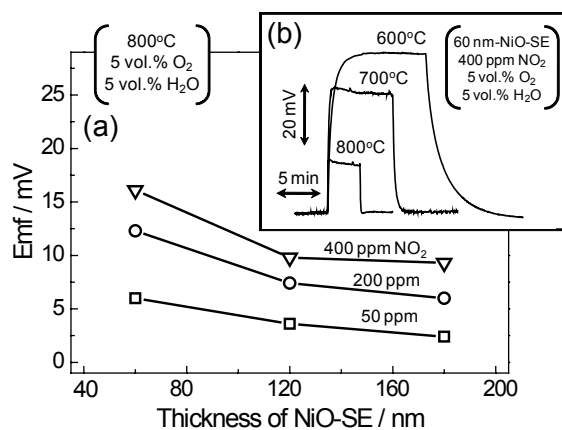


Fig. 6 (a) Dependence of NO_2 sensitivity on thickness of NiO-SE, (b) response transients to 400 ppm NO_2 at various temperatures, for the mixed-potential type YSZ-based sensor.

Meanwhile, we recently proposed a sensor that allows selective detection of NH_3 by using SE made of composite materials, which were formed by screen printing of NiO layer on the sputtered Au layer³⁷. Figure 7 shows the sensitivity of this sensor to various gases at 800°C. Excellent NH_3 selectivity was obtained in this case. Thus, this sensor has a potential to be used for monitoring NH_3 in exhausts emitted from diesel-engine cars that incorporate a urea-SCR system.

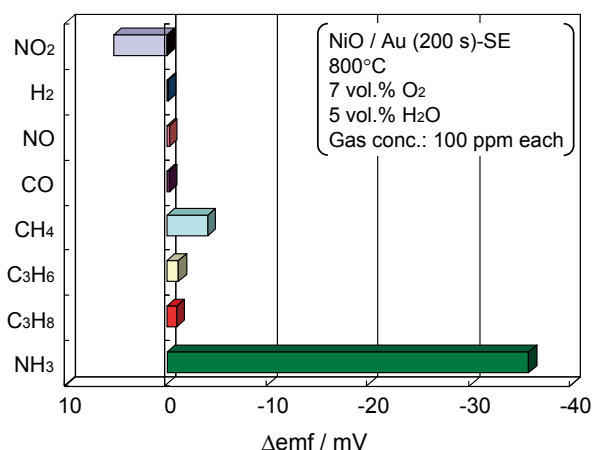


Fig. 7 Comparison of sensitivities to various gases at 800°C for the YSZ-based sensor attached with NiO/Au-SE.

3. New amperometric gas sensor

The sensing signal of an amperometric sensor usually employs the electric current which can be obtained when the target gas is electrochemically oxidized or reduced. This sensor can give a relatively fast response and obtain limiting-current response by controlling diffusion speed of the target gas through the SE layer. However, the sensitivity is sometime not sufficient and the stability of the sensor is usually relatively low due to continuous application of potential to SE. Thus, we examined the possibility of improving the sensing characteristics by proposing the "pulsed-potential method", which is a new measuring method. The sensitivity of a conventional measuring method is defined as the difference between the current values when the gas flow is changed from the base gas to the sample gas, while a certain potential is being applied to SE. On the contrary, in the case of new method, the peak current is measured as a sensing signal when the potential is applied to SE for a very short duration of 0.03 s under a continuous flowing of the sample gas with the fixed concentration.

Figure 8 shows the dependence of the current sensitivity on the C_3H_6 concentration for the YSZ-based sensor using $ZnO(+Pt)$ -SE operating at 600°C under the both measuring modes, when the potential of SE was set at +70 mV vs. Pt reference electrode²⁷. It is clearly seen that the C_3H_6 sensitivity obtained by the pulsed-potential method is about 20 times higher than that obtained by the conventional method. The present sensor also showed

excellent C_3H_6 selectivity with low cross sensitivities to other gases examined. In addition, the sensitivity was hardly affected by the change in water vapor (1.4 - 16 vol.%) and oxygen (3 - 20 vol.%) concentrations. Furthermore, with regards to the stability of the sensor, the sensitivity using the conventional method degraded rapidly down to 25% of the initial value within 5 days from the initiation of the measurement, while the initial sensitivity has maintained almost constantly for over 1 month with the “pulsed-potential method”. These findings indicate that the “pulsed-potential method” can improve very much both of the C_3H_6 sensitivity and the stability of the amperometric YSZ-based sensor.

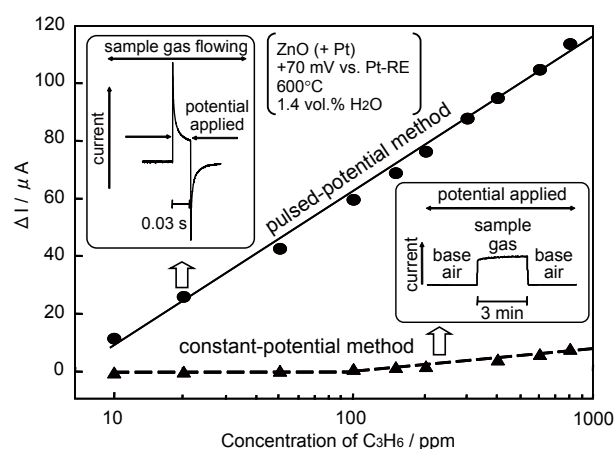


Fig. 8 Sensing characteristics to C_3H_6 for the amperometric YSZ sensor attached with ZnO(+ Pt)-SE operated by two types of measuring methods.

4. Impedancemetric gas sensor

Recently, we have proposed the new-type impedancemetric YSZ-based gas sensor which has a completely different detection method from the above-mentioned mixed-potential type or amperometric gas sensors^{28, 29}). In this case, the change in the complex impedance of the device attached with SE is measured as a sensing signal. Figure 9 shows the comparison of the sensitivities for the mixed-potential type and impedancemetric gas sensors using the same $ZnCr_2O_4$ -SE in the various concentrations of NO and NO_2 . It is seen that the impedancemetric sensor shows the almost identical behavior to NO and NO_2 . This indicates that the present sensor can detect total NOx (NO+ NO_x) in the sample gas. On the other hand, in the case of the mixed-potential-type sensor, the response signals to NO and NO_2 are opposite and the sensitivity to NO_2 is always higher than that to NO.

Figure 10 shows the schematic view of Nyquist plots (a) and the equivalent circuit (b) for the impedancemetric gas sensor. When the sensor is exposed to the sample gas (NO_x), the semicircular arc in the lower frequency range is shrinking in comparison with that for the base gas. The diameter of this semicircular arc indicates the

resistance due to the electrochemical reaction occurring at the electrode interface. With this sensor, the reaction resistance is reduced by introducing the sample gas. The difference between the diameter of the semicircular arc in the sample gas (NO_x) and that in the base gas is defined as gas sensitivity. This sensitivity of the present sensor varies almost linearly with the logarithm of the NO_x concentration and the sensitivity to NO_2 is almost same as that to NO. Therefore, the present impedancemetric sensor does not require the NO oxidation electrode for measuring the total concentration of NO_x , unlike the case of the mixed-potential-type NO_x sensor. We have reported that the impedancemetric sensors can also detect water vapor in a wide concentration range³¹), hydrogen-containing compounds³²) and high concentrations of HCs²⁹).

Furthermore, we have also found that the impedancemetric sensor has relatively high sensitivity to extremely low concentrations of HC³⁰). This suggests the possibility of applying this type of sensor to monitoring of atmospheric environment, similar to the mixed-potential-type sensor attached with In_2O_3 -SE. In particular, the impedancemetric sensor using the laminated ZnO/ SnO_2 SE can detect C_3H_6 selectively in the concentration range of 0.05-0.8 ppm.

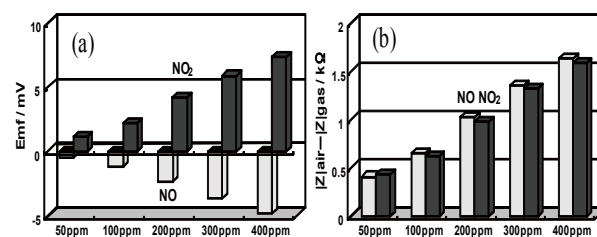


Fig. 9 Comparison of NO_x sensitivities between (a) mixed-potential-type and (b) impedancemetric NO_x sensors using the same $ZnCr_2O_4$ -SE.

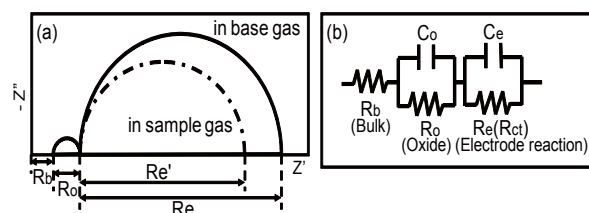


Fig. 10 (a) A schematic view of Nyquist plot, and (b) the equivalent circuit, for the impedancemetric YSZ-based sensor using oxide-SE.

5. Conclusions

In this review, we pointed out that the following important factors to improve the performances of YSZ-based gas sensors; 1) searching of new SE materials, 2) optimization of thickness and morphology of SE, 3) nano-sizing of SE, 4) examination of the most appropriate operation temperature, and 5) proposal of new detection methods. Among them, the most important factor for

obtaining specific and excellent sensing characteristics would be the search for proper SE material. For the commercialization of the sensors, high sensitivity, high selectivity, quick response and especially excellent long-term-stability are definitely required.

Currently, among all types of YSZ-based gas sensors, the air-fuel-ratio sensors are mass-produced and installed in automobiles, as mentioned above. However, in the future, if the NO_x sensors and NH₃ sensor are turned into practical application to control new type of automobile exhaust catalyst such as NO_x storage catalyst and urea SCR system, the fuel efficiency will be drastically improved and the amount of automobile exhaust will be further reduced. Highly sensitive and selective detection of HCs and CO will also be needed in the future, as their exhaust amount will be more strictly regulated all over the world.

Installation of multiple gas sensors in the automobile exhaust will enable to realize the new on-board diagnosis (OBD) system, in which a driver can know the concentration of each exhaust gas as well as the working condition of the catalysts while driving⁴⁵⁾ (Figure 11).

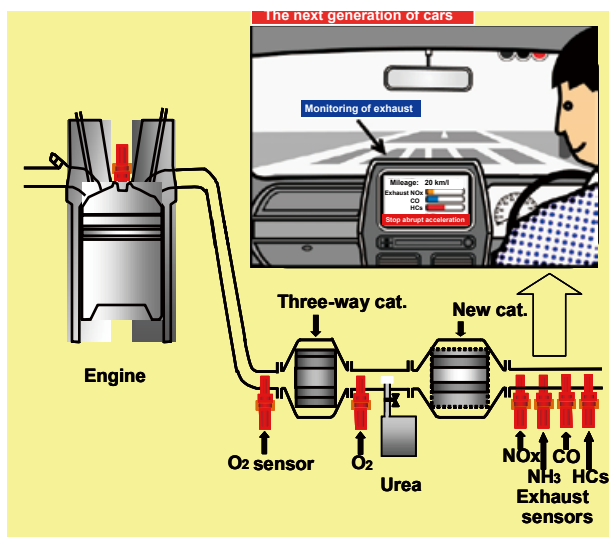


Fig. 11 The next generation vehicle that allows a driver to monitor exhaust gas condition based on the information obtained by the various exhaust gas sensors.

Furthermore, in the field of atmospheric environment monitoring, if the small, low-power-consumption and inexpensive multi-gas-sensors having high sensitivity and high selectivity are realized, the issues with the conventional analytical instruments, such as securing the space, necessity of maintenance and long measurement interval, will be solved. The new sensor can also be installed in much larger number of measurement points compared to the conventional measuring system and can collect larger volume of data. These features will enable us to monitor the air pollutants concentration around the roads in real time or to map out the air pollution condition throughout a city or even a nation. As a result,

we might be able to not only monitor but also predict the environmental pollution^{46,47)}. We hope that this type of sensor research will become even more active and will contribute to the environmental field.

References

- 1) DieselNet: <http://www.dieselnets.com/standards>
- 2) Y. Sasaki, *Jidoshagijyutsu (automobile technology)*, **61**(2), 35 (2007).
- 3) J. Riegel, H. Neumann, H.-M. Wiedenmann, *Solid State Ionics*, **152**, 783 (2002).
- 4) NGK Insulators: <http://www.ngk.co.jp/>
- 5) T. Ono, M. Hasei, A. Kunitomo, T. Yamamoto, A. Noda, *JSAE Rev.*, **22**(1), 49 (2001).
- 6) N. Miura, H. Kurosawa, M. Hasei, G. Lu, N. Yamazoe, *Solid State Ionics*, **86**, 1069 (1996).
- 7) N. Miura, G. Lu, N. Yamazoe, H. Kurosawa, M. Hasei, *J. Electrochem. Soc.*, **143**(2), L33 (1996).
- 8) G. Lu, N. Miura, N. Yamazoe, *J. Mater. Chem.*, **7**, 1445 (1997).
- 9) S. Zhuikov, T. Nakano, A. Kunitomo, N. Yamazoe, *Electrochem. Commun.*, **3**, 97 (2001).
- 10) S. Zhuikov, T. Ono, N. Yamazoe, N. Miura, *Solid State Ionics*, **152**, 801 (2002).
- 11) N. Miura, S. Zhuikov, T. Ono, M. Hasei, N. Yamazoe, *Sens. Actuators B*, **83**, 222 (2002).
- 12) T. Ono, M. Hasei, A. Kunitomo, N. Miura, *Electrochemistry*, **71**(6), 405 (2003).
- 13) N. Miura, K. Akisada, J. Wang, S. Zhuikov, T. Ono, *Ionics*, **10**, 1 (2004).
- 14) P. Elumalai, J. Wang, S. Zhuikov, D. Terada, M. Hasei, N. Miura, *J. Electrochem. Soc.*, **152**, H95 (2005).
- 15) N. Miura, J. Wang, M. Nakatou, P. Elumalai, M. Hasei, *Electrochem. Solid-State Lett.*, **8**, H9 (2005).
- 16) N. Miura, J. Wang, M. Nakatou, P. Elumalai, S. Zhuikov, M. Hasei, *Sens. Actuators B*, **114**, 903 (2006).
- 17) P. Elumalai, N. Miura, *Solid State Ionics*, **176**, 2517 (2005).
- 18) V. V. Plashnitsa, T. Ueda, N. Miura, *Inter. J. Appl. Ceram. Tech.*, **3**, 127 (2006).
- 19) V. V. Plashnitsa, T. Ueda, P. Elumalai, N. Miura, *Sens. Actuators B*, **130**, 231 (2008).
- 20) P. Elumalai, M. Hasei, N. Miura, *Electrochemistry*, **74**, 197 (2006).
- 21) J. Wang, P. Elumalai, D. Terada, M. Hasei, N. Miura, *Solid State Ionics*, **177**, 2305 (2006).
- 22) N. Miura, J. Wang, P. Elumalai, D. Terada, T. Ueda, M. Hasei, *J. Electrochem. Soc.*, **154**, J246 (2007).
- 23) N. Miura, T. Raisen, G. Lu, N. Yamazoe, *Sens. Actuators B*, **47**, 84 (1998).
- 24) N. Miura, T. Shiraishi, K. Shimanoe, N. Yamazoe, *Electrochem. Commun.*, **2**, 77 (2000).
- 25) T. Ueda, P. Elumalai, V. V. Plashnitsa, N. Miura, *Chem. Lett.*, **37**(1), 120 (2008).
- 26) N. Miura, G. Lu, N. Yamazoe, *Sens. Actuators B*, **52**, 169 (1998).
- 27) T. Ueda, V. V. Plashnitsa, M. Nakatou, N. Miura, *Electrochem. Commun.*, **9**, 197 (2007).
- 28) N. Miura, M. Nakatou, S. Zhuikov, *Sens. Actuators B*, **93**, 221 (2003).
- 29) M. Nakatou, N. Miura, *Sens. Actuators B*, **120**, 57 (2006).
- 30) R. Wama, M. Utiyama, V. V. Plashnitsa, N. Miura, *Electrochem. Commun.*, **9**, 2774 (2007).

- 31) M. Nakatou, N. Miura, *Electrochem. Commun.*, **6**, 995 (2004).
- 32) M. Nakatou, N. Miura, *Solid State Ionics*, **176**, 2511 (2005).
- 33) P. Elumalai, V. V. Plashnitsa, T. Ueda, N. Miura, *Electrochem. Commun.*, **10**, 745 (2008).
- 34) V. V. Plashnitsa, T. Ueda, P. Elumalai, T. Kawaguchi, N. Miura, *Ionics*, **14**(1), 15 (2008).
- 35) N. Miura, S. Mori, R. Wama, P. Elumalai, V. V. Plashnitsa, M. Utiyama, *Electrochem. Solid-State Lett.*, **11**(9), J69 (2008).
- 36) Y. Fujio, V. V. Plashnitsa, P. Elumalai, N. Miura, *Electrochem. Solid-State Lett.*, **11**(10), J73 (2008).
- 37) P. Elumalai, V. V. Plashnitsa, Y. Fujio, N. Miura, *Electrochem. Solid-State Lett.*, **11**(11), J79 (2008).
- 38) V. V. Plashnitsa, P. Elumalai, N. Miura, *J. Electrochem. Soc.*, **155**(11), J301 (2008).
- 39) R. Wama, V. V. Plashnitsa, P. Elumalai, T. Kawaguchi, Y. Fujio, M. Utiyama, N. Miura, *J. Electrochem. Soc.*, **156**(5), J102 (2009).
- 40) V. V. Plashnitsa, P. Elumalai, T. Kawaguchi, Y. Fujio, N. Miura, *J. Phys. Chem. C*, **113** (18), 7857 (2009).
- 41) C. O. Park, J. W. Fergus, N. Miura, J. Park, A. Choi, *Ionics*, **15**(3), 261 (2009).
- 42) P. Elumalai, J. Zosel, U. Guth, N. Miura, *Ionics*, **15**(4), 405 (2009).
- 43) P. Elumalai, V. V. Plashnitsa, Y. Fujio, N. Miura, *J. Electrochem. Soc.*, **156**(9), J288 (2009).
- 44) V. V. Plashnitsa, P. Elumalai, Y. Fujio, N. Miura, *Electrochimica Acta*, **54**(25), 6099 (2009).
- 45) N. Miura, T. Ueda, V. V. Plashnitsa, "Nano Ionics, Latest technology and its foresight". CMC Publishing, Chapter 9, 254 (2008).
- 46) N. Miura, T. Ueda, R. R. Wama, Y. Fujio. *Material Integration*, **21**(5), 43 (2008).
- 47) N. Miura, P. Elumalai, V. V. Plashnitsa, T. Ueda, R. Wama, M. Utiyama, *Solid State Gas Sensing*, Springer, Chapter 5, 181 (2009).

Research Report

Development of High-performance Zirconia-based Gas Sensors Using Nano-structured Sensing Electrodes

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The present study is overviewed the recent developments in yttria-stabilized zirconia (YSZ)-based planar sensors using nano-structured sensing electrodes (SE) aiming at sensitive and selective detection of exhaust gases and ammonia slip in automobiles. Particular attention is focused on the fabrication of nano-structured Au-SEs and evaluation of its sensing characteristics in a wide operating temperature range. It was observed that the sensing performance of nano-structured Au-SEs depended to a large extent on the size and shape of Au nano-particles as well as on the morphology of YSZ substrate.

A growing production of automobiles and implementation of industrial combustion furnaces especially in developing countries enforce a strong concern globally on environmental pollution due to release of various hazardous gases (NO_x , hydrocarbons (HCs) and CO). As for the automobiles are concerned, conventional three-way catalyst (TWC) and selective-catalytic reduction (SCR) systems are used to oxidize CO, NO_x and HCs to environmentally safe CO_2 , N_2 and H_2O ⁽¹⁾. Thus, the minimization of concentrations of exhausted gases will result in keeping the clean environment and CO_2 reduction. The control of functionality of TWC and SCR systems requires the development of high-performance solid-state gas sensors workable in harsh environments and high temperature.

The yttria-stabilized zirconia (YSZ)-based gas sensors using the different kinds of sensing electrodes (SE) are capable of providing the sensitive and selective responses to various gases. Furthermore, new attractive findings

in a field of nano-structured materials allow applying their distinguished features to improve the selectivity and sensitivity to a target gas. In fact, we have recently reported that the YSZ-based sensor attached with Au-SE fabricated by r.f. sputtering (sub-micron Au particles) gave sensitive and selective response to NO_2 ⁽²⁾.

Thus, to examine the effect of size and shape of Au nano-particles on its gas sensing characteristics, Au-SEs were fabricated by applying the colloidal gold solution with the particle size of 5 nm on different YSZ plates (porous rough- polycrystalline (rp) YSZ: grain size and roughness of about 300 nm; dense polished-polycrystalline (pp) YSZ: grain size – about 5 μm , roughness – 150 nm; and atomically-smooth single-crystal (sc) (100) and (111) YSZ: roughness is less than 0.5 nm). Figure 1 shows the morphology of Au-SEs fabricated on (a) rp-, (b) pp-, and (c, d) sc-YSZ plates after annealing at 1000°C for 2 h. It was observed that almost all Au colloids diffused into the surface layer of rp-YSZ (Fig. 1, a) and this sensor gave the highly selective and sensitive response to C_3H_6 at 550°C (Fig. 2). Such a behavior is attributed to the formation of intermediate compounds (propylene oxide or acrolein) in the vicinity of nano-Au/YSZ interface with

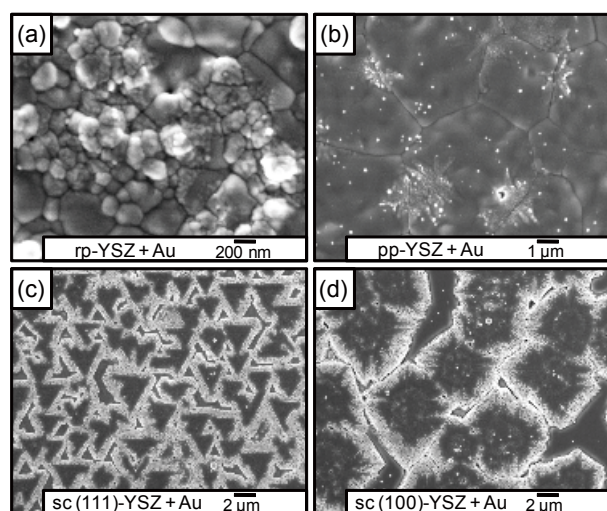


Fig. 1. Crystallization of 5 nm-Au colloids on (a) rp-, (b) pp- and (c, d) sc-YSZ ((111) and (100), respectively) plates, after annealing at 1000°C for 2 h.

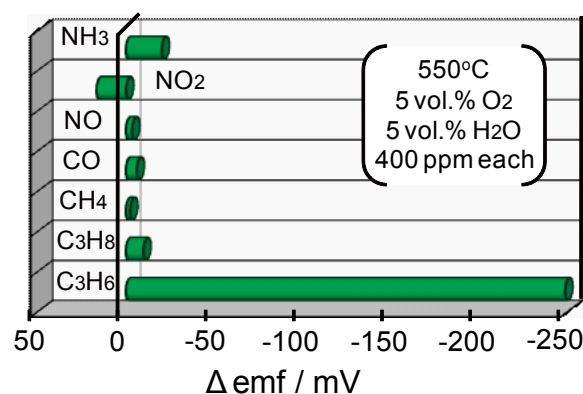


Fig. 2. Cross sensitivities to various gases (400 ppm each) at 550°C under the wet (5 vol.% H_2O) for the sensor based on rp-YSZ treated with 5 nm-Au.

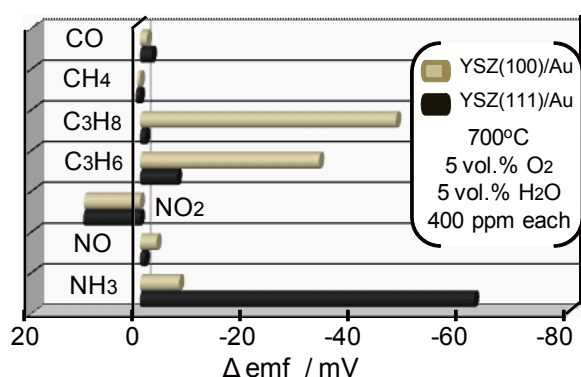


Fig. 3. Comparison of the cross sensitivities to various gases (400 ppm each) at 700°C under the wet condition for the sensors based on each of sc-YSZs attached with Au-SE.

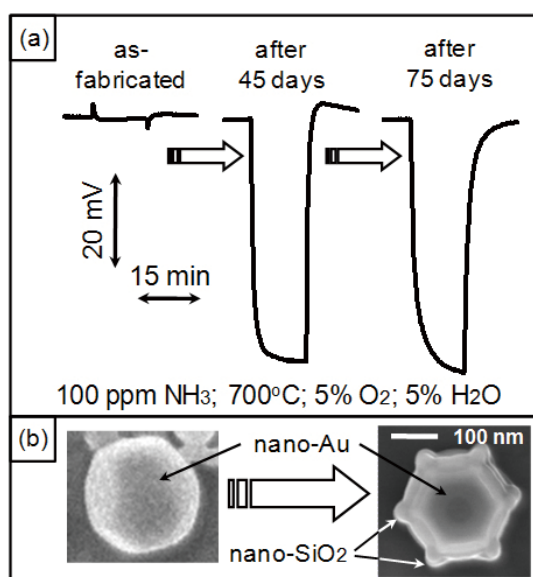


Fig. 4. (a) Response transients to 100 ppm NH_3 at 700°C under the wet condition for the sensor based on pp-YSZ treated with 5 nm-Au; (b) change of the shape of spherical Au particles to hexagonal-like Au-SiO₂ composite.

the help of adsorbed oxygen³⁾.

In the case of sc-YSZ plates, the gold followed the crystalline orientation of YSZ and formed the conductive (100)- and (111)- oriented Au domains with square- and triangular-like geometry, respectively (Fig. 1, c and d). As a result, the sensor based on YSZ(100) with Au-SE exhibited high but not selective responses to HCs at 700°C, whereas the sensor based on YSZ(111) gave selective and sensitive response to NH_3 . Such a discrepancy in the sensing characteristics can be attributed to the dissimilar affinity and catalytic activity of variously-oriented Au domains to different gases.

The morphology of pp-YSZ can be considered as an intermediate between rp- and sc-YSZ plates. So, only partial Au clustering was found along the grain-boundaries and considerable amount of Au nano-particles were observed on the YSZ surface (Fig. 1, b). The as-fabricated pp-YSZ-based sensor using Au-SE did not show attractive sensing characteristics. However, after 45 days of operation at 700°C, the present sensor was found to give sensitive and selective response to NH_3 and the NH_3 response was not altered even after 75 days of operation (Fig. 4, a). SEM and EDX analyses revealed a gradual accumulation of nano-SiO₂ impurities on the surface of nano-Au particles (Fig. 4, b) changing their shape from spherical to hexagonal. In turn, it might result in change of its catalytic activity to gas-phase oxidation because some of active Au clusters are hidden by SiO₂. Additionally, high NH_3 sensitivity can be promoted by possible acid-basic interaction where acidic SiO₂ nano-particles catch and bind basic NH_3 gas molecules.

Thus, based on the obtained results, we are currently designing and constructing the high- performance YSZ-based sensor using nano-structured SEs for the selective and sensitive detection of carbon monoxide.

References

- 1) S. Matsumoto, *Catal. Today*, **90**, 183 (2004).
- 2) V.V. Plashnitsa, P. Elumalai, N. Miura, *J. Electrochem. Soc.*, **155**, J301 (2008).
- 3) V.V. Plashnitsa, P. Elumalai, T. Kawaguchi, Y. Fujio, N. Miura, *J. Phys. Chem. C*, **113**, 7857 (2009).

Research Report

Improvement in sensing characteristics of Zirconia-based Total Hydrocarbon Sensor

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In order to improve the stability of the mixed-potential-type yttria-stabilized zirconia (YSZ)-based propene (C_3H_6) sensor attached with $ZnCr_2O_4$ -sensing electrode (SE), the several modifications of the SE material and YSZ powder were examined. As a result, the sensor using the laminated $ZnCr_2O_4$ /YSZ-SE gave the stable *emf* response against 100 ppm C_3H_6 at 550°C for about one month. The fabricated sensor was found to exhibit the linear dependence of sensitivity on the logarithm of C_3H_6 concentration in the range of 10–800 ppm as well as on the logarithm of total concentration of various hydrocarbons (HCs) in the range of 90–2600 ppmC.

Introduction

For a last few decades, the number of automobiles has been drastically increasing. As a consequence, the emission control for automobiles containing the gasoline and diesel engines have been severely regulated all around the world. Among the various air pollutants, some of hydrocarbons (HCs) can cause a photochemical smog or greenhouse effect on an environmental eco-system. Thus, in order to control the efficiency of the three-way-catalyst (TWC) system, the sensor for continuous monitoring of residual concentration of HCs is strongly demanded downstream of TWC. So far, there have been several reports about yttria-stabilized zirconia (YSZ)-based HCs sensors using noble metal¹⁾ or metal oxide²⁾ sensing electrodes (SEs). Due to the fact that real car exhausts are usually a multi-component gas mixture containing different fractions of the saturated and unsaturated HCs, the measurement of total concentration of various HCs would be the greatest advancement for a future on-board diagnosis (OBD) system.

Quite recently, we have reported that the mixed-potential-type YSZ-based sensor attached with $ZnCr_2O_4$ -SE showed sensitive response to each of non-methane HCs, such as C_2H_6 , C_2H_4 , C_3H_8 , C_3H_6 , C_3H_4 , n - C_4H_{10} , *iso*- C_4H_8 and 1- C_4H_8 , and negligible response to other co-existing gases, such as CO, NO_x (NO and NO_2), H_2 , and CH_4 at 550°C even in the presence of 5 vol.% H_2O .³⁾ Furthermore, this sensor exhibited a good linearity between the sensitivity and the logarithm of total concentration of various HCs mixture (various volume ratios of 1- C_4H_8 , C_3H_6 , and C_2H_6 , ppmC). However, the response of the present sensor was found to be stable only for 10 days. Thus, in the present study, $ZnCr_2O_4$ -SE was modified with YSZ powder to enhance the long-term stability of the present sensor and the obtained sensing characteristics for the newly-fabricated sensors are reported and discussed here.

Experimental

A commercially available one-end-opened YSZ-tube (8 mol.% Y_2O_3 doped) was used for the fabrication of a sensor device. Each of the commercial oxide powders ($ZnCr_2O_4$ and YSZ) or their mixture were thoroughly mixed with α -terpineol, and the resulting pastes were applied on the outer surface of the YSZ tube to form the SE. A commercial Pt paste was applied on the top of the inner surface and outer surface of the YSZ tube to fabricate a reference electrode (RE) and a counter electrode (CE), respectively. The YSZ tube coated with the oxide and Pt pastes was sintered at 1100°C for 2 h. Here, three different structures of SEs were fabricated: (i) the single $ZnCr_2O_4$ -SE, (ii) the composite ($ZnCr_2O_4$ + 10 wt.% YSZ)-SE, and (iii) the laminated $ZnCr_2O_4$ /YSZ-SE.

The gas sensing characteristics of the fabricated sensors were evaluated in a conventional gas-flow apparatus equipped with an electric furnace operating at 550°C. The sample gas containing each of various target gases were prepared by diluting each parent gas with the base air (dry synthetic air + 5 vol.% H_2O). The difference in electromotive force (*emf*) between SE and RE of the tubular sensor was measured with a digital electrometer as a sensing signal.

Results and discussion

Initially, the stability of *emf* response to 100 ppm C_3H_6 for each of the fabricated sensor attached with $ZnCr_2O_4$ -, ($ZnCr_2O_4$ +YSZ)-, and $ZnCr_2O_4$ /YSZ-SEs was examined at 550°C in the presence of 5 vol.% H_2O . As a result, the *emf* responses to 100 ppm C_3H_6 for both the sensors using the single $ZnCr_2O_4$ -SE (Fig. 1(a)) and the composite ($ZnCr_2O_4$ +YSZ)-SE (Fig. 1 (b)) increased drastically after about 10 days. Furthermore, the cross sensitivity to 100 ppm NO_2 was also increased for both sensors. On the contrary, the sensor attached with the laminated $ZnCr_2O_4$ /

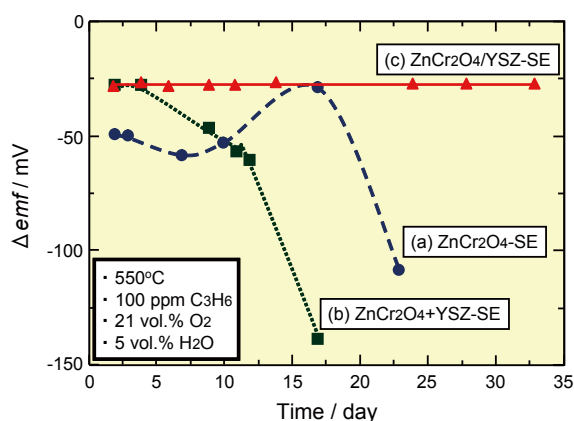


Fig. 1: Time course of C_3H_6 sensitivity at 550°C for the sensors attached with each of (a) $ZnCr_2O_4$ -SE, (b) $(ZnCr_2O_4+YSZ)$ -SE, and (c) $ZnCr_2O_4/YSZ$ -SE.

YSZ-SE exhibited very stable *emf* response to 100 ppm C_3H_6 even after 30-day operation at 550°C, as shown in Fig. 1(c), and the sensitivities to other examined gases (CO , NO_x , and H_2) were still negligible.

In general, the sensing characteristics of the mixed-potential-type sensor are affected by both the catalytic activity for gas-phase reaction in SE matrix and the catalytic activities for two competing electrochemical reactions at SE/YSZ interface. Since only one kind of SE ($ZnCr_2O_4$) was used in the present study, it can be speculated that the *emf* response is more influenced by the catalytic activities for the electrochemical reactions at the $ZnCr_2O_4/YSZ$ interface rather than that of gas-phase reaction. Thus, it seems that the addition of secondary YSZ layer between the $ZnCr_2O_4$ -SE and YSZ tube stabilizes the interface and resulted in much better stability of the present sensor. In fact, the stability of the newly-created interface between $ZnCr_2O_4$ and YSZ layers was confirmed by periodical impedance measurements and SEM observations.

Since various kinds of HCs exist simultaneously in automotive exhausts, it is important that the fabricated sensor attached with the laminated $(ZnCr_2O_4/YSZ)$ -SE

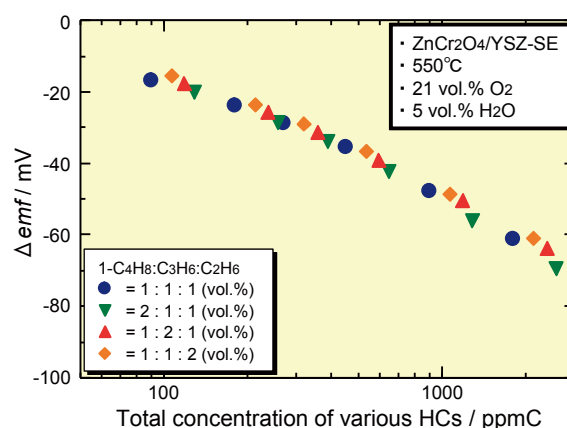


Fig. 2: Dependence of Δemf on the total concentration of various HCs mixtures at 550°C for the sensor attached with the laminated $ZnCr_2O_4/YSZ$ -SE.

can still exhibit the good sensing performance for the total concentration of various HCs. Figure 2 depicts the dependence of Δemf on the total concentration of various HCs mixtures for the present sensor at 550°C in the presence of 5 vol.% H_2O . It is clearly seen that the sensitivities to various HCs mixtures containing different volume ratios of 1- C_4H_8 , C_3H_6 , and C_2H_6 vary almost linearly with regard to the logarithm of total concentration of HCs (ppmC) in the examined range of 90-2600 ppmC. Thus, it is considered that the present sensor could be a possible candidate for the actual total HC sensor operating in automotive exhausts.

References

- 1) V. V. Plashnitsa, P. Elumalai, T. Kawaguchi, Y. Fujio, and N. Miura, *J. Phys. Chem. C*, **113**, 7857 (2009).
- 2) N. Miura, T. Shiraishi, K. Shimanoe, and N. Yamazoe, *Electrochem. Commun.*, **2**, 77 (2000).
- 3) Y. Fujio, V. V. Plashnitsa, P. Elumalai, and N. Miura, *Electrochem. Solid-State Lett.*, **11**(10), J73 (2008).

Micro Review

Advanced Energy Conversion of Useful Resources toward Low-Carbon Society

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The numerous actions for reduction of carbon dioxide concentration in air and for saving of energy supply from fossil fuel resources have been considered and developed to realize a low-carbon society. In our laboratory, advanced biodiesel synthesis from waste recycle oils such as an electrolysis method and a rapid catalytic method in microtube reactor were investigated. Basic research of CO₂/O₂ gasification of coal was started as a subject of Novel Carbon Resources Sciences.

1. Introduction

Global warming is the biggest and serious problem us in this century. Cool Earth 50 is a Japanese plan to reduce global greenhouse gas (GHG) emissions 50% by 2050. Ministry of Environment released the visions for reducing GHG emission by 80% in the developed country to protect the global warming on August 2009. METI recently created the Cool Earth Innovative Energy Technology Program to promote the development of innovative energy technologies toward achieving the goal of halving the world's total GHG emissions by 2050. Based on this program, the following 21 technologies were selected.

(Power generation/transmission)

- High efficiency natural gas fired power generation
- High efficiency coal fired power generation
- Carbon dioxide capture and storage (CCS)
- Innovative photovoltaic power generation
- Advanced nuclear power generation
- High efficiency superconducting power transmission

(Transportation)

- Intelligent transport system (ITS)
- Fuel-cell vehicle
- Plug-in hybrid electric vehicle/electric vehicle
- Production of transport biofuel

(Industry)

- Innovative material, Production/Processing Technology
- Innovative iron and steel making process

(Commercial/residential)

- High-efficiency house and building
- Next-generation high-efficiency lighting
- Stationary fuel cell
- Ultra high-efficiency heat pump
- High-efficiency information device and system
- HEMS/BEMS/local-level EMS

(Cross-cutting technologies)

- High performance power storage
- Power electronics
- Hydrogen production, transportation and storage

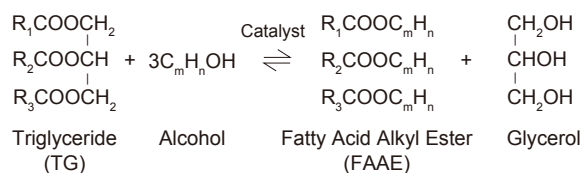
In order to reduce CO₂ emission, construction of huge process such as atomic power plant, innovative iron and steel making process and CCS by 2050 would be difficult. There are many disturbing problems accompanied with the widespread use of solar power generation, electric vehicle, LED lamp and biofuel, for example a relatively small reduction effect on CO₂ emission and a shortage of the resources to produce them. One of the best ways is to promote the raising of environmental awareness among the people. In any way, the continuous efforts of researchers will bring efficient solutions to global warming problem in the near future.

The COE program NCRS aims at establishing a new field of science for efficient use of carbon resources for energy and chemicals and education of young researchers in such a field. In my laboratory, the fundamental research of O₂/CO₂ gasification for the project of NEDO Innovative Zero-emission Coal Gasification Power Generation Project has been investigated. As for the details of our results for the gasification, refer to the research report by Dr Irfan in this journal. Another topic in my laboratory is the development of high efficiency synthesis of biodiesel fuel (BDF). Among the biofuels, bioethanol production is an experimental stage in Japan. On the other hand, there are many small BDF plants all over Japan. However, research on BDF seems to be considered low technology and does not receive as much attention as that on bioethanol in Japan. There is no doubt that the proportion accounted for the biofuels increased year after year due to a rise in crude oil price. Steady research efforts to BDF production may lead to the resolution of global warming problem.

2. High efficient synthesis of biodiesel fuel

BDF is biodegradable and renewable energy and expectable as an alternative diesel fuel.¹⁻³⁾ Conventional production method of BDF is catalytic transesterification

of triglyceride (TG) with alcohol to form fatty acid alkyl ester (FAAE).



Reaction rate of transesterification with a base catalyst is higher than that with an acid catalyst. Therefore a base catalyst is usually used in the BDF production process. Meanwhile an acid catalyst has an activity for esterification of free fatty acid (FFA) which contains in waste cooking oil. Enzymatic transesterification of TG is a good alternative to chemical processes but there are two major problems which are high cost of enzyme and its inactivation by alcohol. Non-catalytic transesterification of TG in supercritical alcohol has been proposed. However the key issues to realize the commercial process are high energy consumption and high equipment cost.

The production cost of BDF is much higher than that of petroleum diesel. Approximately 70-80% of the production cost is occupied by the cost of raw material⁴⁾. Price of vegetable oils became high due to increase in the amount of BDF production in EU and USA. Accordingly the raw material for BDF production was shifted from vegetable oil to raw quality oils such as waste cooking oil, animal fat and inedible oil. There are many small scale plants for BDF production from waste cooking oil in Japan at present. The development of the advanced large scale BDF production process would be desired.

The reaction rate is limited by the mass transfer of TG to oil and methanol phase^{1,2)}. Our results of the BDF production in segmented reaction system in a microtube or in the homogeneous reaction system for reducing the mass transfer resistance are reported.

2-1. BDF production in microtube reactor³⁻⁵⁾

Transesterification of oils to biodiesel was carried out in a microtube reactor with a T-type mixer. To obtain clear images of the flow patterns in the microtube, a methanol solution was dyed with inert red pigment. Details of the flow patterns along the microtube were observed and characterized using an optical microscope equipped with a digital camera as the reaction progressed.

As shown in Fig. 1, transesterification in batch reactor and microtube reactor was completed within 600 and 240 s, respectively. The enhancement of the apparent reaction rate in the microtube reactor was caused by the increase in mass transfer rate, which can be enhanced through segmentation by providing a large specific interfacial area and phase internal flow. As shown in Fig.2, when the size of microtube was decreased, the flow rate in the microtube became high and therefore the oil conversion was increased due to small molecular diffusion distance. Sunflower oil was completely converted to BDF even if the residence time was as short as 112 s at a reaction temperature of 60°C for a microtube reactor (1 mm i.d. and 160 mm in length).

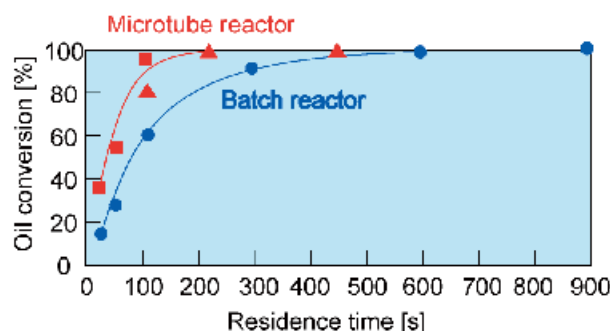


Fig. 1 BDF synthesis in microtube reactor.

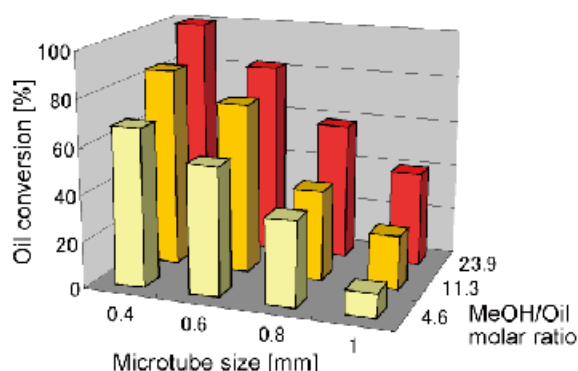


Fig. 2 Effects of tube size and molar ratio of methanol to oil on oil conversion in microtube reactor.

The flow pattern at the entrance region of the microtube was segmented flow of the methanol and oil phases. As the reaction progressed, fine droplets composed of the produced glycerol and methanol was dispersed and circulated in the oil segments. At a methanol/oil molar ratio of 23.9 at 60°C, a quasi-homogeneous phase formed approximately 300 mm from the reaction inlet where the oil was completely converted to FAME. Meanwhile, Fine droplets were unobservable when using waste cooking oil.

2-2. Homogeneous BDF production by using dimethyl ether^{4,6-8)}

Since the oil and alcohol phases in a transesterification system are immiscible, the mass transfer between the two phases becomes a significantly factor that affects the reaction rate. In this study, dimethyl ether (DME) was used as a co-solvent for homogenization of a methanol-oil system under slightly pressurized conditions and would separate easily after depressure. DME has little toxicological effect on health and the environment, and it exists as a gas in ambient conditions.

When DME was used as a co-solvent in a pressurized batch reactor, the oil conversion reached 100% at KOH concentration of 1 wt% within 60 s at room temperature. When a diethyl ether as a co-solvent was introduced into a microtube reactor, the flow pattern at the entrance

region of the microtube was homogeneous. The reaction was enhanced due to the disappearance of mass transfer resistance that existed in the heterogeneous phase. However, as the reaction proceeded, glycerol was formed and separated from the homogeneous phase, and fine drops of glycerol were observed in the microtube. A portion of glycerol fine drops gradually aggregated to form larger drops, and finally, long segments were formed in the microtube.

2-3. BDF production by electrolysis method⁹⁾

Electrolysis method to produce BDF without using base catalyst has been developed. THF was added into the reaction mixture of methanol and corn oil for homogenization. In order to permit conduction between two Pt electrodes, a small amount of sodium chloride and water was mixed in the solution. As shown in Fig.3, the evolution of chlorine or oxygen might occur on the anode. On the other hand, hydroxyl ions and hydrogen were formed on the cathode. The transesterification of TG with methanol requires an active species, i.e., methoxide ion, in order to obtain reasonable FAME yield. Methoxide ion can form when methanol reacts with a hydroxyl ion, and once formed, the methoxide ion attacks TG to produce FAME.

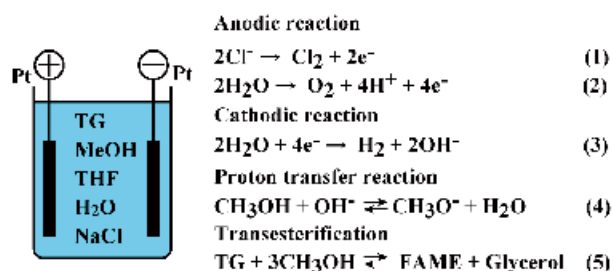


Fig. 3 Elemental reaction in BDF synthesis by electrolysis method.

To clear the role of the basicity in the solution and the electrolysis, FAME yields were determined after the interruption of the electrolysis. As shown in Fig.4, when the electrolysis was stopped at 10 min. in the case of 0.1 wt% H_2O , FAME yield reached 96.8% for 1h, which was identical to that in the case of continuous electrolysis. However, when the electrolysis was stopped at 5 min, the FAME yield at the reaction time of 1 h was almost the same, but the reaction rate became low compared to that in the case of continuous electrolysis because of low basicity in the solution. These results indicate that the transesterification rate was significantly affected by basicity in the solution produced by the electrolysis when the amount of water in the reaction mixture was small. Although the evolution of harmful Cl_2 predicted by the electrolysis was confirmed, no Cl_2 gas was detected for all the cases.

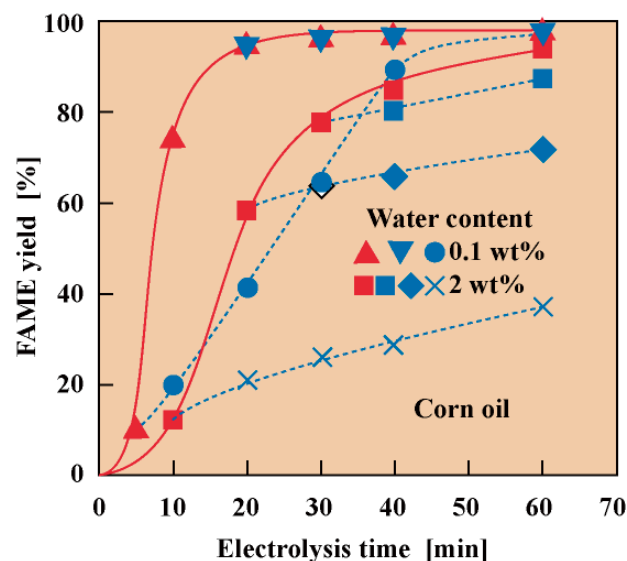


Fig. 4 FAME yield after electrolysis. Real line: continuous electrolysis, dotted line: catalytic reaction after electrolysis, cell voltage = 18 V, molar ratio of methanol to oil = 24, molar ratio of THF to methanol = 0.25.

3. Conclusions

Research on catalytic BDF synthesis has been carried out eagerly in EU (especially Germany), China and Southeast Asia. A lot of attention was focused to the research on second generation biodiesel. Meanwhile, research on the high efficiency catalytic production of BDF would be also important for commercialization.

References

- 1) G. Gual et al., Kagakusouchi, 29 (2008). (Japanese)
- 2) G. Guan et al., Kankyoujyokagijutsu, 8(7), 29 (2009).
- 3) G. Guan et al., Chem. Eng. Trans., 14, 237 (2008).
- 4) G. Guan et al., Chem. Eng. J., 146, 302 (2009).
- 5) G. Guan et al., Ind. Eng. Chem. Res., 48, 1357 (2009).
- 6) G. Guan et al., Chem. Lett., 36, 1408 (2007).
- 7) G. Guan et al., Fuel, 88, 81 (2009).
- 8) G. Guan et al., Fuel Proc. Technol., 90, 520 (2009).
- 9) G. Guan et al., Chem. Eng. J., 153, 159 (2009).

Biodiesel Production from Sunflower Using CaO Catalyst under Reflux Conditions

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Transesterification of sunflower oil (SFO) with methanol was performed using CaO catalyst at 80-120°C under reflux conditions. The effects of the reaction temperature, the catalyst concentration and the molar ratio of methanol to oil on fatty acid methyl ester (FAME) yields were investigated. The CaO catalyst showed good catalytic activity under reflux conditions. In addition, the fuel properties of the BDF produced at 120°C with 5 wt% CaO catalyst satisfied the values required in the EU standard for biodiesel fuel (EN-14214).

Introduction

BDF is catalytically synthesized through the transesterification of triglyceride in vegetable oils and animal fats with excessive methanol, and is used as an alternative petroleum diesel fuel because of its similar combustion properties¹⁻³. BDF is environmentally attractive because a reduction in emissions of greenhouse gases, SO_x and aromatics can be achieved when it is used in place of petroleum diesel fuel.

BDF is produced using a homogeneous catalyst such as KOH, NaOH, HCl and H₂SO₄ under the mild conditions⁴⁻⁷. Homogeneous catalysts caused problems such as equipment corrosion and the need for wastewater treatment after removing the dissolved catalyst from BDF with a large amount of water⁴. However, heterogeneous solid catalysts can solve these problems due to the easy separation of the catalyst from the FAME and to the reusable properties of the catalyst^{4, 8, 9, 10}.

In this study, transesterification of SFO with methanol using CaO catalyst in a reactor with a condenser was investigated at a temperature higher than the boiling point of methanol. The fuel properties and quality of the produced BDF were examined.

BDF Production Process

Transesterification of oil with methanol was performed in a 100 mL flask equipped with a magnetic stirrer, a thermometer and a reflux condenser. The methanol/oil molar ratio was changed within the range of 6:1 to 18:1. The weight concentration of CaO catalyst based on the oil was varied from 1-10 wt%. The flask was immersed in an oil bath. The reaction temperature was varied from 60-120 °C. The reaction product was centrifuged at 6000 rpm for 20 min. The upper ester layer was rinsed with deionized water and the mixture was centrifuged again. These procedures were repeated several times until the pH value in the aqueous phase reached 7.0. Then 0.1 ml of the rinsed sample was diluted by 3 ml of hexane for analysis. The concentration of unreacted oil that remained in the BDF was analyzed using a high performance liquid chromatograph (HPLC, Tosoh Corp., Japan) equipped with a silica-gel column (Shimpack CLC-SIL, Shimadzu Corp., Japan) and a refractive index detector. The standard

tests (JIS K 2390) of fuel properties of the BDF including flash point, pour point, metal content, iodine value, and impurity concentrations, were carried out by Shimadzu Techno-Research Inc.

BDF production from SFO

The effect of molar ratio of methanol to oil on FAME yield for transesterification of SFO is shown in Fig. 1. The molar ratio in the mixture of oil and methanol loaded in the flask before heating was adopted in Fig. 1. FAME yield increased as the molar ratio of methanol to oil increased and reached a maximum value. A decrease in FAME yields at higher levels of methanol content was caused by the dilution effect of catalyst and reactants⁸. A molar ratio of methanol to oil higher than the stoichiometric ratio has generally been adopted for BDF production, to obtain a high FAME yield. The optimum molar ratio of methanol to oil for the transesterification of SFO with KOH catalyst at 25 °C was in the range of 6:1 to 8:1¹¹). In the case of CaO catalyst, Kouze *et al.*¹² adopted a 12:1 molar ratio of methanol to oil for the transesterification of soybean oil and waste cooking oil with refluxed methanol. Liu *et al.*¹³ reported that the optimum molar ratio for the transesterification of soybean oil at 65 °C was 12:1. As

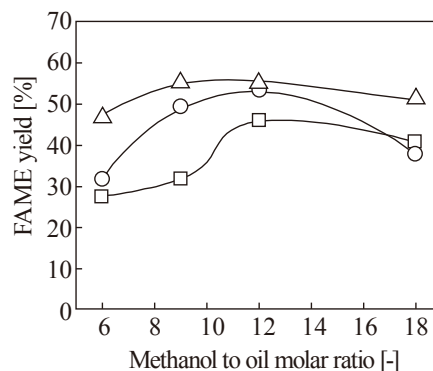


Fig. 1. Effect of the molar ratio of methanol to oil on the FAME yield for transesterification of SFO: Reaction temperature, □, 80 °C; ○, 100 °C; △, 120 °C; 5 wt% CaO catalyst; Reaction time = 30 min.

shown in Fig. 1, the optimum molar ratio at the reaction temperatures of 80 and 100 °C was 12:1, and shifted to 9:1 at 120 °C.

The effects of reaction time and temperature on the FAME yield for transesterification of SFO are shown in Fig. 2. As the reaction time progressed, the FAME yield showed S-shape curves, which, according to Kouzu *et al.*¹²⁾ could be explained that by a variation of the reaction order as transesterification progressed. Transesterification obviously occurred at the boundary between oil and methanol in the early stage, where the reaction rate might be zeroth-order kinetics with respect to oil concentration. The reaction rate was then changed from the zeroth to first order kinetics, due to good miscibility in the reaction mixture. Guan *et al.*⁷⁾ observed the flow behavior in a microtube reactor during the transesterification of SFO and reported that a quasi-homogeneous flow of dispersed fine droplets of glycerol and methanol in the continuous FAME/oil phase was formed above the oil conversion of 70%. As shown in Fig. 3, FAME yields reached more than 92% after 90 min of reaction time.

Fig. 3 shows the effect of reaction temperature on FAME yield for the transesterification of SFO.

Transesterification of oil with methanol in the presence of heterogeneous catalysts is a three-phase reaction system. Accordingly, the reaction rate might be reduced due to mass transfer resistance on the boundary between the oil and methanol phases. FAME yield increased as reaction temperature increased, due to the enhancement of miscibility at high temperatures. Liu *et al.*⁸⁾ indicated that methanol was vaporized at high temperature and formed a large number of bubbles which inhibited the reaction on the three phase interface. However, the evolution of bubbles enhanced the turbulence in the reactor and reduced mass transfer resistance in this study.

Fig. 4 reveals that the FAME yield increased as the concentration of CaO catalyst increased, due to the increase in the total number of available catalytic active sites for the reaction^{13, 14)}. The FAME yield was also affected by mass transfer between the reactant and

catalyst^{8, 13, 14)}. Accordingly, high catalyst concentration caused the reactant mixture to be more viscous, which caused a decrease in the reaction rate due to mass transfer resistance^{15, 16)}.

Fuel properties of the produced BDF

BDF samples for the analysis of fuel properties were produced from the transesterification of SFO with 5 wt% CaO at 60 and 120 °C for 2hr and washed with water several times. The BDF properties obtained using CaO catalyst were compared with that obtained those using 3 wt% KOH catalyst. Table 1 summarizes the fuel properties of the produced BDF.

The pour point is the lowest temperature at which frozen oil can flow, and is often used to specify the cold temperature usability of fuel oil^{17, 18)}. The pour points evaluated by JIS K2269 were -7.5 and -2.5 °C for BDF samples produced with CaO catalyst at 60 and 120 °C, respectively. The flash point is the lowest temperature at which liquid oil can form an ignitable mixture in air. All the flash points evaluated by JIS K2265 were higher than the values described as the minimum requirements for BDF in the European standard (EN-14214).

The amounts of alkali metal and alkali earth metal were evaluated using the EN14108 and EN14538 standards, respectively. The amount of alkali earth metal in unwashed BDF was as much as 1.3 wt%, perhaps Ca compounds such as calcium methoxide and calcium diglyceroxide were partially dissolved in the FAME at high temperatures. After washing the FAME phase with water, the amount of alkali earth metal in the FAME produced with CaO catalyst at 120°C was lower than the minimum value (5 ppm) stipulated by the EN-14214 standard.

The results of iodine values evaluated by JIS K0070 were close to the maximum value (120 gI/100g) stipulated by the EN-14214 standard. The iodine value is related to the number of double bonds of fatty acids, and mainly depends on the origin of the vegetable oil.

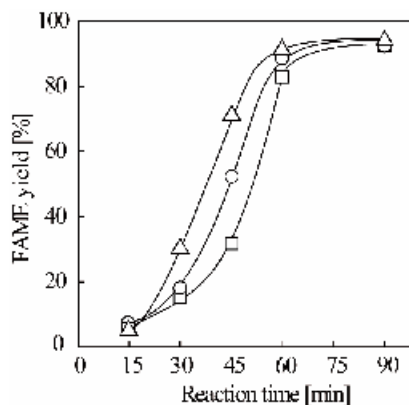


Fig. 2. Effects of reaction time on FAME yield for transesterification of SFO: □, 80 °C; ○, 100 °C; △, 120 °C; 3 wt% CaO; Molar ratio of methanol to oil = 6:1.

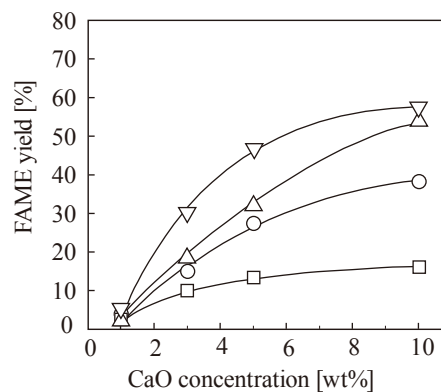


Fig. 3. Effects of reaction temperature on FAME yield: □, 3 wt% CaO; ○, 5 wt% CaO; ▽, 10 wt% CaO; Molar ratio of methanol to oil = 6:1; Reaction time = 30 min.

Monoglyceride, diglyceride, and glycerol were formed during the transesterification of triglyceride, and these compounds should be removed from BDF. The total glycerin results, which include the amounts of mono-, di- and triglyceride and glycerol, were lower than the minimum requirements for BDF in the European standard (EN-14214). In particular, the amounts of intermediates (mono- and triglyceride) of BDF obtained using CaO catalyst were lower than those obtained using KOH catalyst. Thus, the quality of BDF produced using CaO catalyst at 120 °C was acceptable, judging from the quality required in the European standard (EN-14214).

In summary, high temperature BDF production using CaO catalyst under reflux conditions was proposed. The FAME yield for transesterification of SFO indicated a maximum value in the molar ratio range from 6:1 to 18:1. The FAME yield of SFO reached more than 92 % at a molar ratio of 6:1 and a reaction temperature of 80 °C for 120 min with 3 wt% CaO catalyst. Thus, CaO catalyst showed good catalytic activity under reflux conditions. In addition, the fuel properties of the BDF produced at 120 °C with 5 wt% CaO catalyst satisfied the values

required in the EU standard for biodiesel fuel (EN-14214). The results obtained in this study are suitable for commercialization.

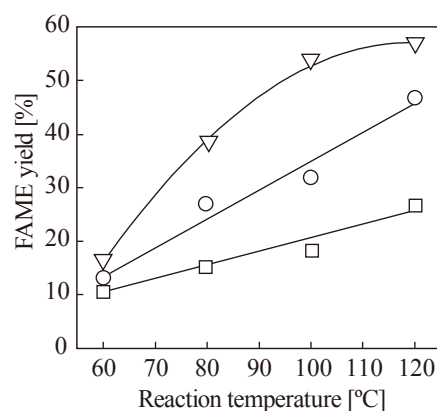


Fig. 4. Effects of catalyst concentration on FAME yield: Reaction temperature □, 60 °C; ○, 80 °C; △, 100 °C; ▽, 120 °C; Molar ratio of methanol to oil = 6:1; Reaction time = 30 min.

Table 1. Fuel specifications of BDF from sunflower oil

BDF sample	Catalyst	3wt% KOH	5wt% CaO	5wt% CaO	EU guide line
	Reaction temp.	60°C	60°C	120°C	
Pour point (°C)		-7.5	-7.5	-2.5	-
Flash point (°C)		188.5	178.5	182.5	≥120
Alkali metal Na (ppm)		<2	-	-	≤5
Alkali metal K (ppm)		<2	-	-	≤5
Alkali earth metal Ca (ppm)		-	<14 (4600) ^a	<2 (13000) ^a	≤5
Alkali earth metal Mg (ppm)		-	<2 (<2) ^a	<2 (<2) ^a	≤5
Iodine value (gI/100g)		119	123	123	≤120
Monoglyceride (wt%)		0.53	0.12	0.26	≤0.80
Diglyceride (wt%)		0.07	0.04	0.04	≤0.20
Triglyceride (wt%)		<0.05	<0.05	<0.05	≤0.20
Free glycerin (wt%)		<0.005	<0.005	<0.005	≤0.20
Total glycerin (wt%)		0.15	0.04	0.07	≤0.25

a : unwashed BDF

Reference

- 1) M.S. Graboske, R.I. McDormick, , *Prog. Energy Combust. Sci.* **24**, 125 (1998).
- 2) U. Schuchardt, R. Sercheli, R.M. Vargas, J. Braz. *Chem. Soc.* **9**, 199 (1998).
- 3) F. Ma, M.A. Hanna, *Bioresour. Technol.*, **70**, 1(1999).
- 4) G. Vicente, M. Martinez, J. Aracil, *Bioresour. Technol.*, **92**, 297 (2004).
- 5) L.C. Meher, D.V. Sagar, S.N. Naik, *Renew. Sustain. Energy Rev.*, **10**, 248 (2006).
- 6) G. Guan, N. Sakurai, K. Kusakabe, *Chem. Eng. J.*, **146**, 302 (2009).
- 7) G. Guan, K. Kusakabe, K. Moriyama, N. Sakurai, *Ind. Eng. Chem. Res.*, **48**, 357 (2009).
- 8) X. Liu, H. He, Y. Wang, S. Zhu, X. Piao, *Fuel*, **87**, 216 (2008).
- 9) H.K. Kim, B.S. Kang, M.J. Kim, Y.M. Park, D.K. Kim, *Catal. Today*, **93**, 315 (2004).
- 10) M.P. Dorado, E. Ballesteros, F.J. Lopez, M. Mittelbach, *Energy Fuels*, **18**, 77 (2004).
- 11) H. Fukuda, A. Kondo, H. Noda, *J. Biosci. Bioeng.*, **92**, 405 (2001).
- 12) M. Kouzu, T. Kasuno, M. Tajika, Y. Sugimoto, S. Yamanaka, J. Hidaka, *Fuel*, **87**, 2789 (2008).
- 13) X. Liu, X. Piao, Y. Wang, S. Zhu, H. He, *Fuel*, **87**, 1076 (2008).
- 14) X. Liu, X. Piao, Y. Wang, S. Zhu, *Energy Fuels*, **22**, 1313 (2008).
- 15) S. Yan, H. Lu, B. Liang, *Energy Fuels*, **22**, 646 (2008).
- 16) W. Xie Z. Yang, *Catal. Lett.*, **117**, 159 (2007).
- 17) J. van Gerpen, B. Shanks, R. Pruszko, D. Clements, G. Knothe (Eds). *National Renewable Energy Laboratory, Colorado*, 37 (2004).
- 18) J.M. Encinar, J.F. Gonzalez, A. Rodriguez-Reinares, *Fuel Process. Technol.*, **88**, 513 (2007).

Research Report

Pulverized Coal Pyrolysis & Gasification in $N_2/O_2/CO_2$ Mixtures by Thermo-gravimetric Analysis

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The combustion characteristics of Datong coal in the different $N_2/O_2/CO_2$ environments have been extensively studied by using thermo-gravimetric technique. The effects of combustion environment, oxygen and CO_2 concentrations and different heating rates were considered. Moreover, different models have also been applied and the values of Arrhenius activation energy (E) and pre-exponential factor (A) have also been estimated from the TGA data obtained at different heating rates.

Introduction

Concerns over the role of greenhouse gases in forcing global warming have led to international agreements that have set targets for controlling carbon dioxide emissions. Achieving these goals will require emissions trading, increasing energy efficiency, fuel substitution, and changes in combustion practice. Coal is an abundant, low cost fuel but with a high ratio of carbon to hydrogen, making control of CO_2 , a major concern for the future use of coal. As stationary sources emitting large amounts of CO_2 , pulverized coal fired power stations could be the best candidates to install CO_2 capture system. In lieu of our growing energy demands, carbon sequestration provides an alternative to sharply reducing coal use. Carbon sequestration can be defined as the capture and secured storage of the carbon that is emitted as a result of human activities as well as the carbon that is already present in the atmosphere. However, it is necessary that the concentration of CO_2 in the gas or liquid stream be more than 90% before it can be injected into the oceans or deep underground geological formations.

The carbon- CO_2 reaction is of great importance in coal gasifiers and in numerous industrial operations hence this gasification process has been examined extensively by many investigators¹⁻⁹. Turkdogan and Vinters¹⁰ reported the effect of CO_2 concentration on the carbon- CO_2 reaction rate. The reaction rate of the C- CO_2 reaction with respect to CO_2 concentration is approximately first order at low pressures (pressures much below atmospheric) but approaches zeroth order at high pressures (pressures above 15 atm)¹¹. The carbon- O_2 is also important in overall gasification scheme because the reaction is rapid even with chars, exothermic and not limited by equilibrium. Thus some char is reacted with O_2 to produce the heat and temperature required to drive the carbon reaction¹². Moreover, prior to or concurrent with the other reactions in a gasifier, pyrolysis of coal takes place. As the behavior of pyrolysis is not yet properly established but however, it is known that the rate of pyrolysis and the amount and composition of volatile products from a given sample of coal or char depends upon several factors such as heating rate, final decomposition temperature attained, vapor residence time, the environment under which the

pyrolysis takes place, pressure coal particle size and coal type^{13, 14}. The char- CO_2 reaction, after the pyrolysis reaction is completed, takes place on the char surface and is essentially a carbon- CO_2 reaction. As the later starting only after the former stage is essentially completed and as the pyrolysis process is completed at high temperature so it is better to gasify the coal at oxy-fuel combustion conditions by which the internal surface area increases markedly¹⁵.

Oxy-fuel combustion technology could be successfully used to retrofit existing coal fired power plants or alternatively be used to design and build new coal fired power plants with almost zero emissions¹⁶. In a recent review, oxy-fuel combustion technology for coal fired power generation has been described in detail and demonstrated to be a cost effective method of CO_2 capture¹⁷. However differences in thermal properties of N_2 and CO_2 make oxy-fuel combustion quite different from conventional air combustion. Buhre¹⁷ also reported that the presence of CO_2 in high concentrations during oxy-fuel combustion affects the heat transfer, flame ignition, coal burn out, emissions, and ash properties. Comparison of the reactivity of coal/char in air and oxy-fuel combustion environments under various O_2/N_2 and O_2/CO_2 conditions have been studied and number of factors have been identified to cause the difference^{18, 19}. This difference in reactivity are due to the differences in properties of bulk gases, the lower rate of diffusion of oxygen through CO_2 and the higher specific heat capacity of the CO_2 and may be the coal type (rank) also play a significant role in the reactivity and hence burnout²⁰.

The aim of the present study is to see the effects of different combustion environments of bulk gases, oxygen and CO_2 concentrations, pyrolysis conditions and different heating rates on coal gasification reaction. Most importantly the simultaneous processes of pyrolysis and gasification reactions have been studied on coal. Different models have been applied and from them different activation energies values have been calculated at different heating rates for different weight fractions of the coal.

2. Experimental

2.1 Material and its characterization

A coal imported from China, Datong coal, was selected for the thermo-gravimetric analysis experiments. The raw coal was first crushed and pulverized firstly using the mortar & pestle in the laboratory and then sieved using screen vibrator. The proximate and ultimate analyses of coal sample are summarized in Table 1.

Table 2 shows the physical properties of the resulting coal.

Table 1: The proximate and ultimate analyses of Datong coal sample

Coal Analysis			
Proximate analysis (dry %)		Ultimate analysis (dry %)	
Moisture	3.89	C	73.92
VM	27.28	H	3.82
F C	61.54	O	10.24
Ash	11.18	N	0.27
		Total S	0.61
		Comb. S	0.57
		Uncomb. S	0.04
		Cl	90 (mg/kg)
		F	150(mg/kg)
		Na	470 (mg/kg)
		K	1600 (mg/kg)
		Hg	0.07 (mg/kg)
		Se	0.0001
		Cd	1 (mg/kg)
		As	0.0002
		B	0.0011

Table 2: The physical properties of the Datong coal sample

Property	Datong Coal
BET surface area (m ² /g)	5
Pore volume (cm ³ /g)	0.016
Average pore diameter (nm)	13.2
Particle size (μm)	100 – 300
Specific density (-)	1.47
Heat capacity (J/Kg K)	1170
Melting point (°C)	1490
Softening point (°C)	1290
Calorific value (kJ/Kg)	28.780

2.2 TGA measurement and analysis

Pyrolysis and CO₂ gasification experiments were carried out in a TGA apparatus connected with the computer having thermo plus 2 software for analyzing the coal sample. The procedure can be summarized as follows: about 10 mg of the sample having a particle size range of 100 – 300 μm in diameter was placed in a quartz pan. The sample was packed loosely and placed the pan over the TG holder of which one end was suspended and another was attached to the microbalance. The temperature of the sample was measured by a thermocouple placed at the beneath of the holder. The coal sample was heated at a heating rate of 10 K/min from room temperature to 1273 K in the mixture of O₂/N₂ or O₂/CO₂ with various oxygen concentrations from 2% to 100% for combustion tests and different pyrolysis tests using N₂ or CO₂. Pyrolysis and gasification processes were also taken place simultaneously. Initially, the system was purged with high purity nitrogen at heating rate of 10 K/min and then the flow of N₂ was switched to different mixtures of O₂/CO₂ at the same heating rate of 10 K/min. In order to verify the influence of heating rate, the non-isothermal tests runs proceeded at different heating rates of 10, 15, 20 and 50 K/min. For all the experiments, the gas flow rate was kept at 50 cc/min. The weight change of the sample, time and temperature were recorded simultaneously for all the experiments.

3. Results and Discussion

3.1 Coal combustion in different environments

This Fig. 1 shows the comparison of coal pyrolysis experiments in different gas environments with the variation of gas temperatures by thermo gravimetric analysis technique. In case of pure streams of CO₂ and N₂ environments, the mass loss rate of coal pyrolysis in the presence of N₂ was lower than that in pure CO₂ environment at both high and low temperature regions but

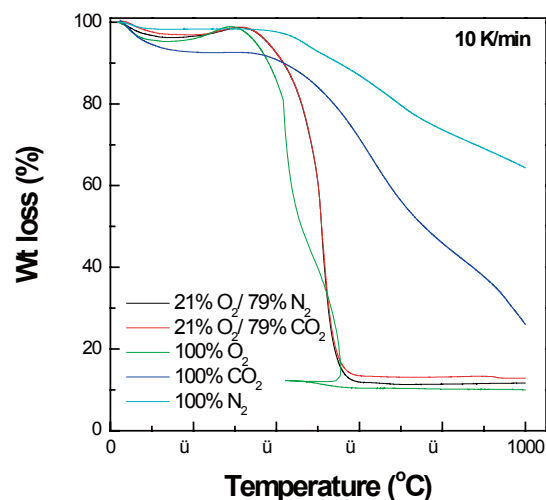


Fig. 1. TG curves of Datong coal combustion in environment of bulk gases at heating rate of 10 K/min.

Table 3. Data of ignition points of Datong coal in different environments

Comp.	100% O ₂	20% CO ₂ /80% O ₂	50% CO ₂ / 50% O ₂	70% CO ₂ /30% O ₂	79% CO ₂ /21% O ₂	79% N ₂ / 21% O ₂
IT (°C)	417	421	434	472	479	488

this difference is marginal at high temperature. This may be understood by the stages of coal pyrolysis process. In case of 100% N₂ environment, the coal pyrolysis process has two stages: release of moisture content and devolatilization but the process of coal pyrolysis in high 100% CO₂ environment can be divided into three stages: moisture release, devolatilization and char gasification by CO₂ in high temperature zone¹⁸. Also, this difference may be explained due to the density difference and transport properties of these gases which are quite different (the mass of the CO₂ molecule is different from that of N₂). Moreover, the formation of char particles is larger and its surface area is also higher than that of the N₂ char particles as observed by Rathnam¹⁹) hence the weight loss observed in CO₂ environment is higher than the N₂. In case of high concentration of O₂ all the coal was fully combusted immediately and sharply lost its weight and reached to the ignition point immediately which is around 417 °C as shown in Table 3 and also indicated as a horizontal peak in the Fig. 1.

Different mixtures of these gases were also investigated as shown in Fig. 1 and it can be clearly seen that the difference among them is very meager i.e. almost same except at high temperature zone where there some difference is found.

It is seen in Fig. 1 that at high temperature region the weight loss in O₂/CO₂ environment is little bit less than O₂/N₂ environment that may be due to the thermo-physical difference of combustion mixtures and due to the lower rate of diffusion of oxygen through CO₂¹⁹) but this difference is so small that can be ignored. This meager difference can be explained by this way that, the presence of the same concentration of O₂ in the gas mixture dominates the combustion process over the pyrolysis process and hence the individual effect of CO₂ and N₂ gases in the mixtures becomes insignificant and as a result TGA profiles show the same curves. On the other hands, Li¹⁸) claimed that, in O₂/CO₂ mixture, the loss rate of coal sample is little smaller than that in O₂/N₂ condition and the burning time is little bit longer hence the replacing of N₂ only by CO₂ is unfavorable to the burning and burn-off of the coal char. But this paper deals with the reaction of coal with CO₂ in order to overcome the environment issues as the increase of CO₂ concentration causes a global warming. However, this combustion performance in the presence of CO₂ can be improved by increasing oxygen concentration in the gas mixture as described in the next section.

3.2 Effect of different O₂/ CO₂ mixtures

During non-isothermal heating process, the normalized TG curves in different combustion environments are

shown in Fig. 2. It can be seen that the rate of mass loss increases with the increase of oxygen concentration in O₂/CO₂ mixture. When the concentration of oxygen is so high then the TG profiles decreased sharply and reached to the ignition point immediately. The details of ignition points with the use of different oxygen compositions are shown in Table 3.

As mentioned in above section that the coal reactivity in O₂/CO₂ environment is little smaller than that in O₂/N₂ environment at the same oxygen concentration, but coal reactivity increases with the increase of oxygen concentration and that is found to be proportional to the O₂ concentration in O₂/CO₂ environment¹⁸). In fact, under oxygen enriched char combustion conditions, CO oxidation in the boundary layers of char particles and the gasification of the char by CO₂ becomes significant and that pulverized coal char particles burn under increasing kinetic control in elevated oxygen environments, despite the higher burning rates²¹). It is also seen in the combustion profiles that each profile shows a peak which appears at about 350 °C i.e. before ignition temperature for all the TGA profiles. In fact, TGA profiles must show the decreasing trend of loss of volatile matters but instead of decreasing, it indicating the increase of coal mass. This increase in coal mass may be due to the reaction of oxygen with the functional groups present in the coal sample. In order to support this point, it is clearly seen from the Fig. 1 that when there is no oxygen in the gas stream then there is no peak which can cause the increase of mass. So it can be claimed that this increase in mass is due to the reaction of oxygen with the functional group present in

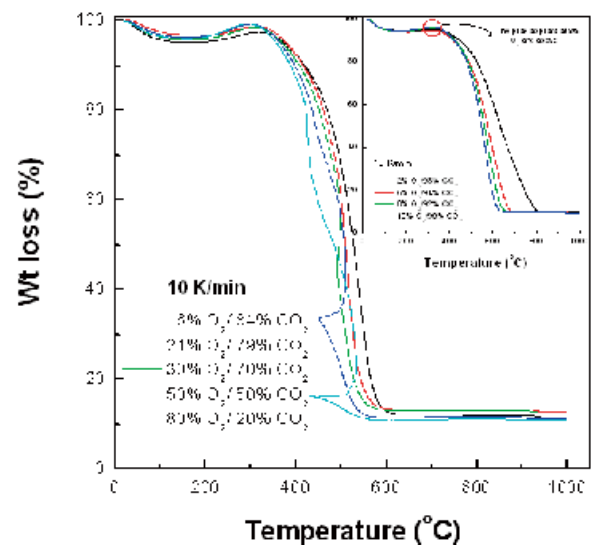


Fig. 2. TG curves of Datong coal combustion in a mixture of different gases at heating rate of 10 K/min.

the coal sample. This Fig. 2 also contains one small Fig which is required to find out the optimum value of O_2 i.e. how much oxygen is stoichiometrically needed to react with the present functional groups in the coal sample. It is clearly indicated in the small Fig. that with the use of 2% & 6% O_2 , there is absolutely no peak appears but with the increase of oxygen concentration from 6 to 8% O_2 , then the peak starts to appear so this shows that 8% O_2 appears to be optimum value. However, the use of lesser amount of O_2 shifted the TGA curves to the higher temperature zone and as a result the burning rate of coal is decreased and the burnout time is also delayed.

3.3 Effect of different pyrolysis temperatures

The figures 3, 4 and 5 show the influence of different pyrolysis temperatures on coal sample in both isothermal and non-isothermal conditions. The Fig. 3 showed different TGA profiles with the effect of different pyrolysis temperatures on coal sample. In this experiment, the coal was first pyrolysed at different temperatures started from 300 to 825 °C and then gasified with 21% O_2 / 79% CO_2 gas mixture. The mass loss rate profiles after 500 to 825 °C when gasified dropped down sharply as they were already reached at or beyond the ignition points as mentioned in the Table 3. But in case of 300 and 400 °C, when gasified, the mass rate loss decreased slightly up to the ignition temperature and then dropped down sharply to complete the combustion reaction. As the ignition point lies between 400 and 500 °C, so as a result, the prior use of gasify medium is useless. So there is need to perform pyrolysis from room temperature to 400 or 500 °C, either at isothermal or non-isothermal conditions.

Fig. 4 (a,b) showed the pyrolysis process at 400 and 500 °C at non-isothermal condition with heating rate of 10 K/min with different compositions of oxygen and carbon dioxide. It can be seen from Fig. 4(a) that TGA curves slightly moved ahead up to the ignition point and completed the gasification reaction smoothly except at

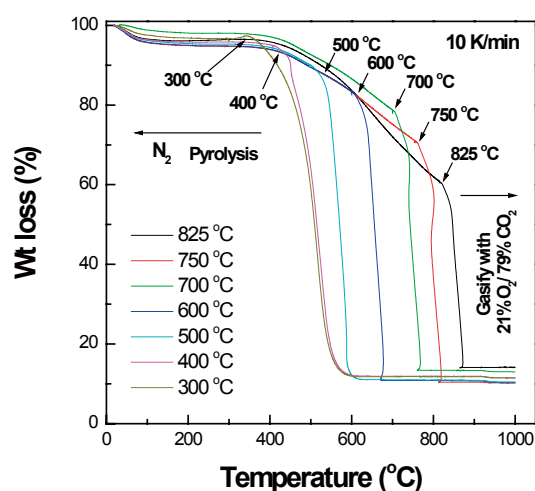


Fig. 3: Influence of different pyrolysis temperatures on coal in non-isothermal conditions at heating rate of 10 K/min.

the high composition of oxygen and carbon dioxide (i.e. 50%).

At high ratio of O_2/CO_2 , the TGA curve first moved ahead slightly as rest of the TGA curves but at a sudden lost its weight and immediately reached to its ignition point due to the excess amount of oxygen and then smoothly decreased and completed the gasification reaction. On the other hand, in Fig. 4(b), it can be seen that all the TGA curves were dropped immediately as these were already beyond the ignition point but at high concentration of oxygen 30% and 50% the curves were moved back and reached up to their respective ignition points and finally completed the gasification reaction. On comparing with Fig. 4(a) and Fig. 4(b), it can be claimed that weight loss in both the figures is almost same or may be weight loss is very slightly less in former Fig than the later one but at relatively low temperature. This claim can be explained

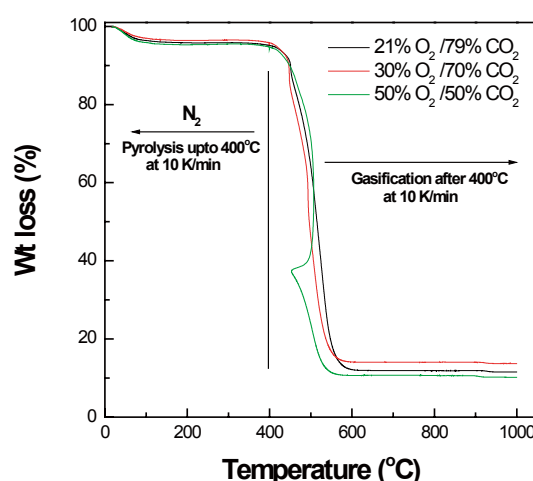


Fig. 4(a): Effect of different pyrolysis temperatures on coal in non-isothermal conditions at a heating rate of 10 K/min.

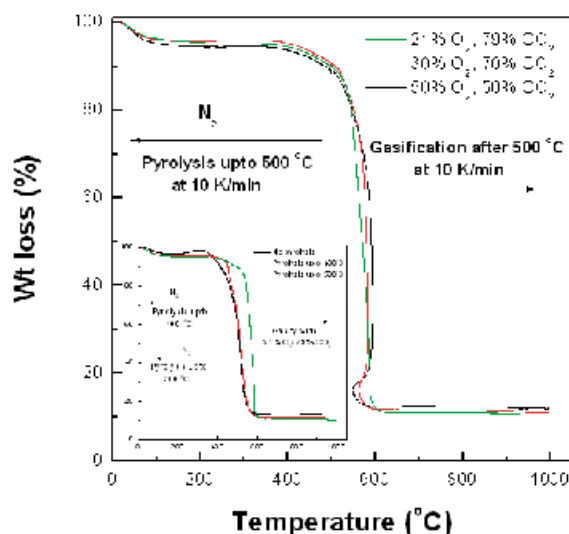


Fig. 4(b): Effect of different pyrolysis temperatures on coal in non-isothermal conditions at heating rate of 10 K/min.

from Fig. 4(c) which is located within the Fig. 4(b). Fig. 4(c) showed the comparison of coal sample with the char sample at different pyrolysis temperatures. The weight loss of coal sample under non pyrolysed condition and the sample pyrolysed at 400 °C were almost same but comparatively at less temperature than the coal sample pyrolysed at 500 °C. There are number of advantages of this prior process of pyrolysis than to the gasification process:

- 1) Simultaneous production of fresh char in one continuous process by removing the moisture content and volatile matters
- 2) Avoiding the excess use of gasifying medium
- 3) No increase of coal sample mass as there is no reaction between oxygen and the present functional group. However, it doesn't affect significantly on

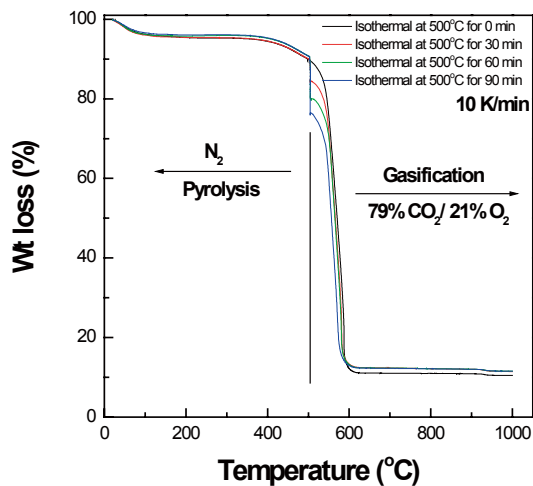


Fig. 5(b): Influence of different pyrolysis temperatures on coal sample at a heating rate of 10 K/min with the variation of different isothermal time.

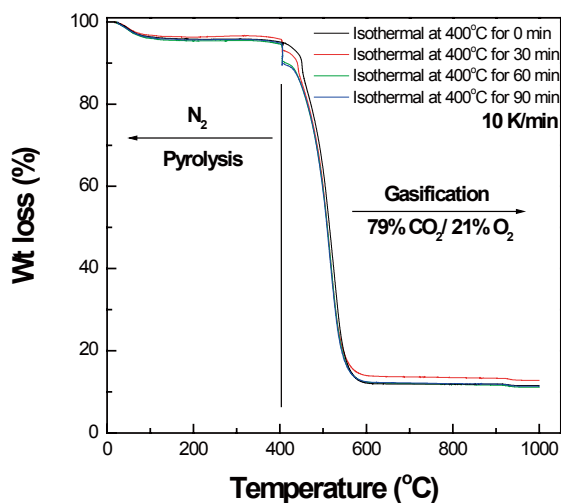


Fig. 5(a): Influence of different pyrolysis temperatures on coal sample at a heating rate of 10 K/min with the variation of different isothermal time.

the combustion reaction mechanism.

Fig. 5 (a,b) shows the influence of pyrolysis process with the extension of heating rate at isothermal condition for particular period of times.

In this coal sample was first pyrolysed up to 400 °C at a heating rate of 10 K/min and then keep the sample at 400 °C for different times from 0 to 90 min and then the coal sample was gasified with the mixture of 79% CO₂/ 21% O₂ at a heating rate of 10 K/min. These experiments were performed just to remove more volatile matters from the coal samples but these experiments having constant heating rate at isothermal conditions were found to be not attractive because of excessive time and may be due to need of multiple experiments. It is seen in Fig. that the weight loss is almost same as that of Fig. 4(a) except the length of experiments performed. So these experiments seem not to be fruitful because of the passage of excessive time.

3.4 Effect of heating rate on combustion characteristic of coal

Coal combustion experiments were also carried out at four different heating rates (10, 15, 20 and 50 K/min) from room temperature to the final temperature i.e. 1000 °C and their combustion profiles were presented in Fig. 6.

It is shown in figure that with the increase of heating rate, TGA curves shift to higher temperature zone. As the heating rate increases from 10 to 20 and finally to 50 K/min, the weight loss rates at respective heating rates were also decreased. In case of 10 to 20 K/min heating rates, the weight loss rates were almost same but on the other hand at 50 K/min the weight loss rate was comparatively less. It may also indicate that the increase in heating rate only shortens the time approaching the final temperature but little influence on its combustion mechanism. On these

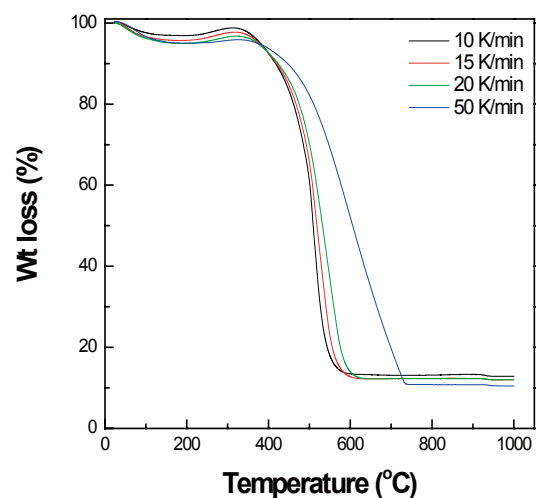


Fig. 6: Effect of heating rates on coal combustion profiles

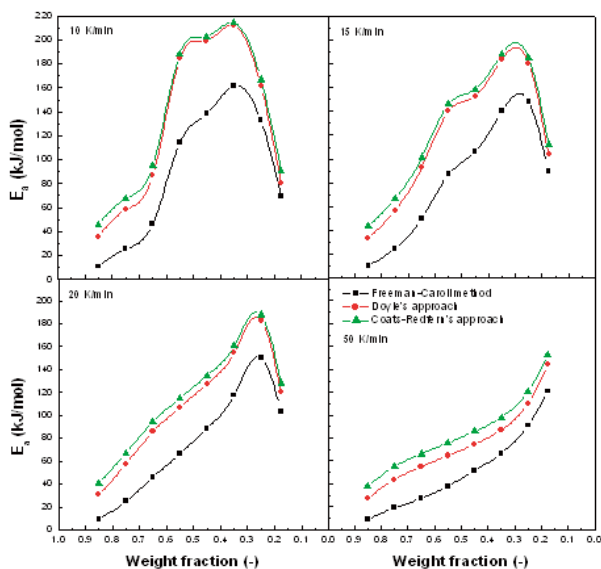


Fig. 7: Activation energy values calculated by different methods with in temperature range of 400 to 600 °C.

heating rates, values of activation energies at different weight fractions were also found by different correlations at non-isothermal analysis condition as shown in Fig. 7.

In case of non-isothermal analysis, the temperature changes at a constant positive rate. Brown²²⁾ developed a rate equation of weight loss in the differential form.

$$\frac{d\alpha}{dT} = \frac{A(1-\alpha)}{\beta} \exp(-E/RT) \quad (a)$$

Integrate this equation using initial conditions $\alpha = 0$, $T = T_0$.

$$\ln(1-\alpha) = -\frac{A}{\beta} \int_{T_0}^T \exp(-E/RT) dT$$

As the ignition point lies after 400 °C hence the limits of the integral are conventionally changed to

$$\int_0^T \exp(-E/RT) dT,$$

hence the function $p(x)$ may be introduced such that:

$$p(x) = \int_x^\infty \frac{e^{-x}}{x^2} dx$$

where $x = E/RT$, hence eq (a) becomes

$$\ln(1-\alpha) = \frac{AE}{\beta R} p(x) \quad (b)$$

where $\alpha = \frac{m_o - m_t}{m_o - m_f}$

m_o is the initial mass of coal, m_t is the mass of coal at a time t and m_f is the final mass of coal after the reaction and β is the heating rate.

The problem with this equation is that this equation is not analytically solvable. The function $p(x)$ however can be expressed by some approximate equation. There are many approximations have been derived but in this paper two simple approaches have been used: Doyle's²³⁾ and Coats-Redfern's²⁴⁾ approximations. These are selected for their simplicity and resulting ease of manipulation of eq (b) into linear forms.

Doyle's approximation of $p(x)$ is derived by observing

a linear relationship between $\ln p(x)$ and x :

$$p(x) = \exp(-5.33-x)$$

Hence eq (b) comes out to be

$$\ln[\ln(1-\alpha)] = \ln\left(\frac{-AE}{\beta R}\right) - 5.33 - 1.052\left(\frac{E}{RT}\right) \quad (A)$$

Hence for a given heating rate, E and A values can be estimated by plotting the $\ln[\ln(1-\alpha)]$ versus $1/T$. In case of Coats-Redfern approach only the first term of an asymptotic expansion of $p(x)$ is retained:

$$p(x) = \frac{e^{-x}}{x^2} \left[1 - \frac{2!}{x} + \frac{3!}{x^2} - \frac{4!}{x^3} + \dots \right] + (-1)^n \frac{(n+1)!}{x^{n+1}} + \dots$$

So $p(x)$ comes out to be $p(x) = \frac{e^{-x}}{x^2}$

Hence the equation may be incorporated into a linear equation as

$$\ln[-\ln(1-\alpha)/T^2] = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \quad (B)$$

The values of A and E may be estimated from the intercept and slope respectively of a plot of $\ln[-\ln(1-\alpha)/T^2]$ versus $1/T$. Further, the E and A values may also be calculated from very well known correlation i.e. Freeman-Carroll method²⁵⁾.

$$\Delta \log \frac{d\alpha}{dt} = n \Delta \log(1-\alpha) - \frac{E}{2.303R} \Delta \left(\frac{1}{T} \right) \quad (C)$$

The plot of $\log \frac{d\alpha}{dt}$ vs $\frac{1}{T}$,

gives the value of E and A from the curve.

It is also seen in Fig. 6 that activation energies appear to decrease with increasing heating rates²⁶⁾. There is a difference of about (40 kJ/mol) in the values of E from using 10 and 50 K/min heating rates. As observed in Fig. 6, at 600 °C, more than 80 % of the material was reacted at a heating rate of 10 K/min whereas around 50% of the original material was reacted at a heating rate of 50 K/min. At different heating rates, different methods such as Freeman-Carroll method, Doyle's and Coats-Redfern's approaches were used for the determination of activation energies. These values were found to be at different weight fractions starting from 90% of the original coal material to the 15% of the retained coal material within the temperature range of about 400 to 600 °C. This range of temperatures and weight fractions have only been selected because the main reaction i.e. gasification lies within these temperature ranges and weight fractions. At each heating rate, the values of E calculated by Coats-Redfern and Doyle's approaches were found to be high and close enough to each other but on the other hand the values of E calculated by Freeman-Carroll method were found to be lower. Moreover, the activation energy profiles obtained by each method showed the same trend i.e. parabolic curve. For these methods, the maximum values of E were found to be between the weight loss fractions of 30 to 40% at 10 K/min but these E values were shifted to lowest weight fractions from 20 to 30% when heating rate of 20 K/min was applied and so on. It is clearly seen from the Fig. 7 that parabolic curves of these values of E were obtained by all the calculation methods. These parabolic curves may be explained by this way that at the

start, the lower activation energy values were due to the combination of fixed carbon and volatile matters present in the coal and then these curves showed maximum peaks which may indicate the presence of high concentration of fixed carbon and almost zero concentration of volatile matter for the gasification reaction and then again the activation energy values go down may be because of the combination of low concentration of fixed carbon and comparatively high quantity of ash contents.

4. Conclusions

Gasification of coal/char in a CO₂ atmosphere can be divided into two stages, the first stage due to pyrolysis (removal of moisture content and devolatilization) which is comparatively at lower temperature and char gasification by different O₂/CO₂ mixtures at high temperature. In N₂ and CO₂ environments from room temperature to 1000 °C, the mass loss rate of coal pyrolysis in N₂ is lower than that of CO₂ may be due to the difference in properties of the bulk gases. The gasification process of pulverized coal in O₂/CO₂ environment is almost same as compared with that in O₂/N₂ at the same oxygen concentration but this effect is little bit delayed at high temperature. This may be due to the lower rate of diffusion of oxygen through CO₂ and the higher specific heat capacity of CO₂. However with the increase of O₂ concentration the mass loss rate of coal also increases and hence it shortens the burn out time of coal. The optimum value of O₂/CO₂ for the reaction of O₂ with the functional group present in the coal sample was found to be about 8%. The combination of pyrolysis and gasification process can be the unique and fruitful technique as it can save the prior use of gasifying medium and the production of fresh char simultaneously in one process. With the increase of heating rate, coal particles are faster heated in a short period of time and burnt in a higher temperature region, but the increase in heating rate has almost no substantial effect on the combustion mechanism of coal. Also the increase of heating rate causes a decrease in activation energy value. Activation energy values were calculated by different well known methods at different fractions from 90% to 15% of the original coal within the temperature range of about 400 to 600 °C and it was found that Coats-Redfern approach showed the highest value of E and Freeman-Carroll method showed the least value of E at every fraction of converted coal.

References

- 1) G. S. Liu, and S. Niksa, *Prog. Energ. Combust. Sci.*, **30** (2004), P. 679.
- 2) S. Kajitani, N. Suzuki, M. Ashizawa, and S. Hara, *Fuel*, **85** (2006), P. 163.
- 3) S. Kasaoka, Y. Sakata, and C. Tong, *Int. Chem. Eng.*, **25** (1984), P. 160.
- 4) R. C. Everson, H.W.J.P. Neomagus, H. Kasaini, and D. Njapha, *Fuel*, **85** (2006), P. 1076.
- 5) T. Adschiri, and T. Furusawa, *Fuel*, **65** (1986), P. 927.
- 6) A. T. Knight, and G. D. Sergeant, *Fuel*, **61** (1982), P. 145.
- 7) G. S. Liu, P. Benyon, K. E. Benfell, G. W. Bryant, A. G. Tate, R. K. Boyd, D. J. Harris, and T. F. Wall, *Fuel*, **79** (2000), P. 617.
- 8) G. Q. Lu, and D. D. Do, *Carbon*, **30** (1992), P. 21.
- 9) G. S. Liu, A. G. Tate, G. W. Bryant, and T. F. Wall, *Fuel*, **79** (2000), P. 1145.
- 10) E. T. Turkdogan, and J. V. Vinters, *Carbon*, **7** (1969), P. 101.
- 11) S. Dutta, C. Y. Wen, and R. J. Belt, *Ind. Eng. Chem., Process Des. Dev.*, **16** (1977), P. 20.
- 12) I. Fernández-Morales, F. J. López-Garson, A. López-Peinado, C. Moreno-Castilla, and J. Rivera-Utrilla, *Fuel*, **64** (1985), P. 666.
- 13) D. Gray, J. G. Cogoli, and R. H. Essenhigh, *Prep. Pap. Natl. Meet. Div. Fuel Chem. Am. Chem. Soc.*, **18** (1973), P. 135.
- 14) D. B. Anthony, J. B. Howard, H. C. Hottel, and H. P. Melssner, M. I. T. Cambridge, *private comm.*, (1975).
- 15) E. A. Gulbransen, and K. F. Andrew, *Ind. Eng. Chem.*, **44** (1952), P. 1039.
- 16) Y. Tan, E. Croiset, M. A. Douglas, and K. V. Thambimuthu, *Fuel*, **85** (2006), P. 507.
- 17) B. J. P. Buhre, L. K. Elliott, C. D. Sheng, R. P. Gupta, and T. F. Wall, *Progress in Energy and Combustion Science*, **31** (2005), P. 283.
- 18) Q. Li, C. Zhao, X. Chen, W. Wu, and Y. Li, *J. Anal. Appl. Pyrolysis*, **85** (2009), P. 521.
- 19) R. K. Rathnam, L. K. Elliott, T. F. Wall, Y. Liu, and B. Moghtaderi, *Fuel Processing Tech.*, **90** (2009), P. 797.
- 20) P. A. Bejarano, and Y. A. Levendis, *Combustion and Flame*, **153** (2008), P. 270.
- 21) J. J. Murphy, and C. R. Shaddix, *Combustion and Flame*, **144** (2006), P. 710.
- 22) M. E. Brown, editor. *Introduction to thermal analysis: techniques and applications*. 2nd ed. London: Kluwer Academic; (2001).
- 23) C. D. Doyle, *J. Appl. Polym. Sci.*, **6** (1962), P. 639.
- 24) A. W. Coats, and J. P. Redfern, *Nature*, **201** (1964), P. 68.
- 25) E. S. Freeman, and B. Carroll, *J. Phys. Chem.*, **62** (1958), P. 394.
- 26) E. Sima-Ella, G. Yuan, and T. Mays, *Fuel*, **84** (2005), P. 1920.

Effective Utilization of Lignocellulosic Biomass with Hot-compressed Water Treatment

Satoshi Kumagai

The Research and Education Center of Carbon Resources, Kyushu University

We have been studying effective utilization of lignocellulosic biomass using hot-compressed water treatment as an environmentally friendly technology. Biomass could be converted to various chemicals such as sugars, organic acids, furan compounds and solid fuels by the treatment.

Because of rising global environmental problems and diminishing fossil resources, renewable and carbon-neutral lignocellulosic biomass has gained attention as an environmentally friendly carbon resource. However, effective conversion technology for the lignocellulosic biomass is yet to be established. Lignocellulosic biomass consists of three components—cellulose, hemicellulose, and lignin. The first two components are sugar polymers, and the latter is an aromatic polymer. Hence, fractionation technology is expected to enable effective utilization of lignocellulosic biomass.

Our research group has proposed a new technology for the conversion of lignocellulosic biomass by using hot-compressed water (HCW) (showed in Fig.1).

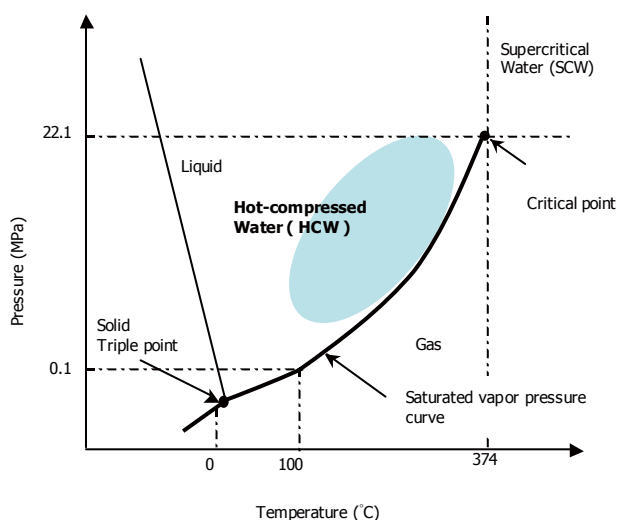


Fig. 1 Phase diagram of pure water.

Decomposition behavior of various sources of lignocellulosic biomass in HCW, such as rice hull, barley straw, rice straw, and Japanese cedar have been investigated. The temperature of HCW was increased in a stepwise manner by using a percolator-type reactor. The elution behavior of sugars from rice hull in response to HCW treatment is shown in Fig. 2.

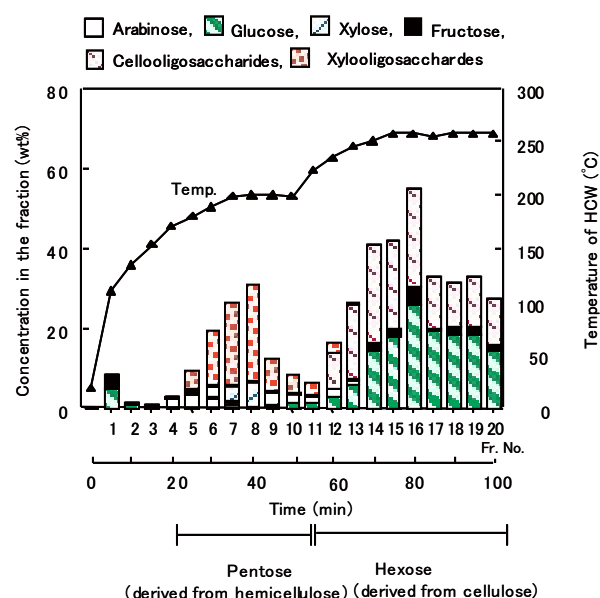


Fig. 2 Elution behavior of sugars from rice hull.

The free sugars, namely, glucose and fructose, were eluted first. Thereafter, the hemicellulose-derived sugars, namely, arabinose, xylose, and xylooligosaccharides, were eluted at temperatures ranging from 140–200°C. Finally, the cellulose-derived sugars, namely, fructose, glucose, and cellooligosaccharides were obtained at temperatures above 230°C.

This saccharification behavior indicates that hemicellulose and cellulose can be fractionated separately by merely controlling the temperature of HCW¹⁾.

This could be achieved because HCW can mediate hydrolysis by increasing the ion products. For example, at approximately 250°C, the number of ion products in HCW is approximately a thousand-fold higher than that in water at normal atmospheric temperature and pressure.

Furthermore, the fractionated decomposition products could be used as functional food components and be converted to their constituent monomeric sugars by enzymatic hydrolysis. These monomeric sugars could

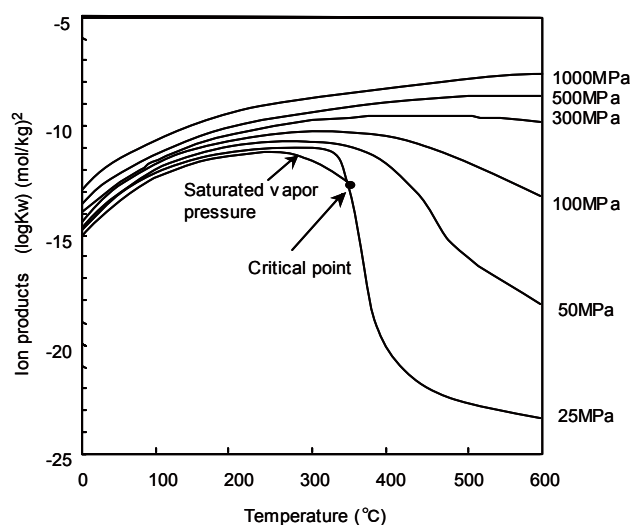


Fig. 3 Ion products.

then be used in the pretreatment processes of ethanol and lactic acid fermentation²⁻⁴⁾.

We are currently investigating whether bamboo and oil palm residues can be effectively utilized using the HCW technology. Hemicellulose- and cellulose-derived sugars could be effectively recovered by HCW treatment⁵⁾.

In addition, the generated monomelic sugars were simultaneously and rapidly converted to organic acids (formic acid, acetic acid, glycolic acid, and

levulinic acid) and furan compounds (furfural and 5-hydroxymethylfurfural) were clarified⁶⁾.

These by-products can be used as sources of various chemicals in biorefineries. Hence, we are investigating the production of these useful substances by HCW treatment.

The HCW treatment also generated solid residues, which are mainly consisted of lignin, a substance with high carbon content. Thus, we attempted to use such residues as a source for solid fuels⁵⁾.

In my current assignment at Hirajima's Laboratory, Department of Earth Resource Engineering, Faculty of Engineering, researches on catalytic production of furan compounds from saccharides and generation of solid fuels with high heating values by HCW treatment are conducting^{7, 8)}.

The author will focus the research on developing a process for the effective utilization of lignocellulosic biomass combined with other previous studies.

References

- 1) Kumagai et al., *J. Jpn. Inst. Energy*, **83**, 776 (2004).
- 2) Kumagai et al., *Jpn. J. Food Eng.*, **6**, 297 (2005).
- 3) Kumagai et al., *Kagaku Kogaku Ronbunshu*, **34**, 458 (2008).
- 4) Kumagai et al., *Jpn. J. Food Eng.*, **5**, 205 (2004).
- 5) Kumagai et al., *Nihon Enerugi Gakkai Taikai* (2009).
- 6) Kumagai et al., *Kagaku Kougakukai Shuki Taikai* (2009).
- 7) Kawada et al., *Shigen Sozai Gakkai Shuki Taikai* (2008).
- 8) Hirajima et al., *Shigen-to-Sozai*, **119**, 118 (2003).

Start on NCRS Forum

Program leader of GCOE NCRS at KU

Hideo Nagashima

Global COE program NCRS, especially in accordance with a rapid economic growth in developing nations, aims at understanding the issues and establishing a new field of science for a global-scale solution against the background that carbon resources such as coal, oil which are chemical materials as well as valuable energy resources become global scramble and head toward exhaustion, indiscreet use of carbon resources causes environmental pollution across the border, burning of carbon resources is a cause of greenhouse gas emissions such as CO₂, and global warming. When COE of Novel Carbon Resource Sciences was adopted, on the comment, a global vision on these issues, in other words, thinking about self-purification capacity the globe itself has, current status that carbon resources consumed exceeding carbon cycle system cause the problem, and what suggestion to make globe sustainable were questioned. This is an assignment discussed among COE members, young

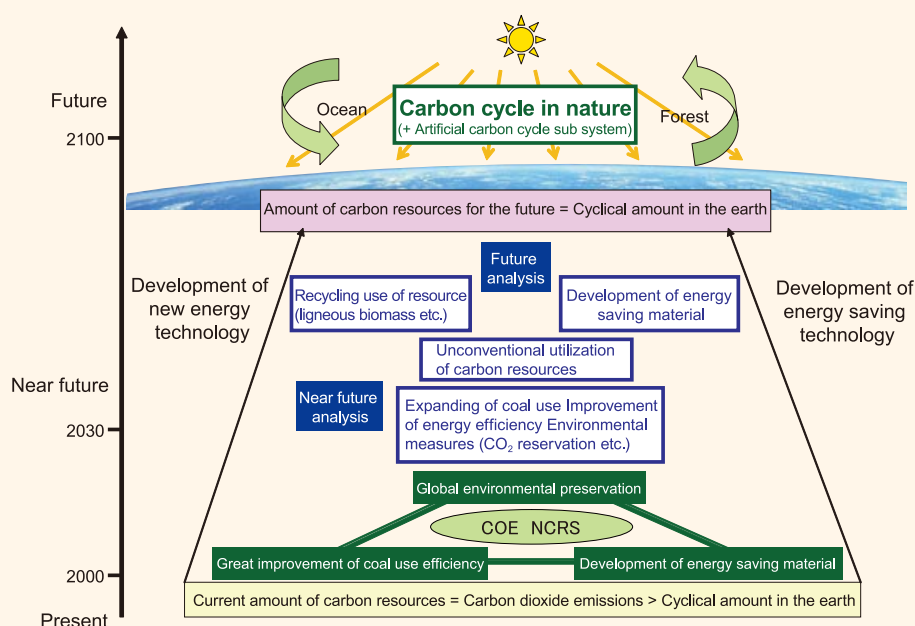
researchers, graduate students to meet a society.

The first year of COE, project implemented construction of infrastructure like an Educational system of COE and establishing of international collaborative scheme. The second year, in spring 2009, inauguration of "NCRS forum" was started to prepare for making proposal as COE on the basis of infrastructure. In this "NCRS forum", COE program members, collaborators in the right places, assistant professors, post doctoral fellows and COE graduate students choose a global theme on carbon resources, invite lecturers to contribute, arrange, and share the subjects through discussion. In particular, forum consists of 3 sub forums, to each of which advisors, young researchers, doctoral students belong. Each of sub forums set a specific theme and has discussion, around 3 or 4 times a year, from one o'clock to five o'clock on Saturday afternoon in principle. Theme related to sub forums

mutually is implemented as a form of Joint Forum. Main theme of sub forums as shown below is integrated into 3 keywords: 'Efficient energy utilization of carbon resources', 'Energy saving technology', and 'Asian environment'. About use of carbon resources, our COE symbolizes 'coal' energy.

Since coal is reserved in rich and evenly distributed around the world, it is main energy resource in many countries. However, quality coal is a world scramble in economic development, besides, in developing countries, most of thermal power plants still using low-fineness coal, energy transformation inefficiency and a low level of environmental measures, which cause mass generation of CO₂ and environmental pollution. Even if a percentage of atomic energy and renewable energy increases, world economy doesn't reach an agreement without using carbon resource such as coal for an energy resource. For this reason, structural strategy of future energy device is thinking globally a bestmix of energy focusing on carbon resources which is realistic energy source and finding a solution to CO₂ problem at once. Forum I features this matter.

On the other hand, Japan doesn't have energy resource and has tried complete energy saving to make the best use of advanced technology since oil shock. Not only energy saving in the industry represented by complete use of waste heat, much energy saving technology is prevailing at homes like an air conditioner, household appliances or a car. In a worldwide energy crisis, the most Japan could demonstrate is that a global unfolding of high energy saving society and a further development of energy saving technology in Japan. To improve a technology to a higher level after this 30 years' effort, innovative material, device and system are needed to



▲Fig. 1 Future vision of carbon cycle system (A figure submitted at hearing).

	ForumI Energy utilization of carbon resources	ForumII Energy saving science technology	ForumIII Asian environment
1	Coal gasification electric power and CCS		
2			Tasks and approaching on Asian energy consumption in low-carbon society
3	Peat fire and CO ₂ restriction		Peat fire and CO ₂ restriction
4	System-based energy saving		
5		Material-based energy saving	
6	Wind generation and solar energy generation		
7			Living condition of megacity in Asia
Fieldwork to Abroad		Singapore	
Fieldtrip to Domestic company		Carbon resources and chemical plant: Chemical companies in Chugoku area (Tosoh Co. Ube Industries. LTD.) Gasification electric power and CCS: in Kanto area (CRIEPI, Nippon Steel Co.)	

▲Table 1 Forum operation in 2009

create from the basic concept. In forum II, picking up these issues, we understand a current status and overlook the future of energy saving material, device and system.

Another forum, forum III is about Asian environment. In NCRS COE, rapid growing Asia is thought to be a practical field of effective use of carbon resources and energy saving technology. Even, KU is taking "direction to Asia" as university's action plan.

Similar to past history of Japan, pollution, environmental destruction, mass occurrence of greenhouse gas become serious in rapid growing Asia. These effects are spreading to others across one country. Asia, without keeping a track of Japan, is desirable to grow to preserve an environment, for that reason, Japan should understand Asian environment and show the way of thinking toward coexistence. In forum III, we study Asian environment from many

sides, understand the feature and think a solution for the future. These 3 forums were planned in spring 2009. After discussing at expanding governing committee which is program conducting meeting, the first meeting, Forum I & II joint meeting was held. Then, 7 times meetings are taking place. Advisors, post doctoral researchers and doctoral students participate in forum. For doctoral students, it is one of educational curriculum. The current number of registered students is 26 in forum I, 24 in forum II, and 20 in forum III. Advisors belong to each forum are also sub-supervisors who admit doctoral students to take a credit of a subject 'NCRS II'. Since many overseas students join in these meetings, topics and discussion are conducted in English, and are developing lively discussion.

Linking with forum, field work to abroad and field trip to domestic company have been also

planned, applicants among the participants meet requirements can take credits of 'Exercises on NCRS I, II'. As for fieldwork to Abroad this year, Forum II implements a visitation to Mitsui Chemicals, Nanyang Technological University, and holds students workshop at National University of Singapore. Fieldtrip to domestic company is planned twice in February.

Forum is being filmed, edited as E-learning material and it is devised that students who couldn't participate in at that time can learn later on. Forum discussion is summarized as a report by mainly young researchers. From now on, summary is going to be reported to this Newsletter. Corpus of 4 years' forum in 5 years COE project is expected to be a COE's proposal toward global carbon cycle system and structure of sustainable society. Hopefully, all members understand this plan.



1st University Collaboration Meeting between Fukuoka and Busan City

March 9th, 2009

Fukuoka city : KU, FIT, KWU, SGU / Busan city : PNU, KMU, DAU, DEU



▲Workshop at Pusan National University

NEWS 02

CONSORTIUM FUKUOKA

as 'center of knowledge' seeking for higher level of education and research with effective use of resources in 4 universities

Leader of CONSORTIUM FUKUOKA
Professor of Faculty of Social and Environmental Studies, FIT

Shigeru OGAWA

The Ministry of Education, Culture, Sports, Science and Technology ? Japan (MEXT) has adopted "CONSORTIUM FUKUOKA" at the master' s level as the "Strategic University Partnership Support Project". The consortium consists of the four national, public and private

universities, which are Fukuoka Institute of Technology (Representative university), Kyushu University, Fukuoka Women's University and Seinan Gakuin University in waterfront areas in Fukuoka city.

Consortium aims to develop high- level environmental human resources — coping with the environment and energy issues and promotion issues of the local economy vigorously and comprehensively — looking at Asia from Fukuoka. The project also tries to promote joint

research focusing on regional issues and utilizing the results actively as the 'center of knowledge'.

This 'center of knowledge' aims to make a contribution to local municipalities and community including local corporations, communicate with government agencies and conduct 'intellectual production' activities such as intellectual exchange with Asian countries.

In order to achieve these objectives, there are four collaborative projects; 1) Educational partnership, 2) Research partnership, 3) Contribution to regional community and 4) Sharing of resources. In these projects the four universities with different installation modes need to build up collaborative education and research system by effective utilization of each university's educational research resources and produce results, evaluating its achievements. The implementation structure of projects is as follows; Consortium Strategy Conference, Consortium Promotion Conference, Program Development Committee and Joint Research Promotion Committee are set up as decision-making system; Consortium Office works as Secretariat Division; Tokyo Office has the function of satellite for information exchange between Fukuoka and Tokyo; and there is Advisory Board as an outside evaluation body.

First, in educational partnership the CONSORTIUM Program aims to develop high-level environmental human resources. The courses related to energy and environment in the four universities were selected and incorporated into curriculum. Anyone who attends the master course of the four universities can take the CONSORTIUM Program and gain credits. In 2009 financial year, 12 subjects in first semester and 14 subjects in second semester are being offered. Remote teaching system enables students to take other graduate schools opening courses just staying in their place.

Furthermore, "Four Universities Joint Seminar" targeted for graduate students of the four universities was held in the early September 2009. The 2 nights and 3 days seminar contained lectures on energy and environment, a tour of facilities and group discussion, with the objectives of broadening their point of view outside their own research areas and deepening exchanges among students. 24 people from the four universities participated in the seminar.



▲Remote lecture

Many of the questionnaires collected after the seminar said that they have broadened their views through exchanges with other universities' students.

In addition to that, since October the job hunting support seminar called "Research Seminar on Industrial World" have been taking place every month, targeting for the first year grade graduates. This seminar is different from general company information sessions. Speakers with active career in various areas talk about appeal of jobs or personnel required by companies with remote teaching system from Tokyo Office. Outright talks based on their experience at workplace are receiving favorable comments every time.

Research aid project was carried out in order to support research partnership among researchers from the four universities and to enhance cooperation among the universities. This project provides one-year research aid to collaborative research by some researchers of the four universities. After public entry within the four universities, 6 subjects of those were approved by Joint Research Promotion Committee. We hope this marks the beginning of continuous research for the following years.

In terms of contribution to regional community, 5 series of public lectures took place from September to explain energy and environment issues to general public in a simple way. The researchers from the four universities as well as

lectures from local municipalities and environment-related NPO offered information in a wide range of areas. About 200 people participated in every lecture and the seminars made a great success. Moreover, we actively cooperate with other organizations such as G-COE of NCRS Kyushu University co-organizing seminars and public lectures.

On the other hand, CONSORTIUM FUKUOKA strives to strengthen partnership with East Asia. A workshop was held in Pusan National University this March. Not only four universities of CONSORTIUM FUKUOKA but also people from Pusan National University, Dong-A University, Dong-eui University and Korean Marine University joined the workshop. The general information of each institute and research on environment and energy were introduced in this seminar. As these universities based in Pusan, South Korea are considering partnership with our universities in a constructive way, we are expecting further collaboration in education and research areas.

We think these projects have been accomplished by staff of the four universities working together and by effective use of each university's merit and specialty. CONSORTIUM FUKUOKA will do our utmost best to live up to expectations.

SYMPOSIUM & WORKSHOP 2009

Hosting

NCRS G-COE Special Seminar

Date: June 5 , 2009

Venue: Building C, Lecture Room 1, Chikushi Campus, Kyushu University

G-COE The 1st Symposium on Human Life and Environment

The Current Status on Indoor Environment and Health & Comfort Prediction

Date: June 27, 2009

Venue: Conference Room, C-CUBE 3F, Chikushi Campus, Kyushu University

G-COE Special Seminar

Date: September 15 , 2009

Venue: KASTEC Bldg. 3F, Training Room, Chikushi Campus, Kyushu University

NCRS GCOE Seminar Lithium-ion battery & Approach of User Company

Date: October 30, 2009

Venue: Chikushi Hall, C-CUBE 1F, Chikushi Campus, Kyushu University

NCRS GCOE & JCOAL: Public Lecture and Exhibition

~Let's think about energy and life that supports our future~

Date: November 1, 2009

Venue: C-CUBE, Chikushi Campus , Kyushu University

The Third International Symposium on Novel Carbon Resource Sciences:

Advanced Materials, Processes and Systems toward CO₂Mitigation

Date: November 2-3 , 2009

Venue: C-CUBE , Chikushi Campus , Kyushu University

International Symposium on Resource Development in the Ocean

Date: December 3, 2009

Venue: Multi-purpose Meeting Room (601), 6F of RIAM, Kyushu University

The 2nd SJTU-KU Joint Workshop on Environment and Energy Issues in Relation with Novel Carbon Resource Sciences

Date: December 11 , 2009

Venue: Shanghai Jiao Tong University, Shanghai, China

The Fourth International Symposium on Novel Carbon Resource Sciences:

Environmental Science and Technology

Date: December 12-13 , 2009

Venue: Shanghai Jiao Tong University, Shanghai, China

Joint Hosting

The 2nd Kyushu University - Korea University Joint Workshop on Functional Materials

Date: May 27-29 , 2009

Venue: Daimaru Ryokan , Oita prefecture

International Workshop on Development of Environmentally Friendly Functional Materials

Date: June 19 , 2009

Venue: Chikushi Hall, C-CUBE 1F, Chikushi Campus, Kyushu University

RIAM Special Seminar : PREDICTING AIR QUALITY

Date: June 26 , 2009

Venue: Chikushi Hall, C-CUBE 1F, Chikushi Campus, Kyushu University

Special Seminar CHIKUHO - Asia Mirai Juku

Date: August 29 , 2009

Venue: Tagawa City Hall

"Light Using Organic and High Polymer Chemistry in Ubiquitous Information Society" Project

Organometal Chemistry • Synthetic Organic Chemistry Student Workshop

Date: September 28 , 2009

Venue: Chikushi Hall, C-CUBE 1F , Chikushi Campus , Kyushu University

The 4th International Symposium for Young Elements Chemists:

2009 Workshop on Organometallic Chemistry

Date: October 28 -29 , 2009

Venue: Common Management Bldg. 3F , Chikushi Campus, Kyushu University

The 13th Symposium of the Society of Silicon Chemistry JAPAN

Date: October 30 – 31 , 2009

Venue: Karatsu Royal Hotel

2nd G-COE International Workshop on Energy and Environment in Chemical Engineering

Date: November 4 , 2009

Venue: Sougou Gakushu Plaza, 2F, Room No 12 ,Ito Campus, Kyushu University

The 2nd International Symposium on Chemistry of Organic & Polymer Materials for Ubiquitous ICT

Date: November 4 , 2009

Venue: Building D-E , Lecture Room 3 , Chikushi Campus, Kyushu University

The 11th Cross Straits Symposium(CSS-11)on Materials, Energy, and Environmental Sciences

Date: November 12-13 , 2009

Venue: Pusan University , Korea

The 2nd Symposium on Human Life and Environment

Architectural Environment and Health maintenance • Enhancement

Date: December 4, 2009

Venue: Kyushu Energy Center

Joint Hosting

International Symposium on Earth Science and Technology 2009 CINEST
Cooperative International Network for Earth Science and Technology

Date: December 8-9, 2009
Venue: Nishijin Palace

2009 Sino-Australian Symposium on Advanced Coal and Biomass Utilization Technologies

Date: December 9-11, 2009
Venue: East Lake Hotel, Wuhan, China

Lecture

Hi-LINK Symposium

Date: June 2, 2009
Venue: International Hall, Hakozaki Campus, Kyushu University

Invitation to Chemistry_Dream & Chemistry21 :

Chikushi Campus, Kyushu University, One-day Experimental Chemistry Class

Date: July 25, 2009
Venue: C-CUBE, Chikushi Campus, Kyushu University

The 3rd INAMORI Frontier Research Seminar

~Fundamentals, Functions and Applications of Ceramic Materials~

Date: November 13, 2009
Venue: Inamori International Hall, Inamori Foundation Center, Ito Campus, Kyushu University

The 137th KASTEC Seminar

Date: November 27, 2009
Venue: KASTEC Bldg. 3F, Training room, Chikushi Campus, Kyushu University

**IMCE lecture : New development of reactor project and catalyst reaction engineering
toward highly effective carbon resource conversion**

Date: December 7, 2009
Venue: IMCE Building 1F Room 111, Chikushi Campus, Kyushu University

Research Performance 2009

Awards & Articles

●Award

Safety of Mine in Kyushu district 2009
(2009/05)

Kikuo Matsui

*In recognition of work with the security of safety of Mine

●Award

The 7th industry-academia-government collaboration contributor honors
(2009/06)

Jun-ichiro Hayashi

"Development of Pyrocoking for Energy/ Material Coproduction from Biomass"

●Award

The 46th joint Kyushu meeting of branches related to chemistries Chemistry Award of Foreign Researcher
(2009/07)

Vladimir V. Plashnitsa

"Nano-structured Au-sensing Electrodes on Single-crystal Zirconia Fabrication and Gas Sensing Characteristics"
Vladimir PLASHNITSA, Perumal ELUMALAI, Yuki FUJIO, Norio MIURA

●Award

Prize for Encouragement from Japan Association of Aerosol Science and Technology
(2009/08)

Toshihiko Takemura

"Development of simulation model for estimation of aerosol effects on climate"

●Award

The Society of Rheology, Japan Award 2008
(2009/08)

Yoshiaki Takahashi

"A research concerning hierarchical structure and viscoelastic properties of diblock and triblock copolymers"

●Award

Incentive Award of The 59th Metallographic Photo Award, The Japan Institute of Metals
(2009/03)

Hajime Matsuo

"High-resolution electron microscopy of twin boundaries in $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}$ "

●Award

Excellent Presentation Award on the 6th Doctoral Student Exchange Seminar, Kyushu University
(2009/08)

Natsuki Watanabe

"Grain Boundary Structure Analysis of High Coercivity NdFeB Sintered Magnet"

●Award

Excellent Research Announcement Prize on Talk shower in Kyushu, Kyushu Branch of the Electrochemical Society of Japan
(2009/09)

Tomomitsu Sato

"Proposal for solid-state electrochemical gas sensor aiming at monitoring of VOC in atmospheric environment"

●Award

Best Poster Award at the 17th JSPP Symposium 2009 by the Japan Society of Polymer Processing
(2009/11)

Hiroshi Ikeda

"Microindentation formation technology to silica glass"

●Award

The 11th Cross Straits Symposium on Materials, Energy, and Environmental Sciences The Best Presentation Award (Oral presentation)
(2009/11)

Yuki Fujio

"Stabilization of Sensing Characteristics for Mixed-Potential Zirconia-Based Hydrocarbon Sensor"

●Award

The 11th Cross Straits Symposium on Materials, Energy, and Environmental Sciences The Best Presentation Award (Poster presentation)
(2009/11)

Natsuki Watanabe

"Effect of Heavy Rare Earth Element Addition on Microstructure of NdFeB Sintered Magnets"

●Award

The 22nd International Symposium on Chemical Engineering Gold Award
(2009/12)

Hiroshi Ikeda

"Preparation of Transparent Silica Glass by Sintering SiO_2 Nano Particles and Its Optical Properties"

●Report

The Research papers published in IChemE Journal was chosen to "the number of cited times TOP75" among research papers published in the Journal during 2006-2009 (2009/06)

Jun-ichi Hayashi

"Gasification of low-rank solid fuels with thermochemical energy recuperation for hydrogen production and power generation" J.-I. Hayashi, S. Hosokai, N. Sonoyama Process Safety and Environmental Protection, Vol.84, Issue 6 (2006) 409-419.

●Report

Prof. Uno at Research Institute for Advanced Mechanics, Kyushu University has reported on Nature Geoscience under the joint research with National Institute for Environmental Studies and Ocean Research Institute, the University of Tokyo that the dust-veiled clouds generated in Asia are transported more than one full circuit around the globe. This excellent results have been mentioned in major news arenas, Daily Mail, Daily Telegraph, AFP (France), Reuters and Times of India. (2009/07)

"Asian dust transported one full circuit around the globe" Itsushi Uno, Kenta Eguchi, Keiya Yumimoto, Toshihiko Takemura, Atsushi Shimizu, Mitsuo Uematsu, Zhaoyan Liu, Zifa Wang, Yukari Hara & Nobuo Sugimoto, Nature Geoscience 2, 557-560 (2009). Doi:10.1038/ngeo583 Nature Geoscience article: <http://www.nature.com/ngeo/journal/v2/n8/abs/ngeo583.html>

●Report

The article was posted on internet Nikkei Bio about his research presentation at the 18th Japan Energy scientific meeting, 30th July, 2009.

(2009/08)

Satoshi Kumagai

"Xylooligosaccharides production from moso-bamboo using a hydrothermal reaction, and fuel production from the treatment residue"

●Report

The Research paper published in Material Letters(Elsevier) by Prof. Norio Miura et al. was chosen to "Top Cited Authors" which contributed to impact factor.

(2009/12)

Norio Miura

"High performance electrochemical supercapacitor from electrochemically synthesized nanostructured polyaniline", Vinay Gupta, Norio Miura

●Report

A research article has been introduced in Synfacts. (2009/06)

Daisuke Noda

"Role of TMEDA in Iron-Catalyzed Coupling Reactions" H. Yamamoto, J.N. Payette, Synfacts 2009, 7, 751. D. Noda, Y. Sunada, T. Hatakeyama, M. Nakamura, H. Nagashima, J. Am. Chem. Soc. 2009, 131, 6078-6079.

●Report

A research was adopted into Academic Challenge at Kyushu university. (2009/06)

Sayo Moriyama

"Immobilization mechanisms of fluoride and borate based on the properties of solid acids and bases of metal oxides and its applications to environmental engineering"

●Report

The photo listed in his prepublication paper was adopted to Cover Art of Tissue Engineering. (2009/08)

Masakazu Inamori

"An Approach for Formation of Vascularized Liver Tissue by Endothelial Cell-Covered Hepatocyte Spheroid Integration" (Abstract)

●Report

The Nikkei (2009/9/4)

Japanese-Australian Meeting on Effective Utilization of Brown Coal

低品質石炭利用
九州と技術研究
九州大学は3日、低品質の石炭「褐炭」の利用技術を開発し、オーストラリアの州政府や大学と共同研究を始める。高品質の石炭は埋蔵量が減っている。活用が進んでいない褐炭を効率的にガス化したり、液化したりする方法を探ることで資源を安定して獲得できるという。

九州大と共同研究に取り組むのは豪ビクトリア州政府とモナシユ大学、メルボルン大学。九州大が日本企業から、モナシユ大が同州政府から資金の提供を受けて研究を進めるほか、両国の研究者が交流する。

九州電力

褐炭研究で覚書
豪ビクトリア州と

九州電力は、オーストラリアの豪ビクトリア州政府と、低品質の石炭「褐炭」の効率的な活用と環境負荷の低減に関する共同研究を始める。同研究は、褐炭のガス化や液化など、高品質の石炭に比べて効率が低く、コストが高い褐炭を有効に活用する技術を開発することを目指す。九州電力は、褐炭の活用に関する研究を進め、環境負荷の低減と資源の有効活用を実現する。同研究は、九州電力と豪ビクトリア州政府、メルボルン大学、モナシユ大学との共同研究で進められる。九州電力は、褐炭の活用に関する研究を進め、環境負荷の低減と資源の有効活用を実現する。同研究は、九州電力と豪ビクトリア州政府、メルボルン大学、モナシユ大学との共同研究で進められる。

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九州大

褐炭「豪」と共同研究
新資源確保へ活用策探る

九州大学は3日、オーストラリアの豪ビクトリア州政府と、低品質の石炭「褐炭」の効率的な活用と環境負荷の低減に関する共同研究を始める。同研究は、褐炭のガス化や液化など、高品質の石炭に比べて効率が低く、コストが高い褐炭を有効に活用する技術を開発することを目指す。九州大学は、褐炭の活用に関する研究を進め、環境負荷の低減と資源の有効活用を実現する。同研究は、九州大学と豪ビクトリア州政府、メルボルン大学、モナシユ大学との共同研究で進められる。九州大学は、褐炭の活用に関する研究を進め、環境負荷の低減と資源の有効活用を実現する。同研究は、九州大学と豪ビクトリア州政府、メルボルン大学、モナシユ大学との共同研究で進められる。

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●Report

Nishinippon Newspaper (2009/9/9)

Japanese-Australian Meeting on Effective Utilization of Brown Coal

Research Performance 2009

Awards & Articles

リン酸鉄リチウム

次世代Li-B用正極材

三井造船、早期事業化狙う

三井造船は、次世代リチウムイオン電池(Li-B)用正極材として、リン酸鉄リチウム(LiFePO₄)の早期事業化を目指す。今秋をめどにパイロット設備の一部を完成させ、高圧で長寿命という特徴を生かして、パワー用として需要喚起、年産30tの生産設備として稼働させる。高圧で長寿命という特徴を生かして、パワー用として需要喚起、年産30tの生産設備として稼働させる。高圧で長寿命という特徴を生かして、パワー用として需要喚起、年産30tの生産設備として稼働させる。

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●Report

The Chemical Daily
(2009/4/23)

Jun-ichi Yamaki, Shigeto Okada

今秋めどに
36t能力
500t超の設備検討

三井造船は、次世代リチウムイオン電池(Li-B)用正極材として、リン酸鉄リチウム(LiFePO₄)の早期事業化を目指す。今秋をめどにパイロット設備の一部を完成させ、高圧で長寿命という特徴を生かして、パワー用として需要喚起、年産30tの生産設備として稼働させる。高圧で長寿命という特徴を生かして、パワー用として需要喚起、年産30tの生産設備として稼働させる。

三井造船、早期事業化狙う

次世代Li-B正極材 コスト競争力追求

九大、産学連携で開発加速

住化と共同でリン酸鉄

ナトリウムイオン電池も視野

住化と共同でリン酸鉄ナトリウムイオン電池も視野。九大、産学連携で開発加速。住化と共同でリン酸鉄ナトリウムイオン電池も視野。九大、産学連携で開発加速。住化と共同でリン酸鉄ナトリウムイオン電池も視野。九大、産学連携で開発加速。

●Report

The Chemical Daily
(2009/11/19)

Jun-ichi Yamaki, Shigeto Okada

石炭の高度利用が未来を築ける

効率的な温暖化防止に貢献

中国で年間200万tの削減

1次エネルギーの90%は石炭

石炭から クリーン・コール・ハ

負の遺産を超える石炭

省エネはもう一つの発生源

太陽エネルギーの創出

日本のクリーン・コール・テクノロジーは低炭素社会の切り札

●Report

Nishinippon Newspaper
(2009/11/21)

FUKUOKA SCIENCE MONTH: G-COE NCRC・JCOAL Public Exhibition

次世代Li-B正極材 コスト競争力追求

九大、産学連携で開発加速

フッ素導入で高容量化

三菱重工などと実用化めざす

フッ素導入で高容量化。三菱重工などと実用化めざす。九大、産学連携で開発加速。フッ素導入で高容量化。三菱重工などと実用化めざす。九大、産学連携で開発加速。

●Report

The Chemical Daily
(2009/11/24)

Jun-ichi Yamaki, Shigeto Okada



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