



# Kenan Center News

The newsletter of the Kenan Center for the Utilization of Carbon Dioxide in Manufacturing  
University of North Carolina at Chapel Hill and North Carolina State University

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## Center Directors

Ruben G. Carbonell      Joseph M. DeSimone  
919-515-5118              919-962-2166  
ruben@ncsu.edu         desimone@unc.edu

## Newsletter Editor

Darlene K. Taylor  
919-962-9532  
dkt@unc.edu

## Website

[www2.ncsu.edu/champagne](http://www2.ncsu.edu/champagne)

## Corporate Sponsors

Air Liquide	Nalco
Air Products	Nomacorc
Ashland	Oak Ridge National Lab
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Daikin	Sandia National Labs
DuPont	Solvay
Michelin	Thar Design
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	MICELL Technologies

The Kenan Center for the Utilization of Carbon Dioxide in Manufacturing is comprised of chemists, chemical engineers, and materials scientists from the University of North Carolina at Chapel Hill and North Carolina State University as well as a team of corporate sponsors. The center seeks to elucidate the fundamental science and engineering principles that facilitate the use of carbon dioxide in conventionally organic and halogenated solvent or aqueous waste stream processes. Our laboratories are uniquely equipped to help industrial partners launch research programs in supercritical fluids R&D, as well as to assist in augmenting proprietary research programs within their corporate R&D laboratories. Please feel free to contact us for a discussion of how the Kenan Center can assist your academic or corporate laboratory in the development and implementation of CO<sub>2</sub>-based technology.

## Directors' Letter

As our Kenan Center enters into its fourth year, we are making extra efforts to establish a strategic plan for our research program. This has become particularly important because of the diverse interests of our large membership. As the major industrial outreach component of the



NSF Science and Technology Center for Environmentally Responsible Solvents and Processes, the Kenan Center membership help us understand the short term needs of industry as they help us to plan for needs that might be 5 to 10 years in the future. We are grateful to all of the company representatives that have

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## New Industrial Partners

The Kenan Center extends a warm welcome to our four newest corporate partners: Air Liquide, Daikin, Michelin, and Nomacorc. Air Liquide, founded in France in 1902, is a global presence with 125 subsidiaries throughout 60 countries. The company specializes in providing industrial and medical gases and related services and is known to take special measures to ensure protection of the environment and full customer support. Daikin Industries, Ltd. is a Japanese company that has its roots in the Osaka Kinzoku Kogyosho Limited Partnership founded in 1924. Daikin is well known for its air-conditioning and refrigeration technologies as well as fluorochemical synthesis. Daikin America, Inc. was established in 1991 and began production of fluorocarbon polymers in 1994. Daikin also offers a global perspective and is very much focused on preserving the Earth's environment. Michelin was formed on

May 28, 1889, by two French brothers - Edouard and André Michelin. The history of this company is an interesting entrepreneurial story and worth a read. The tires with the commercial jingle we know so well - "Because so much is riding on your tires" - were first produced in the US in 1908. Nomacorc, based in Zebulon, NC, separated from its parent company Nomaco in 1999. Nomacorc's specialty is the synthetic cork for wine bottles. These closures are made by an extrusion process and show highly consistent cell density, structure, and dimensional control that, among other advantages, limit oxygen permeation. Nomacorc even offers custom coloring of these 100% recyclable corks. We are very pleased to have each of these companies join us as corporate partners and look forward to continued interactions.

*Sarah Folk*

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## Directors' Letter (*cont'd*)

aided us in this important task.

Prof. Denis Gray from NC State University, an expert in industry-university collaborative research centers, helped us to design a questionnaire to illicit the opinions of our corporate partners as to the project areas that would be of most interest to industry. Dr. Ev Baucom, Deputy Director of the NSF CERSP, collected the necessary information and the results of the survey are shown in one of the articles of this issue of the Kenan Center News.

Not surprisingly, given the make-up of most of our current membership, the largest interest lies in the synthesis of polymers and coating applications for polymeric systems. On the other hand, the responses hint as to what the future might bring. Center researchers are just beginning to make progress in novel applications of carbon dioxide: in drug delivery, petroleum processing, microelectronics, etc. Some of these applications of interest now were undreamed of when we began the Kenan Center in 1997. However, there is one major challenge that needs to be overcome, regardless of the application. There is a need for simplified processing systems to facilitate the goal of providing energy efficient, cost effective and environmentally benign chemical manufacturing operations.

We will continue to be responsive to this and other needs and we are optimistic that with the talent we have assembled in terms of faculty, students, and corporate partners, and with the infrastructure we now have available, we will succeed in reaching our goals.

*Ruben Carbonell*

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### Authors of Contributing Articles:

*Paa-Joe Akoto-Ampaw, Engineering Graduate Student at NC State  
Everett Baucom, Deputy Director of NSF ST CERSP*

*Chad Booth, Post-Doctorate Chemist at UNC-Chapel Hill*

*Sarah Folk, Chemistry Graduate Student at UNC-Chapel Hill*

*Jason S. Keiper, Post-Doctorate Chemist at UNC-Chapel Hill*

*Karen Kennedy, Engineering Graduate Student at NC State*

*Joseph Royer, Post-Doctorate Engineer at NC State*



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# Christine Grant makes her mark at N.C. State

## History:

B.S. Chemical Engineering, Brown University, 1984

M.S. Georgia Institute of Technology, 1986

Ph.D. Georgia Institute of Technology, 1989

Assistant Professor, North Carolina State University, 1989

Associate Professor, North Carolina State University, 1996

## Research:

Removal of calcium salts (a collaboration with NIST), prevention of friction and stiction in MEMS devices (in collaboration with Sandia National Labs) and high temperature lubricant degradation in fiber processing. Her research interests in the NSF-ST CERSP include understanding the governing mechanisms in liquid and  $\text{scCO}_2$  cleaning systems, which is an extension of the research she has done in aqueous based surfactant systems.

Dr. Christine Grant was the first and remains the only African-American woman faculty member in the College of Engineering at North Carolina State University. She is one of only 5 African-American women ChE faculty in the entire country (out of more than 3000 ChE faculty). Being the first of 2 girls, her mom, a science teacher, and her dad, a music teacher, it was no stretch for her to go into academia. Her interest in the environment, science and technology has enabled her to build a vibrant research program on surface decontamination processes, focused on the removal of organic and inorganic films from solid surfaces using environmentally benign systems, Micro-Electro-Mechanical Systems (MEMS) and Textile Fiber Processing.

Having received a B.S. in Chemical Engineering from Brown University in 1984, Christine went on to graduate school at Georgia Institute of Technology where she received her Master's in 1986 and Ph.D. in 1989 under the direction of Dr. Eric Clayfield, a renowned colloid scientist. Her thesis topic of Surfactant Enhanced Electro-Osmotic Dewatering of Mineral Ultrafines is applicable to

environmental systems (e.g. sewage dewatering). She joined the Chemical Engineering Department faculty at NC State as an Assistant Professor in the same year and was promoted to Associate Professor in 1996.

Her research and academic programs have been supported by over \$3.6 million in funding, the majority of which comes from NSF (removal of calcium salts — a collaboration with NIST — and prevention of friction and stiction in MEMS devices — in collaboration with Sandia National Labs) and the National Textiles Center (high temperature lubricant degradation in fiber processing). Her research interests in the NSF-ST CERSP include understanding the governing mechanisms in liquid and  $\text{scCO}_2$  cleaning systems, which is an extension of the research she has done in aqueous based surfactant systems. Her initial role in the CERSP as leader of the Rate Processes Group, under the former center structure, required her to interact with a team of faculty researching fundamental issues of kinetic and transport mechanisms in  $\text{CO}_2$ -based processes. She is also the Co-Director of the NSF-REU program at NC State, which over the next

5 years will support more than 100 undergraduate students from around the country to come to NC State and perform research in green processing. The NSF-ST CERSP supports six of these students every year.

Christine Grant prides herself in the number of undergraduate and minority students she has mentored over the years. Over 40% of her mentees have gone on to graduate school. She currently advises 3 graduate students, 4 post-doctorates and 5 undergraduate students. Her interest in environmental research goes beyond the boundaries of the US to countries like Ghana in West Africa, where she established a partnership between NC State and the University of Science and Technology (UST), Kumasi, with the development of International Environmental/Chemical Computer Educational Aids between 1997 and 2000. She has been a recipient of numerous awards and honors, notably, she was elected to the Council of Outstanding Young Engineering Alumni of Georgia Institute of Technology, YWCA Academy of Women Award in Science and Technology, and she received the National Technical Association (NTA) Top Women in Science and Engineering Award.

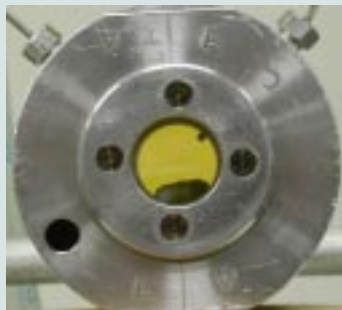
When she is not exploring new research ideas, Christine spends time with her husband (an electrical/computer scientist) and 5-year old son who have both been very supportive of her career. Her faith, desire to be challenged and the support of her family, she says, are what motivate her to such great achievements. On a personal note, she loves to sing, write, read and dance.

*Paa-Joe Akoto-Ampaw*



# Engineering and Science Highlights

## *New Hybrid Fluorocarbon/Hydrocarbon Surfactants for CO<sub>2</sub>*



A clear, homogeneous CO<sub>2</sub> solution can be formed with 2.5 wt.% of surfactant, water, and the solvatochromatic probe methyl orange (MO). MO, which is not readily soluble in dry CO<sub>2</sub>, is presumably stabilized by the surfactant through the formation of nanometer-sized microemulsion droplets.

A series of anionic phosphate-based surfactants have been synthesized that each possess one partially fluorinated chain and one fully hydrocarbon chain. Jason Keiper a post-doctorate working for Joseph DeSimone at UNC-CH has performed the synthesis in a modular synthetic approach that allows for the preparation of systematically varied analogs, and in turn, the capability to evaluate the effects of surfactant structure on their properties in CO<sub>2</sub>. Several surfactants demonstrated the capacity for water uptake, the extent of which was dependent upon surfactant structure.

*Jason S. Keiper*

## *High-pressure Microscopy and Newly Designed Optical Cell*

A Nikon microscope equipped with intermediate working distance objectives has been modified for use in conjunction with a specially developed cell that is capable of pressures up to 5000psi. The cell is equipped with quartz windows and variable temperature control.

*Chad Booth*



A **Virtual Tour** of the laboratory facilities at UNC-Chapel Hill and NC State is now available on CD-ROM. To request a copy of the CD, please visit the website <http://www.nsfstc.unc.edu/> and refer to the section on Center News.



## **Brian Novick receives \$10,000 Fellowship**

Keep North Carolina Clean & Beautiful Foundation awarded Brian Novick with its prestigious Governor and Mrs. Dan K. Moore fellowship. Novick, a chemical engineering graduate student at NC State University, was surprised by the award presentation which took place during the April 23 Kenan Center Review Meeting held at the Friday Center in Chapel Hill. The \$10,000 fellowship and a plaque were presented to Novick as a result of his strong academic standing, his commitment to improving the environment, and his research into the use of carbon dioxide as an environmentally superior solvent in manufacturing coating processes.



NC State Chemical Engineering Department Head, Peter Kilpatrick (left), joins Ruben Carbonell and Joseph DeSimone in congratulating Brian Novick, the recipient of the Keep NC Clean and Beautiful Award. Jane C. Rogers, Managing Director of the Foundation (second from right) presented Novick with the award.



## Carbonell Awarded Alcoa Foundation Distinguished Engineering Research Award

Professor Ruben Carbonell was awarded the Alcoa Foundation Distinguished Engineering Research Award for his outstanding research achievements over the last five years at North Carolina State University. The award was presented to Carbonell on May 7, 2001, and consisted of a certificate and \$5,000 in cash. The Engineering Foundation and College of

Engineering at NCSU allocated the Alcoa Research Awards to encourage research among its faculty and to recognize research achievements.

## DeSimone honored for his contributions to public well-being

Professor Joseph M. DeSimone was awarded the Gustavus John Esselen Award for Chemistry in the Public Interest in recognition of his contributions to a cleaner environment. The award was presented to DeSimone on Thursday, April 19, 2001, in a ceremony at Harvard University's

Mallinckrodt Chemistry Laboratories. Following the presentation DeSimone gave a lecture entitled "Green Chemistry for Sustainable Economic Development." The Gustavus John Esselen Award is presented annually by the Northeastern Section of the American Chemical Society to honor outstanding achievement in scientific and technical work that contributes to the public well-being. DeSimone joins the ranks of F. Sherwood Rowland and Mario J. Molina who were the first to receive the award in 1987 for the discovery of the effect of chlorofluorocarbons on the ozone layer. Past awardees have also included Carl Djerrasi for his work in birth-control drugs and Kary Mullis for development of the polymerase chain reaction used in DNA testing.

## Devin Flowers Designs Photoresists for CO<sub>2</sub>

Imagine if semiconductors were produced commercially in carbon dioxide. Carbon dioxide would replace aqueous and organic solvents currently used in industry and reduce the amount of waste generated by these processes. That could be the future, based on the Kenan Center research of Devin Flowers. Devin's research involves designing and synthesizing CO<sub>2</sub>-compatible photoresists for 193nm and 157nm lithography. The idea is to create photoresists that are soluble in liquid CO<sub>2</sub> at reasonable conditions and that possess the same characteristics required for conventional resist materials, such as thermal stability, low absorbance, solubility contrast, sensitivity, resolution, etch resistance, and purity. In collaboration with NC State graduate student Erik Hoggan and their advisors, Joseph DeSimone and Ruben Carbonell, Devin hopes to prove that high quality photoresist materials can be deposited, developed, and stripped in liquid/supercritical CO<sub>2</sub>.

Devin originally started college as a mathematics major. However, after his sophomore chemistry class, Devin realized that he enjoyed chemistry more than mathematics. Devin completed his bachelors' degree in 1997 at Alabama State University, where he

supercritical fluids and microlithography". He also enjoys the interaction with the various members of the Center.

When Devin's not working hard in the lab, he likes to play sports, read, and spend time with his wife

### History:

B.S. , Alabama State University, 1997

Ph.D. candidate, University of North Carolina at Chapel Hill

*"Being in the Kenan Center has allowed me to attend several conferences and enhance my knowledge of supercritical fluids and microlithography"*

majored in chemistry and minored in mathematics. Devin chose UNC-CH and DeSimone's group to pursue his Ph.D. in polymer/organic chemistry because of the many opportunities for professional development. Devin feels that participating in the center for the last three years has been challenging, but very rewarding. He explains, "Being in the Kenan Center has allowed me to attend several conferences and enhance my knowledge of

Veronica and 4-year old daughter Megan. After graduation, Devin plans to begin his career in industrial research and development. However, he would like to explore more business and management related opportunities as his career progresses. Devin knows that the experience he has obtained in the Kenan Center will have application in his career for many years to come.

*Karen A. Kennedy*



# Kenan Center Members Prioritize Research Projects: Results of Surveys

The vision, mission and goals (see CERSP News Director's message) of the National Science Foundation Science and Technology Center for Environmentally Responsible Solvents and Processes (CERSP) is primarily focused on fundamental research, but with a long-term view to practical applications. With that in mind, we conducted two surveys involving participants of the April 23, 2001, Kenan Center meeting as part of the STC's industrial outreach.

In the first survey, conducted by mail prior to the meeting, participants were asked to rate their interest in 35 broad potential commercialization targets in order to assist the CERSP (as well as the Kenan Center) in establishing realistic focal points for selected programs. Approximately 60% of participants representing fourteen companies responded. Respondents were asked to rate the 35 areas from 1 to 5, with 5 being very important commercially or of great research interest and 1 being of little interest. The ten highest rated categories are highlighted resulting from that survey are shown in Table 1. Five of these categories are in the area of polymer manufacture and three relate to coatings and films. Polymer foaming and nanoparticles complete the "top ten". Results of the survey lend credence to the CERSP's selection of "Macromolecules—Synthesis and Processing" and "Deposition and Dissolution" (including film formation) as two of its three selected "Application Domains"; the third, "Small Molecules", includes nanoparticles.

**Table 1. Priority of Commercialization Targets**  
(Revised to reflect input following April 2001 KC meeting)

<b>Polymer Manufacture</b>	<b>3.5</b>
Continuous polymerization	3.9
Core/shell polymers	3.8
Suspension polymerization	3.4
Chain growth (solid state)	3.4
New polymers (e.g. block, co-, or terpolymers)	3.3
Solution polymerization (e.g. polyacrylates)	3.2
<b>Coatings and Films</b>	<b>3.5</b>
Enhanced barrier coatings (e.g. improved surface fluorination of polyethylene tanks)	3.9
Protective coating (e.g. to prevent corrosion)	3.7
Functional Adhesive Coatings	3.6
Fouling release	2.7
<b>Polymer Extrusion-based Processes</b>	<b>3.0</b>
Polymer foaming	3.5
Reactive extrusion	3.0
Polymer blend facilitation	3.0
Enhanced extrusion	3.0
Dyeing	2.3
<b>Specialties</b>	<b>3.0</b>
Particles	3.8
Surfactants	3.2
Catalysis	2.8
Enzyme and fermentation	2.4
<b>Biotechnology</b>	<b>2.7</b>
Enzymatic catalysis	2.8
Separation from fermentation broths	2.8
Biocommodities	2.8
Pharmaceuticals	2.4
<b>Microelectronics/ Computer Chip Manufacture</b>	<b>2.5</b>
Lithography	2.8
Photoresists	2.8
Lubricants	1.8
<b>Cleaning</b>	<b>2.3</b>
Precision cleaning	2.7
Industrial cleaning	2.5
Dry cleaning	2.1
<b>Nutraceuticals/Food Processing</b>	<b>2.1</b>
Extractions	2.3
Separations	2.1
Fractionations	2.0
<b>Petroleum Production and Refining</b>	<b>1.6</b>
Deasphalting heavy crude oils	1.8
Emulsion breaking	1.8
Tertiary recovery	1.1

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# Events of Past Kenan Center Review Meeting

The spring 2001 Kenan Center Review Meeting was held April 22 and 23. During the afternoon of April 22, Kenan Center members were treated to a tour of the UNC and NCSU facilities as well as an impromptu tour of Raleigh. In the evening, dinner was hosted at La Residence Restaurant in Chapel Hill, followed by an intimate wine, cheese and dessert reception. This provided an excellent opportunity for students, faculty and industrial members to discuss on-going research in a social setting. The scientific portion of the review meeting was held April 23, at the Friday Center in Chapel Hill. A continental breakfast was followed by opening remarks from Ruben Carbonell and Joe DeSimone where they introduced two

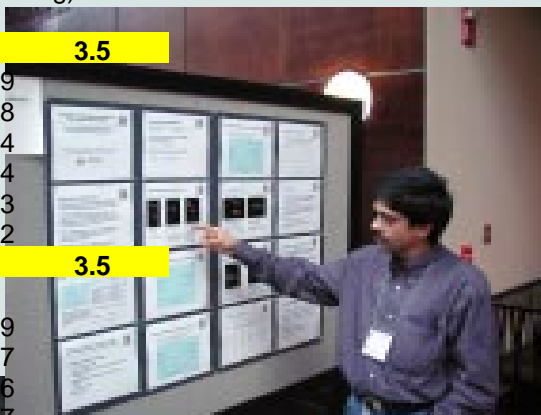
new Kenan Center members, Nomacorc and Daikin Industries. Ten different students and post-doctorate researchers from NCSU and UNC-CH gave research updates in a 10-minute oral presentation format. Selected presentations discussed a variety of topics including partitioning coefficients, PET recycling and depolymerization, CO<sub>2</sub>-based microelectronics research, biocatalysis, polymeric nanogels, hydrogenation reactions, and new hybrid surfactants. A spirited Kenan Center Business Review Meeting followed lunch at the Friday Center. Company representatives were introduced to the reorganization of the NSFST Center for Environmentally Responsible Solvents and Processes (CERSP) including the vision, mission

and goals for the technical programs of the CERSP as well as the revised project teams. In addition, Dr. Everett Baucom, Deputy Director of the CERSP, lead a session during the business meeting to solicit feedback from company representatives. The intent of this session was to identify Kenan Center research projects with the greatest impact and potential for commercialization. The Spring 2001 Kenan Center Review Meeting concluded with a poster session where nearly 50 students and post-doctorate researchers presented their Kenan Center sponsored or partially funded work. The fall meeting will be held September 17, 2001, at the Friday Center in Chapel Hill, NC.

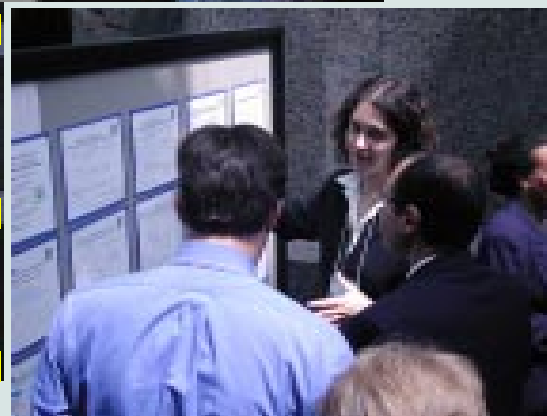
*Joseph Royer*

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Separation from fermentation broths	2.8
Biocommodities	2.8
Pharmaceuticals	2.4
<b>Microelectronics/ Computer Chip Manufacture</b>	<b>2.5</b>
Lithography	2.8
Photolithography	2.2



*Photos by Reto Bolliger*



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In the second survey, conducted at the Kenan Center Meeting and based upon respondents' strong interest in polymer manufacture, Kenan Center participants were asked to rate a series of factors related to that topic. Factors were selected to effect lower capital investment, lower operating costs, higher quality product, and/or reduced development or operating risk. Each participant was given nine votes, three each at three different priority levels, to select from 23 different factors.

Remarkably, the 500 points voted by participants were equally divided between lower cost processes and higher quality products. Scaled values are listed in Table 2. We will use these "knowledge gap" items and their importance ratings to help assign priorities in selecting STC research programs.

*Everett Baucom*



Kenan Center for the Utilization of Carbon Dioxide in Manufacturing  
CB #3290, Venable and Kenan Laboratories  
Department of Chemistry  
University of North Carolina at Chapel Hill  
Chapel Hill, NC 27599-3290

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