Safe Storage of Dilute Ethylene Oxide Mixtures in Water

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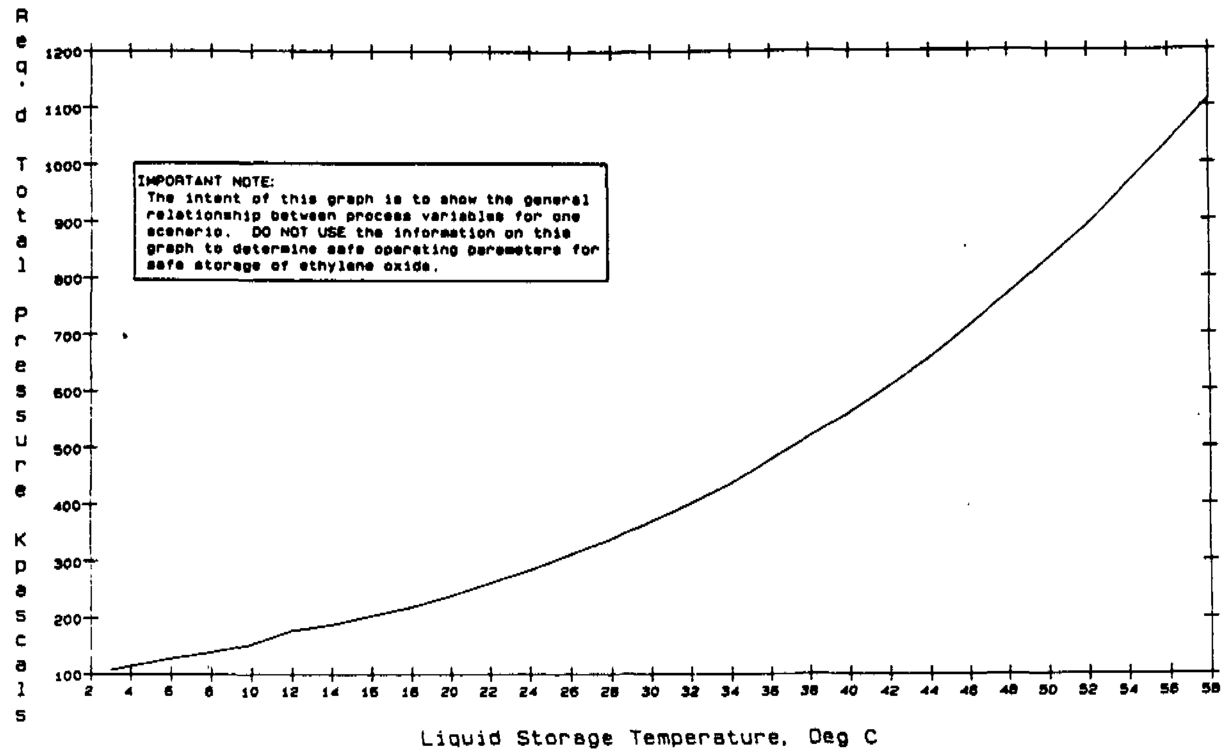
In the past industry has had to rely on a number of "rules of thumb" to provide a means of reasonable analysis for many design, operation, safety and similar issues. The lack of readily available computing facilities made the use of "rules of thumb" a necessary part of doing business in the hydrocarbon processing industry. And these "rules of thumb" have proven useful and allowed many tasks to be accomplished successfully. Today, however, availability of mainframe computers or desktop computing facilities has provided a tool that has decreased the need to rely on "rules of thumb." And in many cases processing improvements can only be accomplished by replacing "rules of thumb" with more rigorous analysis. In the ethylene oxide producing/consuming industry a widely-used "rule of thumb" concerns the storage of ethylene oxide water solutions. A well-publicized "rule" stated that solutions in excess of 1-2 weight percent ethylene oxide in water should not be stored [1]. This "rule" is certainly valid in many situations. However, this guideline may be unnecessarily restrictive in other cases. The impact of several key process parameters impacts the amount of ethylene oxide in water than can be safely stored. This study will show that higher concentrations of ethylene oxide in water can be safely stored under the right circumstances. The study will also discuss the key variables that determine whether aqueous ethylene oxide solutions can be safely stored. Finally, a methodology used in determining how much ethylene oxide in water can be safely stored will be outlined.

FACTORS AFFECTING THE SAFE STORAGE OF AQUEOUS ETHYLENE OXIDE

The factors affecting the safe storage of aqueous ethylene oxide solutions should be examined. First, the safe storage of pure ethylene oxide will be reviewed. Ethylene oxide consumers and producers are generally familiar with the need to maintain an inert gas pad over ethylene oxide in storage. Ethylene oxide has a broad flammability range and even in the absence of oxygen, ethylene oxide vapor concentrations of greater than 75% in nitrogen form a flammable mixture [2]. Thus, a safe storage temperature and inert blanket gas pressure are determined by the need to maintain the resulting ethylene oxide vapor composition below 75%. Figure 1 depicts the relationship between the minimum blanket gas pressure requirement and a given storage temperature. A safety margin is included in the data, but the intent of the relationship is to maintain ethylene oxide vapor compositions below 75%. Storing aqueous ethylene oxide solutions safely also requires that the vapor composition of ethylene oxide be maintained below the 75% flammable limit when stored under a nitrogen pad. But, the "rule of thumb" dictating that 2 weight percent ethylene oxide in water solutions not be stored is not based on a vapor composition limit. The vapor composition of a 2 weight percent ethylene oxide aqueous solution at normal storage temperatures and pressures is much less than 75%. Yet the 75% vapor composition limit should be kept in mind as other factors influencing safe storage are examined.

An aqueous solution of ethylene oxide will undergo a hydrolysis reaction. The reaction would proceed slowly in the absence of a catalyst. But it will occur. As the exothermic reaction progresses the temperature of the stored mixture will rise. A rise in temperature may then result in a corresponding increase in pressure over the liquid. A temperature rise and a pressure rise are two additional factors to be considered in analysis of safe storage for aqueous ethylene oxide solutions. Equipment integrity may be compromised by too high a temperature or, more likely, the inability to vent gas and prevent the overpressurization of a closed vessel becomes the critical concern. Again, the hydrolysis reaction would proceed slowly in the absence of catalyst. But, a "worst case analysis" would require that a contamination of the aqueous ethylene oxide solution has occurred that has promoted the hydrolysis reaction. Still, the large excess of water would act as a heat sink and limit the temperature/pressure rise. The intent of this study is to outline the various process variables that impact the safe storage of aqueous ethylene oxide solutions.

There are many possible reasons for storing ethylene oxide and water mixtures. There are processing steps in ethylene oxide manufacturing that result in the storage of aqueous solutions of ethylene oxide. Maintenance operations in ethylene oxide manufacturing and consuming industries may dictate a need for temporary storage of aqueous ethylene oxide solutions. Hoechst Celanese has utilized safe storage of aqueous ethylene oxide mixtures as a means of reducing environmental emissions generated when water washing process equipment in preparation for personnel entry and maintenance. There may be other reasons that dictate the need to store aqueous ethylene oxide mixtures.



Note: Assumes insulated storage vessel.

Figure 1. Storage pressure for liquid ethylene oxide under nitrogen blanketing gas. (Basis: <75% EtO in vapor space.)

The storage of ethylene oxide-water material can be hazardous. This is the reason for the "2 percent rule." In presenting this analysis "worst case" scenarios will be assumed. First, the storage vessel containing the aqueous ethylene oxide may have a cooling capability for removing the heat of the hydrolysis reaction and limiting the temperature/pressure rise. This analysis will assume that the cooling capability is not available for whatever the reason. Also, an ethylene oxide storage vessel will normally have the ability to vent gas to a vent gas scrubbing facility. This analysis will assume that the vent scrubber is unavailable. The study will further assume that, for environmental reasons, the vent gas will not be vented to the atmosphere. Instead, as the temperature rises the storage vessel will increase in pressure because gas cannot be vented. These worst case assumptions of no cooling capacity and a closed (no vent) storage vessel will provide the basis for the study.

Thus, three factors will be used to determine what is the safe level of ethylene oxide in water than can be stored. First, an ethylene oxide vapor composition limit of 75% must be avoided. Next, the storage vessel temperature limits must not be exceeded should a hydrolysis reaction occur. Finally, and most critical, the storage vessel pressure limits must not be exceeded.

KEY PROCESS VARIABLES AFFECTING THE ANALYSIS

Certain key process conditions determine how much ethylene oxide in water can be safely stored. These conditions include:

1. The initial temperature of the stored material.
2. The initial pressure of the storage vessel.
3. The ratio of vapor volume to liquid volume.
4. The concentration of ethylene oxide in water.

An analysis can be performed that determines how much ethylene oxide in water can safely be stored that incorporates the above process conditions as variables. The analysis can be set up on an electronic spreadsheet, equation solver or other computer-based calculation method. Then, case analysis can be performed to study the sensitivity of each variable on the safe level of ethylene oxide in water for a given system.

CASE ANALYSIS: TEN PERCENT ETHYLENE OXIDE IN WATER

A calculational model was developed on an electronic spreadsheet to study the effect of the identified process variables on the safe storage of ethylene oxide–water solutions. Use of a spreadsheet allows one to alter a given input variable, or set of input variables and "instantly" see the calculated results on the output variables.

The input variables for the model include:

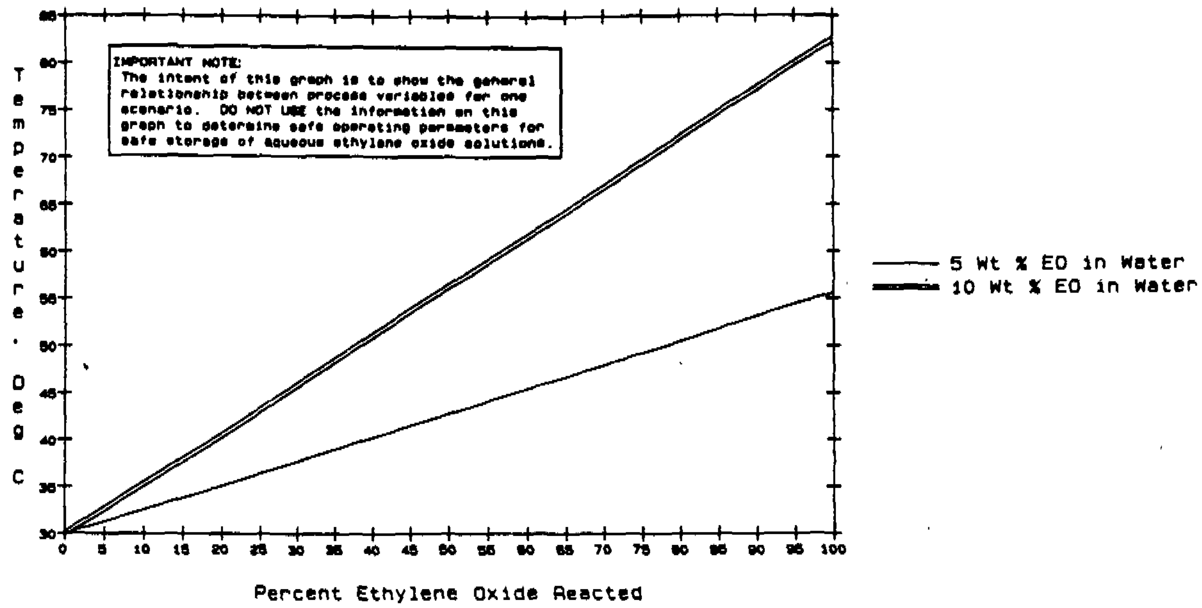
- Composition of mixture (weight percent EtO in water)
- Relative vapor/liquid volumes in storage vessel
- Initial temperature of storage vessel
- Initial storage pressure of storage vessel
- Fraction of ethylene oxide hydrolyzed to ethylene glycol

Key assumptions used in the model are:

- A hydrolysis reaction occurs (EO + $H_2O \rightarrow$ Ethylene Glycol)
- VLE of nitrogen-water-EO-ethylene glycol corrected for nonidealities
- Adiabatic reaction—no heat loss/gain to atmosphere
- Closed system—no venting of gas or dumping of liquid
- No cooling capability exists

The output variables calculated by the model include:

- The composition of the liquid and vapor phases



Basis of analysis: Initial vessel pressure of 244 kilopascals (before filling)
Vessel pressure of 337 kilopascals (after filling, 10 % EO)
Vessel pressure of 311 kilopascals (after filling, 5 % EO)
Initial vessel temperature of 30 degrees C
1/1 vapor to volume ratio

Figure 2. Temperature rise in storage vessel as result of hydrolysis reaction.

The final temperature of the vessel
The final pressure of the vessel

Again, safe storage will be determined by examining the calculated output variables to see they do not exceed the following limits:

Composition of ethylene oxide in vapor phase <75%
Temperature below desired/design temperature of vessel
Pressure below desired/design temperature of vessel

Other important calculational methods built into the model include vapor/liquid equilibrium data for aqueous ethylene oxide solutions, hydrolysis heat of reaction data, heat capacity data, stoichiometry of the hydrolysis reaction, ideal gas relationships for determining vapor density and pressure on the vessel, heat of vaporization data and other calculational steps.

TEMPERATURE RISE FROM HYDROLYSIS REACTION

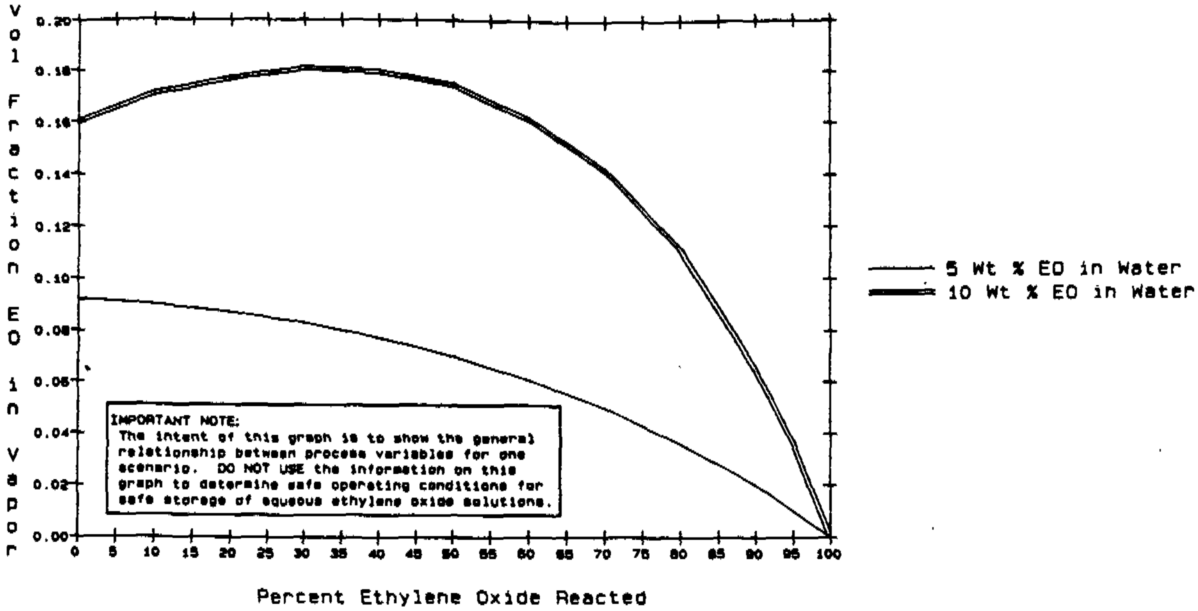
First, the temperature rise resulting from a hydrolysis reaction was quantified. A 10 weight percent ethylene oxide in water solution stored in a vessel that had 1/1 vapor to liquid volume ratio, a starting pressure of 3 kilopascals (6 psig) and an initial temperature of 30°C (86°F) was used as the basis for determining the temperature rise. The results are shown graphically in Figure 2. The temperature rise shows a linear relationship as the hydrolysis reaction proceeds to completion. The maximum temperature reached occurs at 100% conversion of ethylene oxide. This temperature was 82.5°C (181°F). This temperature is below the vessel design temperature.

Next, the concentration of ethylene oxide in the vapor as the hydrolysis reaction proceeds was calculated. Again, the basis was a 10 weight percent ethylene oxide in water solution, a 1/1 vapor to liquid volume ratio, an initial temperature of 30°C (86°F) and an initial pressure of 3 kilopascals (6 psig). The results are shown in Figure 3. It is interesting to note the concentration "plateau" that occurs as the hydrolysis reaction proceeds. The decrease in liquid ethylene oxide concentration and increase in vapor pressure caused by the temperature rise tend to balance out and result in a fairly steady ethylene oxide vapor composition. For this case the ethylene oxide vapor content was well below the 75% limit for non–explosive mixtures. Indeed, the ethylene oxide vapor content was not the limiting constraint in determination of safe operation for any of the cases that the author studied. Either a high pressure or temperature constraint occurs before the high ethylene oxide vapor content limit does.

Figure 4 demonstrates the effects the hydrolysis reaction has on the closed vessel pressure. The storage vessel pressure rise as a result of the hydrolysis reaction is shown for 5 and 10 weight percent ethylene oxide in water solutions. Notice the plateau that occurs in the 70 to 80% hydrolysis region. The maximum pressure occurs before hydrolysis reaction completion because of the combination of ethylene oxide vapor pressure and solution temperature. Further cases will use 75% ethylene oxide reacted as the base "worst" case.

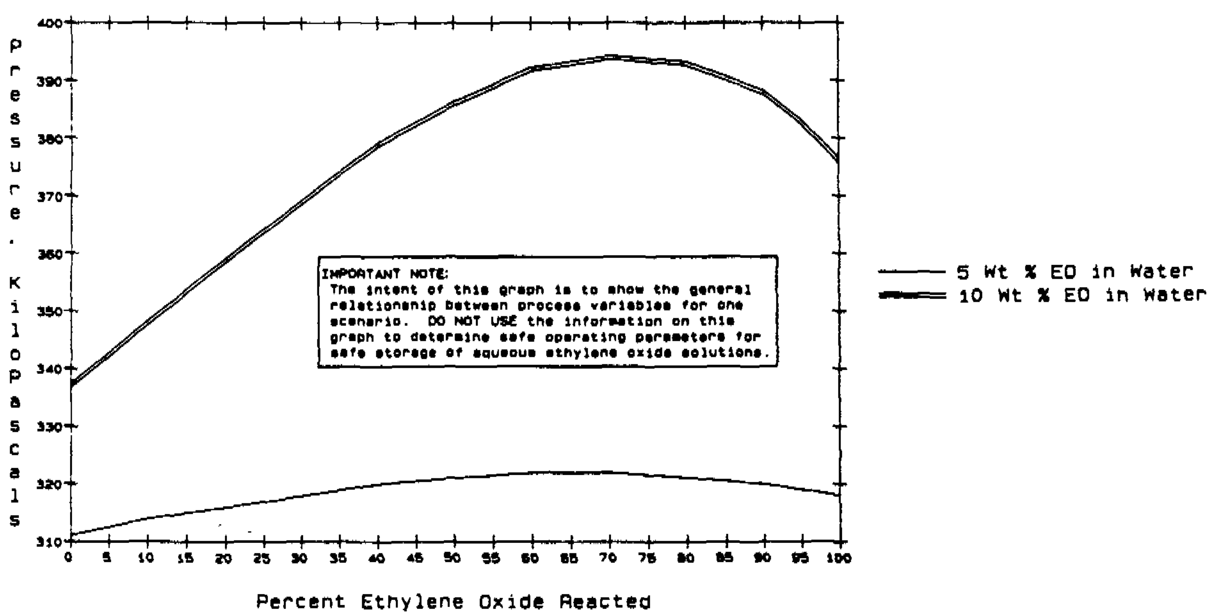
The relative ratio of vapor to liquid volume was then studied. The relative amount of vapor volume available is critical as judged from Figure 5. Note that the analysis was made with 75% of the ethylene oxide reacting because the previous analysis showed that to be worst case in terms of maximum vessel pressure. As the relative vapor volume increases the vessel pressure rise decreases. Further analysis used a 1/1 vapor to liquid volume ratio.

The effects of initial temperature are shown in Figure 6. Obviously, initial temperature has an effect on both maximum temperature and on the maximum pressure achieved. Similarly, Figure 7 shows the effect initial vessel pressure has on the maximum pressure achieved. Initial pressure is obviously an important variable in deter-



Basis of Analysis: Initial vessel pressure of 244 kilopascals (before filling)
Vessel pressure of 337 kilopascals (after filling, 10 % EO)
Vessel pressure of 311 kilopascals (after filling, 5 % EO)
Initial vessel temperature of 30 degrees C
1/1 initial vapor to liquid volume ratio

Figure 3. Ethylene oxide vapor composition resulting from hydrolysis reaction.



Basis of analysis: Initial vessel pressure of 244 kilopascals (before filling)
Vessel pressure of 337 kilopascals (after filling, 10 % EO)
Vessel pressure of 311 kilopascals (after filling, 5 % EO)
Initial temperature of 30 degrees C
1/1 initial vapor to liquid volume ratio

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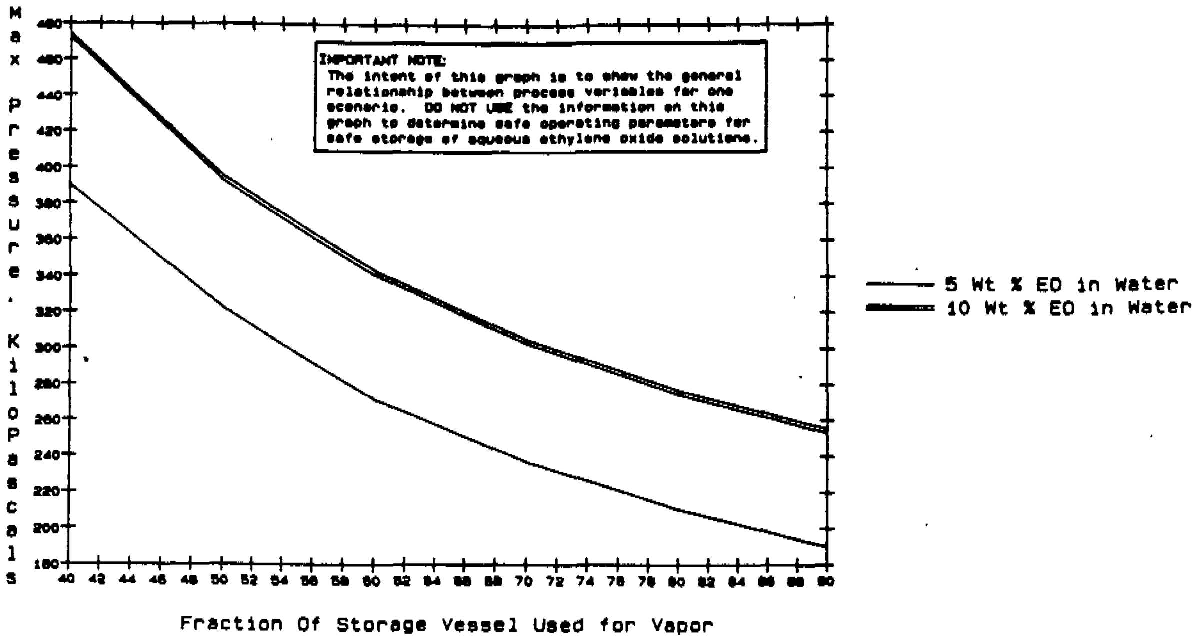
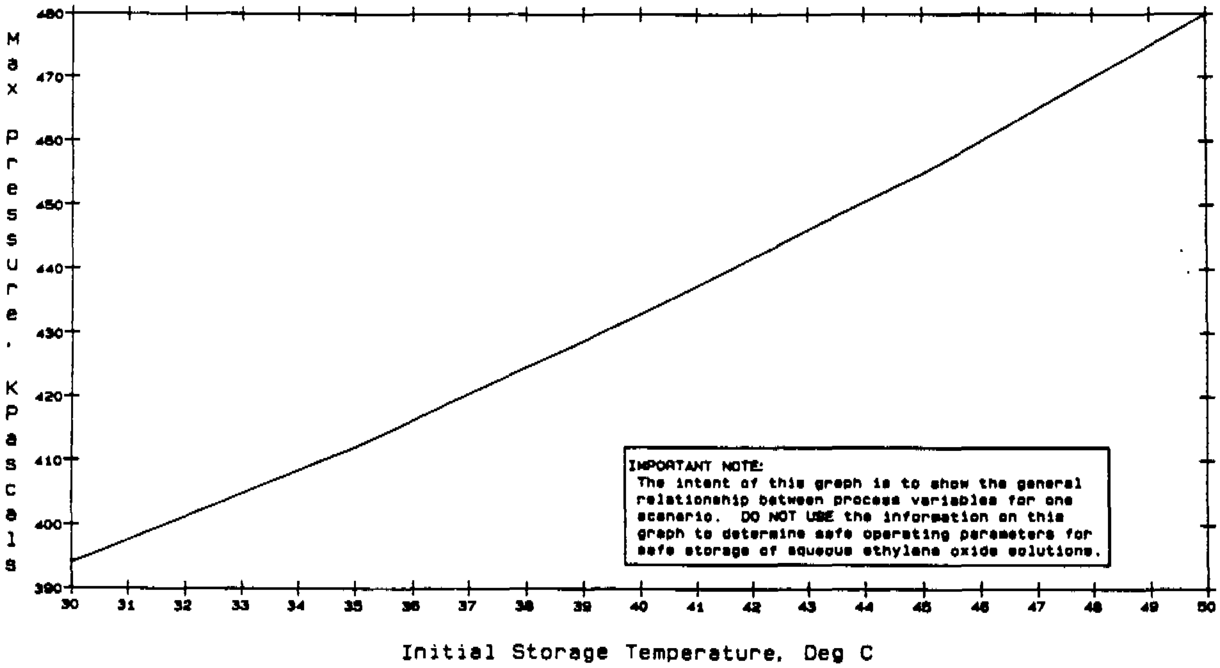
Figure 4 Pressure rise in storage vessel as result of hydrolysis reaction.



Basis of analysis: Initial vessel pressure of 244 kilopascals (before filling)
Vessel pressure after filling varies with volume ratio
Initial vessel temperature of 30 degrees C
Assumed 75 % of EO reacted in hydrolysis reaction

Figure 5. Storage vessel maximum pressure achieved as function of vapor to liquid volume ratio.



Basis of analysis: 10 weight percent ethylene oxide in water
Initial vessel pressure of 244 kilopascals (before filling)
1/1 vapor to liquid volume ratio
75 % of ethylene oxide hydrolyzed

Figure 6. Effect of initial storage temperature on maximum vessel pressure achieved.

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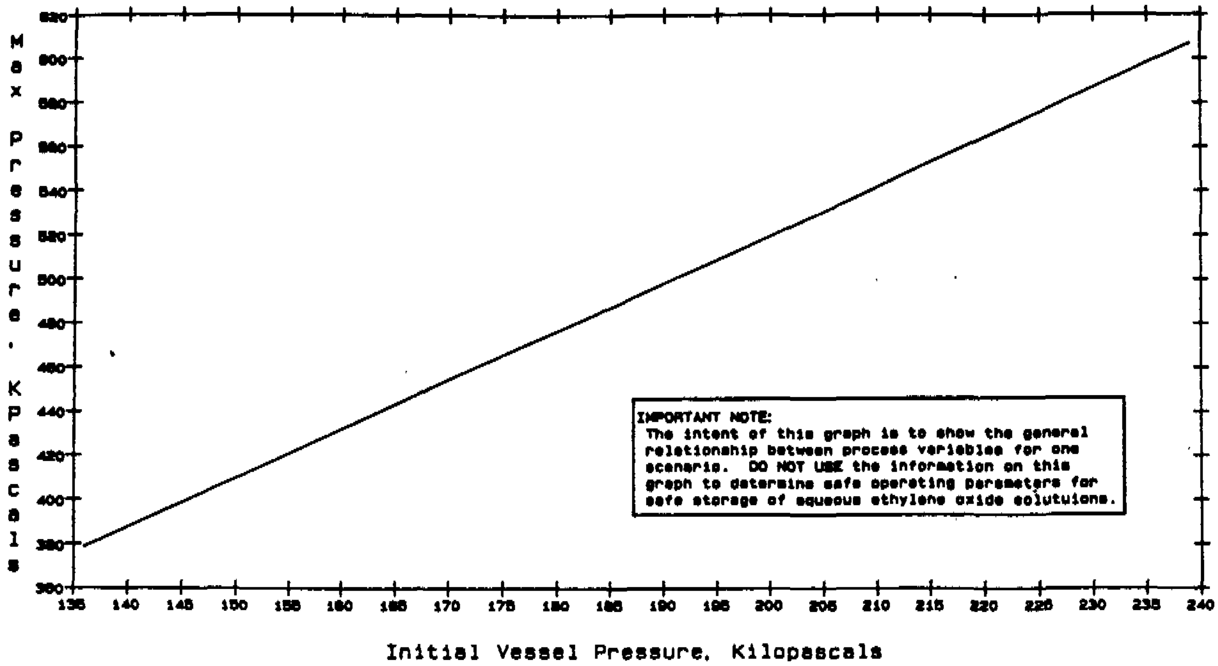
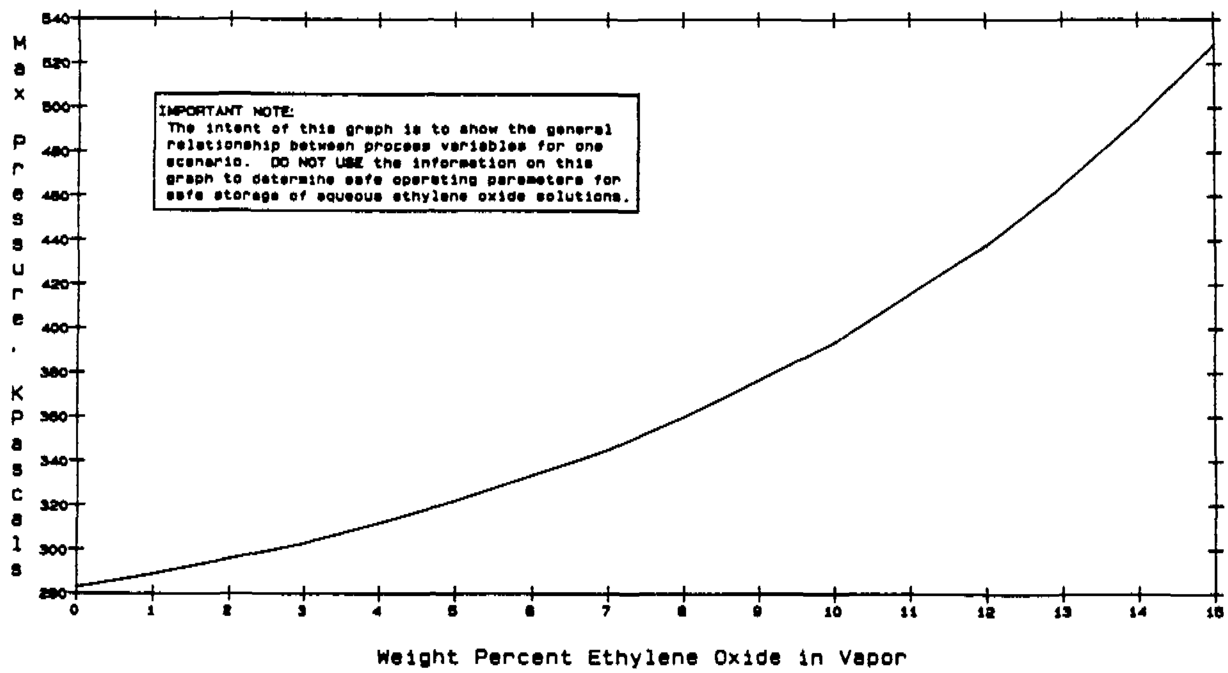


Basis of analysis: 10 weight percent ethylene oxide in water
Initial temperature of 30 degrees C
1/1 vapor to liquid volume ratio
75 % of ethylene oxide hydrolyzed

Figure 7. Effect of initial vessel pressure on maximum pressure achieved from reaction.



Basis of analysis: Initial vessel pressure of 244 kilopascals (before filling)
Initial vessel temperature of 30 degrees C
1/1 vapor to liquid volume ratio
75 % of ethylene oxide hydrolyzed

Figure 8. Maximum vessel pressure achieved for varying levels of ethylene oxide in water.

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