

An Environmental Engineering Approach to Green Chemistry-Catalysis

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Abstract

21st century is the time to evaluate the “total quality” in terms of the environment, energy and resources of the world. All the nations have to unite in resource protection, depollution, reuse and recycling concepts. In order to adopt sustainable development, man has to try the way to find out processes and products that maximize economic and environmental benefits and social responsibility.

Catalysis is an economically and ecologically important field in the production integrated environmental protection. There are numerous examples of catalytic applications in various industries for a cleaner production and non-stop research is going on in the field of green chemistry.

In this study, the developments in the green chemistry and thereby catalysis technology have been reviewed. Also, an evaluation of the clean production conditions in Turkiye is tried.

Introduction

A brief outline of historical development in environmental pollution control in the world in general can be given as the following:

1. In 1970s it was the “control of pollution”,
2. In 1980s energy and environmental performance were considered in parallel and the environmental impact of the product was questioned,
3. In 1990s “total quality” term was added to the environmental management approach; waste minimization, energy efficiency, reuse and recovery possibilities were examined.

Nowadays, in 2000s, the Environmental Management Systems (EMS) and EMS Standards like,

- BS 7750 in UK
- NSF 110 in USA
- EMAS in EU (1993)
- ISO 14000 International Standards

have brought about the idea that economic development should be parallel to the principles of sustainable development!

Among these EMS standards, ISO 14000 Family is of great importance. For example, ISO 14001 is a tool that serves for both internal and external purposes such as:

- it provides environmental management such that

you are in control of your processes and activities and their impact on the environment

- there are no specific levels of environmental performance; ask yourself, can you improve things?
- so it helps companies to find their new ways in cleaner production
- this way their employees and customers become happier!

Trying to fulfill the requirements of such “International Standards”, performing various “International Conferences” and signing many “Agreements” on Environmental Protection, the Nations all over the world have united in the action of clean production.

It is obvious that, in the future:

- Highly selective and resource-protecting synthesis routes have to be developed without the formation of by-products and waste
- Chemicals have to be produced from renewable feedstocks
- Broader utilization of alternative energy sources must be achieved in our daily lives

In this study, an updated review of green chemistry and catalysis has been given. The role of catalysis in the Clean Production is explained giving some examples from the industry. The developments in the application of green chemistry concepts in education have been focused on. Also, an evaluation of the situation in Turkiye is considered and the future expectations are formulated.

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Worldwide actions of green chemistry and catalysis

American Chemical Society, ACS, (2001), has declared the 12 principles of green chemistry:

1. Prevention
2. Atom Efficiency
3. Less Hazardous Chemical Synthesis
4. Designing Safer Chemicals
5. Safer Solvents and Auxiliaries
6. Design for Energy Efficiency
7. Use of Renewable Feedstocks
8. Reduce Derivatives
9. Catalysis
10. Design for Degradation
11. Real-time Analysis for Pollution Prevention
12. Inherently Safer Chemistry for Accident Prevention

Two worldwide New Environmentally Benign Processes have to be mentioned here, these are:

1. US Department of Energy, Office of Industrial Technologies Agriculture program has worked on sustainable development at the national level,
2. Cargill-Dow example to produce biodegradable plastic Nature Works which is made through fermentation of corn and other plants!

Adoption of Sustainable Chemistry is the “*triple bottom line*” approach to designing processes and products that maximize *economic* and *environmental* benefits and *social* responsibility.

Today many developed countries have real life application of this rule such that:

- ✓ *Japan Chemical Innovation Institute*
It aims to contribute realizing sustainable development of society through promotion of innovations in chemical technology in the context of Green and Sustainable Chemistry Network GSCN (1999), (<http://www.gscn.net>)
- ✓ *UK Green Chemistry Awards [1]*
Green Chemistry Network promotes the concepts of Green Chemistry in Schools, Universities and Industry,
 - * *DyStar* ⇒ have developed *more efficient dyes*, which drastically reduce waste and energy consumption.
 - * *Industrial Copolymers* ⇒ incorporated *reactive diluents* to replace large amounts of solvent and polyol in polyurethane finishes in the automotive finishing industry and prevented the VOC release.

- ✓ *The Naval Surface Warfare Center-USA*
Indian Head Division has focused on many pollution prevention technologies in all applications of *explosives and propellants*, referred to as “Green Energetic Chemistry”
Now they have nonpolluting and recyclable formulations! (cramerrj@ih.navy.mil)
- ✓ *DuPont CR&D Experimental Station*
They have made the commitment to “*drive toward zero waste generation at the source*”
They will use the “*Inherently Safer Process Checklist*”
To minimize, substitute or eliminate, modify or simplify conditions for potentially hazardous materials (jalbertmiller@msm.com)
- ✓ *A specialty Chemical Company- Rohm and Haas Company-USA [2]*
Complying with the following regulations:
 - 1- ACC Responsible Care-Product Stewardship
 - 2- ISO 14001; Env.Man.and Audit Scheme (EMAS) in EU
 - 3- Rohm and Haas Env.Improvement Objectives
 They have succeeded in the followings:
 - ❖ Development of environmentally friendly replacements for TBT
 - ❖ Use of renewable, resource based materials
 - ❖ Development of pest-specific insecticide and herbicide leading to minimal non-target effects
 - ❖ Replacement of solvent-based systems with water-based systems
 - ❖ Reducing the level and number of non-essential ingredients in formulations

New synthesis routes and intelligent process design and catalysis

In the fine chemicals manufacture, the classical organic syntheses are being replaced with inorganic processes with cleaner, catalytic alternatives!

The atom efficient catalytic processes include: catalysis by solid acids and bases, catalytic reductions and oxidations, catalytic C–C bond formation, asymmetric catalysis, biocatalysis and catalysis in novel media (ionic liquids and supercritical fluids) [3,4].

Catalysis is an “*economically and ecologically*” extremely important field in the chemical and refinery industries for the *production or reactor integrated environmental protection !!!*

“The function of catalysis in the future should not be to eliminate and destroy harmful substances

in an expensive way at the end of the process, but rather to avoid the formation of such harmful substances in the process by means of primary approaches” says Wolfgang Hoelderich in the Chemical Technology and Het.Catalysis Lab. at the Univ. of Technology RWTH, Aachen Germany, in “Green Chemistry, April 2001”

Catalysts are the key for sustainable development

- in the chemical and refinery industries
- in the exhaust gases of automobiles
- in the denitrification of the flue gases of electrical power plants
- in the production of environmentally friendly optically pure chemicals for the pharmaceutical and agrochemical as well as fragrance industry

The value of the worldwide catalyst market is about 6 billion USD [1]

- ! About 20% of the gross national product in the USA is the added value of the catalytically manufactured products
- ! At least one catalytical step is involved in the production of about 90% of all chemical products

Industrial examples of the use of catalysis in cleaner production

- ①
 - The direct synthesis of *tert-butylamine*, a valuable intermediate for the tire and pharmaceutical industry, is being manufactured from isobutene and ammonia
 - BASF researchers have developed a catalyst for this process with 99% selectivity. No toxic HCN and corrosive H₂SO₄ are involved [5].
- ②
 - The replacement of *chlorine* by the more environmentally friendly H₂O₂ or O₂ in industrial and academic laboratories
 - A BASF process for the production of citral (a high demand intermediate in perfume and household cleaner production) from isobutene and formaldehyde uses a silver partial oxidation catalyst and produce no chlorinated side products with less synthesis steps [5].
- ③
 - Nalco Chemical Company developed *STABREX* microorganism control based on stabilized hypobromite compound designed to mimic bromine antimicrobials produced in the human immune system [6].

- This is an enzymatically catalyzed oxidation process product, which is used in the treatment of industrial wastewater since 1997, replacing chlorine again.

④
 ▪ Craig Hill (Emory University) and Ira Weinstock (USDA) developed a catalytic approach to *separation of lignin from cellulose in pulp and paper processing* [5].

- It utilizes non-toxic and inexpensive organic compounds called polyoxometalates and is an effluent-free process and mimics the processes of nature [6].

⑤
 ▪ Prof.Karen M. Draths and John W.Frost synthesis of *adipic acid* (used in the manufacture of Nylon66) and *catechol* (used in the production of flavors) use biocatalysis and renewable feedstocks.

**Presidential Green Chemistry Challenge 1998 Academic Award by EPA [7]*

- Here, nontoxic glucose is the starting material, which is derived from renewable carbohydrate, and genetically manipulated microbes are synthetic catalysts.

⑥
 ▪ *Disodium iminodiacetate* DSIDA is a key intermediate in the production of an environmentally friendly non-selective herbicide- “Monsanto’s Roundup”

**Presidential Green Chemistry Challenge 1996 Alternative Synthetic Pathways Award by EPA [7]*

- DSIDA is produced not from formaldehyde and HCN and HCl but, from diethanolamine which is dehydrogenated using a copper catalyst (which is filtered and reused)

⑦
 ▪ Prof.Chi-Huey Wong’s, (from the Scripps Res. Inst., one of the most cited chemists in the world), *multi-enzyme system* based on genetically engineered glycosyltransferases with in situ regeneration of sugar nucleotides is a revolution in the field of carbohydrate chemistry and has enabled the large-scale synthesis of complex oligosaccharides for clinical evaluation

- These new enzymatic reactions are carried out under green conditions!

▪ Here *enzymes are used as catalysts* in large scale organic synthesis

**Presidential Green Chemistry Challenge 2000 Academic Award by EPA [7]*

⑧

What cleans the car exhaust is the catalyst again! [8]

- “Exhaust Purifiers” are advanced catalysts bonded to a ceramic honeycomb to achieve high diesel particulate emissions reduction without sacrificing the conversion of hydrocarbons and carbon monoxide!
- “Soot Filters” burn the soot upon contact with a proprietary catalyst coating!
- “Selective Catalytic Reduction” systems use urea, which reacts with NO_x in the catalyst bed to produce nitrogen and water!
- Three way catalysts provide simultaneous control of NO_x, CO and HC in rich burn gas engines
- These catalysts have optimum temperature ranges between 675 to 1100°F
- Different catalysts are designed according to exhaust conditions and fuel type
- Automobile industry makes use of catalysis to reduce toxic emissions from internal combustion engines, *the prevention of pollution at the source!*

Green chemistry in education

American Chemical Society in coordination with US EPA is developing instructional materials and workshop opportunities on green chemistry to faculty and students (1998) [9].

These materials will be available in both print form and on the Internet, in English and German through a collaboration with the Royal Society of Chemistry and the Gesellschaft Deutscher Chemiker for high level secondary school use in all three countries.

The Term “Green Chemistry” is used to describe the design of chemical processes and products to reduce or eliminate the use and generation of hazardous substances, and to conserve materials and energy.

A video and a magazine are produced and Presidential Awards are used.

School of Chemistry, University of Leeds, UK started in 1999 with a final year undergraduate course. Recent papers were analyzed in the course and experiments were developed identifying reagents, reactions and technologies for replacement!

Chemistry Department, University of Scranton, USA, began to green their curriculum in 1996 with an environmental chemistry course [10].

The topics of the Presidential Green Chemistry Challenge were excellent discussion themes for

poster and oral presentations in the class!

Clean production in Türkiye

Environment Law, no 2872, dated 1983 is an application on the “prevention of pollution”.

It is a fact that, being a developing and dependent country, Türkiye cannot update the old technologies that are in use, so easily.

Only the companies doing some foreign trade try to achieve ISO 9001 and 14001 standards and give emphasis on the clean production.

Being a participant in the 1992 Rio Conference, Türkiye has initiated the clean production studies.

“National Environmental Action Plan”, supported by the World Bank, includes long term goal of encouraging the use of clean technologies and clean energy resources,

Agenda 21 works of the Ministry of Environment focus on the clean production, also.

TÜBITAK-TTGV Science-Technology-Industry Discussions Group has made meetings starting by 8th of July 1998. The industrial sector report published in Oct.1999 prepared by the -Clean Production-Clean Product; Environmentally Friendly Technologies Group- has proposed the establishment of a “*Clean Production Center*” for the development of a *structural model* to be applied all over Türkiye [11].

TÜSIAD- Turkish Industry-Businessman Association has prepared a report titled “Environmental Protection Based Technical Problems Related to Foreign Trade - Action Plan for the Turkish Industry” and listed Priority Industrial Sectors for Clean Production in Türkiye as follows:

1. Textile
2. Leather
3. Food
4. Metals Processing
5. Paper
6. Chemistry

The First Application of Clean Production has been in the Textile Industry:

- ✓ In 1997, “8 clean production auditors” from the Danish Technological Institute have consulted 6 pilot textile plants in 3 different regions in Türkiye
- ✓ A “Clean Production Manual” has been prepared
- ✓ Integration of these works with the world applications are being processed to form a wide database

The future plans for the Clean Production in Türkiye

1. Clean production policies should be taken as gov-

- ernment policies
2. Environment Law should be revised
 3. Clean Production Center should be organized
 4. Businessman should cooperate in these works
 5. Privatization should prefer clean technologies and replace the old
 6. Catalytic processes should play their part!

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