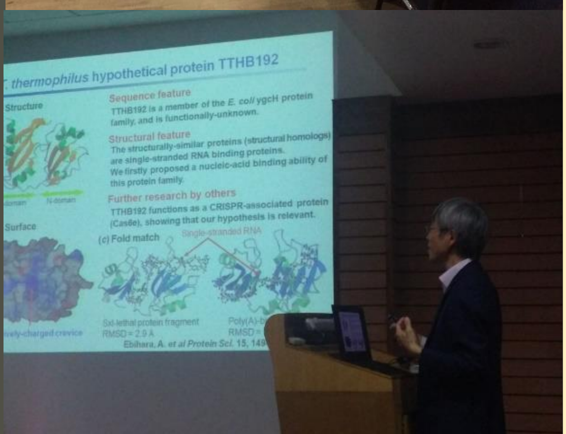

Newsletter

December - 2017

Indian Institute of Chemical Engineers

GUWAHATI REGIONAL CENTRE

Department of Chemical Engineering

IIT Guwahati

Green Fuels using Electrochemical Reduction of CO_2

Prof . Anil Verma
Department of Chemical Engineering, Indian Institute of Technology Delhi

Energy requirements are continuously increasing and putting a lot of pressure on the finite conventional energy resources. According to the projections of International Energy Outlook, the natural gas, coal, and oil will be used for more than three-fourths of the total world energy consumption by 2040. Since fossil fuels are limited as well as responsible for environmental issues, alternate sources need to be explored for sustainable energy supply. As per the recent report of Intergovernmental Panel on Climate Change (IPCC), fossil fuels should be phased out completely in power generation by 2100 to keep their negative environmental impacts in check. The increased use of fossil fuels has resulted higher CO_2 concentration in the atmosphere, which has crossed the level of 400 ppm. On the other hand, natural sinks for CO_2 sequestration such as forest cover are depleting. According to World Resources Institute, ~80% of the earth's forest cover is already vanished due to deforestation in past century. It shows that natural CO_2 absorbers are being deteriorated at a fast rate resulting into the increased carbon balance in the atmosphere. The widening gap between the emitted CO_2 and sequestered CO_2 is the indicator that the existing sink is needed to be assisted by some kind of artificial process that can perform the same function as the trees/forests do. Therefore, scientists are trying to develop such processes, that can not only fulfill the rising energy demands by the production of fuels, but at the same time can also help in minimizing the excess CO_2 of the atmosphere. . In this aspect, electrochemical reduction of carbon dioxide (ERC) has come up as one of the most promising methods, which may convert CO_2 using renewable energy (solar or wind) to value added chemicals that can serve the purpose of fuels. It has been conceptualized and accepted that plant functions can actually be mimicked using ERC.

The electrical energy, preferably generated from renewable energy sources such as solar or wind, is supplied to an electrochemical reactor to carry out ERC. In the electrochemical reactor, CO_2 can be supplied directly in gas phase or after solubilizing in aqueous/non-aqueous medium. The former is termed as direct electrochemical reduction of gaseous CO_2 (dERC) and has higher practical applicability. ERC can result in a variety of products ranging from CO and hydrocarbons to alcohols and acids, wherein the applied potential, electrolyte medium, and electrocatalysts play a decisive role.

In the electrochemical reduction of CO_2, first step is the activation of stable CO_2 molecule. The carbon atom has double covalent bonds with oxygen atom and the two pairs of electrons are shared between the atoms. The electronegativity of carbon is much less than oxygen still, CO_2 is a linear molecule, because there are only two electron pairs on the central carbon atom, which are equally shared by two oxygen atoms on both the sides. Due to the linear sp hybridized structure, the bond strength of CO_2 is very high (~532 kJ•mol-1) thus making it remarkably stable. Therefore, CO_2 needs substantial electrical potential in electrochemical environment to get activated. The activation of CO_2 requires change in its geometry from linear CO_2 to bent CO_2 anion radical ($\bullet CO_2-$) which results in a very slow self-exchange rate for the $CO_2/\bullet CO_2-$ couple, thus making this step rate determining. This is the most energy intensive step in the ERC and it theoretically requires -1.9 V vs. SHE. Therefore, efficient electrocatalysts are required to reduce the activation energy barrier.

Another issue is of simultaneous hydrogen evolution reaction (HER) at cathode, due to the close standard reduction potentials of CO_2 and H_2. Since H+ ions are indispensable for the formation of

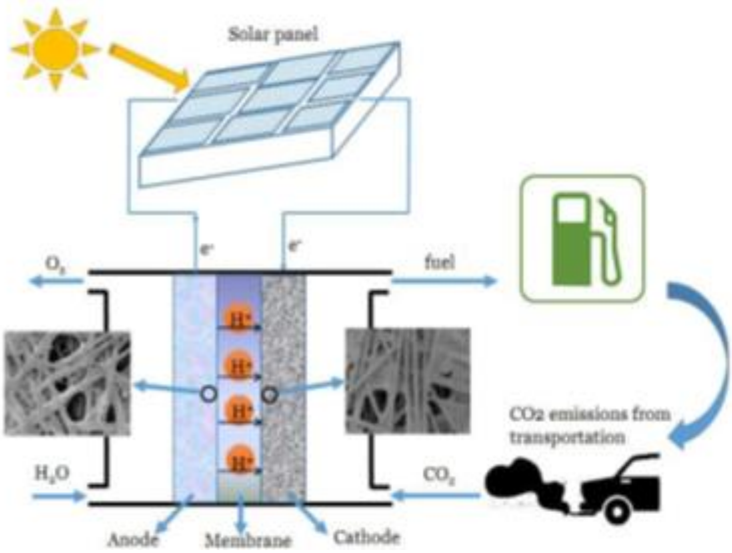

Figure. Conceptual model for the electrochemical reduction of CO_2 to fuel

hydrocarbons and alcohols, its use in ERC is unavoidable. Thus competition takes place between CO_2 electroreduction and hydrogen evolution reaction at cathode during ERC, which results in significant consumption of supplied energy for HER rather getting used up in the CO_2 electroreduction. Hence, current efficiency of the CO_2 electroreduction process is adversely affected. Thus electrocatalysts are required which can selectively catalyze the reduction of CO_2. In view of this, the issue of electrocatalysts seeks the most attention among all other challenges. Moreover, in gas phase ERC, the challenge to increase the mass transfer is addressed by using a gas diffusion electrode (GDE), which increases the CO_2 concentration on the reduction site, whereas in case of aqueous phase ERC, the mass transfer limitation prevails due to very low solubility of CO_2 in water. In IIT Delhi, our research group is working on various challenges of dERC, such as kinetics and mass transfer, solid electrolyte, and electocatalysis.

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Hydrogen and Steel Sector

M. Srinivasarao, A. Syamsundar
Research & Development Centre, RINL – Visakhapatnam Steel Plant

Development of green technologies is need of the hour in all major industrial sectors due to the continuous rise in carbon emissions. Industrial sectors like power, iron & steel, cement, etc. are the major emitters of CO_2 to the atmosphere. With an average emission of 2 - 2.5 tons of CO_2 per ton of steel produced in integrated plants, iron & steel sector is contributing 4-5% of the world's greenhouse gas emissions [1]. Currently, India is the world's third largest producer of crude steel with the production of 95.6 million tons in the year 2016-17 [2]. Still, India's per capita steel consumption is 63 kg whereas World's average is 208 kg [2]. As the Government of India is planning to enhance steel production in the country to 300 MT per year by 2030, it is expected that India will become the second largest steel producer in near future [3]. With the increase in steel production, CO_2 emissions from the steel sector are expected to enhance in the coming years.

Table 1: Crude Steel Production in India [2]

Year	Crude Steel Production in India (Million Tons)	World Rank
2012	77.3	4
2013	81.2	4
2014	87.3	4
2015	89.0	3
2016	95.6	3

In conventional integrated steel plants, blast furnace (BF) and basic oxygen furnace (BOF) are used for the production of liquid iron and steel respectively. More than half of the steel produced in India is through BF-BOF route. In BF, metallurgical coke (produced from coking coal through high temperature carbonization process in coke oven batteries) is used as a reducing agent to convert iron ore into liquid iron. The major reactions take place in a blast furnace is [4]

$$2C + O_2 \rightarrow 2CO$$
$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$$
$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$$
$$FeO + CO \rightarrow Fe + CO_2$$

From the above reactions, it is clear that BF iron making is a carbon intensive process. Further, coking coal is required here for the reduction. India's coking coal reserves are limited and mostly dependent on imports. Considering environmental concern and raw material availability and cost, various other alternative iron making technologies are being developed. Direct reduced iron (DRI) and smelting reduction (SR) are the major alternative iron making processes [5]. DRI is either coal based or gas based process where liquid iron is produced without using high quality coke. Today, India is the largest producer of DRI in the world. Smelting reduction on the other hand is a single or a combination of processes used for production of hot metal from various iron- containing materials by their smelting reduction with the use of non-coking coals. CO2 emissions from DRI and SR technologies are lower than from the conventional BF. Apart from these technologies, hydrogen based steel making is also under development.

Hydrogen based steel making: H_2 being a promising fuel to replace fossil fuels, hydrogen economy has received a great attention from green energy point of view in recent times. It has the highest energy content per unit mass among known fuels. H_2 can be obtained from fossil fuels, renewable sources, electrolysis and nuclear energy. At present, H_2 is produced largely from fossil fuels by natural gas reforming and coal gasification. Being a carbon free fuel, H_2 is environmentally more favourable reductant than coke for iron ore. If H_2 is used in the place of coke as a reducing agent, the CO_2 emissions can be reduced to a great extent [6]. The following main reactions take place in the reduction of iron ore using H_2.

$$3Fe_2O_3 + 3H_2 \rightarrow 2Fe_3O_4 + 3H_2O$$
$$Fe_3O_4 + H_2 \rightarrow 3FeO + H_2O$$
$$FeO + H_2 \rightarrow Fe + H_2O$$

The major limitations of using H_2 are its slow kinetics apart from its high cost compared to coal. To overcome the slow kinetics, hydrogen plasma is proposed over H_2 gas [7]. Kinetics of hydrogen plasma is an order of magnitude faster than H_2 gas. Hydrogen plasma will serve both as a reducing agent and also as a heating source for the smelting process. Currently, this process is successfully tested at lab scale and industrial trails are to be carried out for commercialization. Whether it is gas or plasma, huge amounts of H_2 is required at the industrial scale. H_2 generated from fossil fuels at some other place far from the steel plant not only unfavourable from the economic point of view but also might not serve the overall purpose of reduction in CO_2 emissions. Hence, it is essential to explore various options to generate H_2 within the plant premises from the existing sources or from the renewable sources. One of such existing options is the reforming of coke oven gas (COG), a by- product from coke oven batteries [8]. The COG is hydrogen rich along with significant amount of methane (CH_4). Currently, COG is used as a fuel for various purposes in integrated plants due to its high calorific value. Hence, the innovative technologies are to be developed to produce H_2 with the available resources such as COG at a cost competing price with coal. Though in the coming years, H_2 production cost is expected to decrease, but it will be still costlier than coal. Due to various technical and economical limitations of these new processes, the conventional Blast Furnace (BF) route of iron making will dominate in the near future as well. However, to supplement BF, active research is going on the development of green iron making technologies to reduce carbon emissions, if not eliminated completely.

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Potential of Membrane Reactors in the Developing Hydrogen Economy

Richa Sharma
Department of Chemical Engineering, Indian Institute of Technology Guwahati

Hydrogen has drawn much interest over the last 10 years as a potential alternative to fossil fuel dependent economy. With the advent of the Department of Energy portfolio of clean energy technologies, hydrogen as fuel is immensely sought after to produce electricity. Moreover, an integral part of this technology is the fuel cell that splits the hydrogen into hydrogen ions and electrons to produce electrical current with only water as the by-product. This integration is therefore the driving force for the developing hydrogen economy to establish itself.

Hydrogen to fuel cell using stored, high pressure cylinders has already been launched by many companies such as Hyundai, Honda, BMW, General Motors and Fiat. However, the prototypes lacked commercial success largely due to the risk issues related to hydrogen leak in addition to its enormous price. This challenge can be circumvented using an on-site hydrogen production unit called membrane reactor. Membrane reactor is a unique representation of process intensification that combines in a single reactor generation of a desired product and a semi-permeable membrane to selectively extract the product [1]. This concept got further revolutionized with the unmatched hydrogen selectivity of non-porous palladium foils that have the ability to separate hydrogen with 99.999% purity. Hence, using renewable high energy density but low weight fuels such as methanol, ethanol and glycerol, on-site hydrogen production with membrane reactors is considered a feasible choice. Selective removal of a reaction product through membrane in these devices enhances the per-pass conversion for equilibrium limited reactions such as dehydrogenation compared to conventional fixed bed reactors. According to Le Chatelier's principle, continuous removal of H_2 shifts the equilibrium in the forward direction resulting in enhanced conversion. Moreover, increase in conversion increases the trans-membrane hydrogen partial pressure difference which results in better hydrogen permeation. Thus, this system enables to achieve high flux and high conversion at the same time provided the membrane is low in thickness and non-porous in morphology.

Figure. 1 (a-c) Multi-pass membrane reactor set up

At Chemical Process Engineering Lab (CPEL), IIT-Guwahati we have designed and installed a state of the art modular multi-pass membrane reactor (as shown in Figure. 1) which has been used to produce hydrogen on –site. This system is one of a kind in the entire country and has demonstrated to effectively produce hydrogen up to 0.65 LPM with the integration of in-house synthesized supported Pd-Ag membranes of 30 µm thickness and bi-metallic alloy catalyst in a packed bed configuration. Using the

email: richa.sharma@iitg.ernet.in

multi-pass membrane separator, we have also demonstrated a control in the hydrogen partial pressure across the length of the reactor in addition to enhanced residence time for gas-membrane contacting. Moreover, we have developed our own catalysts as well as membranes prior to their final integration.

What's intriguing about this system is the dense palladium based membrane which plays a key role. Further, the system doesn't require immense pressures to improve its performance. A very high pressure rather deteriorates the hydrogen selectivity through the membrane. In this study, we have performed varying membrane arrangements as a separator as well as a membrane reformer to optimize maximum hydrogen flux. Having achieved a high flux, the cost effectiveness of the system can also be maintained. This however necessitates thinner membranes but yet non-porous. Hence, we have newly installed set ups for physical vapour deposition (PVD), chemical vapour deposition (CVD) which will be targeted in combination with electroless deposition in future to synthesize thinner Pd-alloyed membranes.

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Biodiesel Production from Unconventional Oilseeds and Oil Sources

Venu Babu Borugadda
Department of Chemical and Biological Engineering, University of Saskatchewan

Energy is an essential commodity. Ever increasing consumption of fossil fuel and petroleum products has been a matter of concern for the country for huge out-go of foreign exchange on the one hand and increasing emission causing environmental hazards on the other. The situation offers us incentives as well as an opportunity to look for substitutes of fossil fuels for both economic and environmental benefits to the country. Biodiesel is one such substitute that can be produced from oil-bearing seeds of many plants and blended with High-Speed Diesel for transport vehicles, generators, railway engines, irrigation pumps, etc. Bio-diesel commands crucial advantages such as the technical feasibility of blending in any ratio with petroleum diesel fuel, use of existing storage facility and infrastructure, superiority from the environment and emission reduction angle, its capacity to provide energy security to remote and rural areas and employment generation. It can be stored just like the petroleum diesel fuel and hence does not require separate infrastructure. The major oilseed crops used for this purpose include sunflower, soybean, rapeseed, linseed, cottonseed etc. majority of which are edible in nature. In the Indian context, use of edible oils for biodiesel production is unaffordable and rather illogical as India is an importer of edible oils. Therefore, in India, it is proposed to use non-edible oil for producing Biodiesel. Presently many species are being grown which yield seed containing non-edible oil. A few of them are *Jatropha Curcas, Karanja, Jojoba, Kusum, Mahua, Neem, Sal, Simarouba* etc. However, presently plantations of these biofuel crops are distributed and production units are located away from the plantation sites. The absence of clearly defined high yielding varieties and marketing channels result in inefficiencies in production, which further results in an increase in the cost of biofuel production. Hence, identifications of region-specific feedstock for the production of bio-diesel not only acquired benefits at both regional and local levels but will directly accelerate growth and rural empowerment. The North-East holds great significance from ecological and evolutionary plants as compared to any other part of India. The region is rich in biodiversity and has the largest number of endemic species of borne oilseeds (TBOs) like *Jatropha* species native to Northeast India, tung, rubber seed, nahor and seeds of genus *Litsea Lam*. These trees borne oilseeds yield up to 40% non-edible oil, which is a commercially viable alternative to diesel oil. Hence, it requires immediate attention for the commercial exploration and sustainable utilization of these valuable species for biofuel production (i.e. biodiesel).

email: vbb123@mail.usask.ca

Upcoming Events

Advances in Sustainable Polymers

Fourth International Symposium on Advances in Sustainable Polymers will be jointly organized by Centre of Excellence for Sustainable Polymers, Department of Chemical Engineering, Indian Institute of Technology Guwahati and Polymer Processing Academy during January 8-11, 2018.

The symposium will include plenary talks on recent advances in several aspects of sustainable polymer-based technologies.

Additional details can be obtained from www.iitg.ernet.in/asp17

Indo-Japan Bilateral Symposium on Future Perspective of Bioresource Utilization

"Indo-Japan Bilateral Symposium on Future Perspective of Bioresource Utilization" with special reference to North Eastern Region will be jointly organized by Indian Institute of Technology Guwahati, India and GIFU University Japan during February 1-4, 2018.

The symposium includes the discussion on the lines: Frontier in bio-resource in NER, Harnessing of bio-resource in NER, bio-industries and bio-based economics for further agriculture in NER, bio-based processing and production, Functional food, Food development and Agrofood science. The symposium will be dedicated towards comprehensive elaboration on production and processing of bio-based resources and their utilization.

Additional details can be obtained from www.iitg.ernet.in/ijbs2017/

Research Conclave - 2018

Research Conclave is organized under the banner of Students' Academic Board (SAB) of Indian Institute of Technology Guwahati (IITG) during March 8-11, 2018.

It is a staunch platform to nurture the young minds towards research, innovation and entrepreneurship, which intends to bring the integrity of the students towards both industries and academia to redress the academic research challenges, concerns of the entire student community and upcoming entrepreneurs around the globe. It is a forum to harness innovative mind to level-up the economic strata of current society from research to industries. The Research Conclave work as catalyst for building leaders through holistic, transformable and innovative ideas. It has started in 2015 with great rhythm and passion, and this year with the same enthusiasm we are conducting this event in a broader spectrum.

Additional details can be obtained from www.iitg.ac.in/researchconclave/

Reflux - 2018

Reflux, the annual Chemical Engineering Symposium of IIT Guwahati, is organized during March 16-18, 2018. It has been a pioneer in chemical industrial and entrepreneurial scene of the country.

The aim of Reflux is to provide an opportunity for budding Chemical Engineers to share scientific expertise and knowledge towards the development of new methods and strategies in different fields of Chemical Engineering. The event is planned to be highly interactive and an excellent learning experience for all the delegates.

Additional details can be obtained from http://www.reflux.in/

Guwahati Regional Centre Activities

Seminar Series on *Quantification of Biological Systems: Systems Biology Approach*

Prof. Kalyan Gayen, Department of Chemical Engineering, NIT Agartala delivered this talk on December 8, 2017.

Engineering systems are getting quantified, optimized and optimally operated, where as biology is evolving to be a quantitative science. Engineering principles can be applied to the biological systems in analyzing the working principles of living systems. In other words, nature has created the biological systems and there are constant efforts to understand the working principles of biological systems, which are working efficiently in micro / nano scale with high degree of robustness. Systems biology approach is the application of engineering approachs to understand the biological systems. Challenges lie on the prediction of phenotypes incorporating genome, transcriptome, proteome and metabolome of one complex living system. This Lecture broadly covered about the motivation of systems biology and the different mathematical approaches applied to understand the living systems. In this connection, one case study on the effect of endocrine disrupting elements on steroidogenesis using dynamic modelling is presented. In an another case study, quantification of bio butanol synthesis using steady state modeling namely elementary mode analysis is presented. Further, highlights about the microalgae based bioproducts and conversion of lignocellulosic materials into value added chemicals are delivered.

Seminar Series on *Introduction to Structural biology*

Prof. Akio EBIHARA, Faculty of Applied Biological Sciences, Gifu University delivered this talk on December 13, 2017.

All organisms have the genome, a complete set of DNA including all of the genes. After a gene is transcribed to its corresponding protein, all synthesized proteins work together to control the metabolism. The genome analysis indicates that the number of genes in a genome is finite: ca 4,400 genes in a bacterium Escherichia coli and ca 20,000 genes for Homo sapiens. The biological phenomena can be explained using a finite part list.

Structural biology seeks for functional and mechanistic understanding of how molecular components in a biological process work together at the molecular and atomic level. The advance in this research field allows us to understand a complete picture of biological phenomena on a genome wide scale. In this lecture, he showed two topics relating to structural biology.

(a) Deciphering a code of protein: Interestingly, in all genomes sequenced, a large portion of predicted proteins are functionally unknown proteins, called as “hypothetical proteins”. X-ray crystallography, a powerful tool for structural biology, can determine the shape of protein at atomic level, which tells how the functional groups of a protein are well defined in 3-D space to exert its original function. He showed some examples of research that obtained functional information of “hypothetical proteins” through X-ray crystallography.

(b) Observing a protein complex: The most broadly used method to determine the atomic-resolution macromolecular structures is X-ray crystallography. However, this approach is limited by the bottleneck of protein crystallization. This constraint has imposed limitations in the application to large protein complexes and integral membrane proteins for which multiple conformational or compositional states coexist; these complexes are very difficult to crystallize. The recent advances in single-particle cryo electron microscopy (cryo-EM) are solving this limitation. Cryo-EM now provides us a near-atomic resolution structure of protein complexes and membrane proteins. He showed some examples obtained by cryo-EM.

Seminar Series *on Nanocatalyst Development for Fuels from Biomass at NSF-CREST Bioenergy Center of NC A&T*

Prof. Debashish Kuila, Research Director ,NSF CREST Bioenergy Center delievered this talk on December 19, 2017.

One of the major objectives of our research at NSF-CREST Bioenergy Center is to produce fuels from thermal gasification of biomass using catalytic approaches. The first part of the talk covered catalyst development for Fischer-Tropsch (F-T) synthesis using Si-microchannel microreactors. The status of microrector set-up and catalyst screening using sol-gel and mesoporous silica supported catalysts is discussed.

The second part of this presentation covered development of robust catalysts for steam reforming reactions of bio-derived liquids to produce H_2, especially for the proton exchange membrane fuel cells (PEMFC). Glycerol is readily available as a by-product in biodiesel industry and contains much higher H_2 than that present in methanol or ethanol. Although steam reforming of methanol and ethanol have been extensively studied , limited studies have been reported using different catalysts for steam reforming of glycerol (SRG). We have been investigating different mesoporous catalysts- Co-MCM-41, Ni-MCM-41, Co-SBA-15 and Ni-SBA-15 and those in the presence of MgO, etc. for SRG to examine their comparative performances. The catalysts prepared in our laboratory using one-pot procedure have been characterized using TGA-DSC, N_2 adsorption-desorption, XRD, TEM, ICP-OES, FTIR and H_2-TPR techniques. The prepared catalyst possess high surface area in the range of 540 to 750 m^2/g and pore sizes of 4.8 - 5.9 nm, depending on the metal, mesoporous support and additional metal oxide to enhance the stability of the catalyst. The catalysts were tested for their activity, selectivity and long-term stability for GSR in a tubular fixed bed reactor at different temperatures and glycerol/water molar ratios. The results from his ongoing studies were presented.

No.	Name of the Award and criteria	Speaker
01	Ashland Bharat Ratna Prof C N R Rao Medal and CDS Award	Professor D.D. Sarma, FNA, FTWAS, IISc Bangalore
02	RPG Life Science Prof M M Sharma Medal and CDS Award	Professor Yogesh Joshi SS Bhatnagar Prize Winner IIT Kanpur
03	Asian Paints Padma Vibhushan Dr R A Mashelkar Medal and CDS Award	Dr. Arunima (Ruma) Acharya, Entrepreneur and Philanthropist Founder Ground Technology Inc.(GTI), Founder PfP Industries, LLC, Houston
04	Deepak Group's Padma Bhushan Prof L K Doraiswamy CDS Award	Padmashri Prof. G.D. Yadav VC, ICT, Mumbai
05	Chemical Weekly's Padmashri Dr G P Kane CDS Award	Prof. Xiao Dong Chen, Soochow University, Jiangsu Province, P R China
06	IICT-Avon PadmashriDr G S Sidhu CDS Award	Prof. B.N. Thorat, Head, Department of Chemical Engineering, ICT, Mumbai
07	Hetero Drugs Prof G S Laddha CDS Award	Dr. Basu Saha, Professor of Chemical and Process Engineering, Director, Green Process Engg Research, London South Bank University, London SE1 0AA
08	Hikal CDS Award	Mr. Soumya Chakrabarty Chief Operating Officer, OPAL India
09	Sartorius India CDS (for biotechnology)	Professor G K Suraishkumar Department of Biotechnology, IIT Madras
10	United Phosphorus CDS Award	Professor P.K. Ghosh Former Director, CSMCRI Bhavnagar
11	CSMCRI CDS Award	Professor N.C. Pradhan, IIT Kharagpur
12	CLRI Dr Y Nayudamma CDS Award	Mr. C.K. Tewari, ED, IOCL, Haldia
13	DOST Professor S K Sharma Medal and CDS Award	Dr. Rakesh Kumar Director, CSIR-NEERI Nagpur
14	CHEMCON NEERI Distinguished Speaker Award	Dr. Somnath Basu, PhD, PE Vice President Global Process Engineering & Chief Technology Officer , Houston TX 77041, USA
15	NCL's Prof K Venkataraman CDS Award	Professor Saikat Maitra, Vice-Chancellor Maulana Abul Kalam Azad University of Technology
16	Lab India Professor R. Kumar CDS Award	Professor V.S.R.K. Prasad Director, Indian Institute of Petroleum and Energy, Andhra University Campus, Visakhapatnam

Source: http://www.chemcon2017.com/endowment_lecture.php