Application of Computational Tools to Enhance Understanding of Chemical Kinetics, Mechanisms, and Reactors: Examples in Air Pollutant Formation and Control

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Abstract

Environmental and chemical engineering students are introduced to topics in chemical kinetics, mechanisms, and reactors in many of their fundamental engineering classes. The use of example problems that enable students to better understand product formation from multi-step reactions, as well as how the choice of a reactor (e.g. a batch versus a flowing reactor) influences the predicted product yields are important. Computational tools are useful in enabling the evaluation of multiple scenarios and complicated, multi-reaction systems.

This paper utilizes air quality engineering examples to enable exploration of the effects that varying parameters have on air pollutant formation and control. The influences of initial NO_X and gas-phase hydrocarbon concentrations on ozone formation are explored. Simplified chemical kinetic mechanisms, rate constants, and rate expressions are presented and modeled using the Polymath numerical computational package. Corresponding Matlab inputs are also illustrated. The example that is presented enables faculty to reinforce mathematical principles (e.g. solving differential equations), chemical rates/rate constants/reaction orders, and fundamental reactor concepts of mole balances, conversion, and yield. Moreover, the systems that are discussed enable a broader discussion of air pollutant formation and control. These are areas that students may easily relate to in their everyday lives. Methods by which the tools can be employed in alternative scenarios are also discussed.
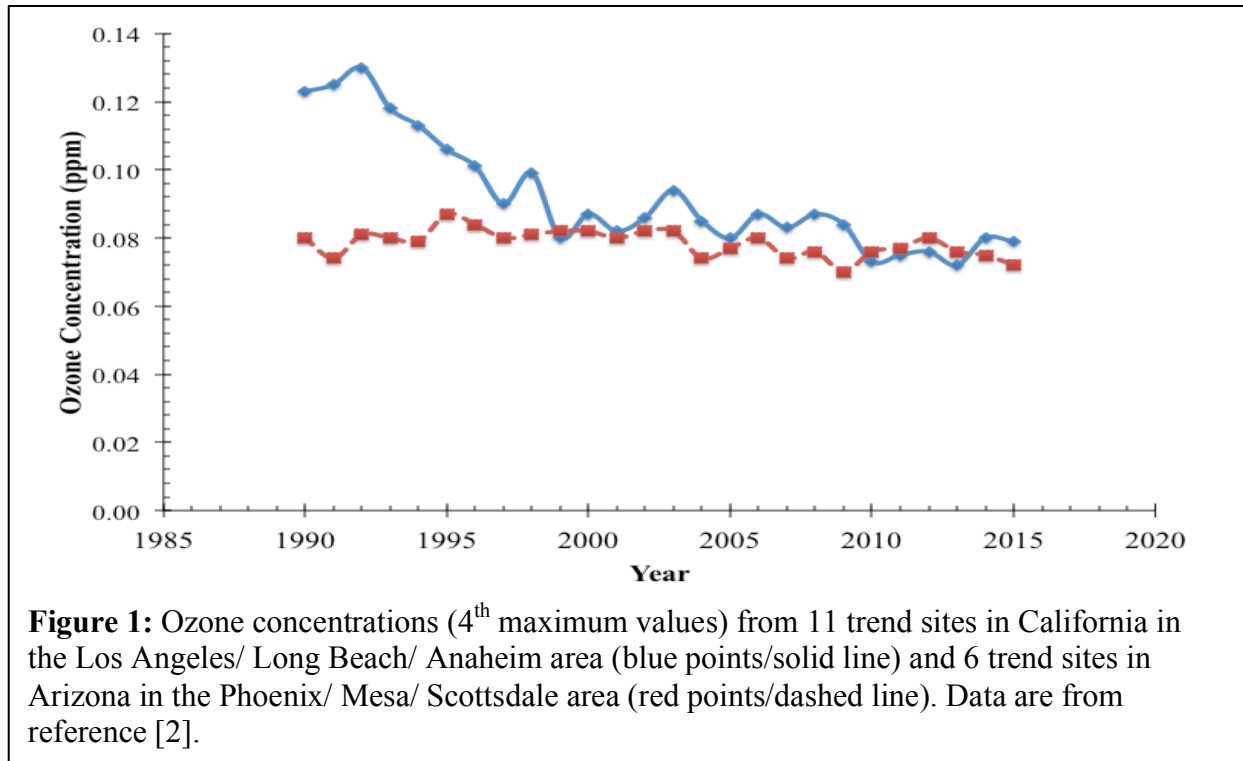
Introduction

Chemical kinetics and reactor design courses can be augmented through the use of example problems that are simplified enough, yet relate to real-world scenarios. The study of air pollutant formation and control provides example problems that may be used to reinforce concepts of reaction order, rate expressions, material balances, and the effects of reactor systems, while simultaneously allowing students to explore environmental themes and also enhancing their computational skills.

Air quality modeling is used by states, cities, and the federal government in order to evaluate the impacts of new or existing sources, understand the impacts of new air pollution control strategies, and to predict future atmospheric conditions so that appropriate advisories can be communicated to the public, among many other uses. Different types of models exist [1]. However, the models all typically include a chemistry component in order to be able to simulate the formation of pollutants such as ozone or particulate matter. Although there are thousands of compounds that could be modeled, air quality modeling efforts typically contain surrogate species that represent classes of compounds [1]. By employing different initial concentrations of compounds, conclusions can be drawn regarding the formation of various pollutants of interest.

Often times cities or states are concerned with determining the concentrations of ozone, a pollutant that forms in the atmosphere as a result of the reactions of NO_X (which consists of NO

and NO_2) and hydrocarbon compounds. The trends in ozone levels in the Los Angeles/Long Beach/Anaheim areas in California as well as the Phoenix/Tempe/Scottsdale areas of Arizona are presented in Figure 1 over the period from 1990 to 2015[2]. The data of Figure 1 represent the 4th maximum highest ozone concentrations over 11 and 6 sites (identified by the US Environmental Protection Agency and identified as "trend sites") in the cities within the states of California and Arizona, respectively, over the specified time frame[2].

Figure 1: Ozone concentrations (4th maximum values) from 11 trend sites in California in the Los Angeles/ Long Beach/ Anaheim area (blue points/solid line) and 6 trend sites in Arizona in the Phoenix/ Mesa/ Scottsdale area (red points/dashed line). Data are from reference [2].

The ozone concentrations in the Los Angeles area have decreased drastically over the past decades, with 8-hour average values as high as 0.400 ppm in the 1960s[3]. On the other hand, the 8-hour average ozone concentrations over the years in the Phoenix area fluctuated slightly, but remained below 0.10 ppm[4]. Recently, the ozone concentrations in both areas have decreased further, even though the 8-hour National Ambient Air Quality Standard (NAAQS) for ozone of 0.070 ppm (as established in 2015) is still exceeded in both areas[2].

Air pollution control strategies can be devised by considering the compounds that influence net ozone formation the most. Ozone isopleth diagrams (an example of which appears in Figure 2) can be used to devise these strategies. The curves in Figure 2 represent lines of constant ozone. These lines are plotted against the initial NO_x and initial hydrocarbon (HC) concentrations in a region. If the ambient conditions in an area are represented by the initial NO_x and hydrocarbon conditions that exist at point A, i.e. high NOx conditions and low hydrocarbon levels or "VOC- limited" conditions, the fastest way to reduce the ozone concentration would be to hold the NO_x level constant while reducing the hydrocarbon level. This action corresponds to a control strategy that follows the path of line 1 rather than line 2. If the ambient conditions in an area are represented by the initial NO_x and hydrocarbon conditions that exist at point B, i.e. low NO_x conditions and high hydrocarbon levels or "NO_x-limited" conditions, the fastest way to
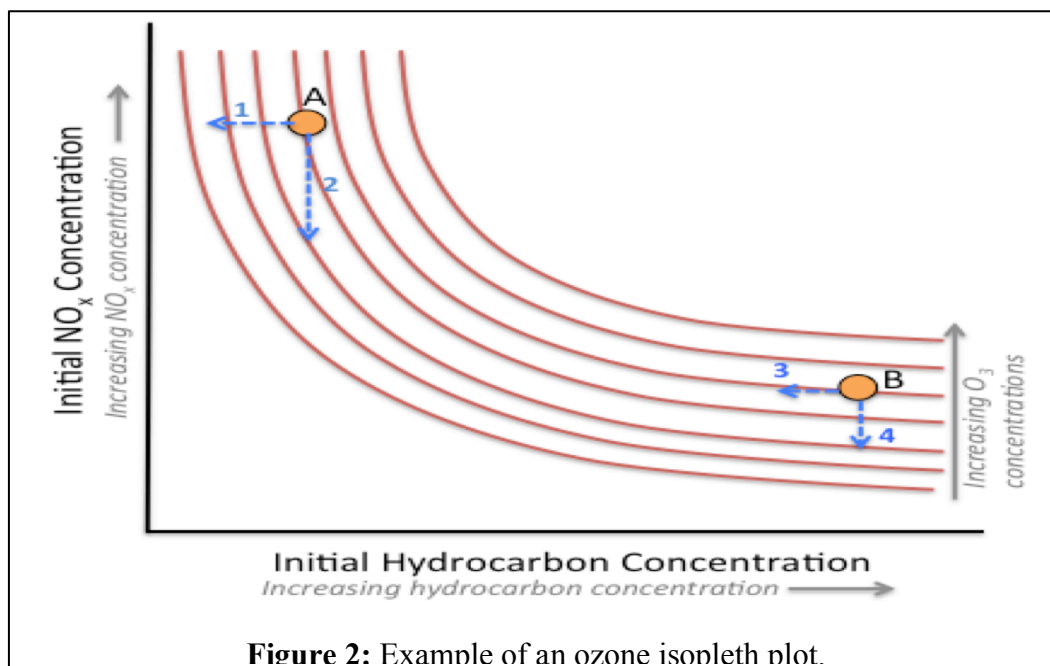
reduce the ozone concentration would be to hold the hydrocarbon level constant while reducing the NO_x level. This control strategy corresponds to following the path of line 4 rather than line 3. Although the path of line 3 (holding the NOx level constant while reducing the hydrocarbon level also decreases the ozone concentration, the decrease is rather small. By knowing the sources of either NO_x or hydrocarbon levels in the area, appropriate source controls could be devised. The major sources of NO_x are combustion systems. Thus, NO_x reductions typically correspond to reducing the number of vehicle miles travelled, improving fuel efficiency standards/vehicle emission systems, and controlling stationary sources such as power plants. Hydrocarbons are emitted from multiple sources, some natural (biogenic) and others man-made (anthropogenic). Thus, reducing hydrocarbon emissions might result in different air pollution control strategies, including installing evaporative control systems at fuel refilling stations, reformulating gasoline so that it is less reactive, or even controlling the types of trees that are planted. These topics are (or can be) discussed in preparation for the modeling exercise or can be assigned to students as a way to broaden their exploration of scientific themes, depending on whether the class is targeted towards an environmental engineering or chemical engineering class.

Modeling Activity

The concept of air quality modeling was introduced to both chemical and environmental engineering majors in a Reactor Design class that is required for chemical engineers as well as multiple Introduction to Air Pollution / Air Quality Engineering classes. The goals of the assignment were to:

1) enable broader thinking through the interpretation of modeling results,
2) expose students to computer-based modeling tools,
3) reinforce unit conversions, and
4) reinforce chemical concepts of rate expressions, reaction order, and material balances.

The modeling assignment is presented in Chemical Modeling Exercise #1. This exercise consists of both thought provoking questions (e.g. questions 1 and 6 of Chemical Modeling Exercise #1) and multiple simulations (e.g. questions 2-5 of Chemical Modeling Exercise #1).

Figure 2: Example of an ozone isopleth plot.

A simplified set of reactions for both ozone formation from the photolysis of NO_2 and the OH radical initiated destruction of C_8H_{18}, a component of gasoline that is also present in the atmosphere due to evaporative emissions, were provided as a mechanism. The gas-phase reactions of only a single hydrocarbon, C_8H_{18}, were provided in this reaction system in order to simplify the overall mechanism. However, as indicated subsequently in this paper, other systems with multiple hydrocarbons were employed in different modeling exercises for different classes. The use of just one hydrocarbon enabled the discussion of the relative trends in NO_x limited or VOC limited areas, and helped to reinforce students' knowledge of fundamental chemical concepts while simultaneously broadening students' critical thinking skills.

Computer-based Modeling Tools

   Although different models are available for real-world air pollution modeling activities[1], these tools are much too complicated to incorporate as a small module/homework assignment in either a required chemical engineering Reactor Design course or an Introduction to Air Pollution /Air Quality Engineering course. Also, these models are essentially "black boxes" where only inputs such as the pollutant mix or the initial concentrations are added. In order to enhance understanding of fundamental chemical concepts, as well as to enable the use of computational tools that students had ready access to, students were encouraged to set up their code either in Polymath[5], a computational program that is utilized in the "Essentials of Chemical Reaction Engineering" textbook [6] that is used in many chemical engineering programs around the nation, or Matlab, a widely available program. Although Microsoft Excel does have a differential equations solving component[7], the process of solving the equations would be impractical given the number of differential equations that must be solved simultaneously, even in the relatively small mechanism that was provided. Excel was therefore not recommended to the students as the tool for the modeling portion of the activity. However, Excel was recommended as the tool to use to easily generate plots of the final data.

Unit Conversions

   As seen in Chemical Modeling Exercise #1, the initial concentrations and rate constants were provided in different sets of units. Thus, students had to determine a consistent set of units. Given the temperature, pressure and Avogadro's number values of 298 K, 1 atm, and 6.02×10^{23} molecules mol^{-1}, respectively, and assuming that the ideal gas law (PV=nRT, where P, V, n, R, and T are, respectively, pressure, volume, moles, the gas constant, and absolute temperature) applied, the following conversion factors could be determined by students:

   1 part per million=1 ppm = 1 μmol mol^{-1} = 2.463×10^{13} molecules cm^{-3}, and, similarly,

   1 part per billion=1 ppb=1 nmol mol^{-1} = 2.463×10^{10} molecules cm^{-3} = 10^{-3} ppm.

Given these conversion factors, the initial concentrations and rate constants that had to be altered for the example shown in Chemical Modeling Exercise #1 are presented in Table 1.

Table 1: Converted rate constants and initial concentrations assuming a temperature and pressure of 298 K and 1 atm, respectively.

Reaction	Provided Rate Constant ($cm^3 molecule^{-1} s^{-1}$)	Rate Constant Used in the Model ($ppm^{-1} min^{-1}$)
5	k5 = 3.57×10^{-12}	k5 = 5.28×10^3
6	k6 = 1.00×10^{-12}	k6 = 1.48×10^3
7	k7 = 5.79×10^{-12}	k7 = 8.56×10^3
8	k8 = 2.48×10^{-12}	k8 = 3.66×10^3

Specie	Provided Information	Initial Concentration Used in the Model (ppm)
C_8H_{18}	50, 100, or 300 ppb	0.050, 0.100 or 0.300
NO	85% of 100 ppb	0.085
NO_2	15% of 100 ppb	0.015
OH	1.13×10^6 molecules cm^{-3} *	4.59×10^{-8}
HO_2	1×10^8 molecules cm^{-3}	4.06×10^{-6}

*Note: In the original modeling exercise, this value was 10^6 molecules cm^{-3}. However, a recent paper[8] updated the level. This updated value is presented in this paper and new output data are included from the models.

Rate Expressions and Material Balances

Rate expressions are typically introduced to both chemical and environmental engineering students when the subject of chemical reaction kinetics arises. Although actual rate expressions can only be determined through the use of experiments, initial information can be obtained by simply assuming that the rate expression may derived directly from the molecularity of the system. Thus, elementary reactions with the following forms:

$$\text{(Reaction a)} \quad A \rightarrow \text{Products,}$$
$$\text{(Reaction b)} \quad B+D \rightarrow \text{Products}$$
$$\text{(Reaction c)} \quad E+F+G \rightarrow \text{Products}$$

and rate constants k_a, k_b, and k_c, respectively, would have reaction rates of :

$$\text{rate for reaction a } (r_a) = k_a * C_A \qquad \text{(Equation 1)}$$
$$\text{rate for reaction b } (r_b) = k_b * C_B * C_D \qquad \text{(Equation 2)}$$
$$\text{rate for reaction c } (r_c) = k_c * C_E * C_F * C_G \qquad \text{(Equation 3)}$$

where the C_i are the concentrations of species in the reaction. Reaction "a" represents a unimolecular reaction that is first order overall. When considering photolysis reactions, i.e. of the form $A + h\nu \rightarrow$ Products, these reactions are considered to be first order reactions, even though a photon is required to initiate the chemistry. The rate constant for this type of reaction varies based on time of day, location, and season. However, the rate constant is easily calculated by knowing the absorbtion coefficient of the reacting specie and solar intensity values at the specified location. Reaction "b" represents a bimolecular reaction that is second order overall and first order each with respect to compounds B and D. The reactions that typically take place in the atmosphere are usually first or second order overall; true gas-phase termolecular reactions (similar to Reaction "c") are rare. The rate constants that were provided to the students were calculated or obtained from the published literature. Sources for the rate constants are provided in Table 2.

Table 2: Reactions and rate constants used in Chemical Modeling Exercise #1.

Reaction	Rate Constant	References
(1)$NO_2 + h\nu \rightarrow NO + O^{\cdot}$	k1= 0.5 min^{-1}	Calculated using [1] [9]
(2) $O + O_2 \rightarrow O_3$	k2=21.83 ppm^{-1} min^{-1}	[9]
(3) $O_3 + NO \rightarrow NO_2 + O_2$	k3=26.6 ppm^{-1} min^{-1}	[9]
(4) $HO_2^{\cdot} + NO \rightarrow {}^{\cdot}OH + NO_2$	k4=1.2 x 10^4 ppm^{-1} min^{-1}	[9]
(5) $C_8H_{18} + {}^{\cdot}OH \rightarrow {}^{\cdot}C_8H_{17} + H_2O$	k5 = 3.57 x 10^{-12} cm^{3}molecule^{-1} s^{-1}	[10],[11]
(6) ${}^{\cdot}C_8H_{17} + O_2 \rightarrow {}^{\cdot}O_2C_8H_{17}$	k6 = 1.0 x 10^{-12} cm^{3}molecule^{-1} s^{-1}	[10],[11]
(7) ${}^{\cdot}O_2C_8H_{17} + NO \rightarrow {}^{\cdot}OC_8H_{17} + NO_2$	k7 = 5.79 x 10^{-12} cm^{3}molecule^{-1} s^{-1}	[10],[11]
(8) ${}^{\cdot}OC_8H_{17} + O_2 \rightarrow C_7H_{17}CHO + HO_2^{\cdot}$	k8 = 2.48 x 10^{-12} cm^{3}molecule^{-1} s^{-1}	[10],[11]

The type of reactor that is used for a process plays a critical role in determining the extent of conversion that may occur. A generalized material balance may be written as:

$$\frac{dN_i}{dt} = F_{i \ at \ t=0} - F_i + Generation \qquad \text{(Equation 4)}$$

Where N_i = moles of "i", F_i = molar flowrate of "i", and t= time. In considering air quality modeling efforts, as a first approximation, one can model the chemistry in the atmosphere as a simple well-mixed reactor, similar to an ideal constant volume batch reactor system. Given this

information, the generation term on the right reduces down to r_iV, where r_i is the rate of formation of component i and V is the volume of the batch reactor. Given a constant volume system, where the concentration of specie "i" is equivalent to the number of moles per volume (i.e. $C_i = N_i / V$). The material balance reduces to:

$$\frac{dN_i}{dt} = Generation = r_i V \qquad \text{(Equation 5)}$$

$$\frac{d\left(\frac{N_i}{V}\right)}{dt} = \frac{dC_i}{dt} = r_i \qquad \text{(Equation 6)}$$

where C_i is the concentration of specie i, t is time, and r_i is the rate of formation of specie i. If the material is a reactant, then r_i is negative. The overall rate of formation of a specie takes into account all formation and loss reactions in a mechanism.

To begin the exercise, students needed to first identify which reactions formed and destroyed each specie in the overall mechanism. After doing so, a material balance on that specie could be developed. As an example, ozone (O_3) was formed in reaction 2 with rate r_2 and destroyed in reaction 3 with rate r_3. Thus, the net rate of O_3 formation was r_2- r_3, and the material balance for O_3 was determined to be:

$$\frac{d\, O3}{dt} = r_2 - r_3 \qquad \text{(Equation 7)}$$

where $r_2 = k_2*O2*O$, $r_3 = k_3*O3*NO$, and the chemical symbol represents the concentration of the compound. Thus, "O3" and "NO" represent the concentrations of ozone and nitric oxide, respectively. Material balances were developed for each unique compound, and the rate constants as well as the initial concentrations were modeled in accordance with the scenarios that were presented in the exercise. An example input from the Polymath modeling is provided in Figure 3. The corresponding Matlab formatted input is available in Appendix 1.

Results:

A sample output file from Polymath is provided in Appendix 2. Table 3 contains all of the initial concentrations that were modeled, as well as the resulting calculated maximum ozone levels. Figure 4 is a plot of the calculated ozone levels as function of varying NO_x levels as the hydrocarbon concentration was held constant at three separate levels : 0.050 ppm, 0.100 ppm, and 0.300 ppm. This plot addressed question 2 of the modeling exercise, including the different starting conditions indicated in questions 4 and 5. The data of Figure 4 indicate that as the starting NO_x level decreased, the ozone level also decreased, irrespective of the initial hydrocarbon concentration that was used. Figure 5 is a plot of the calculated maximum ozone levels achieved in systems where the initial hydrocarbon concentrations were varied while the NO_x concentration was held constant at 0.100 ppm. The plots of Figure 5 indicate that the ozone level did not vary significantly as the hydrocarbon level was lowered. The data that were obtained and are presented in Table 3 as well as in Figures 4 and 5 enabled students to generate data in a manner similar to the type of data that would appear on an ozone isopleth diagram (similar to Figure 2). Using their data, students could conclude that for the initial conditions that were provided, the fastest way to lower ozone in the modeled region would be to focus on lowering the emissions of NO_x in the atmosphere. It is also important to point out that the modeled concentrations result in ozone concentrations that are higher than those actually seen in the greater Los Angeles and Phoenix areas shown in Figure 1. The differences can be attributed

to the simplification of the chemical mechanism (to exclude additional ozone loss mechanisms) and the dilution / transport of pollutants from the points of emission and reaction.

```
# The reaction mechanism incorporates the NO2 and C8H18 mechanisms.
# The following expressions are for the rates of the reactions (r#) with rate constants (k#),
# where all rate constants are in the ppm,minute system of units.
r1=k1*NO2
k1=0.5
r2=k2*O*O2
k2=21.83
r3=k3*O3*NO
k3=26.6
r4=k4*HO2*NO
k4=1.2e4
r5=k5*C8H18*OH
k5=5.28e3
r6=k6*C8H17*O2
k6=1.48e3
r7=k7*O2C8H17*NO
k7=8.56e3
r8=k8*OC8H17*O2
k8=3.66e3
#The following equations represent the material balances for each specie.
#The levels of OH and O2 remain constant.
d(NO2) / d(t)=r3+r4+r7-r1
d(NO) / d(t)=r1-r3-r4-r7
d(O) / d(t)=r1-r2
d(O3) / d(t)=r2-r3
d(C8H18) / d(t)=-r5
d(C8H17) / d(t)=r5-r6
d(O2C8H17) / d(t)=r6-r7
d(OC8H17) / d(t)=r7-r8
d(C7H17CHO) / d(t)=r8
OH=4.59e-8
HO2=4.06e-6
O2=21000
# All initial concentrations are specified below in units of ppm.
NO(0) = 0.085
NO2(0) = 0.015
C8H18(0)=0.100
O(0)=0
O3(0)=0
C8H17(0)=0
O2C8H17(0)=0
OC8H17(0)=0
C7H17CHO(0)=0
# The model must indicate how long the run should last (360 mins).
t(0)=0
t(f) = 360
```

Figure 3: Polymath input file for the scenario where the initial C_8H_{18}, NO, and NO_2 levels were 100 ppb (0.100 ppm), 85 ppb (0.085 ppm) and 15 ppb (0.015 ppm), respectively. A temperature of 298 K and 1 atm was assumed.

Table 3: Modeled scenarios (initial concentrations) and resulting calculated maximum ozone levels.

| Model Run #	Initial Concentrations (ppm)						Calculated Maximum Concentration (ppm)
	NO	NO_2	C_8H_{18}	O_2	OH	HO_2	O_3
1 (base case #1)	0.085	0.015	0.100				0.224
2 (20% decrease in NO_x)	0.068	0.012	0.100				0.200
3 (40% decrease in NO_x)	0.051	0.009	0.100				0.172
4 (60% decrease in NO_x)	0.034	0.006	0.100				0.139
5 (80% decrease in NO_x)	0.017	0.003	0.100	21×10^4	4.59×10^{-8}	4.06×10^{-6}	0.096
6 (20% decrease in C_8H_{18})	0.085	0.015	0.080				0.223
7 (40% decrease in C_8H_{18})	0.085	0.015	0.060				0.222
8 (60% decrease in C_8H_{18})	0.085	0.015	0.040				0.221
9 (80% decrease in C_8H_{18})	0.085	0.015	0.020				0.220
10 (base case #2)	0.085	0.015	0.300				0.235
11 (20% decrease in NO_x)	0.068	0.012	0.300				0.210
12 (40% decrease in NO_x)	0.051	0.009	0.300				0.183
13 (60% decrease in NO_x)	0.034	0.006	0.300				0.150
14 (80% decrease in NO_x)	0.017	0.003	0.300	21×10^4	4.59×10^{-8}	4.06×10^{-6}	0.107
15 (20% decrease in C_8H_{18})	0.085	0.015	0.240				0.231
16 (40% decrease in C_8H_{18})	0.085	0.015	0.180				0.228
17 (60% decrease in C_8H_{18})	0.085	0.015	0.120				0.225
18 (80% decrease in C_8H_{18})	0.085	0.015	0.060				0.222
19 (base case #3)	0.085	0.015	0.050				0.222
20 (20% decrease in NO_x)	0.068	0.012	0.050				0.197
21 (40% decrease in NO_x)	0.051	0.009	0.050				0.170
22 (60% decrease in NO_x)	0.034	0.006	0.050				0.137
23 (80% decrease in NO_x)	0.017	0.003	0.050	21×10^4	4.59×10^{-8}	4.06×10^{-6}	0.094
24 (20% decrease in C_8H_{18})	0.085	0.015	0.040				0.221
25 (40% decrease in C_8H_{18})	0.085	0.015	0.030				0.221
26 (60% decrease in C_8H_{18})	0.085	0.015	0.020				0.220
27 (80% decrease in C_8H_{18})	0.085	0.015	0.010				0.220
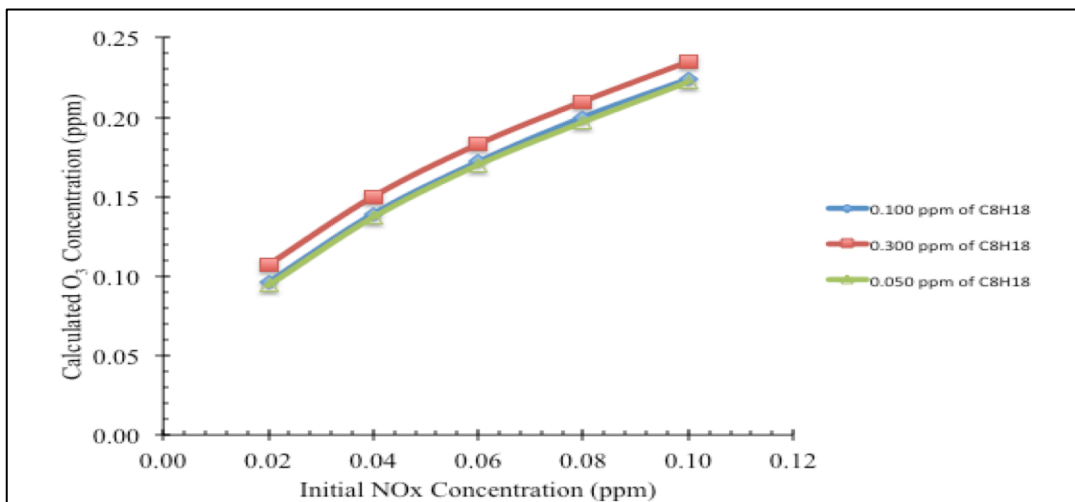
Figure 4: Impacts on the calculated maximum O_3 concentrations obtained by varying the initial NO_x concentration while holding the *C_8H_{18} concentration constant* at either 0.050, 0.100, or 0.300 ppm.
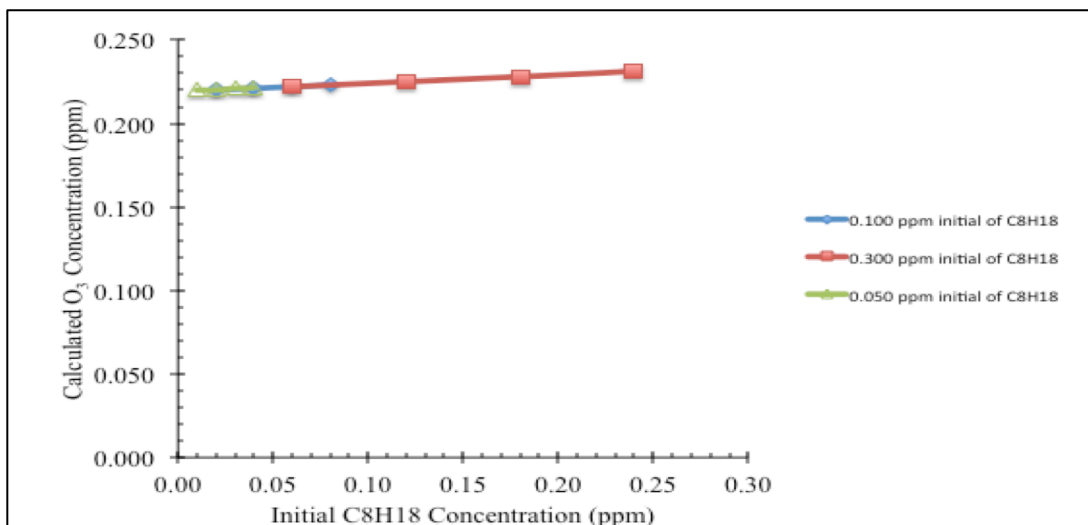
Figure 5: Impacts on the calculated O_3 concentrations obtained by varying the initial C_8H_{18} concentration from a high initial starting value of 0.300, 0.100, or 0.050 ppm, while holding the initial NO_x concentration constant at 0.100 ppm, with 85% of the NO_x as NO, and the remaining as NO_2.

Impacts on Students and Curriculum

The last time that the chemical modeling exercise was implemented was in Spring 2015, in a required junior level Reactor Design class at Arizona State University. All 178 students in the class had some level of introduction to Matlab from previous courses (although not from a single course), and were also exposed to Polymath as an alternative while in the Reactor Design class since the required textbook utilized Polymath-based examples [3]. The assignment was conducted in groups of 2 or 3 students. A separate evaluation was not conducted for this one assignment. However, student scores on the assignment provided a measure of student performance. In addition, students communicated their opinions in the end of year faculty and course evaluations as well as in person. Minimal competence in the grading of the assignment was 70%, corresponding to "C" level performance (the required metric for core courses in the chemical engineering degree program at Arizona State University). Out of the 178 students, only 3 students chose not to submit the assignment. Out of the remaining 175 students, 171 students received scores of 70% or greater. The average score was 90.9%, with a standard deviation of 9.2%. Numerous comments during office hours revealed that students enjoyed the exercise, but struggled tremendously with the coding portion of the work when trying to use Matlab, and also had some difficulties in converting between the units of molecules cm^{-3} and "parts" (e.g. parts per billion, million, or trillion) by volume. These comments were echoed in the end of year course evaluations. Nevertheless, the course evaluations in the 2015 year for Reactor Design were still very high at 4.33/5.

Both of the students' challenges (with units and modeling) were addressed in real-time by providing a mini tutorial on air pollution units, as well as holding additional help sessions to assist with the coding. The challenges that were faced with the unit conversions stemmed from a lack of familiarity with the units of "parts" *by volume*. Some of the chemical engineering students had been exposed to units of "parts" in a water quality class and therefore assumed a mass, not a volume basis. Polymath was chosen as the coding platform that was presented in the additional help sessions, since students found the user interface to be easier to work with than

Matlab. Most students (>85%) ended up using Polymath as the computational tool for the modeling exercise.

The chemical modeling activity was discussed in end-of-year ABET assessment documents that were assembled for the 2015 Reactor Design class, and subsequently addressed in a chemical engineering program faculty meeting. Recommendations regarding the implementation of computational resources in chemical engineering courses were made, and, in 2016, a dedicated numerical methods / computational course for chemical engineering students was established. The chemical modeling assignment that is detailed in this paper was not implemented in the 2016 Reactor Design course due to the timing of the numerical methods/computational course. However, the chemical modeling assignment will be deployed again in the Spring 2017 semester. Feedback will be available and presented at the 2017 American Society of Engineering Education Pacific Southwest (ASEE PSW) conference.

Past Alternative Modeling Options

The exercise that has been discussed was implemented in Introduction to Air Pollution/Air Quality Engineering classes in the past in different ways. These methods included:

1. *Evaluation of the effectiveness of blended fuels in minimizing the maximum ozone concentration.*

   The alternative fuel, E85, a mixture of 85% ethanol (C_2H_5OH) and 15% gasoline was used in the modeling efforts, rather than just gasoline. E85 is a flex fuel that is used in multiple places around the world, including in the US. Additional reactions for the OH radical initiated decomposition of ethanol were provided to the students. Scenarios that were similar to the ones presented in questions 2 through 5 of Chemical Modeling Exercise #1 were posed, and students responded.

2. *Comparison of the use of pure gasoline to the use of methanol.*

   Methanol (CH_3OH) is used as a fuel in car racing. Additional reactions for the OH radical initiated decomposition of methanol were provided to the students. Scenarios that were similar to the ones presented in questions 2 through 5 of Chemical Modeling Exercise #1 were posed, and students responded. Additional work to spark student interest in understanding why methanol is not used as a fuel for everyday vehicles was encouraged.

Future Modeling Exercises

As mentioned previously, in the Spring 2017 semester, alternatives to Chemical Modeling Exercise #1 will be presented to students in the required junior level Reactor Design course. The exercise will be changed so that a flow reactor system is modeled, rather than a batch reactor system. This will allow students to examine the impacts of the reactor type on conversion and product formation. Although students would not be able to compare modeled data to actual data with this system (since the mechanism is even more simplified as compared to the already simplified chemical mechanisms that are used in existing modeling efforts[1]), this exercise would still enable students to consider the effects of flow on the material balances. Molar conversions of the hydrocarbon and product yields will be calculated and compared.

A system that will be implemented in the fall 2017 semester in the Air Quality Engineering class at Arizona State University is the simultaneous control of carbon dioxide and sulfur containing compounds through the use of a catalytic packed bed reactor system. This work would augment the discussion of the formation and control of gases from environmental processes that include the biological degradation of wastes (e.g. at a wastewater treatment plant).

Modeling has already begun on this type of system, and, time permitting, will be presented at the 2017 ASEE PSW conference.

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Appendix 1: Matlab input for the problem shown in Figure 3.
(Note that this file is provided as an example, since most students chose to use Polymath for their simulations. In addition, the input concentration for OH represents the 2016 updated value, as noted in Table 1, and is slightly higher than the value that students used in their simulations.)

```
tspan = [0 360.]; % Range for the independent variable
y0 = [0.015; 0.085; 0; 0; 0.3; 0; 0; 0; 0]; % Initial values for the dependent variables
function dYfuncvecdt = ODEfun(t,Yfuncvec);
NO2 = Yfuncvec(1);
NO = Yfuncvec(2);
O = Yfuncvec(3);
O3 = Yfuncvec(4);
C8H18 = Yfuncvec(5);
C8H17 = Yfuncvec(6);
O2C8H17 = Yfuncvec(7);
OC8H17 = Yfuncvec(8);
C7H17CHO = Yfuncvec(9);
k1 = 0.5;
r1 = k1 * NO2;
O2 = 21000;
k2 = 21.83;
k3 = 26.6;
r3 = k3 * O3 * NO;
HO2 = 0.00000406;
k4 = 12000;
OH = 0.0000000459;
k5 = 5280;
r2 = k2 * O * O2;
k6 = 1480;
k7 = 8560;
r7 = k7 * O2C8H17 * NO;
r6 = k6 * C8H17 * O2;
k8 = 3660;
r5 = k5 * C8H18 * OH;
r4 = k4 * HO2 * NO;
r8 = k8 * OC8H17 * O2;
dNO2dt = r3 + r4 + r7 - r1;
dNOdt = r1 - r3 - r4 - r7;
dOdt = r1 - r2;
dO3dt = r2 - r3;
dC8H18dt = 0 - r5;
dC8H17dt = r5 - r6;
dO2C8H17dt = r6 - r7;
dOC8H17dt = r7 - r8;
dC7H17CHOdt = r8;
dYfuncvecdt = [dNO2dt; dNOdt; dOdt; dO3dt; dC8H18dt; dC8H17dt; dO2C8H17dt; dOC8H17dt; dC7H17CHOdt];
```

Appendix 2: Polymath output for the problem shown in Figure 3.

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	C7H17CHO	0	0	0.0250637	0.0250637
2	C8H17	0	0	2.335E-12	2.144E-12
3	C8H18	0.3	0.2749353	0.3	0.2749353
4	HO2	4.06E-06	4.06E-06	4.06E-06	4.06E-06
5	k1	0.5	0.5	0.5	0.5
6	k2	21.83	21.83	21.83	21.83
7	k3	26.6	26.6	26.6	26.6
8	k4	1.2E+04	1.2E+04	1.2E+04	1.2E+04
9	k5	5280.	5280.	5280.	5280.
10	k6	1480.	1480.	1480.	1480.
11	k7	8560.	8560.	8560.	8560.
12	k8	3660.	3660.	3660.	3660.
13	NO	0.085	0.0073575	0.085	0.0073575
14	NO2	0.015	0.015	0.0926425	0.0926425
15	O	0	0	1.01E-07	1.01E-07
16	O2	2.1E+04	2.1E+04	2.1E+04	2.1E+04
17	O2C8H17	0	0	1.058E-06	1.058E-06
18	O3	0	0	0.2345721	0.2345721
19	OC8H17	0	0	9.442E-13	8.669E-13
20	OH	4.59E-08	4.59E-08	4.59E-08	4.59E-08
21	r1	0.0075	0.0075	0.0463151	0.0463151
22	r2	0	0	0.0463151	0.0463151
23	r3	0	0	0.0459015	0.0459015
24	r4	0.0041412	0.0003591	0.0041412	0.0003591
25	r5	7.271E-05	6.665E-05	7.271E-05	6.665E-05
26	r6	0	0	7.257E-05	6.665E-05
27	r7	0	0	7.257E-05	6.665E-05
28	r8	0	0	7.257E-05	6.665E-05
29	t	0	0	360.	360.

Differential equations

1. $d(NO2)/d(t) = r3+r4+r7-r1$
2. $d(NO)/d(t) = r1-r3-r4-r7$
3. $d(O)/d(t) = r1-r2$
4. $d(O3)/d(t) = r2-r3$
5. $d(C8H18)/d(t) = -r5$
6. $d(C8H17)/d(t) = r5-r6$
7. $d(O2C8H17)/d(t) = r6-r7$
8. $d(OC8H17)/d(t) = r7-r8$
9. $d(C7H17CHO)/d(t) = r8$

Explicit equations

1. $k1 = 0.5$
2. $r1 = k1*NO2$
3. $O2 = 21000$
4. $k2 = 21.83$
5. $k3 = 26.6$
6. $r3 = k3*O3*NO$
7. $HO2 = 4.06e-6$
8. $k4 = 1.2e4$
9. $OH = 4.59e-8$
10. $k5 = 5.28e3$
11. $r2 = k2*O*O2$
12. $k6 = 1.48e3$
13. $k7 = 8.56e3$
14. $r7 = k7*O2C8H17*NO$
15. $r6 = k6*C8H17*O2$
16. $k8 = 3.66e3$
17. $r5 = k5*C8H18*OH$
18. $r4 = k4*HO2*NO$
19. $r8 = k8*OC8H17*O2$

General

Total number of equations	28
Number of differential equations	9
Number of explicit equations	19
Elapsed time	0.000 sec
Solution method	stiff
Independent variable accuracy. eps	0.00001
First stepsize guess. h1	0.0001
Minimum allowed stepsize. hmin	0.00000001
Good steps	410
Bad steps	0

Data file: c:\users\jean\documents\asee_paper_models\no2_c8h18_run1_withho2_initial.pol