Interdisciplinary Learning for Chemical Engineering Students from Organic Chemistry Synthesis Lab to Reactor Design to Separation

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Abstract

A novel approach to the Chemical Engineering curriculum sequence of electives here at West Point enabled our students to experience a much more realistic design process, which more closely replicated a real world scenario. Students conduct the synthesis in the organic chemistry lab, then conduct computer modeling of the reaction with ChemCad and Mathematica, analyze chemical separation processes, and design a reactor system. This interdisciplinary learning approach demonstrated to students that all of their courses are meant to compliment each other, their learning, and experiences.

Introduction

The Chemical Engineering curriculum at the United States Military Academy has the students enrolled in three electives simultaneously in the Spring semester of their 3rd year. The electives taken simultaneously are Organic Chemistry II, Separation Processes and Chemical Reaction Engineering. This juxtaposition allowed us to simultaneously study a common reaction, the Friedel-Crafts alkylation, in each of the respective classes.

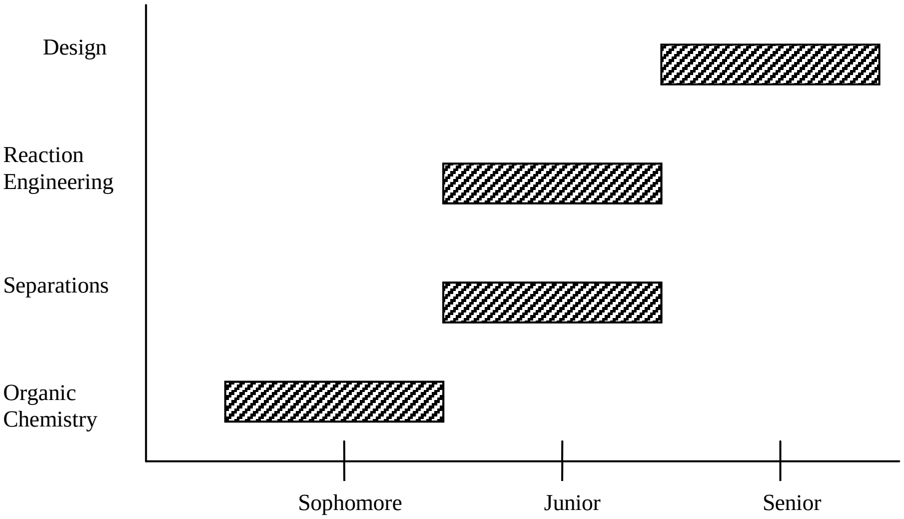


Figure 1. Typical Chemical Engineering Program Order of Electives

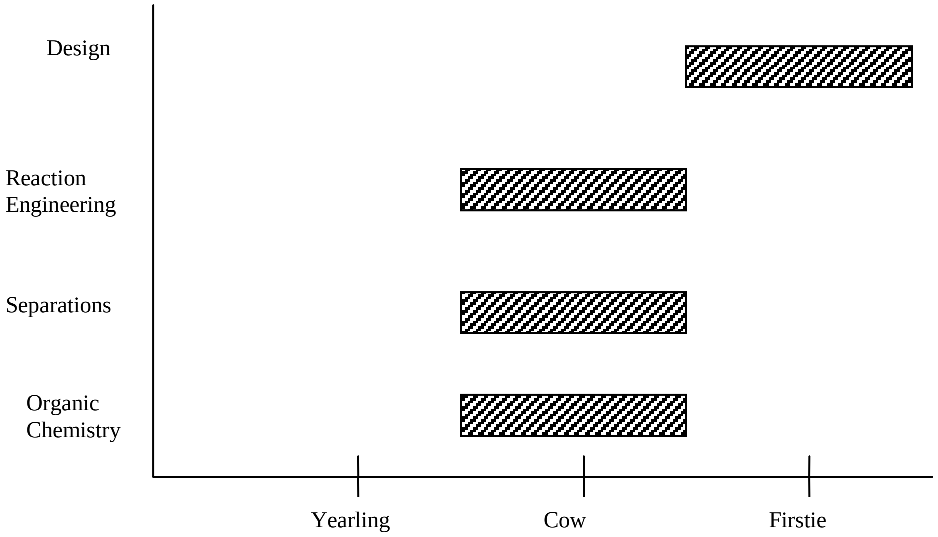


Figure 2. USMA Chemical Engineering Program Order of Electives

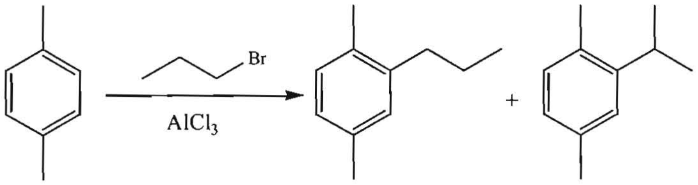
The arrangement, therefore, more closely mirrored the real world Chemical Engineering design process. In addition to its realism, the engineering design process used by our students, in addition to its realism also parallels the Military Decision Making Process (see Figure 8), thus reinforcing military as well as engineering decision making concepts.

Lastly our novel approach to curriculum development allowed for an earlier incorporation of the actual data into the process via ChemCad, the Chemical Engineering software that was used by each student. Typically, use of this software does not occur until later in the design sequence.

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[1]. 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 Friedel-Crafts alkylation reaction which 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.[1] (See Figure 3 and Figure 4).



1 : 2

b.p (°C) 138 204 196

Figure 3. Friedel-Crafts alkylation of *p*-xylene.

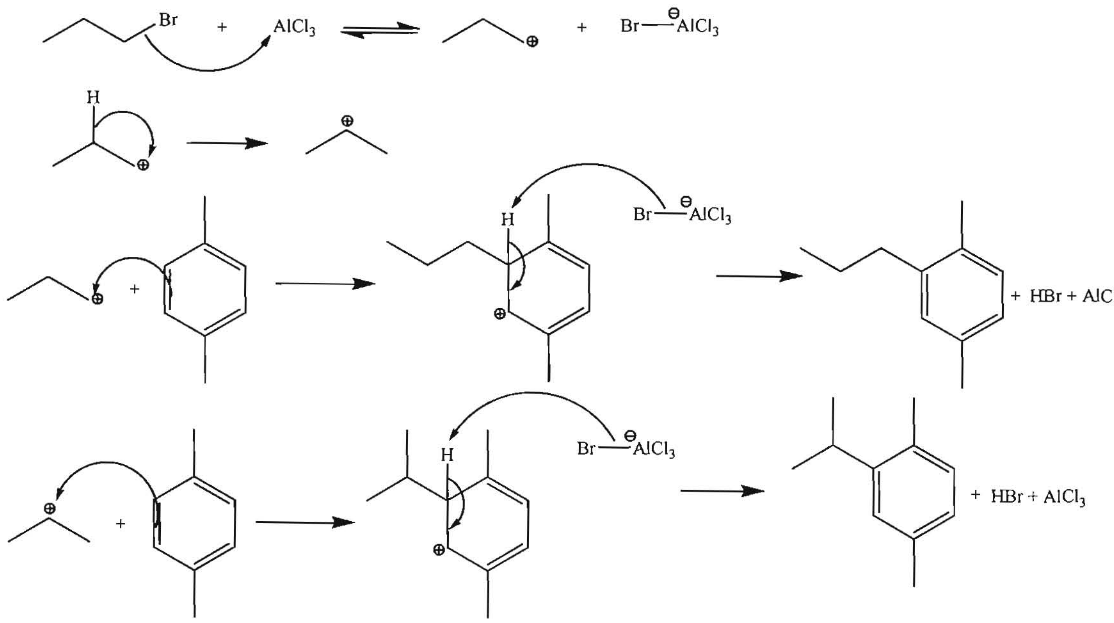


Figure 4. Friedel-Crafts alkylation of *p*-xylene mechanism[1].

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.

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 electives we have provided our students with a more realistic approach that more 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.

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. 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, k_0, 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.

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[2] performance equation:

Starting with the generic second order reaction:

$$\mathbf{A + B \rightarrow products} \qquad (1.1)$$

The corresponding rate equation is as follows[2]:

$$-r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = k_{tot} C_A C_B \qquad (1.2)$$

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

$$ln\frac{1-X_B}{1-X_A} = ln\frac{M-X_A}{M(1-X_A)} = (C_{B0} - C_{A0})k_{tot}t \qquad (1.3)$$

where $M = C_{Bo}/C_{Ao}$.

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}.

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 $k_{tot.}$[2]

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	0.729489603	-0.31541016
	10	3.79	2.36	0.622691293	-0.4737044
	14	3.63	2.2	0.606060606	-0.50077529
	18	3.34	1.91	0.571856287	-0.55886756
	20	3.18	1.75	0.550314465	-0.59726541
311	0	5.29	3.859	0.729489603	-0.315410163
	2	3.8	2.369	0.623421053	-0.472533142
	6	3.3	1.97	0.596969697	-0.515888926
	14	3.1	1.6	0.516129032	-0.661398482
	18	2.88	1.42	0.493055556	-0.707133423
333	0	5.29	3.85	0.72778828	-0.317745
	2	2.83	1.4	0.494699647	-0.703804
	6	2.39	0.96	0.40167364	-0.912115
	10	2.04	0.61	0.299019608	-1.207246
	14	1.73	0.3	0.173410405	-1.752094

Table 1. Friedel-Crafts alkylation kinetic data

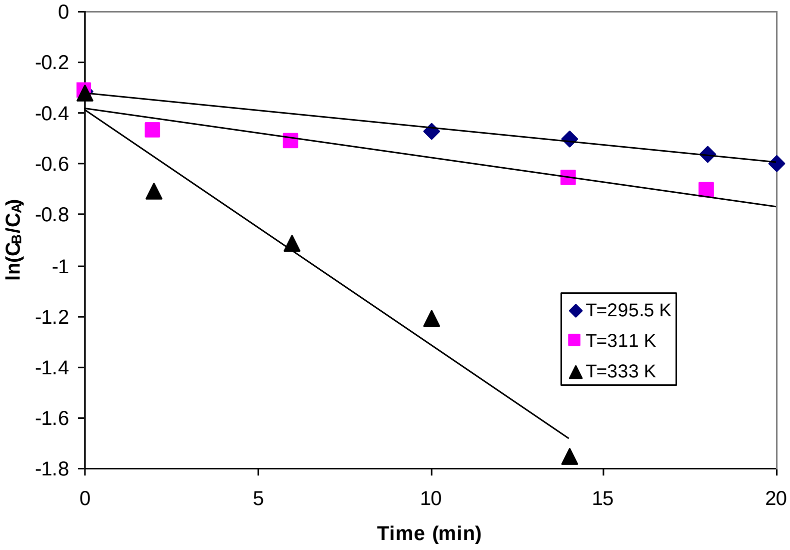


Figure 5. Concentration versus time plot.

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[2]:

$$k_{tot} = k_1 + k_2 \tag{1.7}$$

$$\left(\frac{C_{n-propyl}}{C_{isopropyl}}\right)_{AVE} = \frac{k_1}{k_2} \tag{1.8}$$

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:

$$k = k_0 e^{-E_a/RT} \tag{1.9}$$

Plotting ln k vs 1/T, the slope of this line is $-E_A$, 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.

This information is 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 versus time model. Each student had to demonstrate mastery of this process before using ChemCad at a desk side briefing to the instructor. 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 volume for the initial guess can be estimated. Questions left to resolve are reactor volume, heat duty, and isothermal versus adiabatic operation. Students were free to explore various reactor networks, such as parallel versus 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 $AlCl_3$ using water, and use a series of distillations columns to purify the remaining components. However, much like a real-world design process, 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 capstone design team surprised us by exceeding 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 3rd year students in these separate courses, this team made the logical leap and combined the designs to achieve some additional efficiencies. Figure 6 depicts their ChemCad design flow sheet which incorporates a recycle stream for unconverted reactants.

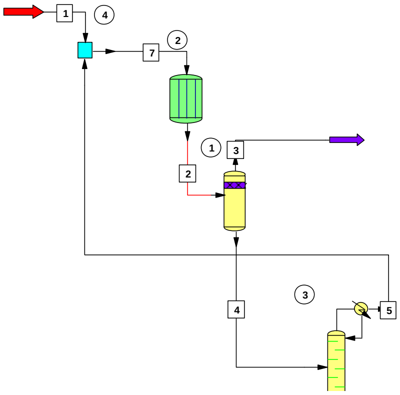


Figure 6. Student Team Fully Integrated Reactor and Separations Design Proposal

Unanticipated benefits

As our students navigated through both projects, we experienced multiple unexpected benefits; some of these have been discussed above. Another significant added benefit was a connection we began to draw between the engineering design process and the Military Decision Making Process (MDMP) taught in 3rd year military science class. As you can see from Figures 7 and 8, 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, but we were able to draw multiple connections across many aspects of our curriculum like the case of engineering design and military science.

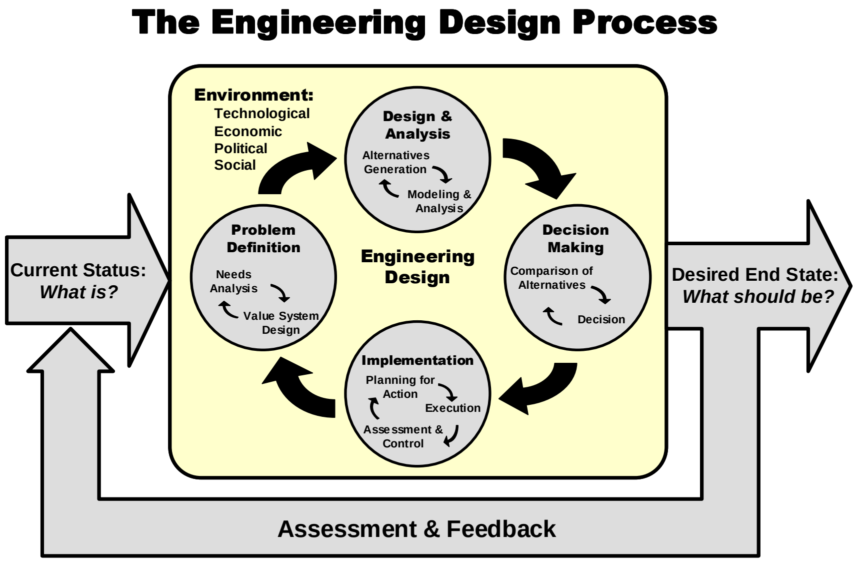
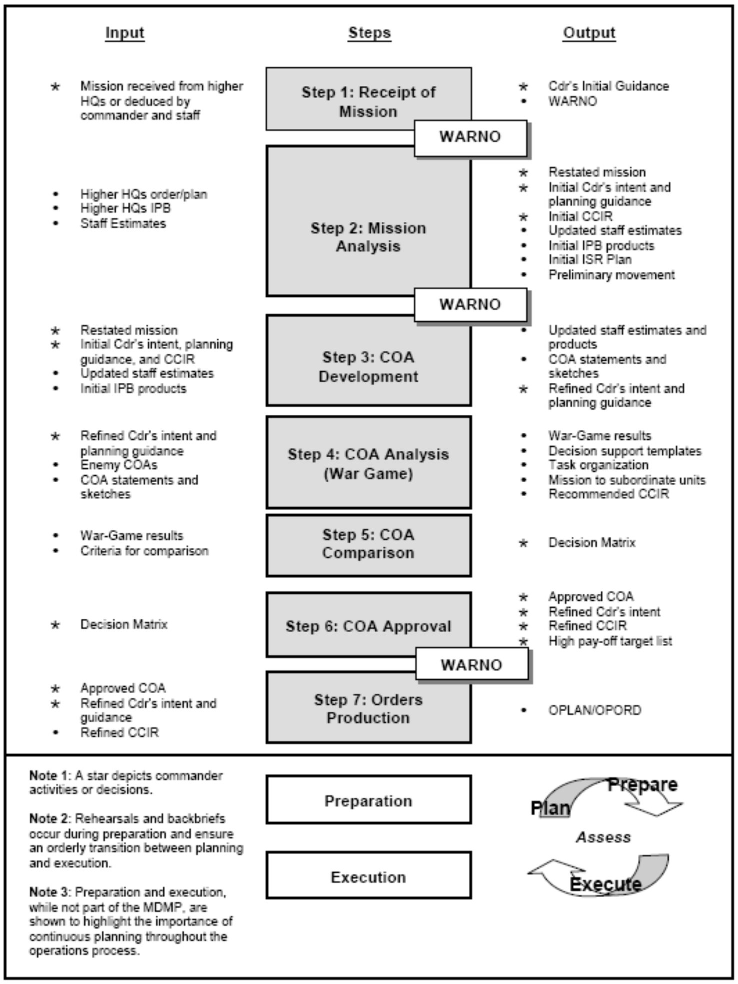


Figure 7: The Engineering Design Process[4]



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 8. The Military Decision Making Process[3]

Analysis of Results

To analyze the results the students were given a quiz 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 project cycle to see if there was improvement, and retention of knowledge. These results are in Table 2.

	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 2. Quiz Results

In addition to this the students were asked the following questions regarding their individual experiences with the capstone project. 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 below in Table 3 accompanied by the average response. Finally, 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.

Question Regarding Individual Experience	**Ave Response**
1. Was this capstone project useful in terms of helping the learning process?	1.64
2. Was this capstone project helpful to wrap up the course material at end of semester?	1.73
3. Did this capstone 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 capstone project?	2.55
6. Do you think the capstone experience helped your Term End Exam preparation?	2.09

Table 3. Questions Regarding Individual Experiences

From the results, it is clear that the Capstone 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 next year and continue to gather data.

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. In fact, we will execute the project again this year to gather more data. 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, to this 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.

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.

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[1] Gilbert, John C. and Stephen F. Martin, Experimental Organic Chemistry A Miniscale and Microscal Approach, *Fourth Edition*, (2006).

[2] Levenspeil, Octave. Chemical Reaction Engineering, *Third Edition*, (1999).

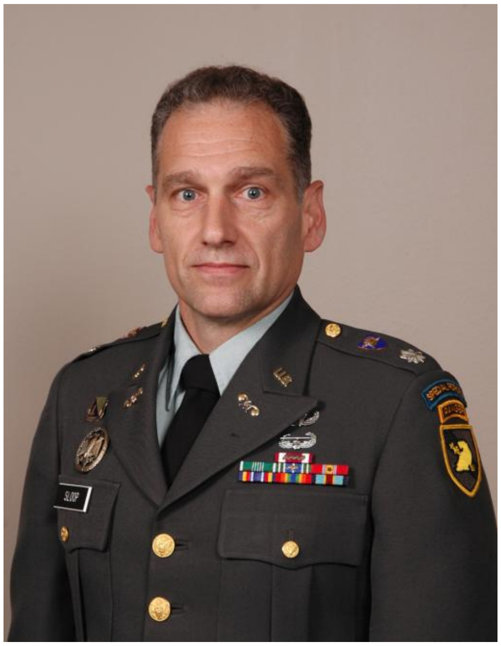
[3] FM 5-0. Army Planning and Orders Production. January 2005.

[4] CE300 Course Book, USMA, 20 June 2007.

BIOGRAPHIES

Colonel Russ Lachance is an Academy Professor supporting our Chemical Engineering Program. His teaching responsibilities include all chemical engineering courses and general chemistry courses. He received his B.S. degree from the United States Military Academy, at West Point NY;his M.S. and Ph.D. in chemical Engineering from MIT, Cambridge, MA. He is the Head Department Academic Counselor for our Department, the ABET coordinator for the Department, and serves on the ABET Committee, the RCI committee and the Faculty Council. He is the Officer-in-Charge of the Cadet Spirit Band, a football mentor, and the PME2 Team Leader for Company B4.

Dr. Andy Biaglow teaches chemistry core and elective courses. He is the director of the Chemical Engineering Program, and responsible for establishing a research program in Chemical Reaction Engineering. Dr. Biaglow received his B.S in Chemical Engineering at Case Western and his Ph.D in Chemical Engineering from University of Pennsylvania. He also did post-doc work at the University of PennsylvaniaDr. Biaglow is a member of the International Zeolite Association, the American Institute of Chemical Engineers, and the American Society of Engineering Educators. He conducts research on reaction pathways and intermediates in solid-catalyzed reactions. He is a member of the Materials Research Society, New York Catalysis Club and the American Chemical Society.



Lieutenant Colonel Joseph Sloop teaches CH383/384, Organic Chemistry I & II. Lieutenant Colonel Sloop's scientific interests include heterocycle synthesis, substituent effects on reactivity in organic systems, and magnetochemistry. He received his B.S. in Chemistry from Davidson College; his M.S. and Ph.D in Chemistry from North Carolina State University, in Raleigh, NC. He is a member of the American Chemical Society, Phi Lambda Upsilon, Phi Kappa Phi, Gamma Sigma Epsilon and the Chemical Corps regiment.

Major Rich Comitz taught CH101/102, General Chemistry last year. He is now the Assistant Course Director for CH383/384, Organic Chemistry I & II, and CH 489/CH490 Individual Research He received his B.S. in Chemistry at the United States Military Academy, at West Point, NY, and his M.S. in Chemistry at the Florida Institute of Technology. MAJ Comitz also serves as an Officer Representative of the Sprint Football Team, and Company Academic Counselor.

Major Matthew Armstrong teaches CH101/102, General Chemistry, CH 364 Chemical Reaction Engineering, CH 489/CH490 Individual Research and also serves as the Department S4. He received his B.S. and M.S. in Chemical Engineering from Rensselaer Polytechnic Institute in Troy, NY. MAJ Armstrong also serves as an Officer Representative for the Cadet Marathon Team, and Company Academic Counselor.