Rev 10/15 JMW/GW

ChE 253M

Experiment No. 6

Statistical Experimental Design

<u>Purpose:</u>

1. To introduce students to the power of statistical experimental design and analysis techniques.
2. To teach techniques of fluid dynamics measurement, and introduce non-Newtonian behavior.

<u>Pre-lab Preparations:</u>

In addition to making a data sheet for the first part of this experiment, you will also have to do some preliminary work with JMP IN to perform an experimental design. Follow the instructions below:

1. Click the **DOE** tab in the JMP Starter window. Then select **Response Surface Design**.
2. A DOE window will appear. Our experiment requires three factors. The default number of factors is two, so press **Add** to add a third factor.
3. In this experiment we are going to be measuring the viscosity of Poly(EthyleneOxide) (PEO) solutions in water at various concentrations, temperatures, and shear rates. So, change the factors names from X1, X2 and X3 to **PEO Concentration**, **Temperature**, and **Shear Rate**. Also set the ranges for the three variables to 1.0 – 4.0, 20 – 50, and 500 – 5000 respectively. (The first Value box with a –1 in it is the lower range, and the box with the 1 in it is the higher range.) Press **Continue**.
4. Select **Box-Behnken** and press **Continue**.
5. Click on the **Randomize** button, and change it to **Sort Left to Right** (typically you'd want to randomize the experiment order, but due to time constraints, we aren't going to do this).
6. Click on **Make Table**.
7. After the design has been generated, **SAVE YOUR DESIGN FOR FUTURE USE!** Go to the **File** menu, select **Save**, and then enter a file name in the correct directory.
8. <u>Print a copy of your design.</u> Dr. Willson will ask to see it before lab begins along with your data sheet for the first part of the experiment.

Theory:

Engineers are often called upon to study complex systems in which the output variables (responses) are dependant on many input variables, (called factors). Ideally, through scientific methods, one would like to find analytical relationships between the variables that derive from a complete theoretical understanding of the system. In reality, there will often be situations in which, due to time constraints or financial limitations, you will be called upon to determine the effects of some factors on a given outcome without being able to fully investigate, or necessarily understand, every aspect of the system. At some point in your engineering career, it is also likely that you will be asked to optimize some system or process and to do so with as few experiments as possible. This lab will introduce you to rigorous methods for accomplishing these goals in the most efficient way possible.

The challenge of understanding systems with a minimum of effort has been studied thoroughly over the years, and a huge number of methods have been devised to tackle the problem. In this experiment, you are going to use JMP IN software to analyze three factors that affect the viscosity of a poly (ethylene oxide) (PEO) solution in water. You will use the "Box Behnken design" which allows you to predict the effect of each variable over its entire range while running an absolute minimum number of experiments. In Figure 1 below, the variable search space is depicted as a cube, and the points at which you will actually take measurements are represented by dots.

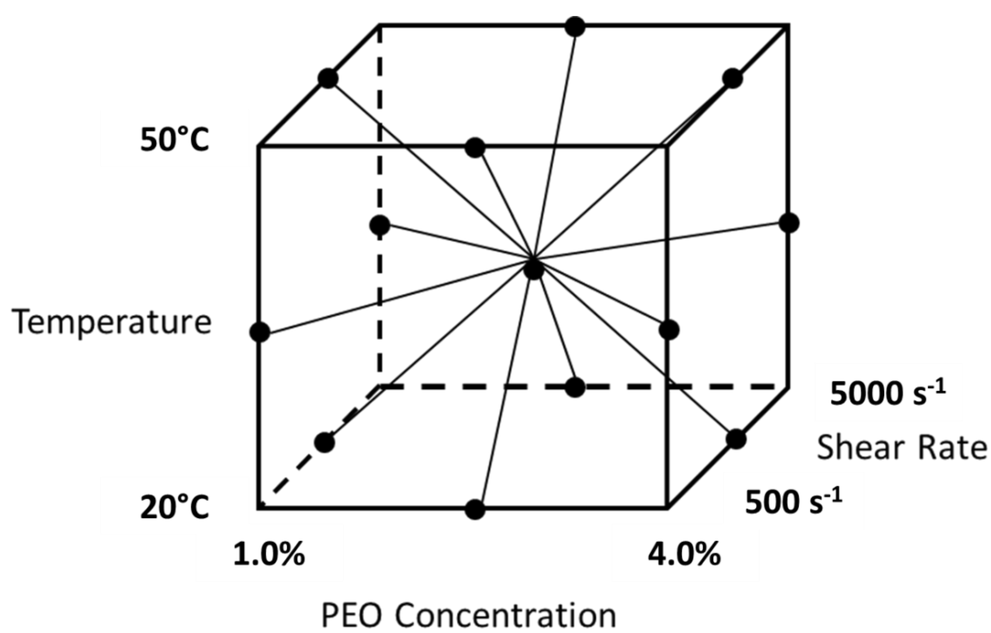

FIGURE 1

One of the three factors of interest is plotted on each axis. One of the measured experimental points is in the very center of the box. The other experimental points are taken where two of the three variables are set at extreme values and the third variable is set at its midpoint. JMP has the ability to use the viscosity response data taken at these points and to perform statistical calculations that allow prediction of the viscosity over the whole box (variable space)! It generates a polynomial that describes the viscosity as a function of PEO concentration; shear rate, and temperature, as follows:

$$\eta = \beta_0 + \beta_1 T + \beta_2 C + \beta_3 \dot{\gamma} + \beta_{12} T C + \beta_{13} T \dot{\gamma} + \beta_{23} C \dot{\gamma} + \beta_{11} T^2 + \beta_{33} \dot{\gamma}^2 + \beta_{22} C^2$$

where η is the viscosity, C is the PEO weight fraction, $\dot{\gamma}$ is the shear rate, and T is the temperature. The coefficients, (β_i's) are calculated fitting factors. The terms that have a product of two variables account for interactions that may occur in the system.

In some cases, you know nothing about the system under study. In that case, you simply have to assume that the relationship between variables and the response is linear or quadratic (or higher order). Often, you can use your knowledge of the theoretical operation of the system you are working with to greatly improve the fit. In this case, we know that the relationship between viscosity and some of the variables is not simply quadratic. For example, the viscosity follows an Arrhenius dependency on the temperature, and follows a "power-law" dependency on the shear rate. Therefore, we will use 1/T , ln(shear rate) and PEO concentration as our input variables, and ln(y) as our output variable.

If you look at the experimental design that you have already prepared (or are getting ready to prepare shortly), you will notice that there are only 13 points used to characterize the box, but that a total of fifteen experiments needed. The reason for this is that three repeat experiments are conducted at the center of the box in order to establish the precision of the viscosity measurement, and this precision is assumed to be the same over the entire variable search space. (In other words, we assume that the rheometer will have the same precision whether it's taking the viscosity at a low shear rate or a high one. This assumption isn't completely valid in this case, but is probably good enough.)

It is important to note that the span of the variables has been set for you in this experiment. Normally the decision about the span for each variable is a very important part of the Statistical Experimental Design process. The extremes can be set based on some knowledge of your process or of the materials or species being studied. If your reactor is not pressurized and water is your solvent, it is not reasonable to study temperatures beyond 100ºC! If you are studying fermentation, it is not reasonable to explore temperatures below the freezing point of your media, etc.

<u>Experiment</u>:

1. You will have to mix up the three concentrations of PEO from a master batch of PEO that is provided. (The PEO that we are using has a very high molecular

weight, and takes a long time to dissolve fully (>1 day), so your TA has prepared a master batch for you.) You will be given a few ml's of 4.0% PEO, and will have to dilute it to 1.0% and 2.5%. You will need approximately 2-3 grams of each of the three solutions to make your measurements.

2. Next you will have to measure the viscosity of the three samples at various temps and shear rates, using your Box-Behnken design. The TA will show you how to use the rheometer in class. The fundamentals behind the measurement are provided at the end of this handout.

3. Take three additional viscosity readings at conditions that are different from those dictated by your experimental design (two inside the variable cube, one outside at a lower shear rate). The TA will tell you the locations of these positions for your group.

JMP IN Analysis:

These instructions describe how to get JMP to do the statistical calculations. (Also, see the Addendum at back of the handout for a couple changes.)

1. Again open JMP
2. Open the design that you saved previously on disk
3. The last title heading in your design sheet should be labeled Y. Click on this heading and change it to read **Viscosity**. Input your data into this column.
4. Click on the **Analyze** menu and select the option **Fit Model**. This option gets you to a dialog box where you can describe the mathematical model. The combinations of variables should be listed in the **construct model effects** window. Your output, **viscosity**, should be listed next to the **Y** box in the upper portion of the window.
5. Click on **Run Model**.
6. The window which comes up is the fit which was made using the basic polynomial fit. Leave this window in the background and return to your data table.
7. Now fit the data using the modified factors that were discussed earlier: **1/T**, **ln(shear rate)** and **concentration**. The output should be **ln(viscosity)**. To do this, add three columns onto your table by clicking on the red triangle next to the **Columns** tab on the left of the window. Name the three columns appropriately.
8. You need to transform the values of your factors and output into your new modified forms (ie. take the ln of all of your viscosity values, and put the new values in the **ln(viscosity) column**, etc). You can either calculate the values in Excel and input them into your new columns, or do it by highlighting a column, selecting the red triangle next to the **Column** tab, and using the **Formula** function.
9. Next, you need to generate a model that you can fit the data with. Hit the **Analyze** tab and select **Fit Model** again. Highlight all the input variables listed in the **onstruct model effects** window, and remove them with the **Remove** button. Next, press the **Ctrl** key on your keyboard, and highlight the three factors which you want to study. Hit the **Macros** key and select **Response Surface**. This

should generate nine combinations of your three factors in the **construct model effects** window.
10. Highlight **viscosity** in the **Y** box, and press **Remove**.
11. Select **ln(viscosity)** from the list of variables in the upper left-hand corner, and press **Y** to cause it to be the output variable.
12. Click on **Run Model**.
13. You will get a modeling window with a large amount of data in it. We will discuss what is relevant in class. In particular, we will discuss the prediction profiler and the contour profiler functions.

Analysis

Your write-up should include:

1. Experimental design sheets

2. The **Summary of Fit** table for both models

3. The coefficient for each term in the fit model. That is, the equations for the fits. Please make a table of these values for both models. These data can be displayed by clicking on the **Parameter Estimates** button.

4. Be sure to include the three dimensional response surface plot.

5. Answer the following questions.

a) Think back to Freshman Calculus. If you were given an analytical expression and you were asked to find the maximum and minimum values of it, how would you do it? (Don't actually answer that question... it is rhetorical.) You have just found an analytical expression for viscosity as a function of three variables. Find the maximum or minimum viscosity of the function. Find the critical points of your function, if there are any.

b) You want to run a reaction to produce a certain chemical. You need to get as much of this material as possible, so you want to maximize the yield of the reaction. You know that the reaction is a function of the concentration of A, the concentration of B, time, temperature and stir rate. Describe how you could use response surface analysis to determine what experimental conditions you should use. How many experiments would need to be run?

c) Did the data points you took outside the box fit well? Why or why not?

d) We used two different models to fit this data. How well did each work? Why? Using the equations that describe the Arrhenius dependence, and the power-law relationship, show why we used the modified factors that we did. If you didn't have any prior theoretical information about the system, how much would you trust the basic polynomial fit?

e) The **Contour Profiler** function enables you to gain an understanding of the sensitivity of the output variable to changes or fluctuations in input variables. This is a very important thing to know, as it can be very difficult to control an input variable exactly, and in a process it is important understand potential deviations from the expected output variable. Using the **Contour Profiler** function, discuss the precision of data taken at a temperature of 20ºC vs. that taken at 50ºC. Which temperature is more sensitive to fluctuations in concentration and shear rate? Discuss.

f) What issues must be considered in choosing the limits for the range of variables in this experiment?

g) List three examples of common materials that display shear <u>thinning</u>.

Experimental Apparatus: Rheometer

In this experiment, measurements are taken using a rheometer made by Paar-Physica. Rheology is the study of the flow and deformation of matter. As the name indicates, rheometers measure rheological properties (like viscosity and elastic modulus) of viscous and visco-elastic materials.

The tool is made up of a drive shaft that has extremely low friction to which we connect a measuring system (in this experiment, a cone and plate). The sample is placed between the cone and plate and a motor drives the shaft. The tool measures the torque that is applied to the system and the resulting rotational speed of the cone. From these two quantities, the shear stress and shear rate are easily calculated, and the viscosity is known. The tool also has excellent temperature control using a Peltier heating and cooling device. See the next Section for a review of the fluid mechanics you should know for this experiment, as well as a discussion of the cone and plate measuring system.

Relevant Fluid Mechanics

Basic fluid mechanics tells us that the shear stress in a fluid is related directly to the shear rate in the manner shown below:

$$\sigma = \eta\dot{\gamma}$$

where σ is the shear stress, η is the viscosity and $\dot{\gamma}$ is the shear rate (which is equal to the change of shear strain per unit time, or in other words, the velocity gradient). For

Newtonian fluids, the viscosity is a constant, regardless of the shear rate. However, many materials exhibit non-Newtonian behavior, including most polymer solutions. In these systems, the viscosity can be strongly dependant on the shear rate, and can be modeled fairly accurately using various theoretical frameworks. The material that is used in this experiment exhibits a phenomenon called "shear thinning". As the name indicates, the viscosity of these materials decreases as the shear rate increases. At very low shear rates, these materials typically behave in a Newtonian manner, up until an "onset viscosity" at which point the viscosity drops quickly. At a much higher shear rate, the materials begin to behave Newtonian again. In between the upper and lower Newtonian regions, as they are called, the viscosity of the material can be fairly well approximated with a power law relationship of the following form:

$$\eta = K \cdot \dot{\gamma}^{(n-1)}$$

where K is called the consistency, and n is a constant less than one. We will use this fact in our analysis in order to fit the data more accurately.

Shear thinning materials have many applications in industry. There are many situations in which a variable shear rate provides significant benefit. For instance, latex paint solutions exhibit shear thinning. This allows the paint to have a high viscosity when the paint is picked up out of the container (no drips) while also having a low viscosity during the high shear rate process of spreading paint onto a wall (resulting in a good, even coat). Also, once the paint is on the wall, it has a high viscosity, since there is little force on it, and as such, the paint does not run down the wall. There are many other examples of the utility of shear thinning materials in our everyday life, including toothpaste, ball-point pen ink, skin cream, etc.

Another relationship that will be used in the analysis is the fact that in most systems, the viscosity follows an Arrhenius relationship:

$$\eta = A \exp(-B/T)$$

The rheometer's measuring geometry for this experiment is called a "cone and plate" geometry. The cone rotates above the stationary plate below it with the sample between the two. The cone is cut at a fixed angle of 1º in our experiment. The resulting shear rate is the same regardless of radial position as long as the angle is small enough. The shear rate is given by:

$$\dot{\gamma} = \Omega_1 / \theta_o$$

where Ω_1 is the angular velocity of the rotating plate, and θ_o is the angle of the cone.

The geometry is shown below in Figure 2.

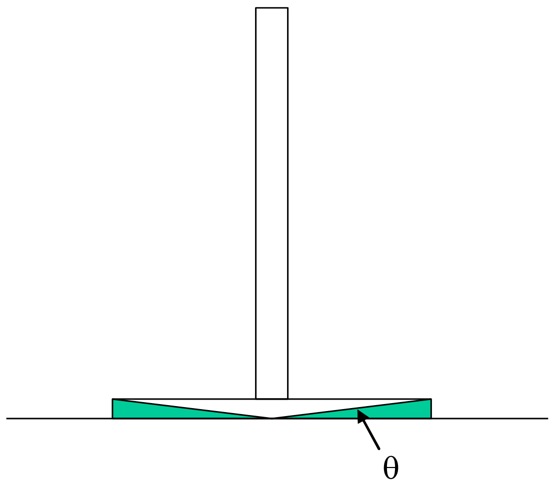

FIGURE 2

Important Note:

The latest version of JMP presents less meaningful polynomial coefficients than we would like. In essence, the program modifies your factor data so that their range is from -1 to 1 by normalizing the data in a simple way. First the program subtracts a constant from each data point, so the middle value is 0 (a process called centering) and then it divides the centered value by half the range of the data (a process called coding). The reason for doing this is to normalize the data relative to each of the factors. This makes the display easy to interpret. However, it produces incorrect, absolute output parameters relative to the polynomial model you are supposed to fit. Two actions are required to turn off coding and centering.

To turn off coding and centering you must:

a) Right click on the column title of your first factor (input variable), and select **column info**…" This will cause a new window to pop up. At the bottom of the window is a list titled **Current Properties**. Highlight **Coding** in the **Current Properties** list, and press **Remove Property**. Click **OK**. Repeat for both of your other factors.

b) When analyzing your data, and working in the **Fit Model** window, before you press **Run Model**, you must click on the red triangle next to **Model Specification** in the right-hand corner of the window. Four possible selections are listed, the first of which, **Center Polynomials** is checked. Select **Center Polynomials** so that the check vanishes.