ChE classroom

Interdisciplinary Learning for ChE Students

FROM ORGANIC CHEMISTRY SYNTHESIS LAB TO REACTOR DESIGN TO SEPARATION

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Interdisciplinary learning and curriculum integration are two very valuable methods to develop our future leaders. Klein (1990) defines interdisciplinary learning as the synthesis of two or more disciplines, establishing a new level of discourse and integration of knowledge.[1] Curriculum integration implies restructuring learning activities to help students build connections between topics.[2] Since our main goal at the United States Military Academy is to develop multidimensional problem solvers, it only makes sense that we as an institution try to integrate interdisciplinary learning into more classes. We saw a perfect opportunity to do this in the Department of Chemistry and Life Science.

At the United States Military Academy, the Chemical Engineering curriculum has the students enrolled in three courses simultaneously in the Spring semester of their third year—Organic Chemistry II, Separation Processes, and

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Chemical Reaction Engineering (Figure 1).

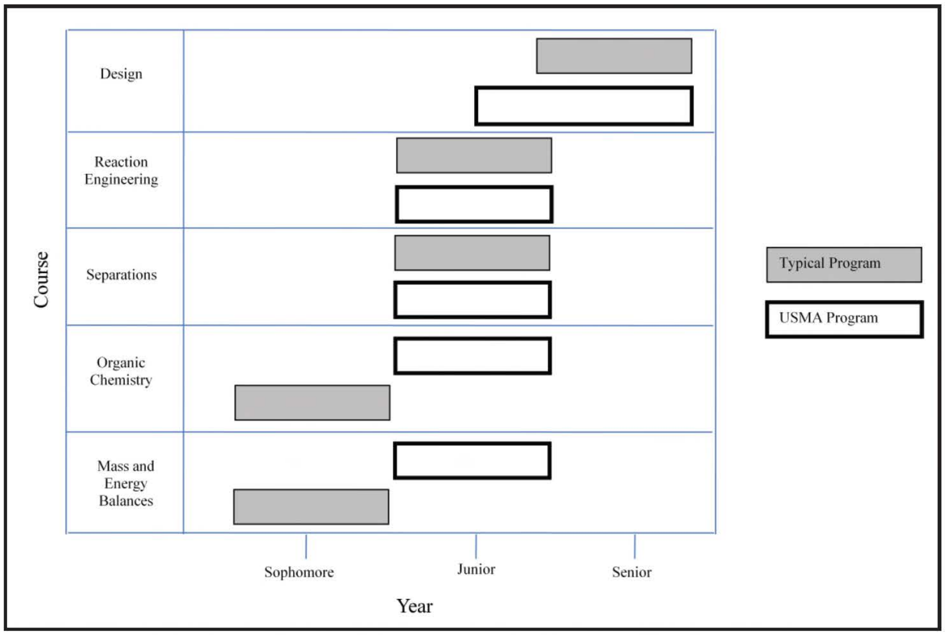


Figure 1. *Chemical Engineering Program order of courses.*

In Organic Chemistry II, students learn the theory behind organic reactions as well as do bench-top experiments that show the practical applications of this theory. In Chemical Reaction Engineering, the students learn how to scale the bench-top experiments up and to design reactors to perform these experiments at industrial levels. Finally, in Separation Processes, students learn how to take this scaled-up process and improve the yield and purity of the final product. This juxtaposition allowed us to simultaneously study a common reaction, the Friedel-Crafts alkylation, in each of the respective classes. During one of the laboratory experiments in Organic Chemistry II, the students performed a reaction in which two products are formed. They were then tasked to separate these two products, but because of time and instrumentation constraints, were mostly unsuccessful. For chemical engineering students, it seems a natural progression to explore solutions to this problem in the context of a chemical separations issue and reactor design. Since these students often take organic chemistry, chemical reactor design, and chemical separations together, an interdisciplinary project such as this provides a practical application to bridge the theory developed in all three courses with an experimental challenge. With our sequencing of courses we have provided our students with an approach that closely resembles the reality of the actual design process, to include the ability to use chemical engineering software in an earlier stage of the development process.

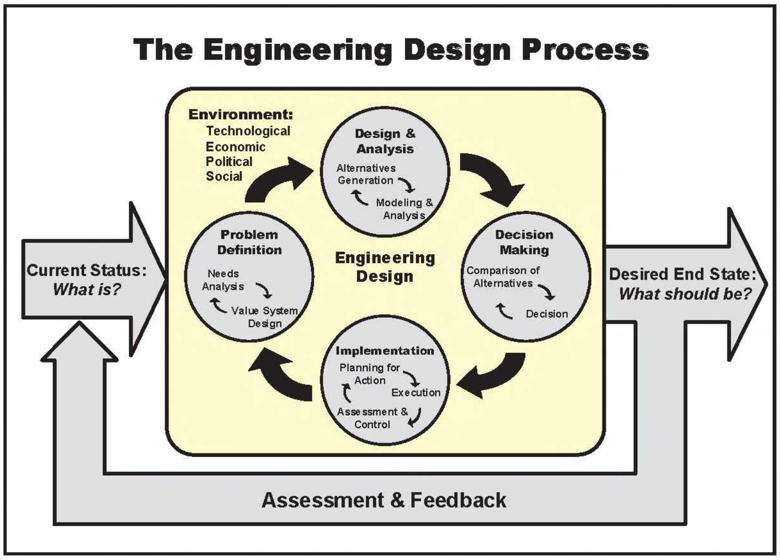


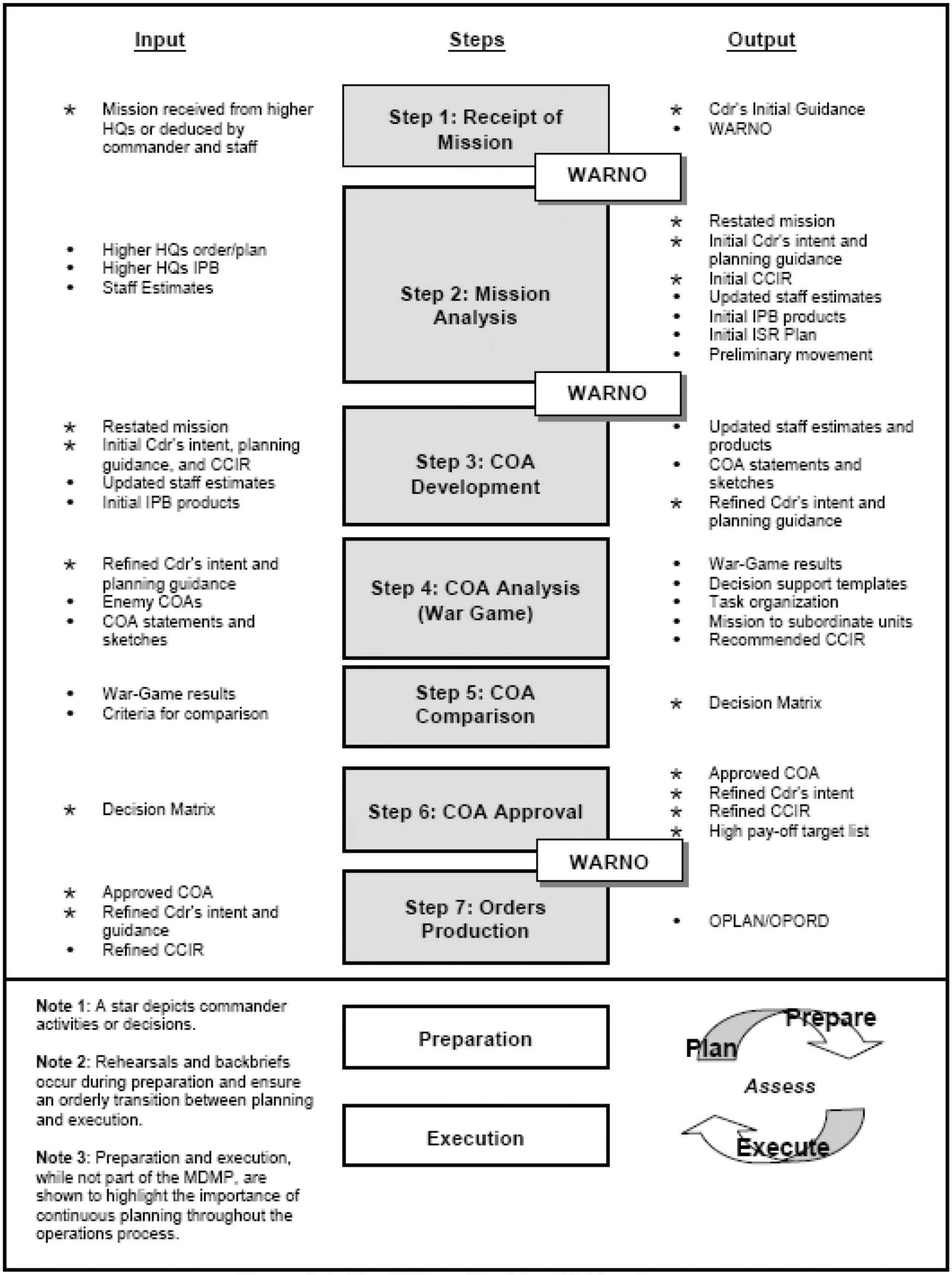
Figure 2. *The engineering design process.*[3]

Another significant added benefit was a connection we began to draw between the engineering design process (Figure 2) and the Military Decision Making Process (MDMP) (Figure 3) taught in third-year military science class. Both processes first define the problem or the mission by examining facts, assumptions, and specified/implied/critical tasks. Both processes then design alternatives and model or test those alternatives so they can be analyzed and compared. Finally, both processes enable us to arrive at a reasonable decision and both are iterative in nature with feedback loops to further refine the design or plan. While this interdisciplinary project was designed to show our students the connections between organic chemistry, reaction engineering, and separations, we were able to draw multiple connections across many aspects of our curriculum like the case of engineering design and military science.

BACKGROUND

The Friedel-Crafts reaction is used in laboratory synthesis as well as in industry in the synthesis of ethylbenzene and its derivatives as an intermediate to make styrene monomers.[3] Therefore, this reaction was a good choice to integrate several different courses.

Laboratory experiments conducted during the second semester of organic chemistry generally illustrate practical application of topics covered in lecture. A convenient Frie-



Input	Steps	Output
★ Mission received from higher HQs or deduced by commander and staff	**Step 1: Receipt of Mission**	★ Cdr's Initial Guidance • WARNO
	WARNO	
• Higher HQs order/plan • Higher HQs IPB • Staff Estimates	**Step 2: Mission Analysis**	★ Restated mission ★ Initial Cdr's intent and planning guidance ★ Initial CCIR • Updated staff estimates • Initial IPB products • Initial ISR Plan • Preliminary movement
	WARNO	
★ Restated mission ★ Initial Cdr's intent, planning guidance, and CCIR • Updated staff estimates • Initial IPB products	**Step 3: COA Development**	• Updated staff estimates and products • COA statements and sketches ★ Refined Cdr's intent and planning guidance
★ Refined Cdr's intent and planning guidance • Enemy COAs • COA statements and sketches	**Step 4: COA Analysis (War Game)**	• War-Game results • Decision support templates • Task organization • Mission to subordinate units • Recommended CCIR
• War-Game results • Criteria for comparison	**Step 5: COA Comparison**	★ Decision Matrix
★ Decision Matrix	**Step 6: COA Approval**	★ Approved COA ★ Refined Cdr's intent ★ Refined CCIR ★ High pay-off target list
	WARNO	
★ Approved COA ★ Refined Cdr's intent and guidance • Refined CCIR	**Step 7: Orders Production**	• OPLAN/OPORD

Note 1: A star depicts commander activities or decisions.

Note 2: Rehearsals and backbriefs occur during preparation and ensure an orderly transition between planning and execution.

Note 3: Preparation and execution, while not part of the MDMP, are shown to highlight the importance of continuous planning throughout the operations process.

Figure 3. *The Military Decision Making Process.*[4]

del-Crafts alkylation reaction that demonstrates the utility of electrophilic aromatic substitution and carbocation rearrangement is that of p-xylene with 1-bromopropane yielding approximately a 1:2 ratio of n-propyl-p-xylene to isopropyl-p- xylene (Figures 4 and 5).[3]

Even with activated arene systems like p-xylene, carbocation rearrangement leads to a substantial proportion of the isopropyl p-xylene. Given that the boiling point difference between the isomeric p- xylenes is only 8 °C, typical microscale distillation techniques and equipment are not adequate to fractionally separate the isomers. So, although the reaction is satisfactory from a synthetic standpoint, the inability to isolate isomerically pure products leaves students with a problem.

RESULTS AND DISCUSSION

Chemical Reaction Engineering Design Project

In the Chemical Reaction Engineering class, the students were given a design project with the following specifications: 1. Volumetric flow rate υ_0 is 52 L/min; 2. A desired product ratio of 50:50 n- propyl-p-xylene to isopropyl-p-xylene at the outlet; and 3. T_{min} is 15 °C and T_{max} is 70 °C. These requirements were dictated in order to focus their problem-solving efforts. The students were directed to use ChemCad to develop their designs, but ChemCad needs frequency factor and activation energy values to correctly model the reactions mathematically. Since these values could not be found in the literature, it was necessary to conduct some preliminary experiments to gather data that the students could use to calculate the frequency factor, k0, and activation energy, E_a, of each parallel reaction, and the overall reaction. Three independent experiments were run at different temperatures to collect the data required for the concentration vs. time plot. These plots were then used to find reaction rate constants, k, for each temperature for each parallel reaction. The kinetic data was collected following the same procedures the students used in the organic chemistry laboratory earlier in the semester.

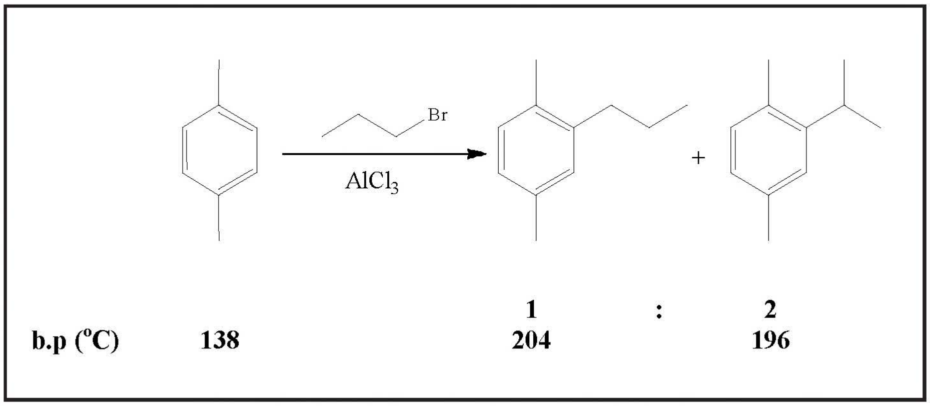


Figure 4. *Friedel-Crafts alkylation of p-xylene.*

TABLE 1
Friedel-Crafts Alkylation Kinetic Data

Temp (K)	Time (min)	[Xylene] (*M*)	[$CH_3CH_2CH_2Br$] (*M*)	C_B/C_A	ln (C_B/C_A)
295.5	0	5.29	3.859	0.729	-0.315
	10	3.79	2.36	0.623	-0.473
	14	3.63	2.2	0.606	-0.501
	18	3.34	1.91	0.572	-0.559
	20	3.18	1.75	0.550	-0.598
311	0	5.29	3.859	0.729	-0.315
	2	3.8	2.369	0.623	-0.472
	6	3.3	1.97	0.597	-0.516
	14	3.1	1.6	0.516	-0.661
	18	2.88	1.42	0.493	-0.707
333	0	5.29	3.85	0.728	-0.3178
	2	2.83	1.4	0.495	-0.704
	6	2.39	0.96	0.402	-0.912
	10	2.04	0.61	0.299	-1.21
	14	1.73	0.3	0.173	-1.75

To calculate the total reaction rate constant a plot of $C_{bromopropane}/C_{p\text{-}xylene}$ vs. time was constructed. To understand this leap it is necessary to derive the irreversible bimolecular-type second order reaction performance equation:[4]

Starting with the generic second order reaction:

$$A + B \rightarrow \text{products} \qquad (1)$$

The corresponding rate equation is as follows:[4]

$$-r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = k_{tot}C_AC_B \qquad (2)$$

It is possible to follow the derivation of this equation in *Chemical Reaction Engineering*, by Octave Levenspiel, in Chapter 3. The following is the end result of the derivations:

$$\ln\frac{C_B}{MC_A} = \ln\frac{1-X_B}{1-X_A} = \frac{M-X_A}{M\left(1-X_A\right)} = \left(C_{B0}-C_{A0}\right)k_{tot}t \qquad (3)$$

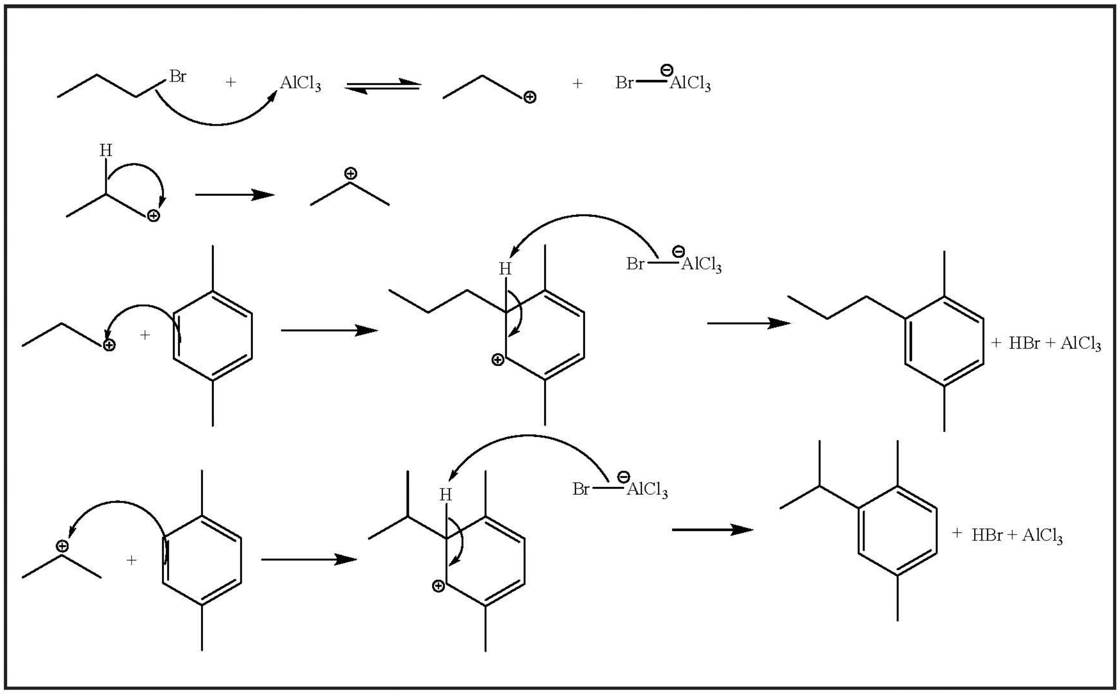


Figure 5. *Friedel-Crafts alkylation of p-xylene mechanism.*[5]

where M = C_{Bo}/C_{Ao}, X = conversion, k = reaction rate constant, reactant A = p-xylene, B = 1-bromopropane.

The implication of this result show that a plot of ln (C_B/C_A) versus time will yield a straight line if indeed the reaction is second order, and first order with respect to each reactant. The intercept will equal M, and the slope will be equal to $(C_{B0}-C_{A0})k_{tot}$.

EXPERIMENTAL

Three experiments were set up identically at temperatures of 295.5 K, 311 K, and 333 K. To 15.0 mL of p-xylene was added 1.00 g of $AlCl_3$. The resulting mixture was allowed to stir while 8.0 mL of 1-bromopropane was added dropwise over a period of 5-10 minutes. At two-minute intervals, a microliter sample was extracted from the reaction vessel, quenched with water, and diluted with diethyl ether. After removal of the aqueous layer, the samples were dried over sodium sulfate. The samples were examined in the Gas Chromatograph/MS to determine the concentrations of reactants and products in each sample.

The reaction progress was monitored by gas chromatography, and the kinetic data recorded in Table 1. By plotting the concentration data from the gas chromatograph found in Table 1, it is possible to calculate the k_{tot}.[4]

With that information and the average ratio of products at each time step it is possible to calculate k_1 and k_2 with the following two equations:[4]

$$k_{tot} = k_1 = k_2 \qquad (4)$$

$$\left(\frac{C_n - \text{propyl}}{C_{\text{isopropyl}}}\right)_{AVE} = \frac{k_1}{k_2} \qquad (5)$$

When all of the reaction rate constants were determined it was then possible to solve for individual frequency factors, k_0, and activation energies, E_a, using the Arrhenius relationship:

$$k = k_0 e^{-E_a/RT} \qquad (6)$$

Plotting ln k vs. 1/T, the slope of this line is $-E_A/R$, and the y intercept is k_0, thus permitting the calculation of both k_0 and E_a for each parallel reaction, and the overall reaction.

The activation energy values and frequency factors are critical to model and scale up the reaction using ChemCad. This entire process was expected to be executed by each student, thus reinforcing the derivation of a concentration vs. time model. Each student had to demonstrate mastery of this process at a desk-side briefing to the instructor before using ChemCad. Upon successful calculation of the reaction rate constants, students were allowed to start the scale-up modeling with ChemCad.

With this data, it was now possible to establish the appropriate kinetic relationships in ChemCAD. The students then used ChemCad to search the most economically feasible reactor design. A cursory analysis of the data yielded an appropriate plot of $1/-r_A$ vs. X_A. Analysis of the plot makes it clear that the best reactor design to minimize volume should be a plug flow setup. Using Mathematica, the mean residence time and

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volume for the initial guess can be estimated. Questions left to resolve are reactor volume, heat duty, and isothermal vs. adiabatic operation. Students were free to explore various reactor networks, such as parallel vs. series reactors and use of recycle. Students were given latitude to explore other unique strategies using ChemCad.

CHEMICAL SEPARATIONS DESIGN PROJECT

The chemical separations design phase of this interdisciplinary project was fairly open ended. The students could use any combination of separations schemes to achieve 90% purity of all components in the system (feed, catalyst, products) and then attempt to achieve a 95% n-propyl-p-xylene product stream. This open-ended approach forced the students to consider all aspects of a realistic separation problem that originated in their organic chemistry lab and that they might see in industry. At first, the students were intimidated because a detailed solution required knowledge beyond their current level, but they eventually enjoyed working on this problem because it truly challenged them to think.

Like the reactor design project, our students began the separations design project by gathering property information. When they could not find certain property information for some of the compounds they quickly learned how to make reasonable approximations and assumptions. We advised the students that a critical task in their design was to determine the best separation technique for each of the components and decide on the most logical sequencing of those techniques. Based on the available property information, most student teams chose to flash off HBr, extract AlCl3 using water, and use a series of distillation columns to purify the remaining components. Much like a real-world design process, however, we forced each team to consider at least two different separation sequences and compare and contrast them. In this way our students learned a great deal about separations processes.

The separations design project also used ChemCad software as the vehicle for the design. Most student teams attempted to jump right into ChemCad without much preparatory analysis, and their initial results clearly emphasized the importance of choosing a reasonable thermodynamic model, and making some preliminary estimates. While students will be expected to use thermodynamic modeling in greater depth later in their curriculum, this exercise served as an excellent tool to emphasize the importance of material yet to come. As a result of creating, manipulating and running ChemCad examples, all students increased their ChemCad proficiency, which is a critical software thread for our entire chemical engineering program.

One design team exceeded our expectations for a truly integrated design solution. This team combined their reactor design with their separations design in the same process flow sheet. Although we expected separate reactor and separations designs from these third-year students in these separate courses, this team made the logical leap and combined the designs to achieve some additional efficiencies. Figure 7 depicts their ChemCad design flow sheet which incorporates a recycle stream for unconverted reactants.

ANALYSIS OF RESULTS

To analyze the results the students were given a quiz at the beginning of the semester consisting of representative questions from the organic chemistry, chemical reaction engineering, and separations disciplines. The same quiz was then re-administered at the end of the semester to see if there was improvement, and retention of knowledge. These results are in Table 3.

In addition to this the students were asked the following questions regarding their individual experiences with the design project at the end of the semester. These questions were answered on a scale of 1 to 5, where 1 represented the most positive feedback and 5 was the least positive. These questions are listed in Table 4 accompanied by the averaged response. A comparison will be made of final examination results from AY06-02 to AY07-2 in the chemical reaction engineering course, to see the impact this had on performance. Although the data only showed a small increase, the students overall exhibited more confidence when approaching these type of problems in other courses.

From the results, it is clear that the design experience had a positive outcome in terms of mastery of the material. The students' responses to the questions were also quite positive. We will conduct the same approach in the years to come and continue to gather data.

TABLE 2
Rate Constant (k) vs. Temperature (K)

Reaction #1 (isopropyl)		**Reaction #2 (n-propyl)**	
k_1	**T**	**k_2**	**T**
0.0296	333	0.00653	295.5
0.0050	311	0.0085	311
0.0029	295.5	0.035	333

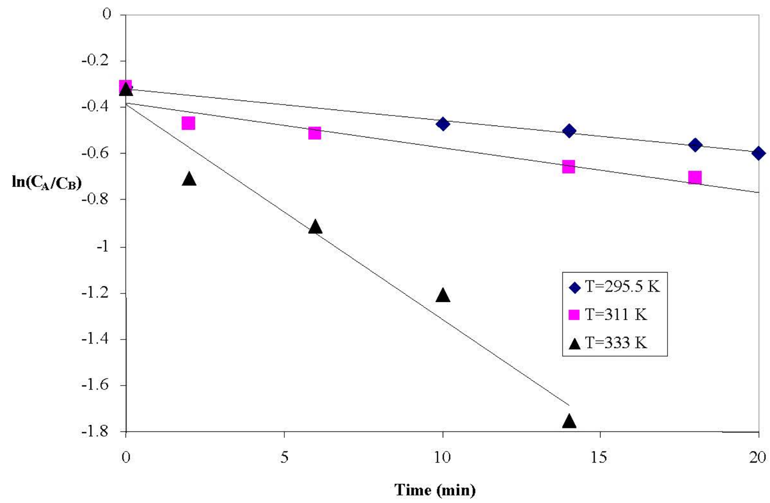

Figure 6. *Concentration vs. time plot.*

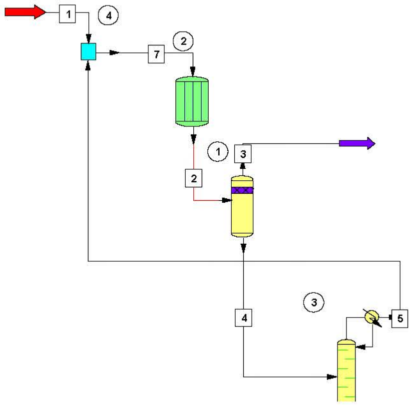

Figure 7. *Student team's fully integrated reactor and separations design proposal.*

TABLE 3
Quiz Results

	Pre-Project:			Post-Project:		
Question	Question #	Correct	Incorrect	Question #	Correct	Incorrect
What is a Friedel Crafts alkylation?	**1**	*5*	*6*	**1**	*7*	*4*
Give an example of one.	**2**	*3*	*8*	**2**	*9*	*2*
Method of calc. k_0 and E_A.	**3**	*2*	*9*	**3**	*8*	*3*
Method of k_1, k_2 calc. parallel rxns.	**4**	*0*	*11*	**4**	*7*	*4*
Can k_1, k_2 be found graphically?	**5**	*0*	*11*	**5**	*2*	*9*
Give two ways to separate gas and liquid phases.	**6**	*8*	*3*	**6**	*10*	*1*
Give two ways to separate two liquid phases.	**7**	*8*	*3*	**7**	*10*	*1*

TABLE 4
Questions Regarding Individual Experiences

Question Regarding Individual Experience	**Ave Response**
1. Was this design project useful in terms of helping the learning process?	1.64
2. Was this design project helpful to wrap up the course material at end of semester?	1.73
3. Did this design project aid your learning in organic chemistry and separations?	2.27
4. Would you recommend this project format next year?	2.09
5. Did you like the design project?	2.55
6. Do you think the design experience helped your Term End Exam preparation?	2.09

CONCLUSION

This idea started out as merely a project for our Chemical Reaction Engineering course, but evolved into a novel educational approach to chemical engineering curriculum development using a technique closely paralleling the actual industry design process. From our results, it is apparent that this is indeed a valid approach. The experience allowed the students to approach the problem as a design engineer in industry would, as well as use the problem-solving techniques previously discussed. Additionally, the students were able to use the chemical engineering software earlier by using the kinetic data given to them. We intend to use this technique again, and recommend it fully to other programs. In fact, the project is in its second iteration and has evolved to include other factors such as cost optimization and environmental impact. As this project becomes a more prominent feature of our program, we will give the students less data, requiring them to decide what information is needed.

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