Incorporating Sustainability Concepts into a Course in Chemical Process Analysis and Design

Final Report

by

Francis A. Gadala-Maria
Department of Chemical Engineering
University of South Carolina

to the

Sustainable Universities Initiative
(Additional funding provided by the
International Paper Foundation)

April 2001
(with additions made January 2002)

Executive Summary

The objective of this project was to incorporate sustainability concepts into ECHE 465 Chemical Process Analysis and Design I. The project, as outlined in the proposal, consisted of the preparation of course modules, the use of the modules, the evaluation of the modules, the dissemination of the modules, and the preparation of the reports. All tasks were completed. Additional work in each of these areas, funded by the International Paper Foundation, is incorporated into this final report.

Introduction

Chemical engineers are in a unique position to make a difference in global sustainability efforts since they are involved in the design of processes. Once they learn to incorporate sustainability concepts into the design of chemical processes, they should be in an excellent position to improve the sustainability of many other types of processes. In the past, chemical processes have been designed without much consideration of sustainability. Thus many processes produce, in addition to the desired product, wastes that need to be disposed of. By giving careful thought to the process at the design stage, it might be possible in some cases to design chemical processes that are at the same time economical and sustainable. This could be done, for example, by choosing raw materials and synthesis routes that produce fewer or no wastes or that produce wastes that can be reused in a sustainable manner. The product itself may also be replaced by a more sustainable alternative. The objective of this project was to prepare, use, evaluate, and disseminate sustainability modules in a course in chemical process analysis and design.

At the University of South Carolina, the chemical engineering undergraduate curriculum culminates in the senior year in a design sequence consisting of two courses: ECHE 465 Chemical Process Analysis and Design I in the fall semester and ECHE 466 Chemical Process Analysis and Design II in the spring semester. This project concerns the first of these two courses. This is a required course offered every fall and taken by all our seniors, 35 to 40 students per year on the average. Since most chemical engineering programs have a similar design course, the sustainability modules introduced as a result of this project could be easily used in similar courses in other schools.

Course Objectives

The course objectives of ECHE 465 Chemical Process Analysis and Design I are listed below:

1. Students will demonstrate the ability to develop a flow sheet for a simple process.
2. Students will demonstrate the ability to perform profitability analysis on simple processes.
3. Students will work in groups and report both orally and in writing on the flow sheet, major pieces of equipment, and economic analysis of a simple process.
4. Students will independently gather information and present in an individual written report their conclusions and recommendations on a problem with global and societal implications.
5. Students will gain an understanding of professional and ethical issues in engineering.

In the past, the individual written report mentioned in the fourth objective of the course has been used to help the students acquire knowledge and formulate reasoned arguments on an open question with some environmental relevance. Topics from previous years include the adoption in this country of product take-back laws similar to those of Germany, the ratification of the Kyoto protocol, and the banning of chlorine and other chlorinated chemicals.

In addition, outside speakers are invited to talk to the class about environmental issues. The last two times the course was taught, Dean Coull of the School of the Environment at USC gave a talk on “Environmental Ethics.”

Proposed Work and Results

The objective of this project was to incorporate sustainability concepts into ECHE 465. The proposed work consisted of the preparation of the modules, the use of the modules, the evaluation of the modules, the dissemination of the modules, and the preparation of the reports. All tasks have been completed. Each of the tasks is listed below with a summary of the steps taken to complete the task.

A. Preparation of Modules

1. Task: choose topics for the individual written report (of the elements of the course) that will require the understanding and use of sustainability concepts.
   Product: A list of seventeen possible topics for the individual report of the course incorporating sustainability aspects has been prepared and is shown in Appendix A.
2. Task: develop homework problems involving the modification of a chemical process to make it more sustainable, and the economic comparison of the original process to the more sustainable process.
   Product: Two problems related to sustainability were assigned as homework. These are presented in Appendix B.
3. Develop the notes for one lecture of a historical nature showing how changes to the chemical process for the production of one product (soda ash, for example) have changed over time and the role that economic, environmental, and sustainability concerns played in the changes.
   Product: The notes for two such lectures (one on soda ash, one on paper) are presented in Appendices C and D. The lecture on soda ash was used when the course was taught in the fall 2000 semester.
4. Develop a questionnaire for the evaluation of the modules by the students in the course. The questionnaire will be developed with the help of the assessment coordinator of the College of Engineering and Information Technology.
   Product: The questionnaire has been developed and is shown in Appendix E together with the responses from the students in ECHE 465 in the fall of 2000.

B. Use of the Modules

The modules developed during the summer were be used when ECHE 465 Chemical Process Analysis and Design I was taught in the fall of 2000.

C. Evaluation of the Modules

The modules were evaluated in three ways:
1. Self-evaluation by the principal investigator after their use.
2. Peer evaluation by other faculty members.
3. Evaluation by the students using the questionnaire developed in the summer.

The results of the evaluation were generally positive and are presented in Appendix E.

D. Dissemination of the Modules.

The modules will be posted in the Sustainable University web page in the form of this final report.

Expenditures

The expenditures followed what outlined in the proposal.

APPENDIX A

Possible topics for the individual written report
(Include the contributions of Lea Lanni during the summer of 2001)

1. To what extent is it practical to replace internal-combustion cars with electrically powered cars? Are they more sustainable than internal-combustion cars?
2. To what extent is it practical to replace internal-combustion cars with hybrid vehicles (powered by gasoline and electricity)? Are they more sustainable than internal-combustion cars?
3. To what extent is it practical to replace internal-combustion cars with fuel-cell powered cars? Are they more sustainable than internal-combustion cars?
4. How sustainable was the Olympic Village developed in Sydney for the 2000 Summer Olympic Games? Which of these sustainability features could be incorporated into the University of South Carolina?
5. To what extent can Columbia, SC become a sustainable city by the year 2020?
6. How sustainable is ethanol as a gasoline antiknock additive? As a substitute for gasoline? (See Chemical & Engineering News, April 17, 2000, p. 29). Should Congress ban MTBE from gasoline in favor of ethanol (See Chemical & Engineering News, March 27, 2000, p. 6; May 8, 2000, p. 40; June 26, 2000)
7. How sustainable is H_2 as an energy source?
8. How sustainable are energy sources that produce CO_2, such as fossil fuels?
9. How can fuel cells help meet our energy and environmental needs? (See C&EN, June 14, 1999, p. 31)
10. What were the causes of the energy crisis in California? What can other states do to prevent a similar situation?
11. How "green" is "green paper"? What are the benefits and drawbacks of its use?
12. How effective is our recycling system? Is it economically viable? How does recycling affect the sustainability of paper?
13. Which of the following would have the greatest impact on reducing the emissions of green house gases?
    - An increased carbon sequestration
    - Increased use of biofuels
    - Switching to less polluting fuels
    - Implement energy-efficient technologies
    - Increasing recycling
    - Increasing incineration with energy recovery
    - Promoting awareness of positive role of wood-based products in carbon cycle
14. How feasible is it to reprocess nuclear fuel?
15. How safe is it to transport spent nuclear fuel by rail?
16. Should food be irradiated?
17. What are the pros and cons of a ban on methyl bromide? (Smithsonian, Dec. 1996, p. 40)

Topics used in previous years:

1. How could the United States minimize its contribution the "greenhouse effect" without significantly affecting the global environment in other ways?
2. To what degree can the United States became self-sufficient in its energy needs?
3. Should the United States adopt zero emission vehicle laws similar to those of California?
4. Should spent commercial nuclear fuel be reprocessed?
5. Should the United States ban the production and use of chlorine, chlorinated organic compounds, and chlorinated oxidizing agents?
6. Should the United States ratify the Kyoto protocol?
7. Should the United States adopt take-back laws similar to those of Germany?
8. How could the reductions in the emission of CO_2 that the Kyoto protocol requires of the United States be accomplished?

All students will write about the same topic, to be chosen by the instructor. The topic will be described in the assignment in some more detail, making it clear what is expected in the reports.

Reports should consist of the following:

A. A cover page with a title, a one-sentence summary of your recommendation, the student's name and signature. The signature is taken to mean that the work of others has not been used except as properly cited in the report.
B. An executive summary, limited in length to 250 words, clearly defining the problem and summarizing the conclusions.
C. A Table of Contents
D. The body of the report organized in the manner considered most appropriate. It may include the following sections: introduction (background information), description of the problem, discussion, personal recommendation, references, table of nomenclature, and appendices.

The reports should be submitted in unfolded 8½"-by-11" sheets of paper, stapled together at the upper left corner. The report must be typed using a word processor, and the file of the report must be submitted as an attachment to an electronic mail message to the instructor at the same time the written report is submitted. The text of the report should be double-spaced in 12 point font, and have at least one-inch margins on all sides. The body of the report (excluding tables, figures, appendices, references, and table of nomenclature) should not exceed 2000 words. The sources of the information you present should be indicated throughout the text. All tables and figures included should be presented in a professional manner, and their source (if they are not yours) indicated. Calculations, if any, included in the appendices need not be typed, but their presentation should be orderly with principal assumptions, data, and other supporting material clearly identified.

APPENDIX B

Homework problems

1. The parties to the Kyoto protocol (the subject of your individual project for this course) were scheduled to meet last month (November 2000) in The Hague, the Netherlands to spell out the mechanisms for reducing the emissions of greenhouse gases into the atmosphere. The meeting was the sixth conference of the parties to the United Nations Framework Convention on Climate Change, called COP6 for short.
   Using a word processor, write a short report listing the points on which the parties agreed at the meeting and the points on which agreement has yet to be reached. Limit your comments to one page of single-spaced text. Cite the source(s) of the information you present.

2. Example 19.8 in our text* (which we discussed extensively in class) showed that by using heat-integration techniques we could reduce the heat input requirements to a particular process from 1900 kW to 100 kW. Estimate the resulting reduction in CO_2 emissions to the atmosphere. Express your answer in terms of metric tons of carbon per year. Compare the savings to the total 1990 US emissions of CO_2, which amounted to $1{,}300 \times 10^6$ metric tons of carbon. (Physics Today, November 2000, p. 29).
   Assume that:
   a. The process operates 8000 hours per year.
   b. The heat is provided by high-pressure steam, which in turn is produced in a boiler burning natural gas (which we can assume to be pure CH_4).

   $$CH_4\ (g) + 2\ O_2\ (g) \rightarrow CO_2\ (g) + 2\ H_2O\ (l) \qquad \Delta H^o_c = -890.36 \text{ kJ/mol}$$

   c. For every mole of methane burned in the boiler, the energy that eventually reaches the process streams as heat is equivalent to 50% of the standard heat of combustion of methane, ΔH^o_c.

* *Analysis, Synthesis, and Design of Chemical Processes* by Richard Turton, Richard C. Bailie, Wallace B. Whiting and Joseph A. Shaewitz. Prentice Hall, 1998.

APPENDIX C

Lecture notes on the role of economic, environmental, and sustainability concerns on changes over time to the chemical process for the production of potash and soda ash.

Introduction

The first U.S. patent was issued in 1791 to Samuel Hopkins for a chemical process. It protected a process to increase the yield of potash and pearl ash (a purer form of potash) from the ashes of trees. Through this lecture we will follow through time some changes in the method of producing potash and soda ash (its substitute) and use in-class discussions to examine the causes for the changes. In particular we will examine the role that environmental and/or sustainability concerns played in the changes.

Colonial Times

During colonial times, most commerce in the countryside involved trading one set of goods or services for another. Very few transactions involved cash. In fact, cash, in the form of coins from several countries, was fairly rare in rural areas. One of the few products that the settlers could sell for cash was potash. They extracted it from the ashes of the trees burned when they cleared their land for planting.

The process involved pouring water on the ashes and filtering the resulting mixture (chemical engineers now call these processes leaching and filtering). The filtrate, free of undissolved solids but containing the dissolved potash was boiled dry (the process we call evaporation). The solids that came out of solution and remained in the pot were the potash.

Potash and pearl ash (its purer form) were important ingredients in glass. They were also important ingredients in soap. A good part of the potash produced in the American colonies was sent to England since England could not afford to burn trees simply to obtain potash. The process was economical in the American colonies because forests were abundant and were being cleared in order to put the land to other uses. Forests are a renewable resource, but at that time they were not being renewed.

Class discussion: How sustainable was this process for obtaining potash from wood ashes?

Kelp ash

During the Napoleonic war early in the nineteenth century, a blockade by the Allies (Britain, Austria, Russia, and Prussia) prevented France from importing saltpeter, an essential ingredient of gunpowder, which in turn was essential to waging war. To circumvent this problem, the French produced saltpeter by boiling calcium nitrate (obtained by mixing urine and dung with powdered limestone) in a vat containing potassium carbonate (potash). The problem now was that the potash was obtained from wood ashes and it was clearly uneconomical to burn wood simply for its ashes. In any case, the use of the forests was limited to shipbuilding by government regulations. In 1811 Bernard Courtois, a French chemist, turned to burning “kelp”, a type of seaweed, as a source for the ashes. (Burke)

The practice of burning kelp for its ashes was already widespread in Britain. Some Scottish lords had incomes from kelp ash of about twenty thousand pounds a year, huge amounts in those days. Demand for kelp ash came at first from glassmakers, who due to shipbuilding regulations similar to those in France were denied access to forest wood simply for its ashes. The growing textile industry, however, became the largest consumer of kelp ash. The alkaline solution that resulted when quicklime (CaO) was added to a solution of kelp ash in water was used as the first stage of bleaching cloth. The ash was also used to make soap to wash raw wool before it was woven. Finally, kelp ash was used in the production of muriate of potash (KCl) for the dying industry.

Class discussion: How sustainable was the use of kelp ash as a source of soda ash and potash?

The LeBlanc Process

LeBlanc process converted two very common and inexpensive raw materials, common salt (sodium chloride, NaCl) and limestone (Ca CO_3) into soda ash (Na_2CO_3). The process, however, involved two other raw materials, sulfuric acid (H_2SO_4) and carbon (C). In addition to the soda ash it produced as byproducts hydrochloric acid (HCl), calcium sulfide (CaS), and carbon dioxide (CO_2). The carbon dioxide was no big problem at the time, and the waste calcium sulfide accumulated in huge piles. The biggest environmental problem, however, was the hydrochloric acid. The acid fumes affected farms downwind of the plants until the absorption of the HCl in water before the gases were released was made compulsory in 1836. This was one of the first environmental regulations. The individual reactions and the overall reaction are shown below, with the inputs and outputs to the overall process shown in bold letters. (Hocking, p. 197)

Individual Reactions

$$\mathbf{2NaCl} + \mathbf{H_2SO4} \rightarrow Na_2SO_4 + \mathbf{2HCl}$$

$$Na_2SO_4 + \mathbf{2C} + \mathbf{CaCO_3} \rightarrow \mathbf{CaS} + \mathbf{Na_2CO_3} + \mathbf{2CO_2}$$

Overall Reaction

$$\mathbf{NaCl + H_2SO_4 + 2C + CaCO_3 \rightarrow CaS + Na_2CO_3 + 2CO_2}$$

The LeBlanc process was also used to convert potassium chloride (KCl) to potassium carbonate (K_2CO_3) after a natural source of potassium chloride was discovered in Germany in 1852. (Hocking, p. 176)

Class discussion: How sustainable was the LeBlanc process as a source of soda ash?

The Solvay Soda Process (also called the Solvay Ammonia-Soda Process)

In 1860, Ernest Solvay developed a process for making soda ash (Na_2CO_3) from the same raw materials as the LeBlanc process, common salt (sodium chloride, NaCl) and limestone ($CaCO_3$). (Meissner)

The overall chemical reaction involved is

$$CaCO_3 + 2NaCl \rightarrow CaCl_2 + Na_2CO_3$$

The reason that soda ash had not been produced before using this reaction is that it does not take place. Under all reasonably attainable operating conditions (combinations of temperature and pressure) the reaction is either thermodynamically unfavorable (it would rather proceed to the left than to the right because of its positive free energy change of reaction) or it is too slow.

The cleverness of the Solvay process consists of replacing this overall reaction with a combination of several other reactions that can take place (each at different conditions and in different pieces of equipment) and which together result in the same overall reaction. The new reactions involve additional compounds (CaO, CO_2, H_2O, $Ca(OH)_2$, NH_4Cl, NH_3, NH_4HCO_3, and $NaHCO_3$) that are produced in some reactions and consumed in the same amount in other reactions so that they are neither raw materials nor byproducts of the overall process.

The six reactions involved, and the temperature at which they take place are shown below (Meissner):

Individual Reactions	**Temperature**
$\mathbf{CaCO_3} \rightarrow CaO + CO_2$	1000°C
$CaO + H_2O \rightarrow Ca(OH)_2$	100°C
$Ca(OH)_2 + 2NH_4Cl \rightarrow \mathbf{CaCl_2} + 2NH_3 + 2H_2O$	120°C
$2NH_3 + 2H_2O + 2CO_2 \rightarrow 2NH_4HCO_3$	60°C
$2NH_4HCO_3 + \mathbf{2NaCl} \rightarrow 2NaHCO_3 + 2NH_4Cl$	60°C
$2NaHCO_3 \rightarrow H_2O + \mathbf{Na_2CO_3} + CO_2$	200°C

Overall Reaction

$$\mathbf{CaCO_3 + 2NaCl \rightarrow CaCl_2 + Na_2CO_3}$$

In addition to the desired soda ash (Na_2CO_3), however, this process produces as a byproduct calcium chloride ($CaCl_2$) in roughly equal amounts (1.04 pounds of calcium chloride per pound of soda ash).

Class discussion: Is the Solvay process more sustainable than the LeBlanc process?

Natural Brines

A large part of the sodium carbonate produced currently is extracted from natural sources, especially natural brines containing the compound. This process eliminates the problem of disposing of the calcium chloride generated in the Solvay process (Hocking, p. 200)

References

Henry M. Paynter, "The First U.S. Patent," *Invention and Technology*, fall 1990, p.18-22.

Herman P. Meissner, *Processes and Systems in Industrial Chemistry*, Chemical Engineering Department, MIT, 1971.

James Burke, *The Knowledge Web*, Simon & Schuster, 1999.

Martin B. Hocking, *Handbook of Chemical Technology and Pollution Control*, Academic Press, 1993.

APPENDIX D

Lecture notes on the role of economic, environmental, and sustainability concerns on changes over time to the chemical process for the production of paper.
(Based mostly on the work by Lea Lanni during the summer of 2001)

Introduction/Brief History

The use of flat surfaces, such as stone, clay, leaves, and animal hides, to record information began long before "true paper" was actually invented. The Chinese implemented the earliest methods of producing this true paper, however, some argue that the Mexicans preceded the Chinese in developing modern papermaking. Nonetheless, the earliest forms of paper were produced when fibers from plants and bark were dried and pressed, or beaten, together to form a sheet. This process was slow and required precise skill by the papermakers.

The Chinese and Japanese techniques spread to Central Asia, Tibet, and India. The Arabs quickly adapted these processes and set up mills in Baghdad, Damascus, Cairo, etc. The spread of papermaking to Europe in the 13th century was made significant by the Italians, who developed the use of water power, the stamping mill, moulds made of wire mesh, the paper press/screw press, and dip sizing.

Over the next few centuries, papermaking became increasingly abundant as more efficient procedures were developed. William Rittenhouse and William Bradford purchased the first paper mill in America in 1690 in what is now Fairmount Park in the city of Philadelphia. From there, mill development continued to grow and by 1810, 202 mills were producing 425,521 reams (500 sheets) of paper in the colonies (Sutermeister, Paperonline).

Raw Materials

As the methods of papermaking evolved with the time, the raw materials used for papermaking were mainly determined by the resources most available to the given area. The papyrus plant, grown extensively in Egypt at the time, was the raw material used in the earliest process that produced the nearest "true paper" thus far. About AD105, the Chinese implemented the use of silk and later mulberry bark. These raw materials produced an even closer resemblance to modern fibrous paper. In the colonies during the 17th, 18th, and mid-19th centuries, linen and cotton rags were the source of papermaking fibers.

Through the 19th century, the preparation of rags for papermaking departed from the Chinese methods. Rags were dusted repeatedly and sorted according to color, grade, and cleanliness. Other non-woody raw materials used include esparto grass, straw, corn stalks, sugar cane, bamboo, manila hemp, and manila rope.

Wood is now considered the universal raw material for the paper industry. While in the past papermakers would use only certain types of wood, almost any kind can be used today. The wood undergoes many modifications once it reaches the mill. The resins are extracted after the wood is chopped up. From here, it is made into a pulp using one or more of the processes described in the next section (Sutermeister).

Pulping

Paper is made from pulp. The process of "pulping" serves to dissolve the lignin that holds the cellulose together and to separate the fibers. Wood can either be chopped into pieces and then cooked in a chemical solution or it can be mechanically ground into a pulp. In the mechanical method of pulping, the weight of the pulp obtained from the weight of the wood is usually 90% or better, since most of the resinous materials in the wood are not removed. Mostly low cost papers are produced from mechanical pulp. One method of mechanical pulping is the stone groundwood method, in which debarked logs are ground against a rotating stone.

The chemical process produces higher quality paper, as it eliminates many unwanted residues, but is also a more time- and resource-consuming process. The wood chips begin in a digester, where they are cooked in a tank at high pressure and temperature. The chips can then undergo various processes to complete pulping.

Chemimechanical Pulping

While this process implements many methods usually associated with mechanical pulping, it is considered a chemical process since it employs use of a pre-soak that defines most chemical pulping methods. This pre-soak, usually in a hot solution of sodium hydroxide (NaOH), will increase the quality of the pulp, as it will decrease fiber damage and the dark color of the wood (Hocking).

Semichemical Pulping

Like chemimechanical and chemical pulping, the chips are first soaked in a digester. In this way, semichemical pulping resembles the chemical process. Most aspects of the soaking in semichemical pulping are at intermediate levels. For instance, the ratios of chemicals to wood are lower than those in chemical pulping, the soaking solution may be closer to neutral, and the cooking times and temperatures may also be decreased. Once the chips are soaked in these conditions, less amounts of refining pulp must be added to the processed pulp than would have to be added to mechanical pulp.

The Soda Process

In the soda process, the first chemical process invented for reducing wood to a pulp, caustic soda (NaOH) is used as the cooking agent. Hugh Burgess and Charles Watt developed this process in England in 1851, and they obtained an American patent in 1854.

In the soda process, the caustic soda is more effective when cooked with the wood at high temperatures. The success of this process depends on the solubility of substances in the wood in the alkaline cooking solution. This will help neutralize the alkali solution. Another action that will help neutralize the alkali solution is the decomposition into acid products of other components of the wood. Neutralizing the alkali solution is very important so that the solution will not be useful until regenerated. In other words, the solution will not react with the pulp until desired so that the pulp will not be completely digested. All of these actions occur in a digester. The wood chips and caustic soda solution, or cooking liquor, are fed into the digester and then steam enters via the bottom of the digester. If the dry weight of the soda remaining in the wood is below a certain amount, the chips will be raw and dark colored. The fibers in this case will not break apart readily, and bleaching these fibers is very difficult. When too much caustic soda is used, the overcooked wood is tender and results in a reduced yield. Therefore, precise measures have to be taken in order to ensure that the resulting fiber contains the desired amount of soda so that these fibers can be modified additionally as they continue the papermaking process.

An important aspect of the soda process is the recovery of the soda; without this feature, the process would not be profitable. There are 3 main steps to this recovery: 1) evaporation of the "black liquor," the liquor in which over half the weight of the original wood has been dissolving, to a concentration that the organic matter present will burn; 2) dissolving the resulting soda after burning; and 3) the conversion of the soda ash to caustic soda by treatment with lime (CaO) (Sutermeister).

<u>The Sulfite Process</u>

The sulfite process, originally invented by Benjamin C. Tilghman , was later improved in 1870 by Fry and Ekman in Sweden. The sulfite process was also known as the "quick cook" process due to modifications developed by Ritter and Kellner in Austria between 1878 and 1882. Usually, calcium acid sulfite (CaO_3S) cooking liquor is used to digest the wood; however, more recently, due to the difficulty of disposing calcium-base liquor wastes, more soluble bases such as sodium, ammonium, and magnesium are being substituted for calcium.

There are two main reactions that define the sulfite process and occur mostly simultaneously. One reaction involves the splitting of the cellulose-lignin complex of the wood by hydrolysis, and the other is the combination of the lignin to calcium bisulfate ($Ca(HSO_3)_2$) to form calcium lignosulfonate. Because reactions in the sulfite process are less drastic than those of other processes, many of the resins remain in the wood. Therefore, less resinous woods must be used, such as spruce, hemlock, and true firs.

Sulfite pulping is superior to the soda process in the amount of lignin it removes and in the degree of whiteness the pulp is able to reach. Pulp made using the sulfite process produces various products including nearly all classes of paper, rayon, and cellophane (Sutermeister, "The Sulfite Process").

<u>The Sulfate ("Kraft") Process</u>

This third chemical process for the preparation of wood pulp was developed in 1883 by Dahl in Germany. The sulfate process is similar to the soda process in many ways, but was developed so that a cheaper substitute for soda ash could be used. Commonly called the "kraft" process, German for "strength," the sulfate process produces paper of a very high strength and dark color.

Sulfate pulps are generally used in the production of paperboard, where physical strength is the most important feature.

Similar to the soda used in the soda process, sodium sulfide (Na_2S) reacts with the wood chips in the digester. However, it is possible that the sodium sulfide first reacts with the water to form sodium sulfhydrate (HNaS), and then reacts with the wood. Unlike the soda process in which all the alkali available is present at the start of the reaction, the sulfate process uses the alkali as needed, creating more controlled cooking conditions. Compared to the unnoticeable byproducts of the soda process, the sulfate process produces methyl mercaptan (CH_4S), which produces a persistent odor.

Because of its name, it might be assumed that sodium sulfate is involved in this process. However, this substance is only useful after it has been reduced to sodium sulfide. The term "sulfate process" is universally used and has never been converted to "sulfide process" (Sutermeister, "The Sulfate Process").

Additional Modifications

Bleaching

Most of the paper used everyday did not go straight from pulp to paper without some sort of bleaching. Different kinds of papers require different kinds of "brightness." The pulp from which all paper comes is usually a yellow or brownish color that is not sufficiently white for the writing paper we use. In order to achieve the desired whiteness, the pulp must be bleached.

Calcium and sodium hypochlorites ($CaCl_2O_2$, NaClO) were the original bleaching chemicals used. Normally, chlorine is passed into milk of lime under specific temperatures and ratios to obtain the desired bleaching solution. The main steps of the modern procedure include chlorination by passing chlorine gas into the mixture of fiber and water, an alkaline extraction to remove chlorinated impurities, followed by bleaching with hypochlorite. The pulp is washed after each step. This process results in a moderate degree of whiteness and strength retention. Additional steps must be added to obtain higher degrees of whiteness (Bleaching and Washing, Sutermeister).

Finishing

Almost all papers must be "beaten" or "refined" before being sent out to the consumer. These beating machines increase the strength of the paper by making the fibers adhere more strongly to each other. Beating methods have been around since the earliest stages of papermaking. Systems in which the sheet of paper was placed on a flat stone or mortarboard and then literally hammered by someone with a rock were common.

Hollanders are common beating machines. These were invented by a Dutchman around 1680. The process of beating by a Hollander involves filling, beating, and dumping (Sutermeister, "Pulp Processing").

The Paper Machine

Gradually, papermaking techniques improved enough to be able to develop machines to complete the processes involved in papermaking. John Gamble received an English patent in 1801 for his paper machine, which was a significant improvement over the machine invented by Nicolas-Louis Robert in 1799. However, in 1803, Henry and Sealy Fourdrinier acquired rights to these machines and because of their significant improvements and promotions, these machines became known as Fourdrinier machines. The first machine built in the United States was made in Connecticut, sold to Amos D. Hubbard, and put into operation in May of 1829. Machine-produced paper was first made in the United States in 1817 at the Gilpin Mill, near Wilmington, Delaware. This paper was made on a cylinder machine, developed by Thomas Gilpin, who patented his design in 1816.

There are two main types of machines: cylinder machines, which are mainly used for heavy paper and paperboard, and Fourdrinier machines. The cylinder machine consists of several screen-covered cylinders that rotate in a vat of stock. Many advancements have been made on the Fourdrinier machine rather than the cylinder machine, so the Fourdrinier machine will be the primary type discussed in these notes.

Fourdrinier machines include many machines that work together to make up the overall Fourdrinier complex. The headbox distributes continuous flow of wet stock at constant velocities as the stock is deposited on the screen. The Fourdrinier table supports many of the presses and rolls of the Fourdrinier complex and is the site for sheet formation and drainage of water. The press section receives the wet sheet and presses it between woolen felts before the sheet is released to the dryer section. The dryer section includes 40 to 70 steam-heated drying surfaces.

The Fourdrinier table is where the bulk of the stretching and water removing occurs. This section supports the table rolls, breast roll, couch roll, suction boxes, and wire rolls. The wire mesh continuously rotates around this table. The dandy roll flattens the top surface of the sheet and improves its finish. After the sheet passes through the dandy roll, watermarks may be added. Upon leaving the Fourdrinier table, the sheet moves on to the presses, where the solids content of the sheet of paper is increased by removing some of the free water in the sheet. The felts used in the press section must be durably woven, yet loose enough to allow water to pass through. Felts also provide cushion for pressing the moist sheets without leaving significant marking (“Pulp Processing”, Formation of paper sheet by machines, Sutermeister).

The Paper Cycle

Paper is part of a process that is continually renewing itself, making it a sustainable process. Most paper can serve as raw material for new paper once it has been used. The papers, if not fit for recycling, can also be used as biofuels. The forest provides a renewable source of raw material, provided it is properly cared for and maintained.

The paper cycle is part of a carbon cycle. The forests take up the carbon dioxide in the atmosphere, which results in sustainable forest management. The timber from forests is turned into wood chips that are used in mills to make pulp. This pulp is used to make paper and paperboard. Most of these products are recycled after use and are returned back to the paper mill for regeneration. Those paper products that cannot be recycled to make additional paper can be sent to an energy recovery plant which completes the paper cycle by releasing carbon dioxide into the atmosphere for the trees to use. Using wood in an eco-efficient manner, by initially making useful products and then using the residues to generate energy, is the basis of sustainability for this process.

The sustainability of this delicate process depends largely on human control. Whether the paper and board products are recovered for recycling or turned over to an energy recovery plant depends on the actions of man. Paper has the potential to be a completely environmentally friendly material, since it is a natural material made from a renewable and recyclable resource (CEPI).

Environmental Awareness/Issues

Recycling

Recycling is the paper industry's key to sustainability. This process reuses paper as a raw material and prevents large amounts of emissions of methane from landfilling paper. With paper that cannot be recycled the use of incineration has recovered large amounts of energy. Recycling is growing at significant amounts. In 1999, the amount of recovered paper used for recycling in Europe was about two thirds greater than it was in 1990.

Not all kinds of paper can be recycled, since some are contaminated during their use. Most papers however, can be reused, such as newspaper, magazines, cardboard, packaging, wrapping paper, etc. In Europe, an average of 50% of the paper is recovered for recycling.

The first step in the recycling process is the cleaning of the used fibers. The fibers are made into a slush substance similar to the solution used when the originally paper was made. Reused pulp is usually not sufficient in strength to be used alone, so new pulp must be added to the mixture of recycled pulp before the paper is made. Depending on the grade of paper desired, large or small quantities of new pulp must be added.

Usually, fibers of recycled paper wear out after about six reuses. Therefore, papermaking is not a closed cycle that can continually regenerate itself without additional materials. New pulp still needs to be produced from trees and other such raw materials. Recycling simply decreases the amount of paper waste in landfills and reduces the amount of new pulp needed to produce a sheet of paper.

"Green" paper is the term used for paper made from recycled materials. Such papers as newspaper and napkins may be entirely "green", while higher quality papers may be made using only a percentage of recycled materials (Paperonline, CEPI).

Water

Water is a major component of the papermaking process. It is used to clean the timber that is brought in from the forests, run some mills by waterpower, and contains the fibers as they are suspended in the water before the paper sheet is made. Often, the water taken from rivers or streams must be cleaned thoroughly before it is used to make paper, so the water returned to these sources is often cleaner than when it was initially removed.

The extent to which streams from paper plants must be purified obviously depends on the amount of difference between the waste stream and the main stream. Some water quality parameters for disposing of wastewater into the streams that may be affected by the kraft process include pH levels, amount of solid in the water, and color of the stream. All of these parameters are considered when preparing to process the wastewater before it is released back into that main water source (CEPI).

Air

A popular complaint about the paper industry is its emissions of such compounds as SO_2 and NO_x into the air. In the last decade, the European paper industry has reduced their sulfur dioxide emissions (CEPI).

Overall, paper production is a highly sustainable process. The use of natural and recycled raw materials ensures a continually available source. The paper industry's minimal contribution to environmental pollution also makes the paper process more appealing. For example, the Kraft pulping process boasts an excellent recovery system that is vital to the success of this chemical procedure. Most of the digestion liquor used in a given batch of chips had been obtained from previous batches' recovered chemicals. The results of this highly efficient recovery mechanism are 1) recovery and regeneration of most of the chemicals used in the original digestion, 2) generating a significant portion of the steam required by the mill by burning the dissolved lignin and other organic components, and 3) avoiding significant pollution by reducing chemical emissions into lakes and streams. This one example shows the immense potential the paper process has as a sustainable process.

References

CEPI/European Paper Industries 2000 Environment Report.
www.paperonline.org/enviro/level3/reports/reports_frame.html

Sutermeister, Edwin. *The Story of Papermaking*. Boston: S.D. Warren Company, 1941.

www.paperonline.org/cycle/recycling/recycling_frame.html

"Formation of paper sheet by machine/papermaking" Encyclopedia Britannica Online.
http://search.eb.com/bol/topic?eu=115049&sctn=17&pm=1. 20 June 2001

"The Sulfate Process." http://palimpsest.stanford.edu/don/dt/dt3383.html. 20 June 2001

"The Sulfite Process." http://palimpsest.stanford.edu/don/dt/dt3384.html. 20 June 2001

"Bleaching and washing/papermaking" Encyclopedia Britannica Online.

http://search .eb.com/bol/topic?eu=115049&sctn=15 20 June 2001

"Pulp Processing." Grolier Online Encyclopedia http://go.grolier.com/discus.html 20 June 2001

Martin B. Hocking, *Handbook of Chemical Technology and Pollution Control*, Academic Press, 1993.

APPENDIX E

Questionnaire for the evaluation of the modules

Student evaluation

The following questions were added to the course evaluation survey administered at the end of the fall 2000 semester. Each of the questions was answered by choosing one of the following five options: Strongly Disagree, Disagree, Neutral, Agree, or Strongly Agree.

31. My awareness of environmental issues in engineering has increased as a result of this course.
33. The lecture by Dean Coull of the School of the Environment helped increase my awareness of environmental issues in engineering.
34. The lecture on the changes to the process for the manufacturing of soda ash helped my awareness of environmental issues in engineering.
35. The homework problems on the climate change meeting and on the reduction of CO_2 emissions helped increase my awareness of environmental issues in engineering.

The table below shows the number of responses in each category for each of these four questions:

	Strongly Disagree	Disagree	Neutral	Agree	Strongly Agree
Question 31	0	2	0	17	12
Question 33	0	2	0	17	12
Question 34	0	6	7	7	11
Question 35	0	6	3	7	15

Although there is some variability, the results are in general positive.

Peer evaluation

Prof. John Weidner of the Department of Chemical Engineering attended the lecture on changes to the process for the manufacturing of soda ash. His assessment is as follows:

"He [Prof. Gadala-Maria] presented a lecture on sustainable manufacturing, using the history of soda-ash production as a case study. I thought the lecture was well researched and effectively presented. I learned a lot and I'm sure the students did as well. My only suggestion for improvement is for him to show the reactions for the earlier manufacturing processes so the material is consistent with his later material. Overall though I thought he did an excellent job."

Self-evaluation

To the lecture on the manufacture of soda ash, I would add the reactions for earlier manufacturing processes as suggested by Prof. Weidner. I would also add some pictures to further liven the lecture.

The homework problems could have been assigned a little earlier in the semester.

The lecture by Dean Coull on environmental ethics was very well received and, if he is willing to do it, could become a regular feature of the course.