A Simulation and Experimental Environment for Teaching Chemical Reaction Process Dynamics and Control

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Abstract: In many undergraduate chemical engineering courses, students are taught about the dynamics of chemical reactions. Examining the textbook literature on reaction process dynamics, there is a gap between the concepts presented in theory and their pedagogical realization in laboratory experiments and complementary simulations. This paper presents a simple, safe, economical approach to provide undergraduate students with an experience in reaction dynamics to match the well-established theory. Optical transmissibility is used as a surrogate for concentration allowing ease of transduction. A simple experiment, costing less than $750 US, is designed and presented along with the results for a crystal violet bleaching reaction. A simulation environment is presented alongside the experimental system. The system's first order dynamics are well established and the simulations match the experiments well. Additionally, influence of temperature on the system's time constant is demonstrated via temperature control. This first order system provides the chemical engineering equivalent to DC motor velocity or RC circuit voltage experiments used in Mechanical and Electrical engineering education. Use of the approach to illustrate simple process reaction control concepts is also demonstrated.

Keywords: Control Education, Chemical Engineering, System Dynamics and Control

1. INTRODUCTION

Understanding of process dynamics is a key part of Chemistry and Chemical Engineering undergraduate programs (Skogestad 2009; Hangos & Cameron 2001). The rates of individual reactions are often the key factor determining process control variables. Typical reactions are provided in textbooks and students are made aware of rates of reactions as functions of time. However, it is fairly standard in undergraduate texts to abstract away the specifics of reactions and replace it with generic reagents (Fogler 1992; Seborg et al. 2004; Marlin 1995; Levenspiel 1999; Davis & Davis 2003; Bequette 1998). For example, a typical problem would describe adding reagents $A+B \rightarrow C$ without a clear physical meaning of what A, B, or C actually are. For example, a continuous stirred tank reactor (CSTR) example from (Seborg et al. 2004) asks the reader to "consider a simple liquid phase, irreversible chemical reaction where chemical species A reacts to form species B." The reaction rate is then written as

$$r = kC_A \tag{1}$$

where r is the rate of reaction A per unit volume, k is the reaction rate constant and C_A is the molar concentration of species A (Seborg et al. 2004).

The differential equations used to determine evolution of species A as a function of time can then be crafted from conservation laws as well as Thermodynamics. For many undergraduate students, the differential equations are insufficient to gain a thorough conceptual understanding of the dynamics of the process.

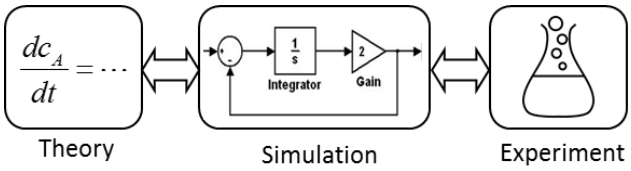

Fig. 1. Coupling among Theory, Simulation and Experiment for student understanding of material.

As illustrated in Fig. 1, it is important to have both simulation and experimental hands-on illustrations of the concepts as a key bridge from the basic theoretical exposition to student understanding. Currently, there exist several excellent educational products for simulating dynamical systems. Matlab/SIMULINK is a standard for undergraduate programs with AMEsim, and Modelica as other suitable packages (MathWorks 2016; Siemens 2016; Modelica 2016). While these are powerful graphical simulation tools, at present much of the attention on so-called packaged simulation toolboxes focus on mechanical or electrical systems. Therefore, many of the chemical process dynamic simulation tools that would be used by students needs to be created. It could be of great value for the younger undergraduate students to focus less on the syntax of simulation languages and more on the content and physical connections in their systems. There do exist some packaged software solutions (Postlethwaite 2016a; Yazdi 2012) but these are not widely available yet and have limitations. Reactor Lab (Herz 2016) does only single components such as one CSTR, has limited rate law options, has limited choices of parameters to vary and still has no

physical meaning since the reactions are all $A+B \rightarrow C$ types without actual chemistry. Similarly, PISim (Postlethwaite 2016b) has limited physical meaning but allows for complex systems to be constructed.

It is equally important there exist educational products that give the student a hands on exposure to certain aspects of chemical process dynamics in the form of experiments. However, the currently available products all focus on demonstrating mass flow, heat flow, or liquid levels as the elements of process dynamics. In particular, Feedback Instruments provides a temperature controlled process and mass flow controlled process (Feedback 2016), which allows the student to understand the dynamics and time domain evolution of temperature or mass flow rate. The pedagogical assumption is that once they know the "mechanical" aspects of the reaction such as temperature/pressure/volume then the chemical aspects will be known through reaction rate laws such as (1). A missing piece of the instructional portfolio is an easy to use simulation environment coupled with experimental demonstration of the dynamics of the reactions. Currently, to the knowledge of the authors, such a product pair is not readily accessible in the market for educational purposes. To be fair, many chemical reactions suitable for study are exothermic, or involve chemicals that require special handling procedures. Therefore, the missing educational products may be due to safety reasons more so than unmet demand.

The purpose of this paper is to present modelling tools and experiments suitable for undergraduate chemistry and chemical engineering courses. In the following, we propose a simple, inexpensive, and safe experimental system that can be used to study the dynamics of processes as well as an intuitive simulation package built on Matlab/SIMULINK that complements the experimental system. The rest of the paper is presented a follows. In section 2, we provide our approach to system modelling in a graphical drag and drop environment. Section 3 presents the design of a simple experiment that can fulfil many of instructional needs illustrating reaction dynamics. Section 4 provides results from a sample laboratory exercise in first order process dynamics and Section 5 provides a simulation example of closed loop control of process concentration using the results of Sections 2-4. A conclusion summarises the main points of the article.

2. SYSTEM MODELING ENVIRONMENT

The developed simulation environment utilizes blocks containing underlying equations governing process behaviour. This includes the reaction dynamics as well as the other process dynamics such as mass flow, temperature, etc. Each block can be connected to upstream or downstream components to move mass from one block to another. As an example, we present a CSTR block as shown in Fig. 2.

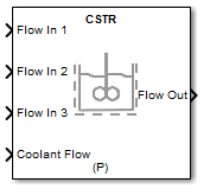

Fig. 2. Icon for a CSTR block.

This block accepts multiple inputs with up to 3 inlet mass flows shown here. Inlet flows contain the fluid temperature (°C), mass flow rate (kg/s), reactant concentration (kg/m^3), density (kg/m^3), heat capacity (J/kg°C), and heat of formation (J/kg). There is also a separate jacket temperature input that is the output from a separate heater block (°C) that would be closely coupled to the CSTR block. A single output flow is assumed. Should the resulting reacted product need to be sent to multiple downstream elements then a flow split component can be used to allocate the output. The reactor itself is characterized by a range of geometric parameters. Fig. 3 illustrates a graphical user interface that easily allows the student to adjust parameters of the reactor vessel.

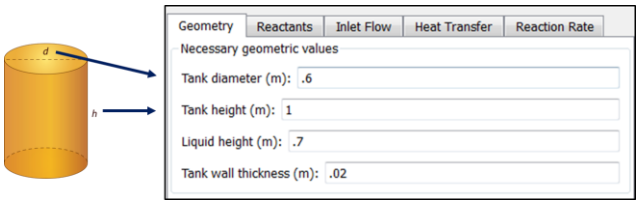

Fig. 3. Example of geometric parameters for a reaction tank.

The reaction dynamics of an exemplar CSTR block would be governed by equations such as an energy balance

$$\frac{dT}{dt} = \frac{UA_r(T_a - T) - \dot{W} - F_{A0}c_{ps}(T - T_0) + \Delta H_{RX}(-kC_A V)}{C_{A0}Vc_{ps}}, \quad (2)$$

a mass/molar balance

$$\frac{dC_A}{dt} = \frac{C_{A0}v_0}{V} - \frac{C_A v_0}{V} - kC_A, \quad (3)$$

and a rate law

$$k = Ae^{\frac{E}{RT}}, \quad (4)$$

where coefficients are defined in Table 1.

Table 1. CSTR parameter and state definitions.

A	pre-exponential factor	R	gas constant
A_r	reactor surface area	T	temperature
C_A	reactant A concentration	T_a	jacket temperature
C_{A0}	inlet concentration of reactant A	T_0	inlet temperature
c_{ps}	solution heat capacity	U	jacket heat transfer coefficient
E	activation energy	V	reactor volume
F_{A0}	inlet mass flow rate of reactant A	v_0	inlet total volumetric flow rate
ΔH_{RX}	heat of reaction	$\dot{W}$	shaft work
k	rate constant		

The collection of elements can be combined in a Matlab/SIMULINK library that allows the user to drag and drop components in a simple to use manner. An example of some available components is shown in Fig. 4. Additional details about the modelling toolkit are included in thesis (Kawamura & Alleyne 2017). The advantage of this approach, much like PISim (Postlethwaite 2016b), is that the student stays focused on the connections and the overall reactions as opposed to the low level programming.

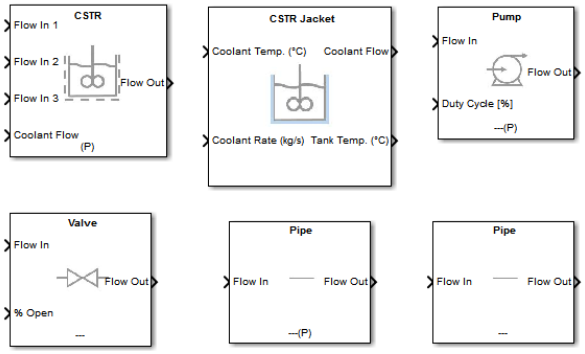

Fig. 4. Subset of library blocks available that can be connected to create a dynamic simulation.

The benefits over other simulation tools in the literature is the ability to customize the blocks, and even the equations under the block masks. Additionally, realistic physical reaction parameters can be utilized. Fig. 5 illustrates the screen shot for a CSTR system where propylene oxide, water, and methanol are combined to form propylene glycol.

The ability to demonstrate simulated results of temperatures and reaction percentage completion is valuable. As illustrated in Fig. 1, it is most valuable if it can be coupled with experiments to validate both the theory and the numerical representation. The challenges of expense and safety prohibit many undergraduate classes from introducing these types of experiments. In the next section we illustrate a simple experiment that captures many of the phenomena of interest for process reaction dynamics.

3. EXPERIMENTAL SYSTEM DESIGN

Determining chemical concentrations, which are at the heart of reaction dynamics, is challenging in general. Usually, samples of the reactants have to be taken from the reaction and run through a slow mass spectrometer analysis to get accurate sensing information. This is often infeasible for the classroom laboratory setting due to the expense associated with instrumentation. The particular experimental system being presented utilizes optical transparency as a surrogate for concentration thereby allowing simpler transduction of reactions that can be performed in real time. The system consists of a custom holder with integrated thermal conduction elements. The holder houses the reaction vessel, which is transparent, as well as a light source and a photodetector positioned on opposing sides of the vessel similar to the classical magnetically levitated ball experiment. The reaction vessel is a beaker with a 30 mL capacity. The holder sits upon a Peltier device which is a thermoelectric element that allows for rapid cooling and heating in an inexpensive manner. The integrated thermal conduction elements within the holder act like a thermal jacket to the reaction vessel and ensure a more uniform thermal environment for the reagents. Fig. 7 below illustrates the experimental system. A data acquisition (DAQ) system completes the control of the thermal environment along with the logging of the analog output of the photodetector.

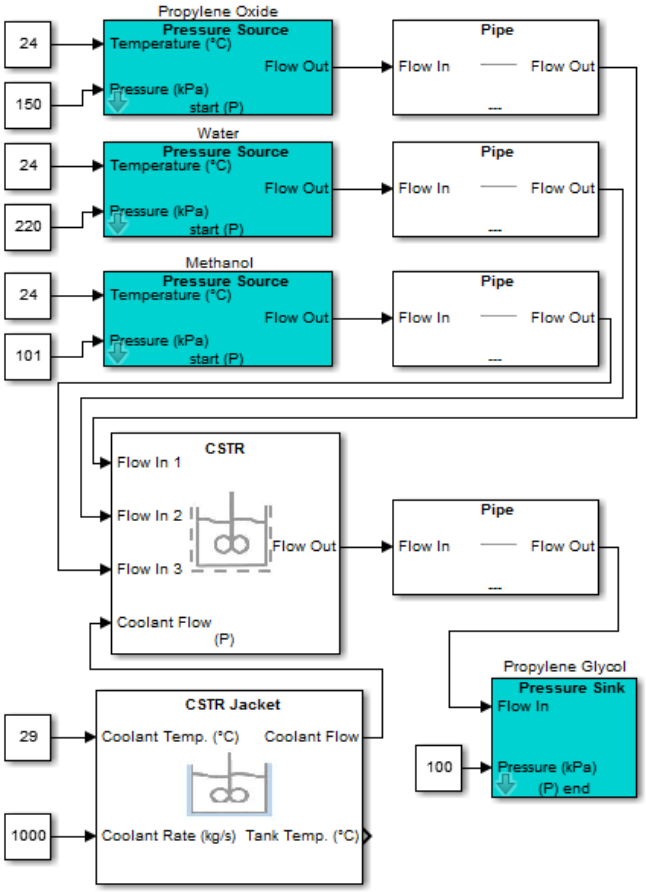

Fig. 5. Complete reaction providing details for an $A+B+C \rightarrow D$ CSTR process.

The total system measures 10cm x 10cm x 15cm without the associated power supply and DAQ interfaces. This compact form factor makes it very suitable for benchtop or desktop exercises. Moreover, a simple DAQ system such as a National Instruments myRIO or Arduino, along with an integrated power supply, can easily make the system self-contained. The reaction vessel shown in Fig. 6 is open to the atmosphere to allow reagents to be pumped in and out if needed to create a true continuous flow environment. Additionally, a stirrer can also be integrated provided it does not block the path between the light source and photo detector. Considering the entire system, including a myRIO and power supplies, the total cost per unit is approximately $750 US and the cost for running each experiment is only the chemical material cost. Since the DAQ system costs approximately ~$250 US, the system cost could be lowered significantly by selecting with a less expensive DAQ system.

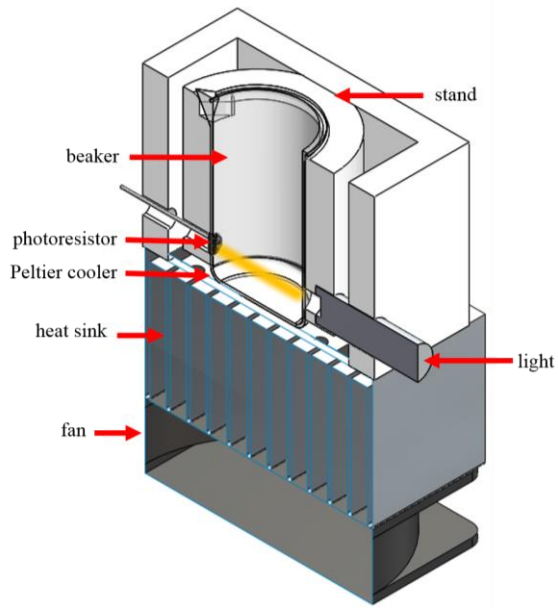

Fig. 6. Experimental system demonstrating hardware elements.

4. EXAMPLE LABORATORY EXERCISE-PROCESS DYNAMICS

One of the simplest dynamic systems to study is the first order system. This is very common in process control. Therefore we use a chemical reaction with a rate that is of first order. The crystal violet bleaching reaction is a simple such a reaction. Key advantages are that it is a low cost experiment to run and is inherently safe so no fume hoods or special protective equipment is needed. This is in-line with the desire for accessibility in our experimental system. Here, a solution of crystal violet is combined with sodium hydroxide (NaOH). The OH^- molecules combine with the crystal violet and the stoichiometry of the reaction is given in Fig. 7.

The reactants and products of Fig. 7 are colorless except for the crystal violet so that as the reaction progresses, and the crystal violet reactant is consumed, the mixture gradually changes from a deep purple to clear. This is easily transduced by photodetector as the optical transmissibility increases. The unforced dynamic equation representing the concentration of crystal violet is given by (5).

$$\frac{dC_{CV}}{dt} = -kC_{CV}; C_{CV}(t=0) = C_{CV}(0) \tag{5}$$

where C_{CV} is the concentration of crystal violet and k is the reaction rate given by

$$k = k(T) = Ae^{\frac{E}{RT}}C_{OH}\,. \tag{6}$$

This is an Arrhenius equation where C_{OH} is the concentration of OH^- and the other parameters are defined in Table 1. Of relevance is the temperature dependence of the reaction rate. Many other reactions are similarly temperature dependent and this gives an easily adjustable process parameter to affect the time constant of the first order system dynamics.

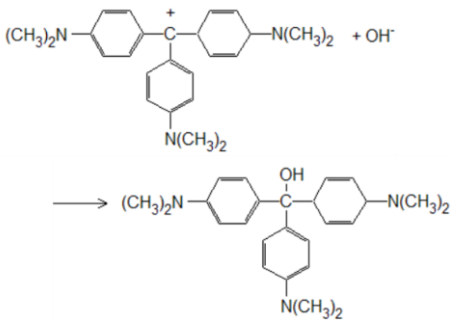

Fig. 7. Stoichiometry of reaction between crystal violet and sodium hydroxide.(Pasco 2016)

To test the efficacy of the experimental system a series of experiments can be demonstrated. Fig. 8 illustrates the series of changes to initial concentration by adding more crystal violet at 400 second intervals. The addition of more crystal violet solution to the existing NaOH is equivalent to resetting an initial condition ($C_{CV}(0)$) on a first order system. This is exactly the equivalent of an impulse response to a first order system. Therefore the students are able to study the effect of convolution of an impulse on a dynamic system.

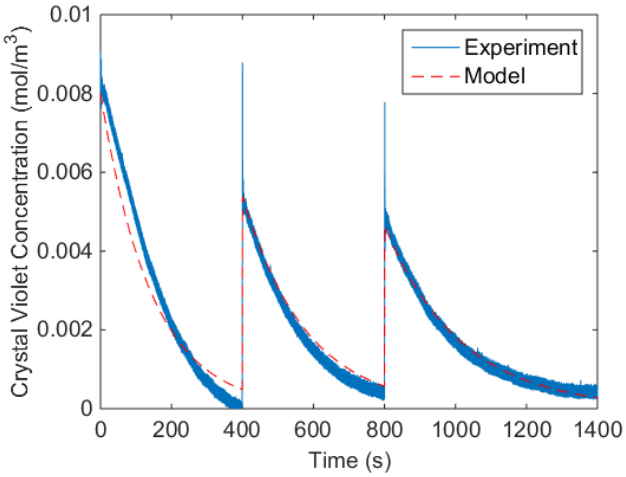

Fig. 8. Response of reaction to impulsive changes to crystal violet concentration.

A second set of experiments examines the temperature effect of the reaction rate, or time constant, given in (6). Fig. 9 illustrates the effect of varying the reaction rate by varying the temperature using the peltier device in the system in Fig. 6. The temperature can be adjusted by 10 degrees Celsius in a matter of minutes thereby making the adjustment process very rapid. By adjusting the temperature, the students can directly see the difference between a slow and fast system and can see the rate dependence effect modelled in (6).

Examining Figs. 8 and 9, it is clear that this is a well characterized first order chemical reaction system with controllable time constant. In addition to time constant studies and impulse response studies, this simple system can be used to study other aspects of process dynamics as well as simple control concepts demonstrated in the next section.

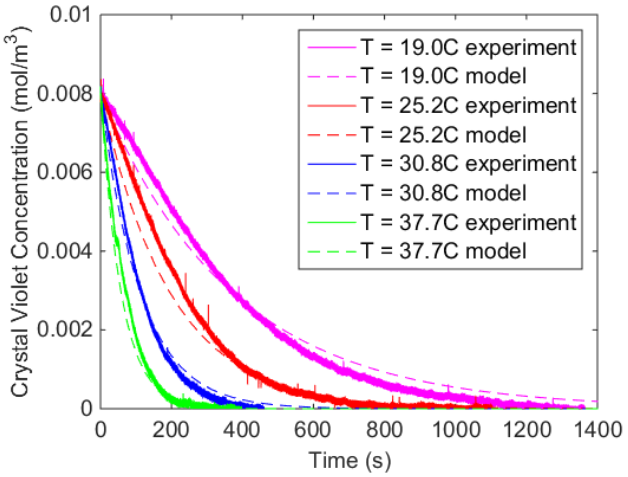

Fig. 9. Effect of reaction temperature on time constant of first order system. The dashed lines are simulated results and the solid lines are data.

5. EXAMPLE: LABORATORY EXERCISE-CLOSED LOOP CONTROL

The open loop system dynamics presented in Section 4 can be complemented by closed loop system dynamics. This can be done in either experiment or simulation once the student has gained confidence that the equations are predictive in terms of model outputs and the model outputs are consistent with data used for validation. Using the same crystal violet reaction in Section 4, a simple closed loop control system is proposed here to regulate the concentration of crystal violet.

For the closed loop system, the following equation governs the concentration of crystal violet

$$\frac{dC_{CV}}{dt} = -kC_{CV} - \frac{C_{CV}v_0}{V} + \frac{C_{CV0}v_{CV0}}{V}. \qquad (7)$$

where k is given by (6), v_0 is total mass flow rate out, V is the total flow, v_{CV0} is the crystal violet mass flow rate in, and C_{CV0} is the concentration of the crystal violet inlet flow. In (7), the crystal violet mass flow rate in, v_{CV0}, is a model input. The other model input is v_{OH0}, the mass flow rate in of sodium hydroxide.

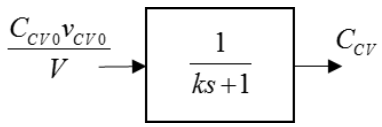

Fig. 10. First order system representing crystal violet concentration within reaction vessel.

Assuming a fixed inflow of NaOH, and a fixed outflow equal to total inflow, the system of (7) is a simple first order system shown in Fig. 10.

This system can be used to expose the students to simple feedback concepts. One such example is the Internal Model Principle and system type related to feedback control systems. A type 0 system in feedback with a proportional gain will have a steady state error to a step reference, or constant disturbance, that is inversely proportional to the low frequency gain of the open loop system. Therefore, a step change in the desired concentration cannot be regulated to zero with a simple proportional control. Fig. 11 shows the feedback diagram with a proportional control.

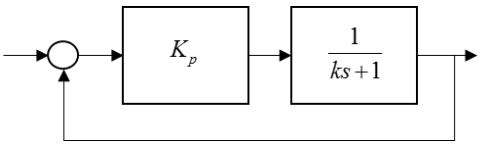

Fig. 11. Proportional control for concentration regulation.

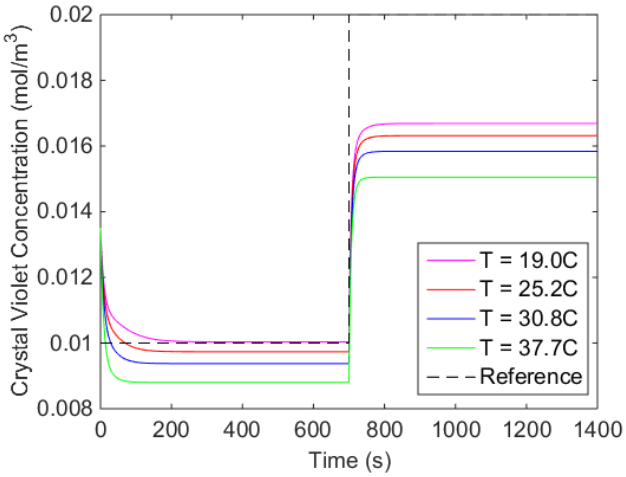

Fig. 12. Proportional control to regulate the crystal violet concentration for different temperatures showing a steady state error.

Fig. 12 illustrates the effect of the system type on the crystal violet reaction plant under varying temperatures. Clearly, the steady state error is non-zero for a change in reference concentration. This is because the open loop transfer function contains no free integrators. Should the control be changed from a proportional to a proportional-integral control, as shown in Fig. 13, the open loop transfer function is now type 1.

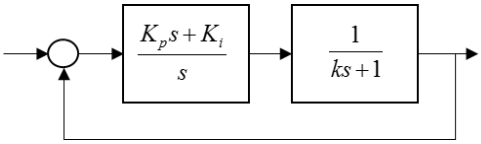

Fig. 13. Proportional-integral control for concentration regulation.

The type 1 open loop transfer function

$$\underbrace{\frac{K_p s + K_i}{s}}_{\text{free integrator}} \frac{}{(ks+1)} \qquad (8)$$

now has a free integrator that provides an Internal Model of the constant reference. As a result, the steady state regulation should be zero. Fig. 14 demonstrates that analytical results presented in a classroom lecture would be borne out in a

concentration regulation system such as the one illustrated in Section 4.

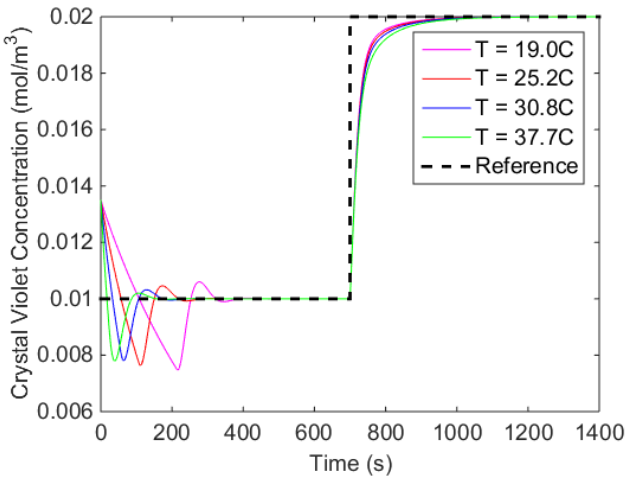

Fig. 14. Proportional and integral control to regulate the crystal violet concentration for different temperatures showing zero steady state error.

As can be seen in Fig. 14, there is zero steady state error over a range of temperatures. Fig. 15 illustrates the adjustment the controller must make in terms of adding the crystal violet reactant as the reaction speed changes.

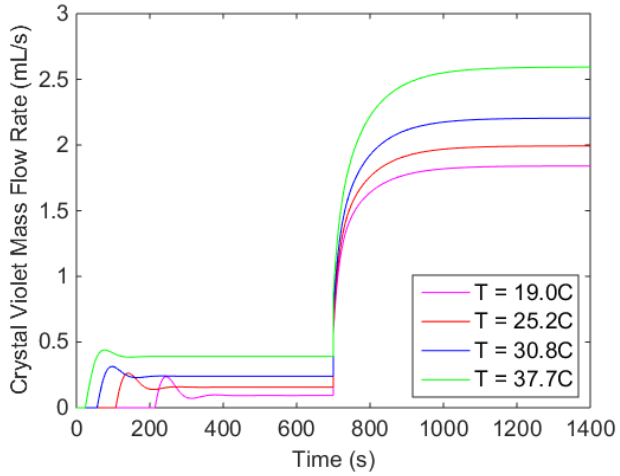

Fig. 15. Crystal violet mass flow rate required for PI control shown in Fig. 14.

The Internal Model example is but one of several control concepts that can not only be explained but also simply demonstrated using chemical reaction dynamics. By analogy, this system provides chemical reaction dynamics that are the equivalent of a DC motor or an RC circuit which are so prevalent for Mechanical and Electrical engineers.

6. CONCLUSIONS

There are several process control experimental systems available for teaching undergraduates. However, to the knowledge of the authors, all current products focus on mass flow or temperature or pressure as the process control variables. There are few, if any, educational experimental systems that illustrate reaction dynamics. This paper presents a simple, safe, and inexpensive manner to teach undergraduate students about reaction process dynamics and span the gap between theory and practice. This first order system provides the chemical engineering equivalent to DC motor velocity or RC circuit voltage examples that are common in other engineering fields when studying system dynamics and control. While only a few exemplar exercises were shown, the reader can extrapolate other types of similar first order dynamics and control examples that can be used in a pedagogically effective manner.

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