# A Course in Environmentally Conscious Chemical Process Engineering

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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.

# 1. Introduction

According to Anastas (1994) the chemical industry is the major source of toxic pollutant release in the United States. Today, efforts to address this are shifting dramatically from the remediation of pollutants to the prevention of pollution in the first place (that is, to be *benign by design*). To a large extent, this trend has been driven by the recognition that, in the long run, prevention is economically more attractive than remediation. Thus, knowledge of technologies and strategies for pollution prevention, 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. This means considering not just waste treatment costs, but also the costs of dealing with regulations, with the community, with potential future liabilities, etc. 2. To provide students with an awareness of strategies for minimizing or reducing the environmental impact of a given chemical process. 3. To give students the opportunity to work on 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. Also, in Spring 2000, a modified version of the course was taught by Professor J. A. Shaeiwitz 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. Our course is

certainly not the only new course dealing with pollution prevention. Various such courses (e.g. Abraham, 2000) have been started in other chemical engineering curricula. However, we believe that, by covering the four components discussed above, the course described here provides a particularly well-balanced treatment of environmentally-conscious chemical engineering, and one that benefits from a strong orientation towards process systems analysis.

## 2.1  Introduction to Pollution Prevention

This first component of the course includes material on basic topics of importance in pollution prevention, and provides a good context for the subsequent process design studies. An excellent source for some of this material is the book by Allen and Sinclair Rosselot (1997). This section of our course includes the following activities:

1.  An introduction is provided to the idea of waste elimination or reduction, and how pollution prevention differs from remediation. This includes a discussion of the waste management hierarchy, as set out by the U.S. Pollution Prevention Act of 1990, that identifies source reduction as the preferred method of waste management.

2.  A discussion is conducted identifying 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.

3.  Since source reduction requires knowledge of the pollution that is currently being produced, some effort is spent discussing 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 (particulates, sulfur dioxide, nitrogen oxides, carbon monoxide, ozone and lead). 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).

4. 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.

5. LCA is complemented with a discussion of industrial ecology. Here a systems approach is introduced focusing on integration of chemical processes, on integration within an industrial sector (e.g., the chemical process industries), or on integration across different industrial sectors. A key idea is that integration can occur when wastes or byproducts from one process or industrial sector can be used as feedstocks in other processes or sectors. In the context of the chemical process industries, a good framework for this discussion is provided by the work of Rudd and coworkers (e.g., Rudd et al., 1981; Stadtherr and Rudd, 1976, 1978; Stadtherr, 1978).

6.    We present some of the simpler "common sense" procedures that can be used to prevent pollution.  These include methods for reducing fugitive emissions and eliminating leaks, and methods for reducing 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.  Another example is the dramatic reduction in styrene and other VOC emissions one can achieve simply by using physical barriers at the edges of fiberglass part forms or around parts to be spray painted.  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.  One recent example is a successful emissions reduction effort based on aggressive use of monitors and alarms to detect small leaks.  Another cited a product design change to mechanical fasteners instead of glued parts that totally eliminated the VOC emissions associated with the glue.  The project on the aggressive use of monitors and alarms is also an excellent example with which to discuss the "human" component of pollution prevention—that it is ultimately the conscientiousness and enthusiasm of numerous *individuals* that determines whether "common sense" pollution prevention is implemented on a day-to-day basis.  In presenting their emission reductions, the company emphasized the "team" approach that they took, assembling groups of operators and mechanics, as well as technicians and engineers, to solicit ideas on how to decrease dichloromethane losses at the plant.  They believed that by involving the individuals who would be responding to the alarms and fixing the leaks in the project development, their ultimate success rate was dramatically improved.

7. Finally, we explore engineering modifications that can be accomplished to reduce wastes and byproduct 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 in the United States 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. Not only is knowledge of these laws important from a legal standpoint, since it is important that chemical engineers know their responsibilities under the law, but it is important since these laws contribute to the impetus for the development of new technologies and waste management strategies. 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. Students were quite adept and enthusiastic about creating some of these scenarios themselves.

## 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 discuss the potential use of aqueous surfactant solutions instead of chlorofluorocarbon solvents in the microelectronics industry (Beaudoin et al., 1995). Liquid and supercritical $CO_2$ have 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-*n*-butyl-3-methyl imidazolium 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). Particular emphasis is given to evaluating different ways that one might recover reaction products from ionic liquids, in the absence of much literature data on the thermodynamics and phase behavior of these systems. Given the expense of laboratory work, what data would be absolutely essential to the preliminary design of a process using ionic liquids?

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 byproduct 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 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. Additional detail about each project is provided below.

## 2.5 Course Syllabus

A sample course syllabus is shown in Table 1. Here the topics are numbered to correspond to the four major course components discussed above. The approximate number of class periods devoted to each topic is shown. These are 50-minute periods; additional class periods for exams and review sessions are not listed. The topics need not be covered in the exact order listed. For example, we generally cover the topics in the order: 1.1-1.2, 2.0, 1.3-1.7, 3.1-3.4. The case studies were assigned throughout the semester, allowing approximately one

month for each.  Two class periods were devoted to each case study, usually one when the project was assigned and another at the end to discuss the results.  In addition to the assignments noted in Table 1, a sample of other assignments used can be found on the assignments page (http://www.nd.edu/~enviro/homeworks.html) of the course web site.  Some assignments are also drawn from the text of Allen and Sinclair Rosselot (1997).  Only the primary reading assignments are shown in Table 1, with other supplemental reading given in the citations above.

## 3.  Design Projects

### 3.1  Decaffeination of Coffee

The first case study explores the decaffeination of coffee with $CO_2$ instead of via the methylene-chloride-based "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 Figs. 1 and 2.

The conventional process (Fig. 1) 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 still required to selectively remove the caffeine from the entire extract, so that the aromas and flavors can be added back to reconstitute the beans.  However, 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.  It is interesting to note that this "water process" was developed as a way to eliminate the need for direct contact between the

beans and the methylene chloride solvent, which was the basis of earlier decaffeination processes.

The $CO_2$ process (Fig. 2) 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 simulations 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 is 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.

## 3.2 Extraction of Soybean Oil

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 concerns due to VOC emissions and safety concerns due to the flammability of the solvent (hexane explosions in soybean oil extraction plants are a known hazard). Rough process diagrams for the two alternatives are given in Figs. 3 and 4.

In the conventional process (Fig. 3) hexane is used to extract the soybean oil. One difficulty is the hexane solvent is not particularly selective. Thus, several downstream refining steps are needed to purify the oil. One such step, the degummer, which is needed to remove the phospholipids, is shown in Fig. 3. Another final refining step, not shown, involves contact with diatomaceous earth, to remove dark colored components in the extracted oil. A further difficulty is that it is hard to get all of the hexane out of the oil. In fact, some hexane ends up in the residual diatomaceous earth from the final refining step, leading to fires in the waste diatomaceous earth, which is commonly landfilled since it is considered a non-hazardous waste.

The $CO_2$ process (Fig. 4) is straightforward, and $CO_2$ is a somewhat poorer solvent, extracting mainly the desired oil and essentially none of the dark-colored higher molecular

weight species nor the phospholipids. Thus, the number of downstream refining steps is greatly reduced. 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 (e.g., a nutraceutical like saw palmetto).

In working with this project, students are able to make the economic comparisons for themselves. They can also explore scenarios under which the $CO_2$ process might become economically attractive. For instance, what if a premium had to be paid for the use of hexane because of increased concern about liability issues arising from explosions and fires? Or, what if an improved scheme for recompressing the $CO_2$ were tried?

## 3.3 Production of *p*-Nitroaniline

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 this way, the need to use chlorine, and to deal with often hazardous chlorinated intermediates, byproducts and wastes is completely eliminated.

In the conventional chemistry (Fig. 5) for production of *p*-nitroaniline, the first step is the chlorination of benzene to monochlorobenzene (MCB). This is not completely selective and

some dichlorobenzene is produced as well. The MCB is then separated and undergoes a nitration step to chloronitrobezene (CNB). The presence of the chlorine atom tends to force the nitrate group into the *para* position; thus chlorine acts as a *para*-director. However, this is not entirely effective, and a ratio of *p*-CNB to *o*-CNB of about 2 to 1 is all that is achieved. Finally, after separation of the *p*-CNB, it undergoes an ammonolysis reaction to yield *p*-nitroaniline (*p*-NA). A rough process schematic for this technology is shown in Fig. 6. The process produces numerous chlorinated waste streams and by-products, and requires multiple energy-intensive distillation column trains. This is a good example of a technology that exhibits bad atom economy. That is, it relies on introducing an atom (chlorine) which is not part of the desired product, and as a result there are waste streams containing that atom.

In the new chemistry (Fig. 7), nitrobenzene (NB) and benzamide (BA) undergo a multistep reaction process, using the stoichiometrically regenerated reagent tetramethylammonium hydroxide dihydrate (TMAOH), to produce the intermediate N-(4-nitrophenyl)-benzamide (NPB). After separation, this intermediate is reacted with ammonia (using a methanol solvent) to yield the *p*-nitroaniline product and regenerate the benzamide feedstock. This is completely selective is producing the *para* isomer. A rough process diagram for this new technology is given in Fig. 8. Though not shown, benzene is still the raw material, and must be nitrated, which will generate waste; however, this process now involves no chlorinated waste, eliminates the production of the toxic chlorobenzene intermediate, and exhibits much improved atom economy in comparison to the conventional technology.

As in the other two projects, students can again study the comparative economics of the two alternatives and consider a variety of scenarios. In this case, the economics of the new

technology are relatively favorable. In fact, this same type of chemistry is now used commercially on a large scale to make a similar product.

## 4. Discussion

### 4.1 Teaching Experience and Assessment

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. 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 equilibrium, 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.

## 4.2 Related Work

The development of the course described here represents just one part of a larger project on Minimizing the Environmental Impact of Chemical Manufacturing Processes, which was

funded by the National Science Foundation under the Combined Research Curriculum Development Program, and was conducted at the University of Notre Dame (Professors J. F. Brennecke, M. A. Stadtherr, M. J. McCready and R. A. Schmitz), West Virginia University (Professors J. A. Shaeiwitz and R. Turton) and the University of Nevada, Reno (Professor W. B. Whiting). The three comparative case studies described above are among a larger number of environmentally-related chemical process design projects that we have developed in connection with this larger project. A list of these comparative case studies, as well as some of the other design projects can be found in Table 2. Additional details about these projects can be found at the project web site: http://www.nd.edu/~enviro. Also available at this web site is further information about the new course described here, as well as information about another new course (Ecology and the Environment) on ecological modeling developed by Professor R. A. Schmitz, and various other course materials, including lecture modules and problem assignments, for introducing environmentally-related materials into the core chemical engineering curriculum.

## 5. 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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List of Figure Captions

Figure 1.  Conventional "water process" for decaffeination of coffee beans.

Figure 2.  Decaffeination of coffee beans using supercritical $CO_2$.

Figure 3.  Conventional process for soybean oil extraction using hexane.

Figure 4.  Process for the extraction of soybean oil using supercritical $CO_2$.

Figure 5.  Chemistry for production of *p*-nitroaniline using the conventional technology.

Figure 6.  Conventional process for the production of *p*-nitroaniline.  The process chemistry is shown in Fig. 5.

Figure 7.  Chemistry for production of *p*-nitroaniline using the new technology.

Figure 8.  New process for the production of *p*-nitroaniline that uses nucleophilic aromatic substitution and eliminates chlorobenzene as an intermediate.  The process chemistry is shown in Fig. 7.

**Table 1.  Sample Course Syllabus.**

| Topic | Number of Class Periods | Reading and Assignments[*] |
|---|---|---|
| 1.1  Introduction | 1 | Chapter 1, Allen and Sinclair Rosselot, 1997 |
| 1.2  Current Environmental Challenges | 2 | Search of popular and technical publications; Assembly of "scrapbook" throughout semester |
| 1.3  Waste Inventories | 3 | Chapter 2, Allen and Sinclair Rosselot, 1997; Use of AIRS, TRI and BRS databases (see text) |
| 1.4  Life Cycle Analysis | 2 | Chapter 4, Allen and Sinclair Rosselot, 1997 |
| 1.5  Industrial Ecology | 2 | Chapter 3, Allen and Sinclair Rosselot, 1997 |
| 1.6  Common Sense Pollution Prevention | 3 | Chapters 5-7, Allen and Sinclair Rosselot, 1997 |
| 1.7  Engineering Modifications | 3 | Chapters 6-7, Allen and Sinclair Rosselot, 1997 |
| 2.0  Environmental Regulations | 4 | Lynch, 1995 |
| 3.1  New Technology – Solvent Substitution | 3 | McHugh and Krukonis, 1994; Beaudoin et al., 1995; Brennecke, 1996; List et al., 1989; Seddon, 1996; Blanchard et al., 1999 |
| 3.2  New Technology – Renewable/Less Toxic Raw Materials and Intermediates | 3 | Draths and Frost, 1990; 1994a,b; Mathews, 1999; Riley et al., 1994; Stern et al., 1992; Stern and Cheng, 1993; Stern, 1994 |
| 3.3  New Technology – More Selective Catalysts and Reactor Systems | 2 | Gavriilidis et al., 1993; Pena et al., 1998; Wu et al., 1995 |
| 3.4  New Technology – Process Integration | 2 | Chapter 8, Allen and Sinclair Rosselot, 1997; El-Halwagi, 1997 |
| 4.1  Case Study – Decaffeination of Coffee | 2 | McHugh and Krukonis, 1994 |
| 4.2  Case Study – Extraction of Soybean Oil | 2 | List et al., 1989 |
| 4.3  Case Study – Production of p-Nitroaniline | 2 | Stern et al., 1992; Stern and Cheng, 1993; Stern, 1994 |

[*]Supplemental reading materials are cited, and additional assignments are discussed, in the text.

**Table 2.  Summary of Design Projects Illustrating the Minimization of the Environmental Impact of Chemical Manufacturing Processes**

| Project | Type | Comments | Contact |
|---|---|---|---|
| Extraction of gingerol from ginger root using supercritical carbon dioxide | Solvent substitution | Batch extraction from ginger root, mass transfer modeling is key to extractor design to obtain contact times | Shaeiwitz |
| Decaffeination of coffee using supercritical carbon dioxide | Solvent substitution | Two processes, WVU:  mass transfer modeling for extraction of caffeine followed by reverse osmosis to concentrate caffeine, ND: comparison of supercritical and conventional processes, nitrogen stripping to concentrate caffeine | Shaeiwitz or Stadtherr |
| Soybean oil extraction using supercritical carbon dioxide | Solvent substitution | Comparison of conventional and new processes | Brennecke |
| Removal of phenol from waste water stream using supercritical carbon dioxide | Waste stream treatment | Extraction of phenol from water followed by phenol recovery and carbon dioxide recycle | Shaeiwitz |
| Removal of phenol from waste water stream using supercritical water oxidation | Waste stream treatment | Phenol destroyed by oxidation in supercritical water as solvent | Stadtherr |
| Concentration of ethanol using supercritical carbon dioxide | Alternative, less energy-intensive process | Alternative to distillation, reduced energy costs so less fossil fuel use | Brennecke |
| Production of refrigerant R-134a | Environmentally-friendly replacement chemical | This is one of the processes currently used to manufacture the new refrigerant | Shaeiwitz |
| New route for production of *p*-nitroaniline | Alternative reaction path | Eliminates need for chlorine and chlorinated organics | Brennecke |
| Production of dimethyl carbonate | Alternative reaction path | DMC is a potential oxygenated fuel additive, it can also replace phosgene as raw material, alternative reaction path does not use phosgene as raw material for DMC | Shaeiwitz |
| Production of polyurethanes from dimethyl carbonate | Alternative reaction path | Phosgene replaced as raw material | Shaeiwitz |
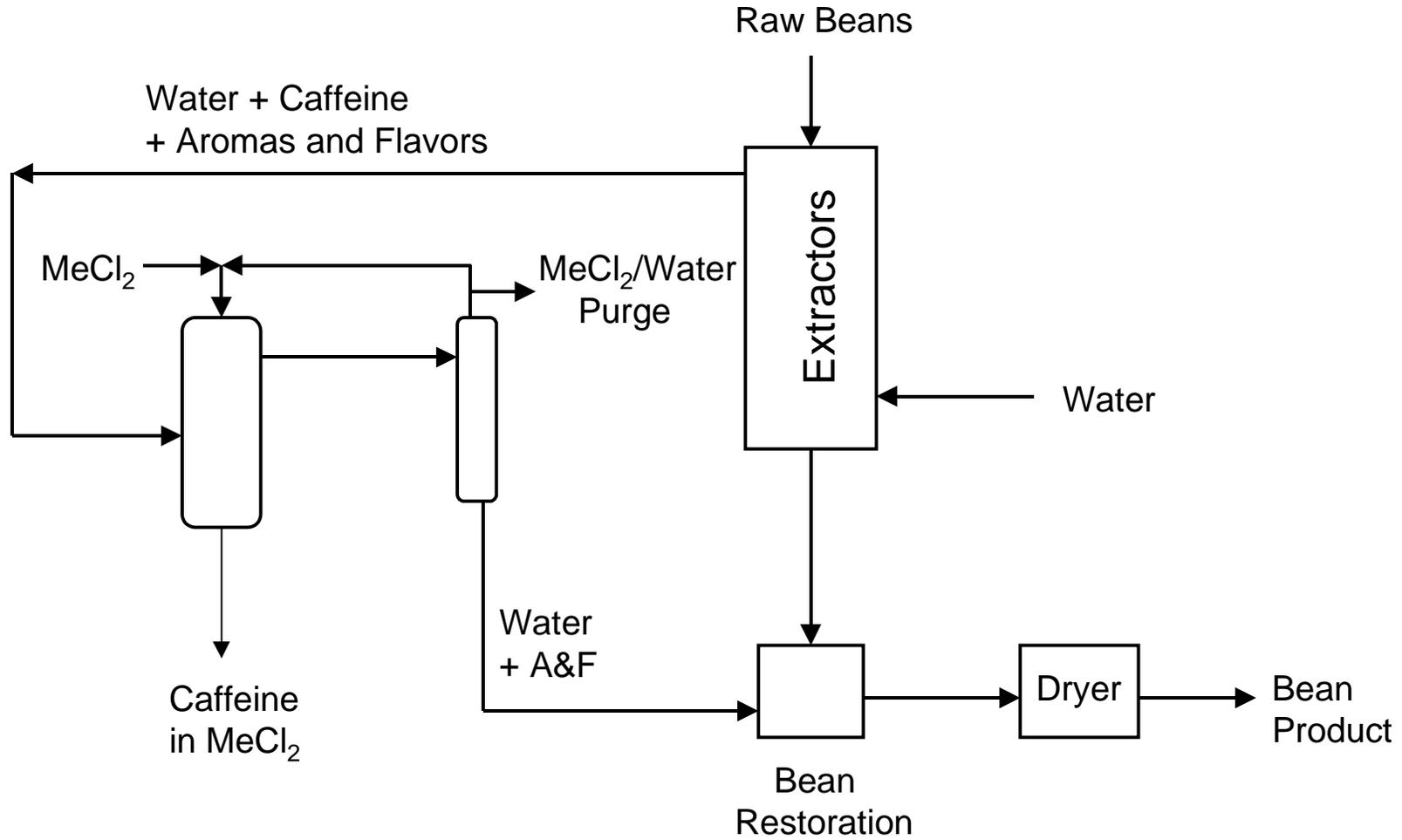
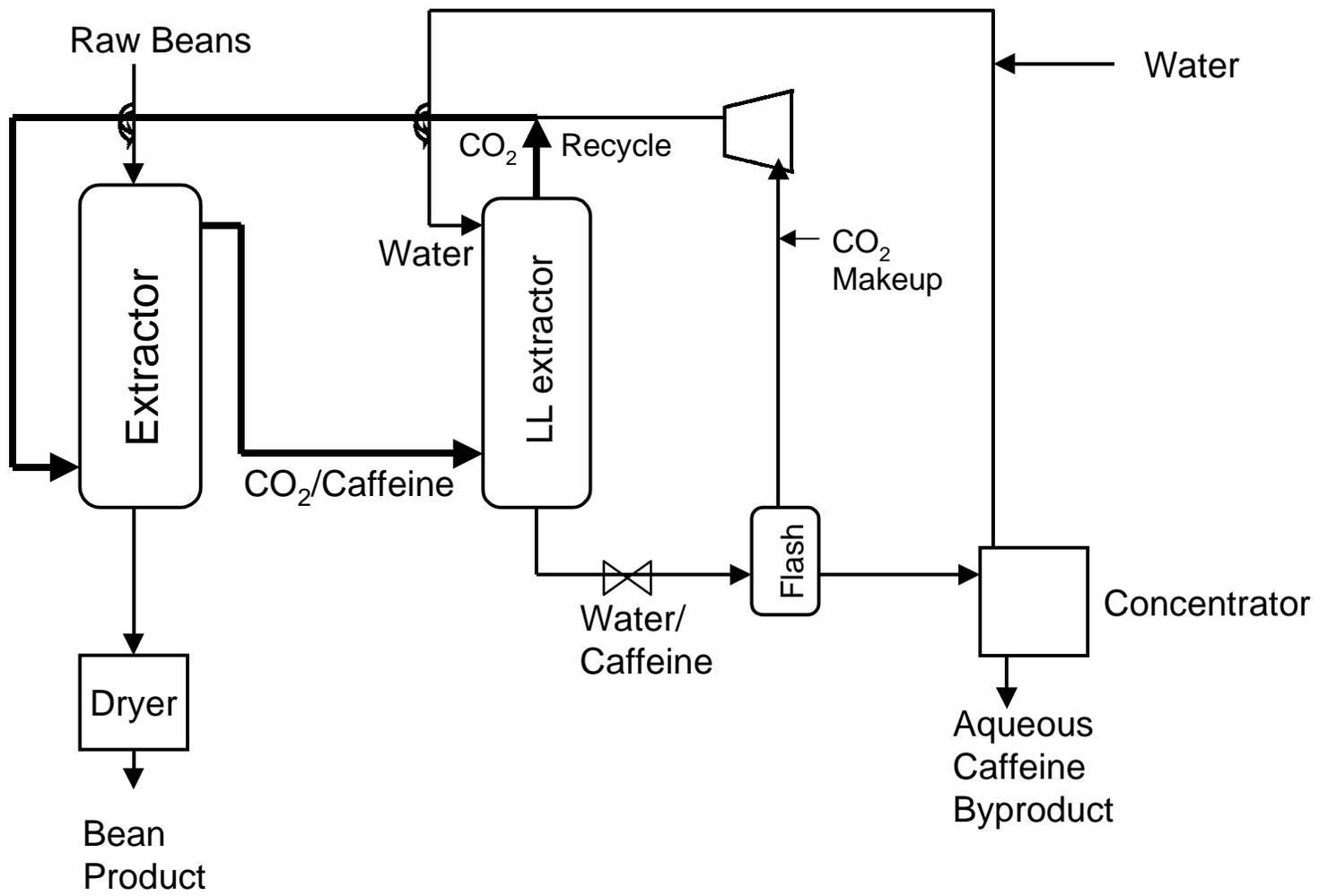Figure 1. Conventional "water process" for decaffeination of coffee beans.

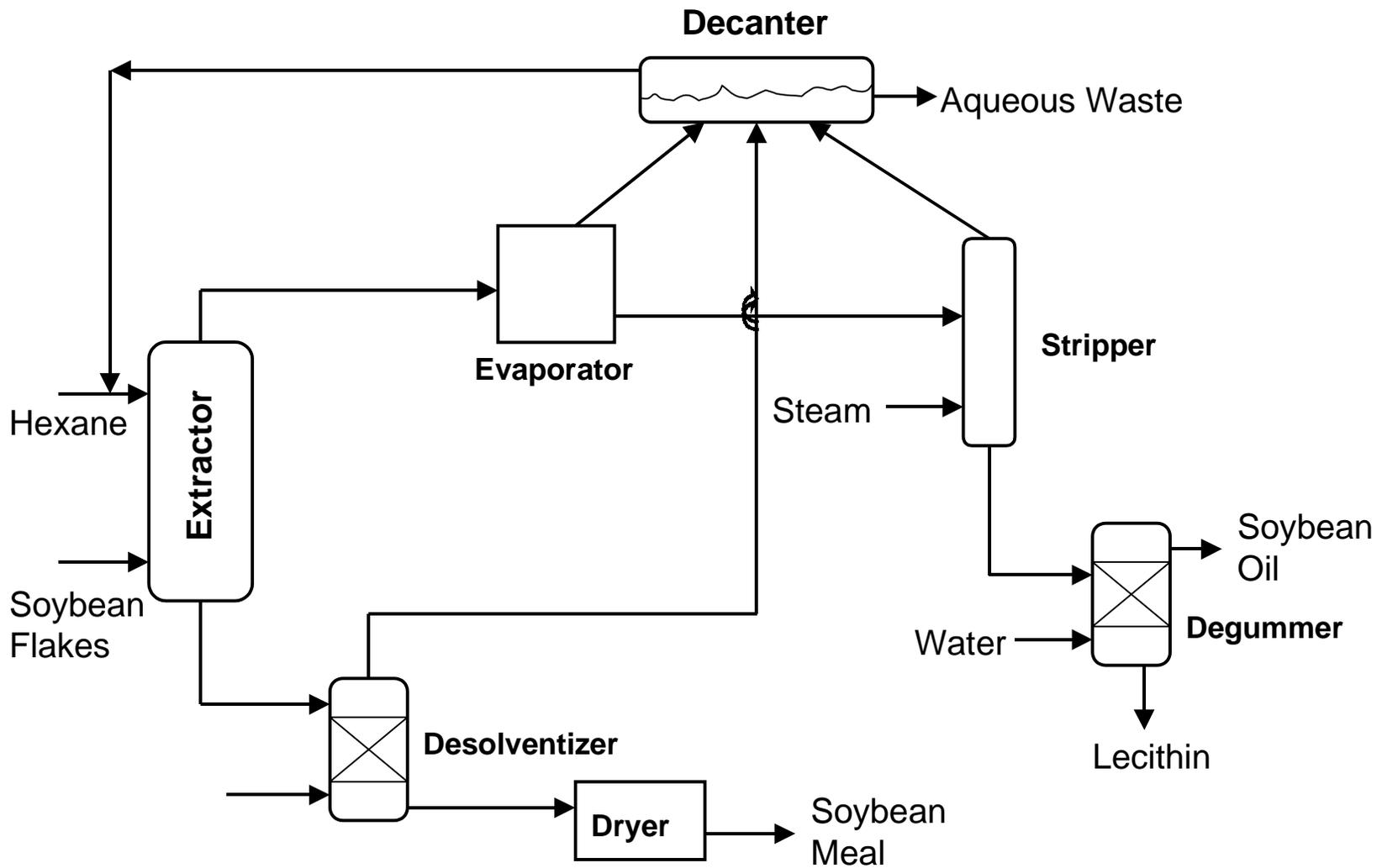Figure 2.  Decaffeination of coffee beans using supercritical $CO_2$.

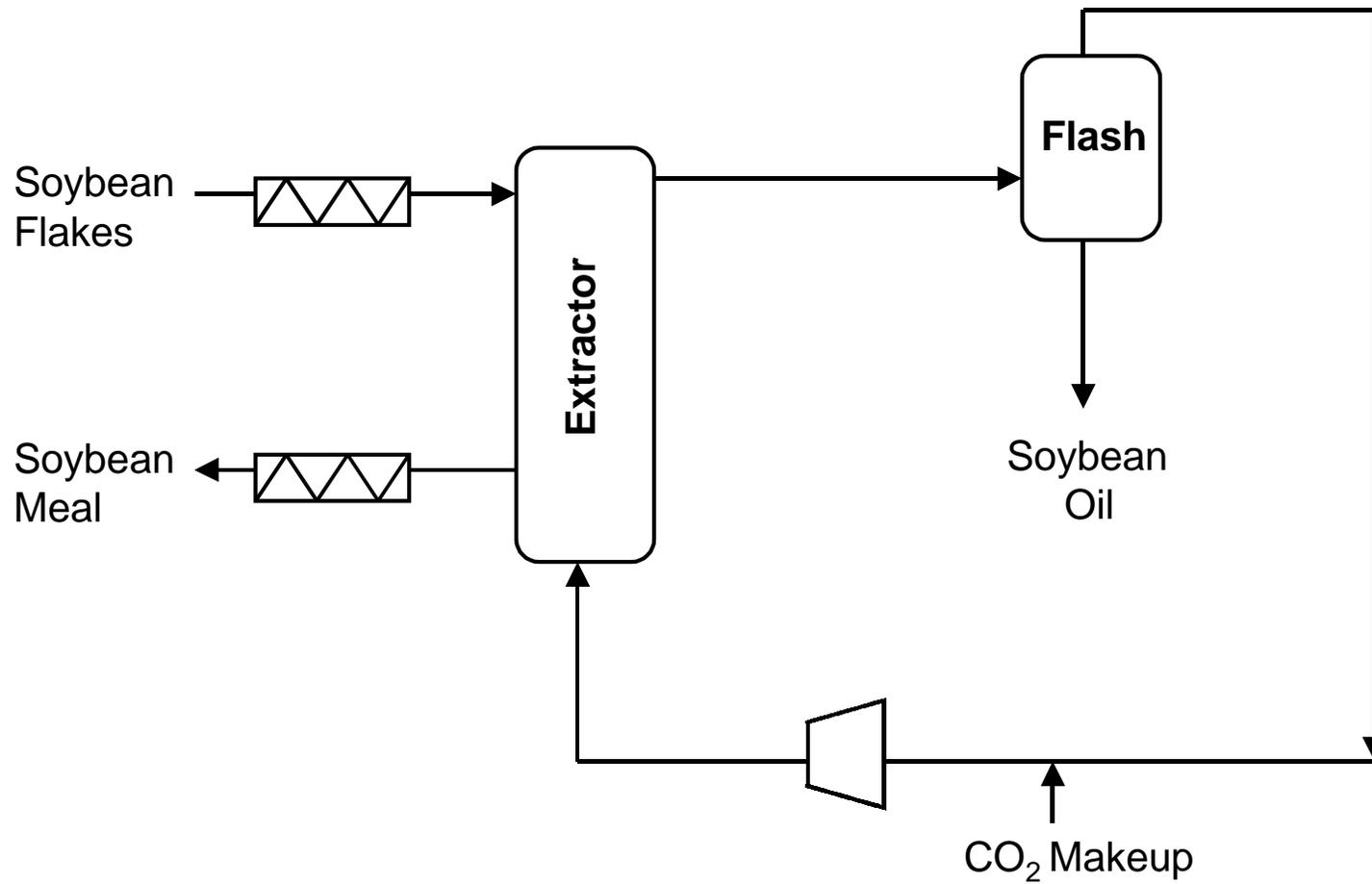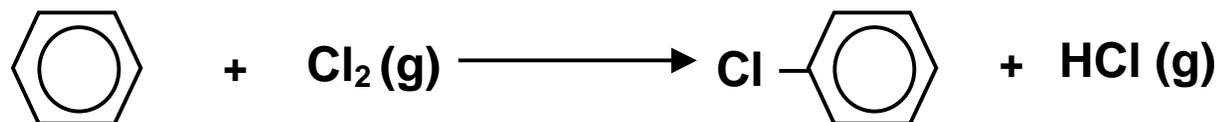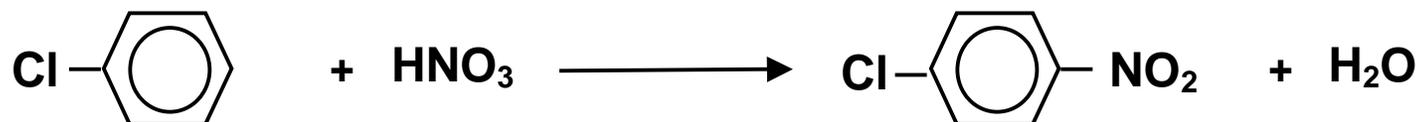Figure 3. Conventional process for soybean oil extraction using hexane.

Figure 4.  Process for the extraction of soybean oil using supercritical $CO_2$.

## 1. Chlorination of benzene



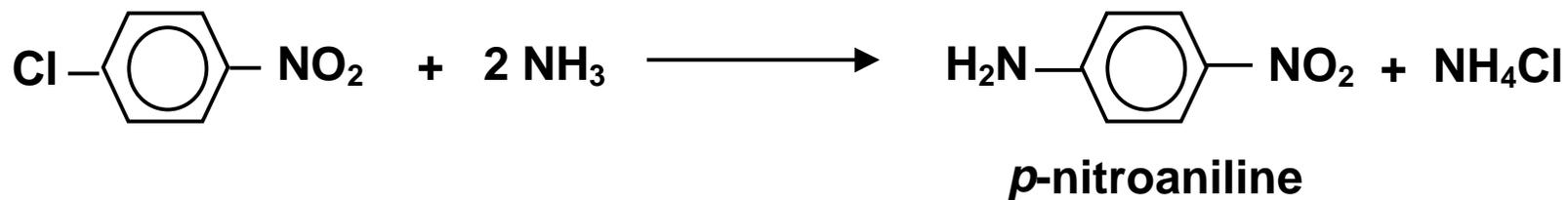## 2. Nitration of chlorobenzene



## 3. Ammonolysis of *p*-chloronitrobenzene



*p*-nitroaniline

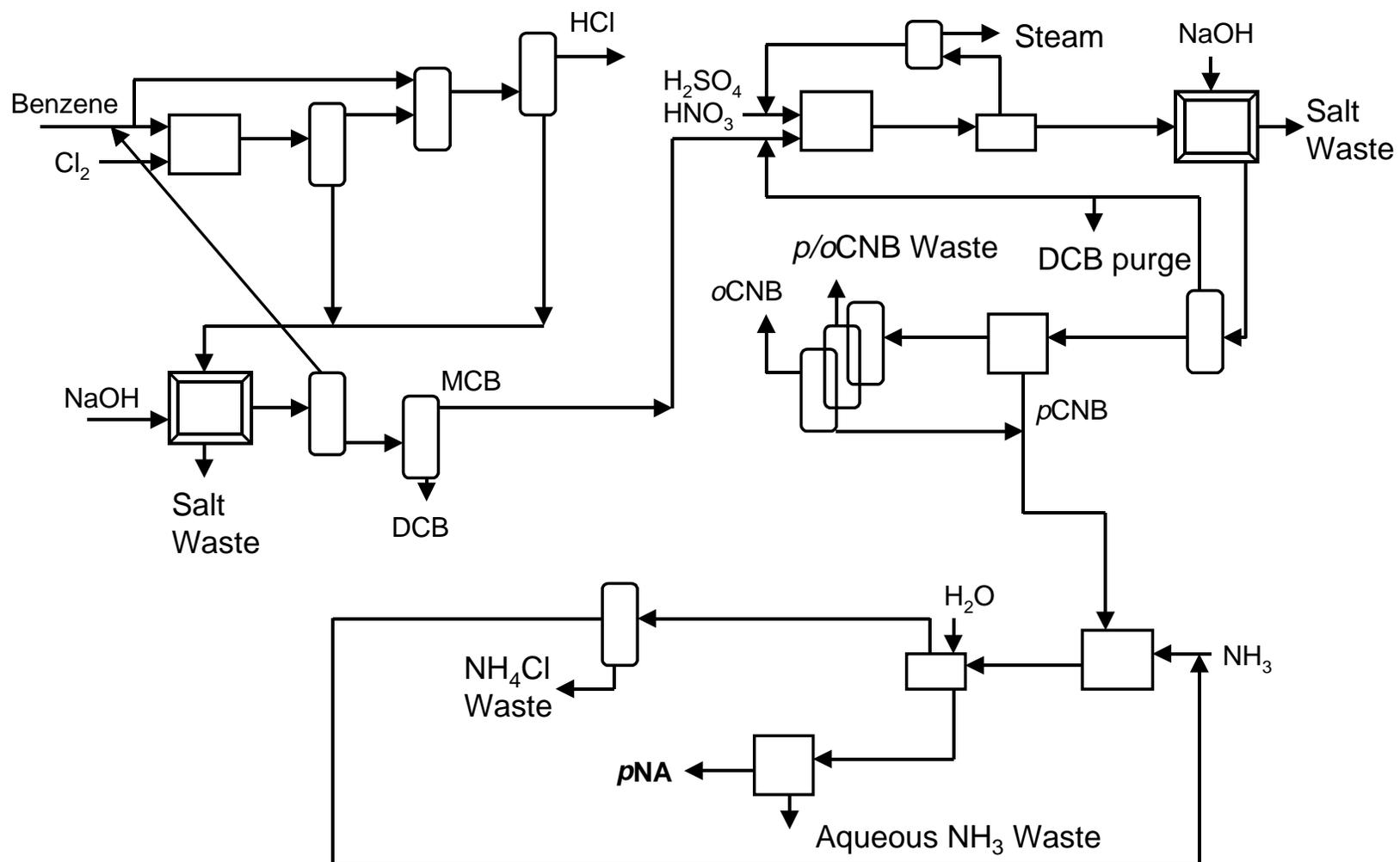Figure 5. Chemistry for production of *p*-nitroaniline using the conventional technology.

Figure 6. Conventional process for the production of *p*-nitroaniline. The process chemistry is shown in Fig. 5.
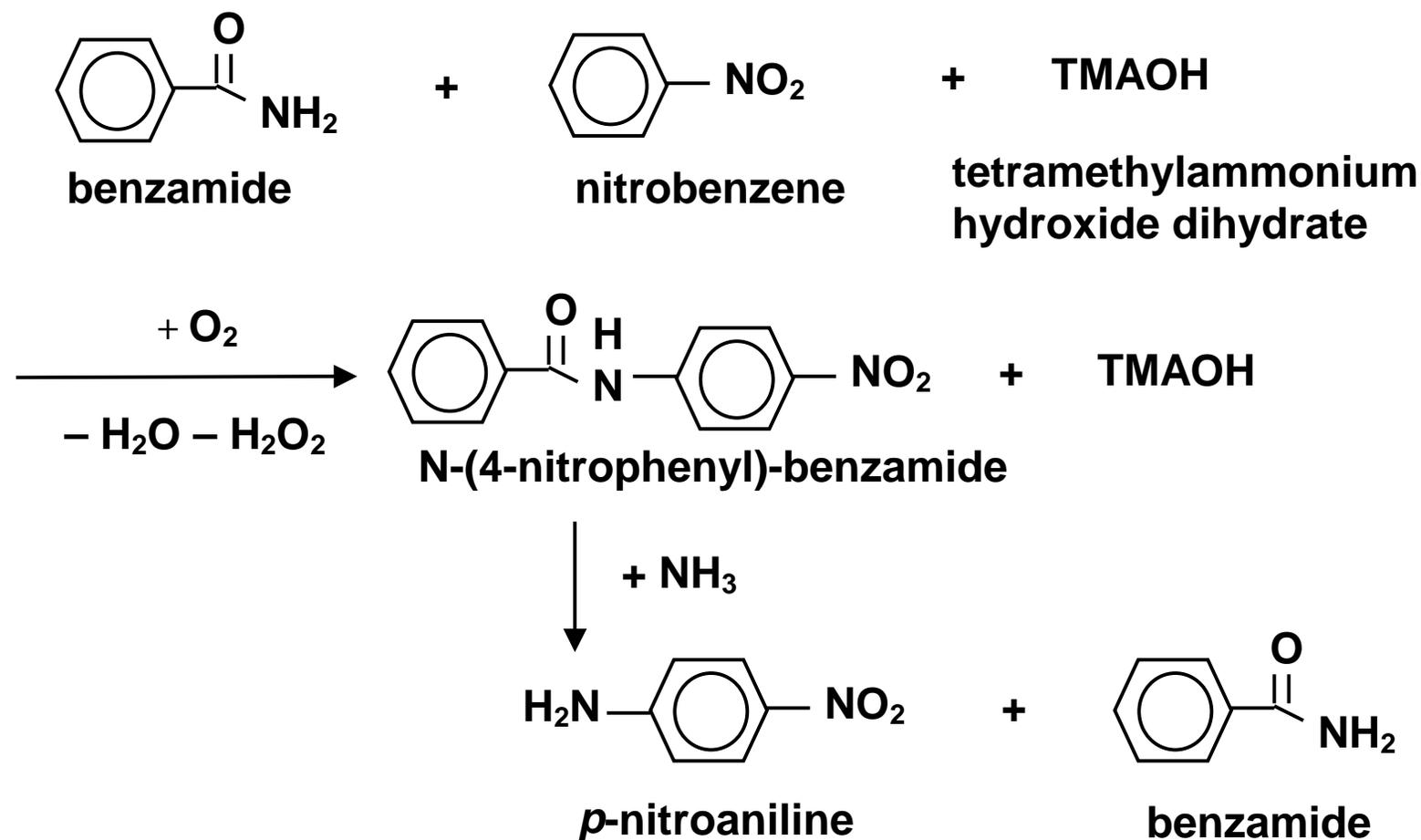
Figure 7. Chemistry for production of *p*-nitroaniline using the new technology.

BA=benzamide
NB=nitrobenzene
TMAOH=regenerated reagent
NPB=intermediate
PNA=*p*-nitroaniline

BA + TMAOH Recycle

BA
NB
TMAOH

**Reactor**

NB

NB + NPB

**Crystallizer**

NPB

NH₃
Methanol

**Reactor**

NH$_3$ + Methanol Recycle

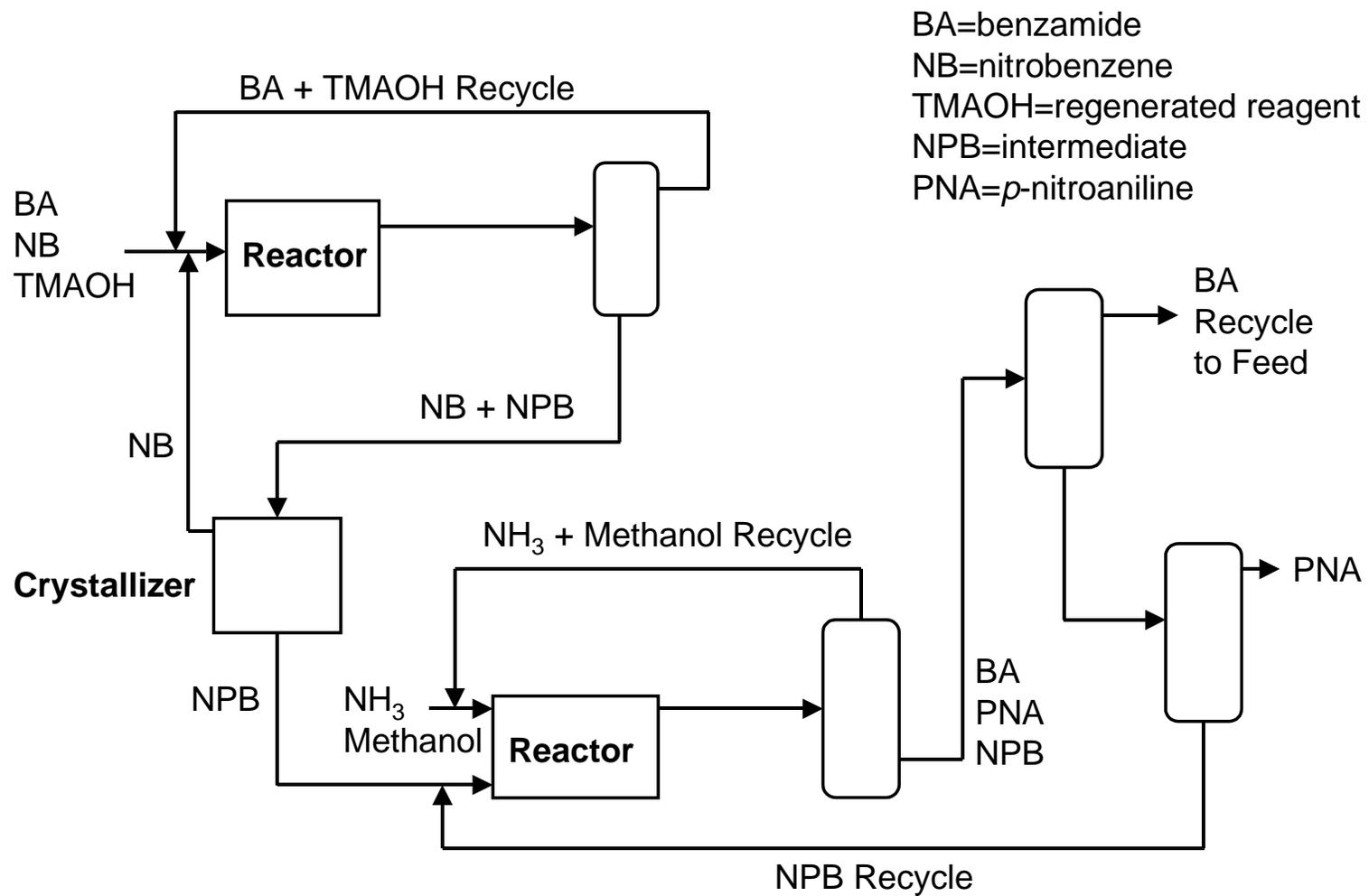BA
PNA
NPB

BA
Recycle
to Feed

PNA

NPB Recycle

Figure 8. New process for the production of *p*-nitroaniline that uses nucleophilic aromatic substitution and eliminates chlorobenzene as an intermediate. The process chemistry is shown in Fig. 7