A Course in Environmentally Conscious Chemical Process Design

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Abstract: To uniquely equip students with the active knowledge and the ability to implement pollution prevention technology, we have developed a design-oriented senior-level elective course on minimizing the environmental impact of chemical manufacturing processes. The objectives of the course are to educate students on the real costs of operating processes that release pollutants to the environment, to provide them with strategies to minimize or reduce the environmental impact of a given chemical process, and to examine the design of processes using new technologies that totally eliminate pollutants at the source. Design-oriented projects form the core of the course, and bring together the students' skills in design, analysis and decision-making in the face of multiple and sometimes competing objectives. We believe this course contributes to the development of our graduates into chemical engineering professionals who are equipped with the awareness, knowledge, and ability to minimize the environmental impact of the chemical manufacturing processes that they oversee.

Keywords: Environmentally Conscious Design, Green Chemistry, Pollution Prevention, Education

1. Introduction

Knowledge of technologies and strategies for pollution prevention and the remediation of hazardous pollutants, as well as the environmental impact of pollutants that are released into the environment, is an increasingly important part of the average Chemical Engineer's job responsibilities. While integrating pollution prevention and waste minimization ideas and techniques throughout the Chemical Engineering curriculum is vital, we believe that a concentrated course will uniquely equip students with the active knowledge and the ability to implement pollution prevention technology. Thus, we have developed a design-oriented senior-level elective course on minimizing the environmental impact of chemical manufacturing processes.

The objectives of the course are 1) to educate students on the real costs of operating processes that release pollutants to the environment, 2) to provide them with strategies to minimize or reduce the environmental impact of a given chemical process, and 3) to examine the design of processes using new technologies that totally eliminate pollutants at the source.

To date, the new course has been taught at the University of Notre Dame three times, in Spring 1997, Spring 1998 and Fall 1999. In Spring 2000, a modified version of the course will be taught by colleagues at West Virginia University. At Notre Dame, class enrollment has ranged from seven to thirty three, depending on whether Juniors were allowed to enroll and in which semester the course was taught. With the two larger classes, the course was taught in a traditional lecture format, although significant discussion was encouraged. With the smallest class, the course was conducted in a pure discussion format. The students were given "preparation assignments" for each class, which usually consisted of reading material, working out a problem, or putting together a preliminary flowsheet for a process. That material was then discussed and elaborated upon in class. Some discussion of these two different course formats is given below.

2. Course Components

The course includes four major components. First, we provide an introduction to pollution prevention. This includes management and maintenance procedures, as well as simple process modifications that can prevent pollution, especially through the reduction of fugitive emissions. Second, we discuss pertinent environmental regulations that impact the design and operating costs of chemical processes. Third, we include a survey of new technology and current research efforts to develop alternative technologies that minimize waste or eliminate pollutants through, solvent substitution, the use of different raw materials and intermediates, and the development of more selective catalysts and reactor systems. The fourth and key part of the course involves the development and comparison of chemical process designs that juxtapose conventional chemical processes with new, environmentally benign technologies.

2.1 Introduction to Pollution Prevention

In order to provide a context for the process design studies, the course begins with an introduction to the idea of waste elimination or reduction, and how pollution prevention differs from remediation. This

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introduction includes a discussion of the waste management hierarchy, as set out by the Pollution Prevention Act of 1990, that identifies source reduction as the preferred method of waste management. The introduction also identifies the scientific bases for many of our most problematic environmental challenges, such as acid rain, ozone depletion, greenhouse gas formation and its potential link to global warming, and persistent environmental toxins. Since source reduction requires knowledge of the pollution that is currently being produced, some effort is spent on methods for conducting waste audits at a particular facility, as well as identifying useful information from national waste inventories, such as the Aerometric Information Retrieval System (AIRS), the Toxic Release Inventory (TRI) and the Biennial Report System (BRS). The AIRS database can be accessed from the EPA website at http://www.epa.gov/airs/airs.html, and gives emissions from industrial sites and results from monitoring stations, as well as attainment and non-attainment areas for the six criteria air pollutants. The TRI and BRS give information on toxics and hazardous wastes, respectively and can be searched by geographic area, facility, industry, or generated-received-transferred wastes. The TRI and BRS information is available on the Right-to-Know net, and can be accessed directly from the Right-to-Know website under databases (http://www.rtk.net). Life-cycle analysis (LCA) is discussed as a useful tool for evaluating processes and products. LCA brings out the challenge in identifying all direct and indirect sources of pollution from a process or product, as well as the difficulty in arriving at quantitative comparisons of the impact of different types of pollution (i.e., does a pound of styrene emitted into the atmosphere have more or less impact on the environment than if it is released to a river in a thousand gallons of wastewater?) In the context of chemical processing facilities, LCA demonstrates the dramatic effect that decommissioning and ultimate site cleanup and plant disposal can have on the overall process economics. LCA is complemented with a discussion of industrial ecology, where chemical processes can be integrated so that wastes or by-products from one process can be used as a feedstock for another process. An excellent source for this material is the book by Allen and Sinclair Rosselot (1997).

In the introductory material we present some of the simpler procedures and process modifications that can be made to prevent pollution. These include many of the "common sense" solutions, such as methods for reducing fugitive emissions and eliminating leaks. In addition, we focus on ways to reduce solvent use and solvent emissions, especially during cleaning operations. For instance, one can design piping systems to drain by gravity so less solvent is needed for flushing and cleaning. Each year, we have been able to draw several excellent real-world examples that fit into this category from the Governor's Awards for Excellence in Pollution Prevention (http://www.state.in.us/idem/index.html under awards) that are given out annually at the Indiana State Pollution Prevention Conference. Finally, we explore engineering modifications that can be accomplished to reduce wastes and by-product formation. These include tuning reactor temperatures and pressure to optimize selectivity, exploring combined reaction/separation schemes, using less purge gas, and improving separation units.

2.2 Environmental Regulations

The second section of the course focuses on the pertinent environmental regulations that impact the design and operating costs of chemical processes. Environmental regulations of particular interest include the Clean Air Act, the Clean Water Act, the Pollution Prevention Act, the Resource Conservation and Recovery Act, the Occupational Safety and Health Act, the Comprehensive Environmental Response, Compensation and Liability Act, the Emergency Planning and Community Right-to-Know Act, the Federal Insecticide, Fungicide and Rodenticide Act, and the Toxic Substances Control Act. These laws are the real impetus for the development of new technologies and waste management strategies, and it is important that chemical engineers know their legal responsibilities. A nicely condensed version of these laws is available from the National Pollution Prevention Center (Lynch, 1995). An excellent way to discuss these laws is through the development of various scenarios to augment some of the actual cases that are discussed in the publication from NPPC. For instance, if an engineer goes out to the plant and determines that a valve has accidentally been left open and 100 gallons of benzene have been released into the river, what must he/she do? What laws apply? A dozen or so well-crafted scenarios can hit most of the important points of the major federal laws listed above.

2.3 New Technology and Current Research

Since the passage of the Pollution Prevention Act in 1990 there has been a tremendous growth in the development of alternative technologies that minimize waste or eliminate pollutants. Students' familiarity with these new technologies and ongoing research efforts will be vital to their ability to implement process designs and modifications that prevent pollution. These alternative technologies generally fall into one of three categories: solvent substitution, the use of different (renewable or less toxic) raw materials and intermediates, and the development of more selective catalysts and reactor systems. Sources of this material include the literature, Green Chemistry and Engineering conferences, and guest lecturers.

In the area of solvent substitution, we have focused on aqueous-based solvents, liquid and supercritical CO_2, and room temperature ionic liquids. For instance, we discussed the potential use of aqueous surfactant solutions instead of chlorofluorocarbon solvents in the microelectronics industry (Beaudoin et al., 1995). Liquid and supercritical CO_2 has found numerous industrial applications. As explored in one of the design projects discussed below, it has been used for the decaffeination of coffee instead of methylene chloride or a combined hot water/methylene chloride system (McHugh and Krukonis, 1994). Also, CO_2 is used commercially for the dry-cleaning of clothes (http://www.globaltechno.com and http://www.micell.com), where it replaces perchloroethylene, and for spray-painting (the UNICARB process (Brennecke, 1996)), where it replaces chlorofluorocarbon or flammable gas (propane or butane) propellants. Although not commercially attractive, supercritical CO_2 can be used to extract soybean oil from soybeans (List et al., 1989), where it would replace hexane, which is extremely volatile and, subsequently, highly flammable. This project is also explored in more detail as one of the case studies. Room temperature ionic liquids, such as 1-butyl-3-methyl imidizolium hexafluorophosphate, are organic salts that in their pure state (i.e., not dissolved in water) are relatively low viscosity liquids at temperatures around ambient. They are being explored as potential environmentally benign solvents for reactions and separations because they have negligible vapor pressures. Most normal solvents are quite volatile, and this volatility is frequently the source of their negative environmental impact through evaporation and atmospheric emission. Room temperature ionic liquids may represent a whole new class of industrial solvents (Welton, 1999; Blanchard et al., 1999).

An exciting area of new chemistry that uses renewable raw materials is biocatalysis. Starting with biomass instead of petroleum products, it is now possible to use natural and/or engineered biocatalysts to facilitate a variety of transformations. For instance, there are new chemical routes to adipic acid, catechol and hydroquinone that use glucose instead of benzene as a starting material (Draths and Frost, 1990; 1994a; 1994b). In making adipic acid (one of the two major components in Nylon 6,6) from glucose, one not only uses a renewable raw material, but it totally eliminates the use of benzene, which is a carcinogen, and the emission of N_2O. Biocatalysis can also be used to produce calcium magnesium acetate, a biodegradable road salt that has less environmental impact, much more economically than the normal synthetic route (Mathews, 1999). This process uses lactose, which is a waste in the whey from cheese production, as its starting material.

Other new synthetic chemistries focus on the elimination of toxic raw materials or intermediates. A dramatic example is the generation of urethanes from amines and carbon dioxide instead of from the highly toxic phosgene (Riley et al., 1994). In addition, in this new process, developed by Monsanto, it is no longer necessary to proceed through isocyanate intermediates (recall the devastating effects of the accidental release of methyl isocyanate in Bhopal, India). Another intriguing new chemistry is the production of *p*-nitroaniline without the use of chlorine (which is normally needed as a para-director) and, subsequently, without the production of the intermediate chlorobenzene (Stern et al., 1992; Stern and Cheng, 1993; Stern, 1994). This new process, developed by Monsanto, is explored as one of the design case studies discussed below.

The development of more selective catalysts and reactor systems focuses on the elimination of by-product formation. For instance, it has been shown that for supported catalysts, the optimal radial distribution of the catalyst in the pellet is a Dirac delta function, with its specific radial position determined by the details of the reaction system (Gavriilidis et al., 1993). Also, we discuss the benefits of various types of catalytic membrane reactions (Pena et al., 1998). Finally, we present new research on the effect of mass transfer on the selectivity of catalytic reactions in packed bed reactors (Wu et al., 1995).

Another important area of current research that is covered in the course are the advances in process optimization and process integration for pollution prevention. In particular, we discuss, as an example of such approaches, the use of integrated mass exchange networks for waste and process streams. This approach is covered peripherally in Allen and Sinclair Rosselot (1997) and more extensively, along with an introduction to other related topics in pollution prevention, in El-Halwagi (1997).

2.4 Projects

Examination of a series of case studies that compare designs of conventional chemical processes to those using new, environmentally benign, technologies is the real core of this course, and gives the students the opportunity to examine and optimize processes side-by-side to compare old technology to new, more environmentally friendly, technologies. The three case studies, which we have developed as ASPEN PLUS simulation modules with costing and economic evaluation, give the students the opportunity to develop preliminary designs, as well as improve the processes and perform a variety of "what if" studies that attempt to project the viability of the conventional technology into the future. They learn how preliminary designs can

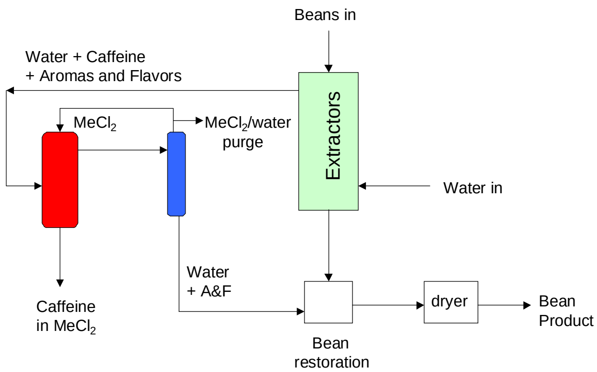

Figure 1. Conventional water/$MeCl_2$ process for decaffeination of coffee beans.

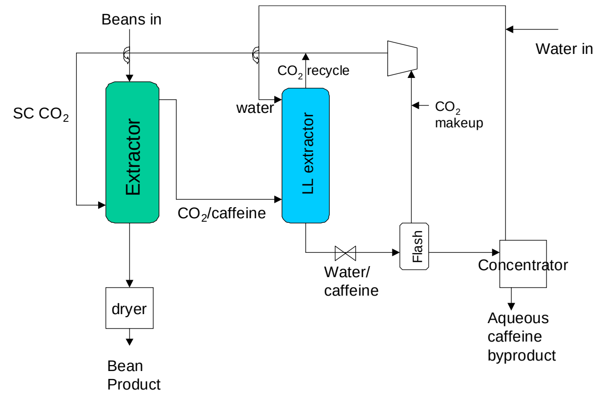

Figure 2. Decaffeination of coffee beans using supercritical CO_2.

be used to estimate the potential economic attractiveness of the new technology. They are also encouraged to address ethical issues surrounding the value of an inherently safer process that has less impact on the environment. As mentioned above, two of the designs use supercritical CO_2 as an environmentally benign replacement solvent for extractions and the third project looks at a new process for the production of *p*-nitroaniline.

The first case study explores the decaffeination of coffee with CO_2 instead of via the "water process." The advantage of the CO_2 process is that CO_2 selectively removes the caffeine from the raw coffee beans. There are now several commercial plants using supercritical CO_2 for tea and coffee decaffeination worldwide (McHugh and Krukonis, 1994). Rough schematics of the two processes are shown in Figures 1 and 2. The conventional process uses hot water to extract the caffeine from the beans. Unfortunately, the solubility of caffeine in water is relatively low and the extraction is not selective; i.e., the desired aromas and flavors are removed as well. Subsequently, methylene chloride is required to selectively remove the caffeine from the entire extract, so that the aromas and flavors can be added back to reconstitute the beans. Unfortunately, there is some contamination of the aqueous aromas and flavors stream with methylene chloride. Since methylene chloride addition to the beans is unacceptable, this requires additional separation stages and results in an aqueous methylene chloride purge stream. The CO_2 process requires extraction with supercritical CO_2 at high pressures, on the order of 350 bar. Fortunately, the extraction is extremely selective, leaving the aromas and flavors with the beans. One way of separating the caffeine from the CO_2 would be depressurization to conditions where the caffeine is no longer soluble. However, recompression of the CO_2 would be quite expensive. Alternatively, the caffeine can be washed out of the CO_2 with water at high pressure, so that the CO_2 can be recycled without recompression. Thus, this is an excellent example where the new, environmentally friendly, technology is economically attractive only when clever design strategies are implemented. A small amount of CO_2 comes out of the water after it is depressurized and this can be recompressed for reuse; however, the vast majority of the recycled CO_2 remains at high pressure.

The comparative design projects are generally given in two stages. First, the students are asked to develop rough process designs for the two processes based on literature provided to them and some discussion in class. They can then compare their process concepts to the full ASPEN PLUS designs that we have developed for the two processes. In the second part of the assignment, we ask the students to compare and evaluate the alternative processes in order to make an assessment of the two technologies and formulate a recommendation on which design should be pursued. Since ASPEN PLUS economic evaluation does not currently take environmental impact into account, the students are asked to identify all waste streams and potential sources of emissions in order to determine which streams would require permits and reporting on the TRI or BRS. One way they quantify the cost of environmental impact is by determining the sensitivity of the process profitability on waste disposal costs and the cost of purchasing hazardous raw materials and solvents (i.e., the methylene chloride for the conventional decaffeination process). They are asked to look for ways to make both processes more attractive (from both profitability and environmental standpoints) and asked to look at the influence of process production rate. The coffee decaffeination process in one in which the new technology is more cost effective than the conventional process. For the base cases used in the

ASPEN PLUS designs the return on investment (ROI) is 9.3% for the conventional process and 16.7% for the CO_2 process.

The second case study looks at soybean oil extraction with CO_2 and is based on the work of King and coworkers (List et al., 1989). This process would replace hexane extraction, which poses both environmental and safety concerns. Unfortunately, extremely high pressures (on the order of 700 bar) are required to achieve reasonably high oil solubilities in the CO_2. Since soybean oil is a relatively low value product, the economics for the new technology are not favorable. A significant difference between this example and the coffee decaffeination is that in coffee decaffeination the dilute extracted compound is not the product, although the caffeine can be sold. Rather, it is what remains, the decaffeinated beans, that are the major product. For a supercritical extraction process, in which the product is the dilute extract, to be economically attractive, usually requires a high-value product.

The third case study exploits some new chemistry developed by researchers at Monsanto (Stern et al., 1992; Stern and Cheng, 1993; Stern, 1994). By using nucleophilic aromatic substitution for hydrogen, they are able to eliminate the need for chlorine to activate benzene. For example, they are able to produce *p*-nitroaniline without proceeding through chlorobenzene, which is the standard technology. In fact, the conventional technology requires three separate steps: chlorination, nitration and ammonolysis. This process produces numerous brine waste streams and by-products, and requires multiple energy-intensive distillation column trains. This third case study compares the processes using the old and new chemistries.

These three comparative case studies are among a larger number of environmentally-related chemical process design projects that we have developed in collaboration with Professors Joseph Shaeiwitz and Richard Turton at West Virginia University as part of a larger NSF-funded program on Minimizing the Environmental Impact of Chemical Manufacturing Processes.

3. Discussion

The major outcome of this course appears to be a dramatic increase in the students' knowledge of environmental regulations, as well as pollution prevention concepts and technologies. This is supported by the results of a questionnaire given to the students at the beginning and the end of the course. Several questions on the assessment designed to probe student attitudes do not indicate any systematic changes. A more substantial discussion of these assessment results can be found elsewhere (Brennecke et al., 2000). Informal conversations with students indicate that both before and after the course they had an understanding that industrial activity does have an impact on the environment. However, after the course they indicate that they have a much greater appreciation of how much can be done to reduce pollution, from simple "common sense" measures, to process modifications and the implementation of entirely new process technologies.

The comparative process designs are an excellent tool to expose the students to new technologies, as well as involve them in the design decision-making process. In addition, many students indicated that seeing full process designs, changing process variables, examining the economic impact of various waste streams, and seeking improvements to the designs substantially improved their understanding and performance in their regular capstone chemical process design course. However, we found that within a normal semester it was really only possible to adequately explore two of the three (e.g., coffee decaffeination and *p*-nitroaniline production) comparative case studies in sufficient detail.

Finally, it should be noted that the discussion format used when the class enrollment was small was highly successful. The regular "preparation assignments" required significant out-of-class time commitment from the students but the rewards in the richness of the in-class discussion were substantial. Every student contributed in each class with questions and comments. It was clear that students were making connections between current topics and topics previously discussed or covered in other chemical engineering courses. This included most of the basic chemical engineering core courses, such as mass and energy balances, phase equilibria, mass transfer and reaction engineering. It seemed particularly rewarding to the students when they realized that a practical curiosity-driven question (e.g., does the local newspaper report that the PCBs in Lake Michigan are polluting the atmosphere and causing a significant health risk to residents of the state of Michigan make sense?) required them to draw on both their thermodynamics and transport know-how. The students were encouraged to stay abreast of current environmental issues (by a semester-long assignment to keep a scrapbook of environmental articles from scientific and popular publications) and to bring them to class for discussion. When covering environmental laws, the students developed the interesting scenarios to be analyzed. The students especially appreciated discussing real-world pollution prevention examples and opportunities that they shared with each other from their summer employment and plant-trip experiences. In addition, we found that this course is particularly well-suited to a discussion format due to the many ethical, social, political and psychological ramifications of implementing pollution prevention technologies.

4. Concluding Remarks

This course provides practical information, as well as exposure to the strategies of process systems analysis and the new technologies that are currently being developed for pollution prevention. With this course, the goal is for our graduates to become chemical engineering professionals who are equipped with the awareness, knowledge, and ability to minimize the environmental impact of the chemical manufacturing processes that they oversee.

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