The object of this column is to enhance our readers' collections of interesting and novel problems in chemical engineering. Problems of the type that can be used to motivate the student by presenting a particular principle in class, or in a new light, or that can be assigned as a novel home problem, are requested, as well as those that are more traditional in nature and that elucidate difficult concepts. Manuscripts should not exceed ten double-spaced pages if possible and should be accompanied by the originals of any figures or photographs. Please submit them to Professor James O. Wilkes (e-mail: wilkes@umich.edu), Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136.

Incorporating GREEN ENGINEERING *Into a Material and Energy Balance Course*

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Through the support of the US Environmental Protection Agency (EPA), a Green Engineering Project has fostered efforts to incorporate green engineering into the chemical engineering curriculum. Green engineering is defined as the design, commercialization, and use of processes and products that are feasible and economical while minimizing generation of pollution at the source and risk to human health and the environment.

The Green Engineering Project has supported several initiatives, including development of a textbook, *Green Engineering: Environmentally Conscious Design of Chemical Processes*,[1] and dissemination through regional and national workshops.[2] The latest phase of this project supports the development of curriculum modules for various chemical engineering courses.[3] This paper describes how the green engineering topics are "mapped" into a material and energy balances course and presents a sample of the types of problems that were developed for instructor use.

Green engineering principles should be familiar to and used by all engineers, and the need to introduce the concepts to undergraduates has become increasingly important.[4-6] The most common method of incorporating it into the curriculum has been through a senior/graduate elective course on environmental engineering or pollution prevention.[7-9] Integrating green engineering principles into various chemical engineering courses has been more challenging;[10] it is most often integrated into the design sequence.[11] Incorporating environmental issues into a material balance course has been reported by Rochefort[12] by using a material balance module developed by the Multimedia Engineering Laboratory at the University of Michigan.[13] The uniqueness of the problem module described in this paper is that it can be easily integrated into a material and energy balances course and that it maps many of the green engineering principles and underlying concepts to topics covered at this level, thus providing the basis for further integration of green engineering in subsequent courses.

The introductory material and energy balances course is a logical place to put basic terminology and concepts of green engineering. The initial goal of this module was to "map" some topics from the *Green Engineering* text to those taught

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in the material and energy balances course, which predominately uses the text *Elementary Principles of Chemical Processes*.[14] The curriculum module developed[15] has 25 problems (with solutions) that can be used by an instructor for in-class examples, cooperative learning, homework problems, etc.

Two to four problems have been developed for each main topic in material and energy balances and the majority of them have multiple parts. Most require a quantitative solution, while others combine both a chemical principle calculation with a subjective or qualitative inquiry. The problems take a topic from a particular subtopic/topic (section/chapter) and then find a green engineering analog. Some cover specific terminology, principle, or calculation covered in both texts, such as in the calculation of vapor pressures of volatile organic compounds (VOCs), while others introduce concepts only covered in a green engineering text.

Presenting a topic found only in the green engineering text is the most challenging integration of course material. For example, the concept of occupational exposure is introduced by having students perform a unit conversion with a dermal exposure equation. In a similar way, workplace exposure limits are introduced in the context of calculating concentration using mole and mass fractions. This helps optimize time usage and course flow, since as prior papers on various subjects have pointed out, "to put in X, you need to take out Y." By taking basic material and energy concepts and designing a problem to introduce a green engineering concept, a unique integration of concepts occurs.

Some problems have additional questions that require students to investigate the literature, go to a web site, or perform a more qualitative analysis of the problem. For example, in the dermal exposure problem, the student must go to an EPA or related web site to determine threshold limiting values and permissible exposure limits for other chemicals. The level of green engineering material is quite elementary since the objective is to give students some familiarity with concepts that would form the basis for more substantial green engineering problems in subsequent courses such as transport, thermodynamics, reactor design, separations, plant design, etc.

An overall conceptual view of green engineering topics mapped to those in a material and energy balances course is presented in Table 1. The mapping is done in a very generic way so that an instructor can see the general outline of the topics taught in a material and energy balances course and some of the general areas of green engineering concepts. Not all of the concepts covered in a material and energy balances course have a green engineering analog and *vice versa*. That is why the EPA-supported Green Engineering Project has multiple modules developed for other courses in the chemical engineering curriculum. The material in this module was developed to be used at the first-semester sophomore level and therefore integrates green engineering concepts in a way that a student starting a chemical engineering program can readily understand. Several problems from the module have been presented below, following the order of in-

TABLE 1
Conceptual Mapping of Green Engineering Topics in a Material and Energy Balances Course

Green Engineering Topic	*Material and Energy Balances Topic**
• How green engineering is used by chemical engineers in the profession	Chap. 1: What Some ChEs do for a Living
• Unit conversions typically used in green engineering process calculations • Various defining equations used in green engineering	Chap. 2: Intro. to Engineering Calculations
• Typical method of representing concentrations of pollutants in a process (%, fractions, ppm, etc)	Chap. 3: Process and Process Variables
• Overall "closing the balance" of a chemical manufacturing process • Balances on recycle operations in green engineered processes • Green chemistry in stoichiometry • Combustion processes and environmental impact	Chap 4: Fundamentals of Material Balances
• Use of various equations of state in green engineering design calculations for gas systems • Pollutant concentrations in gaseous form	Chap. 5: Single Phase Systems
• Representation and calculation of pollutant volatility using vapor pressure • Condensation calculations (gas-liquid equilibrium) for vapor recovery systems • Liquid-liquid extraction balances for pollutant recovery systems	Chap. 6: Multiphase Systems
• Representation of various forms of energy in a green engineering process	Chap. 7: Energy and Energy Balances
• Recovery of energy in a process-energy integration • Use of heat capacity and phase change calculations • Mixing and solutions issues in green engineering	Chap. 8: Balances on Nonreactive Processes
• Energy use in green chemistry reactions, combustion processes • Overall integration of mass and energy balances in green engineering on an overall plant design basis	Chap. 9: Balances on Reactive Processes
• Use of various simulation tools and specifically designed software for green engineering design	Chap. 10: Computer-Aided Calculations
• Representation of mass and energy flows for transient processes with green engineering significance	Chap. 11: Balances on Transient Processes
• Industrial case studies of green engineered manufacturing processes	Chap. 12-14: Case Studies

• From Felder & Rousseau[14]

corporation in the course. A full set of solved problems is available at <http://www.rowan.edu/greenengineering>.

PROBLEM 1

Occupational Dermal Chemical Exposure Equation

Problem Statement

Undesired occupational exposure to chemicals contacting the skin during sampling, splashing, weighing, transfer of chemicals, process maintenance, etc., can be estimated as the sum of the products of the exposed skin areas (cm^2) and the amount of chemical contacting the exposed area of the skin (mg/cm^2/event). The dermal exposure equation given below can be used to estimate the exposure to a chemical absorbed through the skin.

$$DA = (S)(Q)(N)(WF)(ABS) \qquad (1)$$

where

- DA dermal (skin) absorbed dose rate of the chemical (mass/time)
- S surface area of the skin contacted by the chemical ($length^2$)
- Q quantity deposited on the skin per event ($mass/length^2$/event)
- N number of exposure events per day (event/time)
- WF mass fraction of chemical of concern in the mixture (dimensionless)
- ABS fraction of the applied dose absorbed during the event (dimensionless)

Roberta Reactor, a process technician, is sampling a reactor containing acrylonitrile. Unfortunately, she is not following proper safety procedures for personal protection and is not wearing the required gloves. As plant safety officer, you are asked to estimate her dermal absorption rate (mg/workday) for this unwanted exposure. Data from US EPA indicates that batch process sampling yields between 0.7 and 2.1 mg/cm^2 for the quantity Q in the dermal exposure equation.

a) Show that this equation is dimensionally homogeneous using the following units for the parameters: DA (g/min); S (cm^2); Q (mg/cm^2/event); N (event/day).

b) Using the following data, determine DA in the units of mg/workday for this exposure using the upper limit of Q. During the workday, which is an 8-hour shift, Roberta samples the reactor every hour and exposes one of her hands. The mass fraction of acrylonitrile in the reactor is 0.10 and the fraction of the applied dose absorbed during the sampling is 1.0 (representing that all of the acrylonitrile contacting the skin is absorbed).

c) What personal protective equipment must Roberta wear?

(Problem can be used in Sections 2.2 and 2.6 of Felder and Rousseau.)

Problem Solution

This problem introduces students to the concept of workplace exposure to chemicals and methods for presenting the associated risk. The parameters needed to solve the problem are either given in the statement, found in the literature, or must be measured. The surface area of the hand can be found in texts—or for more fun, have the students trace their hands on engineering paper and estimate the area, model the hand as a trapezoid (palm) with cylinders (fingers), or use a planimeter. This part of the problem gives the "hands-on" characteristic to the learning experience.

To prove the equation is dimensionally correct, the student inputs the units from the problem to show that they cancel on the left-hand and right-hand sides of the equation. To solve for the dermal absorption, the values are put into the equation and units are converted. A value of 325 cm^2 for a student's hand surface area is measured (literature value[1] is 408.5 cm^2 for median size of one adult woman's hand).

$$DA = \frac{325\,cm^2}{}\left|\frac{2.1\,mg}{cm^2\langle event\rangle}\right|\frac{8\,event}{day}\left|\frac{0.1}{}\right|\frac{1.00}{} = 546\,\frac{mg}{day} \qquad (2)$$

Information on the hazards associated with contact with this chemical can be obtained by going to <http://hazard.com/msds> and viewing a representative material safety data sheet (MSDS) on acrylonitrile. Students will see that exposure to it causes skin irritation, is harmful if absorbed through the skin, may cause skin sensitization (an allergic reaction), that prolonged and/or repeated contact may cause defatting of the skin and dermatitis, and that it is toxic in contact with skin. They will also note from the web site that proper personal protective equipment (gloves, safety goggles, and respirator) must be used.

Students may also suggest that a method other than manual sampling could be used to reduce risks to the technician and avoid discharges into the workplace. This is a good practical exercise and would help any student in a hazards and operability study (HAZOP) performed in subsequent laboratory or project-based courses.

PROBLEM 2

Concentration Determination Using Threshold Limit Value and Permissible Exposure Limits

Problem Statement

Two parameters that are used to establish workplace limits for concentrations of chemicals are the Threshold Limit Value (TLV) and Permissible Exposure Limits (PEL). TLV is the level at which no adverse effect would be expected over a worker's lifetime. It is a guideline set by a nongovernmental body, but the PEL is set by the U.S. Occupational Safety and Health Administration (OSHA) and is considered the legal limit in manufacturing facilities.

The solvent n-heptane is used in the manufacture of metal components for washing the parts to remove oils used in the cutting step. Several meters are used to monitor airborne concentration values in the plant. Your job as a process engineer is to convert the data provided for TLV and PEL values for n-heptane into the units used by the concentration meters shown below.

a) Meter A: ppb
b) Meter B: mole fraction
c) Meter C: mass fraction
d) What are the consequences of an unwanted release of n-heptane?
e) Suggest a more environmentally benign solvent for the washing operation.

(This problem can be used in Section 3.3 of Felder and Rousseau.)

<u>Problem Solution</u>

This problem involves the concept of concentration and incorporates the green engineering principle relating that concentration to workplace exposure limits of TLV and PEL. The solution will involve the student first going to one of the EPA-suggested websites and looking up the TLV and PEL for n-heptane. By going to <http://hazard.com/msds> and using the Mallinckrodt Baker MSDS for n-heptane, the values of TLV = 400 ppm and PEL = 500 ppm are obtained. This problem can also involve students in learning how to read an MSDS (which is shown later when they examine the consequences of unwanted exposure). Next, students convert to the desired units using conversions from ppm to ppb, mole fraction, and mass fraction.

<u>PEL Meter A</u>

$$\frac{500\text{ ppm}}{}\left|\frac{10^3\text{ ppb}}{\text{ppm}}\right. = 5.00\times 10^5\text{ ppb} \qquad (3)$$

<u>PEL Meter B</u>

$$\frac{500\text{ ppm}}{}\left|\frac{y_i}{10^6\text{ ppm}}\right. = 5.00\times 10^{-4}\text{ mol } C_7H_{16}\text{ / mol} \qquad (4)$$

<u>PEL Meter C</u>

Choosing a basis of 100 moles and starting with the mole fraction for meter B

$$\frac{\dfrac{5.00\times10^{-4}\text{ mol } C_7H_{16}}{\text{mol}}\left|\dfrac{100\text{ mol}}{}\right|\dfrac{100.2\text{g}}{\text{mol}}}{\dfrac{5.00\times10^{-4}\text{ mol } C_7H_{16}}{\text{mol}}\left|\dfrac{100\text{ mol}}{}\right|\dfrac{100.2\text{g}}{\text{mol}} + \dfrac{\left(1-5.00\times10^{-4}\right)\text{mol Air}}{\text{mol}}\left|\dfrac{100\text{ mol}}{}\right|\dfrac{29\text{ g}}{\text{mol}}} = 1.73\times10^{-3}\text{ g } C_7H_{16}\text{ / g} \qquad (5)$$

To determine the risk associated with undesired release of n-heptane in the plant workplace, students examine the MSDS and see a health rating of 2, and for the section on hazards/ potential health effects they see the following for inhalation: inhalation of vapors irritates the respiratory tract; it may produce light-headedness, dizziness, muscle incoordination, loss of appetite, and nausea; and higher concentrations can produce central nervous system depression, narcosis, and unconsciousness.

In the last part of the problem, students investigate whether an alternate solvent is more environmentally benign. Thinking of what solvents they might be using in a chemistry lab, they might chose acetone, for which the same website would give an overall health rating of 1, or slight, and PEL = 750 ppm and TLV = 750 ppm. So the solvent acetone is slightly better environmentally than n-heptane to use. A listing of solvents and their physical properties can be found using EPA's free green chemistry expert system software.[16]

PROBLEM 3

Mass Balance on Reverse Osmosis Process for Electroplating Waste Reuse and Recovery

<u>Problem Statement</u>

Reverse osmosis is a separation process used for pollution prevention in many industries. It is an environmentally effective separation process since it can be used for material recovery and recycle while it eliminates unwanted discharges from a chemical manufacturing operation. In reverse osmosis, a liquid feed stream under pressure passes across a semipermeable membrane filter that allows the passage of water, but rejects organic and inorganic contaminants. In this operation, the purified water stream produced is called the "permeate," and the stream of concentrated impurities is called the "retentate."

You have been hired as a process development engineer for Shiny Electroplaters, and your first assignment is to look at the reduction of chromium discharge from its operation, as shown in Figure 1. Considering the process to be a steady-state continuous operation, determine

a) The permeate quantity (kg/hr) and chromium concentration (mass fraction) being produced.

b) The potential uses for the permeate and retentate streams in a "green" process design.

c) The advantages this process has over other pollution prevention techniques.

(This problem can be used in Section 4.3 of Felder and Rousseau.)

Problem Solution

This problem gives an example of a green manufacturing process that uses a modern separation system such as reverse osmosis for pollution prevention. It makes students think about how the separation is used to make the manufacturing operation "green." The problem is solved using a material balance working on a continuous process at steady state. The student performs a total mass balance and balance on chromium over the process, yielding the following two relationships:

$$\dot{m}_1 = \dot{m}_2 + \dot{m}_3 \qquad x_1\dot{m}_1 = x_2\dot{m}_2 + x_3\dot{m}_3$$

$$210\,\text{kg/hr} = 50\,\text{kg/hr} + \dot{m}_3 \qquad (0.10)(210\,\text{kg/hr}) = (0.40)(50\,\text{kg/hr}) + x_3(160\,\text{kg/hr})$$

$$\dot{m}_3 = 160\,\text{kg/hr} \qquad x_3 = 0.00625$$

Students can brainstorm the potential uses of the permeate and retentate to make this a "green" process by recycle and reuse (see Table 2) and can then redraw the overall process to show mass integration (Figure 2). Students speculate on the advantages of this process from a green engineering standpoint and find that it simultaneously produces a purified water stream and concentrate with no phase change required—energy savings: no by-products produced, no additional chemicals required, operates at ambient temperature.

PROBLEM 4

Heating Value of Renewable Fuels

Problem Statement

Energy use, conservation, and the environmental impacts of the production and use of fuels are important green engineering topics. Currently available oil and coal reserves are nonrenewable and have air-quality issues associated with their use. Although there is no perfect fuel from an economic and environmental perspective, there are alternatives that should be considered.

Ethanol is considered a "green fuel" since it can be made from renewable and sustainable resources and burns cleaner than fossil fuels. The process to produce ethanol can use a renewable resource such as domestically grown crops and thereby lessens the need for importation of crude oil. Since ethanol contains none of the carcinogenic compounds that are found in fossil fuels, worker exposure risk is reduced. In addition, when it is burned, ethanol generates fewer undesired by-products than gasoline.

a) Investigate and draw a process flow diagram for the production of ethanol from corn. Suggest methods of mass and energy integration in this process to make it more environmentally efficient

b) Calculate the higher heating value (HHV) and lower heating value (LHV) of ethanol (kJ/mol).

c) How does this compare to the HHV of fuel oil gasoline at 44 kJ/g? What are other comparisons of fuel oil/gasoline combustion and ethanol combustion?

d) The use of hydrogen as a potential fuel of the future

TABLE 2

Potential Uses of the Permeate and Retentate to Make a "Green" Process by Recycle and Reuse

Permeate Uses	***Retentate Uses***
Process water	Recovery of Chromium; send concentrate to an electrolytic cell
Wash water/rinse water	Recycle to plating bath for make-up of chromium losses
Water for dilution	
Heat exchanging (energy integration)	

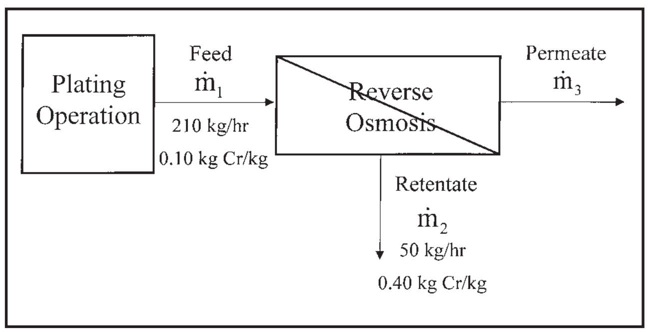

Figure 1. *Process flow diagram of reverse osmosis for the reduction of chromium discharge from electroplating operation.*

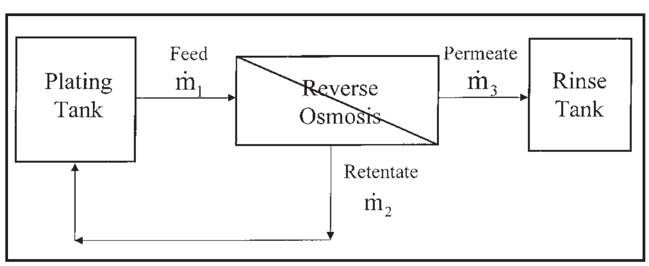

Figure 2. *Process flow diagram showing the integration of permeate and retentate streams.*

has received much recent attention. What is its HHV (kJ/mol) and what are the environmental issues and challenges related to its use?

(Problem can be used in Sections 9.4, 9.6, and Chapters 12-14 of Felder and Rousseau.)

<u>Problem Solution</u>

This problem requires that students investigate the production and use of ethanol fuel from a renewable and sustainable resource. To find a suitable flow diagram for the production of ethanol from biomass, students should be required to go to the library and report the literature source used, such as a biochemical engineering text or a technical encyclopedia.[17,18] Students typically find the corn-to-ethanol process uses fermentation followed by various separations (including distillation, membranes) that also show overall process integration of mass and energy.

Students next determine the heating values of ethanol yielding HHV = 1366.9 kJ/mol and LHV = 1234.9 kJ/mol. A comparison of the heating values to gasoline is made and students are asked to investigate other comparisons. From a green engineering perspective, students are asked to investigate the combustion products of gasoline and other fuel oils. They will find that a 10% blend of ethanol reduces CO, CO_2, VOCs from evaporation, SO_2, particulate matter, and aromatics compared to burning gasoline.[19]

Finally, students are asked to examine hydrogen and determine heating values and other combustion issues. Here they find that on a mole basis the HHV is 285.8 kJ/mol, but on a mass basis, HHV is 141.5 kJ/g, which is higher than gasoline or ethanol. They also see that H_2 burns much more environmentally efficiently since only water is produced as a combustion product. A major issue in the use of hydrogen is its source, which is typically a hydrocarbon.

Upon investigation, students will also see that it currently costs more to produce hydrogen. Technology needs to be developed to use it in the next generation of vehicles, and the infrastructure to transport and dispense hydrogen fuels needs to be developed.

CONCLUSIONS

Green engineering concepts can be integrated into a material and energy balances course by using uniquely developed examples and problems. These problems introduce terminology and basic concepts that lay the groundwork for more extensive incorporation of green engineering in subsequent courses. Problems were developed within the framework of a material and energy balances course and teach students about topics such as workplace exposure routes/limits, recycle and recovery processes, green chemistry, combustion, and mass and energy integration. By using in-class examples or home problems with a cooperative learning approach, students can learn the concepts needed in both a material and energy balances course and green engineering.

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