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Dynamic Simulation of Inertization Step in a Batch Reactor

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Ethylene oxide (EO) is a highly flammable, explosive, and reactive monomer. This component is widely used in several areas of industry, especially to obtain surfactants and solvents through the ethoxylation reaction. Due to its thermal instability and high reactivity with other chemicals, many industrial accidents involving EO have been recorded over the years. To avoid dangers due to the presence of air during the ethoxylation reaction, the inertization process – in which an inert gas is fed to the reactor – is used as a safety measure before the ethoxylation process can be initiated. Subsequently, this reactor is subjected to vacuum, reducing the volume of air and the combustion potential. There are no studies in the literature that simulate the inertization step in a batch reactor. In this study, the inertization of an ethoxylation loop reactor is simulated using the software Aspen Plus® and Aspen Plus® Dynamics. The simulation is used to analyze the maximum vacuum time before starting the ethoxylation reaction. In addition, it is investigated the number of required pressurizations and purges to achieve an amount of oxygen equal to that of a completely tight reactor. To perform these analyses, it is necessary to simulate the leak tightness test, which estimates the amount of air that can enter the reactor depending on its leak tightness. The results show the importance of carrying out the leak tightness test in reactors. Also, it is verified a dependency between the time that the reactor takes to reach certain pressures (vacuum) and the amount of oxygen that can return to the reactor, which would invalidate the inertization process and be a hazard during the ethoxylation reaction.

1. Introduction

Ethylene oxide (EO) is an essential chemical in the industry. Its molecule has highly tensioned angles, making it unstable and very reactive (Pekalski et al., 2005). This reactivity is the reason EO takes part in various exothermic reactions, such as isomerization, polymerization, and decomposition. Therefore, EO is often applied to produce non-ionic surfactants, solvents, polyesters, and antifreezes (Liu et al., 2017). However, EO requires several precautions to be handled; in both liquid and vapor phases, it is considered a dangerous chemical. For this reason, EO was the cause of several accidents in the history of the chemical industry. In 1962, an EO storage tank burst violently. The cause was a highly exothermic reaction, generated from an aqueous ammonia reflux to the EO storage (Gustin, 2001). The latest accident occurred in January 2020 in Spain: the explosion started in a reactor that, then, set fire to the nearby storage tank (The Chemical Engineering, 2020). Other countries have already registered accidents with EO, such as Switzerland, Italy, and Germany.
In the case of ethoxylation reactions, the reaction occurs between EO and hydrophobic compounds containing active hydrogen – e.g., alkylphenols, fatty alcohols, fatty acids, mercaptan, and alkylamides (Schick, 1987). Several studies investigating the dangers regarding EO in ethoxylation processes have been found in the literature. Salzano et al. (2007a) evaluated the additional risks due to the recirculation cycle in three different types of reactors: Semi-Batch Tank reactor (STR, the gas phase is dispersed in the liquid phase); Venturi Loop Reactor (VLR, the gas phase is dispersed in the liquid phase); and Spray Tower Loop Reactor (STLR, the liquid phase is dispersed in the gas phase). The VLR and STLR presented a lower risk of decomposition/explosion when compared to the STR. In the same year, Salzano et al. (2007b) evaluated the ethoxylation of dodecanol and concluded that there is a great risk of explosions when there are large releases of material from the reactor. Pekalski et al. (2005) conducted an experimental and theoretical investigation on ethylene oxide decomposition.

The authors experimentally determined safety-related parameters, considering EO in its pure form and diluted in nitrogen. Palazzi et al. (2014) studied the partial oxidation of ethylene. They developed a physical-mathematical model to predict the phenomena of ignition and flame propagation in the presence of explosive gas mixtures. Pio et al. (2019) conducted an experimental and numerical investigation on the flammability limits for binary mixtures of ethylene or propylene in air, pure or mixed with methane, concluding that the ability to predict flammability limits with respect to operating conditions may represent a crucial aspect for process safety.
To test the integrity against fluid leaks through the walls of the equipment, the leak test is used. So-called tight equipment is one whose structure is free of holes, cracks, or porosity that can let out some of its content (Copens, 1973). When the equipment is not completely tight, inertization is an alternative to maintain process safety. The inertization consists of diluting EO with inert materials, such as nitrogen. This dilution makes the mixture safer in the vapor phase, preventing explosions. Tanks and reactors must be initially purged to remove any air present. Besides, they must be kept under an inert atmosphere in a non-flammable band during all transfers from/to tanks or equipment (Hess, 1950). To inhibit ignition and combustion, the inert atmosphere above the flammable liquid must be composed of less than 13% oxygen. If nitrogen-rich air contains less than 10% oxygen, it will provide an extremely inert atmosphere (MecNeil et al., 2007). Hence, this current study aimed at developing a dynamic simulation of the inertization stage in a semi-batch reactor, which precedes the ethoxylation reaction. It was investigated how the controllers used in this process can contribute to safety. Based on the leak test (or pressure test), the number of required purges for the reactor were identified, and for how long these purges are still valid when the ethoxylation reactions do not occur immediately after the inertization process.

2. Process Description

This work investigates the inertization stage in the production process of an ethoxylated product. Sorbitan monolaurate is the alcohol that will react with ethylene oxide. This reaction is catalyzed by potassium hydroxide in an STL reactor. To obtain the product, a sequence of operational procedures is required: leak test; raw material loading; inertization; addition of ethylene oxide; and neutralization of the product. Each of these procedures requires precautions to ensure the safety of operation.
To perform the leak test, different procedures may be used. One option is to pressurize the vessel with nitrogen to 4 bar and leave it to rest for 15 minutes. During this period, a pressure drop is observed. If the pressure drops below 0.1 bar, the vessel is considered tight and safe for use. Otherwise, it would not be safe to operate, and any leak would have to be rectified (Chiu, 2005). Another option is to apply a vacuum to the vessel and evaluate the pressure increase after 15 minutes.
After confirming the operation safety, the raw material is loaded. This material is subjected to drying to remove the remaining water. The drying occurs through the reactor loop, responsible for heating the material.
After the drying step, the reactor temperature is maintained at 110°C and the inertization step is started through pressurization with nitrogen. In the next step, nitrogen and air are purged through a vacuum system. Chiu (2005) suggests purging nitrogen three times so that the reaction can occur safely later. Depending on the time it takes for the reactor to reach the desired pressures, purges can be invalidated. Therefore, the pressure control must be carefully monitored.
The reaction is initiated with the injection of EO, which must happen immediately after inertization. The time that the reactor remains in a vacuum before the reaction starts depends on the tightness of this reactor.

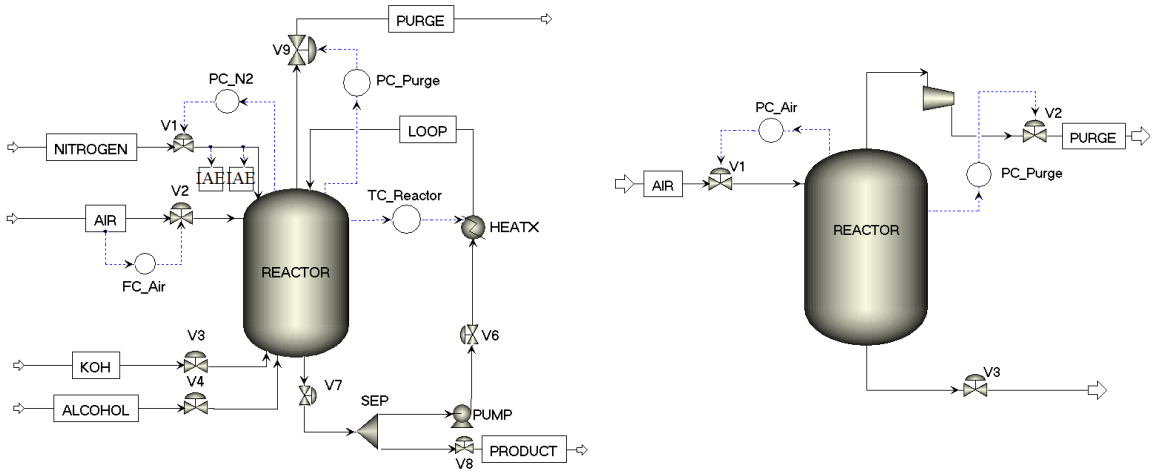
3. Modeling and simulation

The simulated case is a semi-batch loop reactor used for ethoxylation processes. The control of nitrogen injection and purges performed through an ejector was evaluated using Aspen Plus® Dynamics, the software in which the set of differential-algebraic equations is solved. In this situation, an initial condition is necessary. That is obtained through the steady-state process simulation in Aspen Plus®. As the inertization is carried out before the reaction, it was not necessary to model the ethoxylation. For this reason, the reactor was represented by a flash vessel.
Initially, catalyst and alcohol are fed into the system. Then, the inertization is performed. In Figure 1a, the nitrogen feed is used to pressurize the reactor. The purge represents the vacuum made by an ejector.
The geometry of the reactor and the operating conditions of the process, shown in Table 1, were based on Salzano et al. (2007) and Pekalski et al. (2005).
After consolidating the steady-state simulation, the model was exported to Aspen Plus® Dynamics using the Pressure Driven mode. The simulation of the semi-batch reactor's dynamic behavior was implemented according to the procedure developed by Brito et al. (2018) for a semi-batch reactor for nitrile production.

Table 1: Reactor data and process operating conditions.

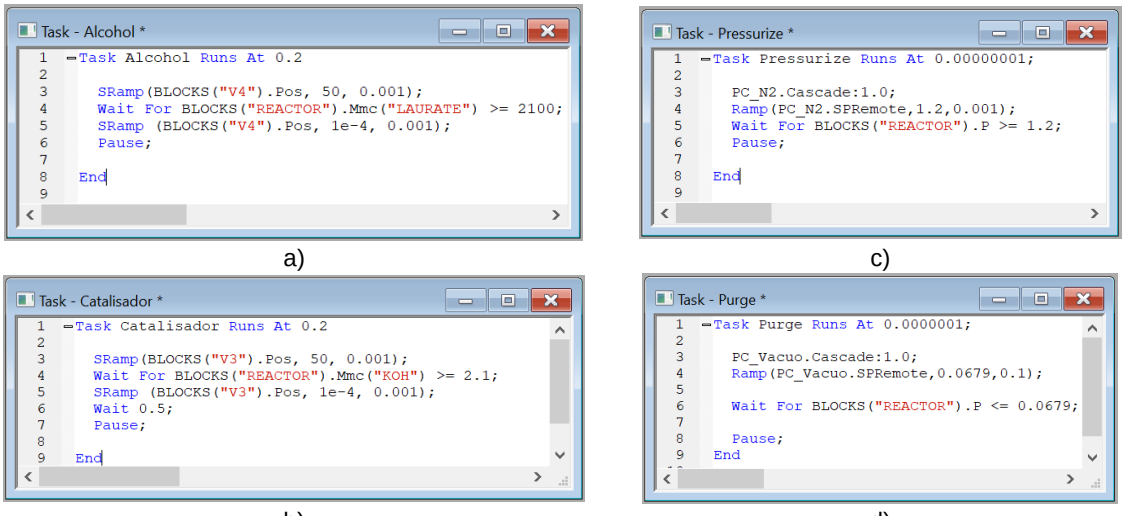
Reactor volume (m³)	8.5
Temperature (ºC)	110
Vacuum pressure (bar)	0.066
Pressurization with nitrogen (bar)	1.2
Catalyst (KOH) (kg)	5.5
Alcohol initially charged (kg)	2150

Control of pressure (through the addition of nitrogen and purge) and temperature of the reactor were included. Figure 1a shows the reactor with the added controls. As the inertization procedure is performed through a sequence of commands, it was necessary to use the Aspen Plus® Dynamics *task* tool. The sequence was: interrupting the energy supply; emptying the reactor; closing all valves; adding alcohol; adding catalyst; vacuum drying; and inertization. The created *tasks* are shown in Figure 2.



a) b)

Figure 1: Stage of a) inertization and b) leak test on Aspen Plus® Dynamics.



a) c)

b) d)

Figure 2: Tasks created for a) transferring alcohol to the reactor, b) adding the catalyst to the reactor, c) pressurizing, and d) purging.

The evaluations were carried out based on the amount of air that was in the reactor before and after the purges. The ideal situation is a completely tight reactor. For situations where the reactor is not completely tight, an air stream was added to the model. The speed at which air enters the reactor is obtained through the leak test and the operating pressure.

When the reactor was not considered completely tight, the leak test was simulated, as shown in Figure 1b. For this test, the reactor was initially at a vacuum condition under a pressure of 0.04 bar and two scenarios of leakage were simulated. For the first air leak, a pressure difference of 0.02 bar was considered; the second leak had a pressure difference of 0.06 bar, both after 15 minutes. From these simulations, it was possible to calculate the approximate speed with which the air is leaked into the reactor.

4. Results and discussions

4.1 Inertization and leak test

The reactor inertization was simulated according to the procedure described in the previous section, using three purges. The situation in which the reactor is considered completely tight was used as the base case. Table 2 presents the results for this case. The results show that with three purges it is possible to remove all the air inside the reactor, replacing it with nitrogen. In practice, a completely tight reactor would not require this amount of purges, since there is no air leakage into it.

Table 2: Results obtained for the base case (completely tight *reactor).*

	Beginning (kmol/kmol)	After the 1st purge (kmol/kmol)	After the 2nd purge (kmol/kmol)	After the 3rd purge (kmol/kmol)
Air	1	0.055	0.003	0
Nitrogen	0	0.945	0.997	1

Simulations that consider the leakage of air into the reactor use the leak test to estimate the leaked airflow. This flow depends on the pressure variation after 15 minutes of the reactor closure. The air leakage is pressure-dependent and, therefore, not constant. This means that when the pressure is above 1.01 bar (ambient pressure) air can't go into the reactor. The airflow only increases as the pressure decreases (vacuum). The maximum airflow values that were found with the leak test are shown in Table 3. As expected, the increase in pressure variation over time results in increased air leakage into the reactor. These results are used in the simulations of the following subsections.

Table 3: Leakage scenarios considered for the leak test.

Base case	$\Delta P = 0$	$v_{air} = 0$
Type 1	$\Delta P = 0.02\ bar$	$v_{air} = 0.81\ kg/hr$
Type 2	$\Delta P = 0.06\ bar$	$v_{air} = 2.44\ kg/hr$

4.2 Pressure control

The control of the nitrogen supply and the opening and closing of the ejector valve to create a vacuum play a crucial role in the inertization stage. In general, the addition of nitrogen happens quickly, making it easier to control. On the other hand, the pressure control to create a vacuum is more dependent on external factors, requiring a longer time to reach the desired pressure. For that reason, four different time intervals were considered for the pressure to reach the desired value for the vacuum during inertization. That was done by changing the time value of the ramp control. The results for the air concentrations obtained after each purge, for each simulated time and leakage scenario, are shown in Tables 4 and 5.

Table 4: Molar concentration of air and nitrogen for different time intervals of control of the ejector opening (vacuum) for the type 1 leakage.

		Beginning (kmol/kmol)	After the 1st purge (kmol/kmol)	After the 2nd purge (kmol/kmol)	After the 3rd purge (kmol/kmol)
2 min	Air	1	0.055	0.003	0.0003
	Nitrogen	0	0.945	0.997	0.9997
6 min	Air	1	0.062	0.025	0.023
	Nitrogen	0	0.938	0.975	0.977
10 min	Air	1	0.07	0.053	0.052
	Nitrogen	0	0.93	0.947	0.948
20 min	Air	1	0.106	0.177	0.18
	Nitrogen	0	0.894	0.823	0.82

Table 5: Molar concentration of air and nitrogen for different time intervals of control of the ejector opening (vacuum) for the type 2 leakage.

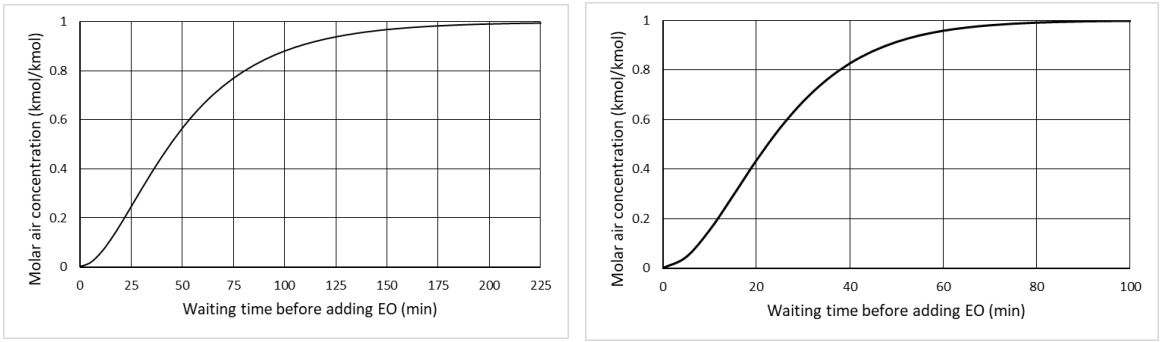
		Beginning (kmol/kmol)	After the 1st purge (kmol/kmol)	After the 2nd purge (kmol/kmol)	After the 3rd purge (kmol/kmol)
2 min	Air	1	0.056	0.004	0.0006
	Nitrogen	0	0.944	0.996	0.9994
6 min	Air	1	0.076	0.066	0.066
	Nitrogen	0	0.924	0.934	0.934
10 min	Air	1	0.097	0.133	0.138
	Nitrogen	0	0.903	0.867	0.862

Considering the molar concentrations of vapor-phase after each purge, presented in Table 4, for the case in which the purge takes 2 minutes to reach the desired pressure, the molar percentage of oxygen inside the reactor at the end of the inertization is below 10%. According to MecNeill et al. (2007), this amount of oxygen is acceptable to consider the vessel inert, indicating that, under these conditions, the reactor can be used safely. The same happens for 6 and 10 minutes. When the controller presents a slower response, taking 20 minutes to reach the pressure, the amount of air that enters through the leak during this period is greater than the amount that can be removed through the purge, reaching an air molar percentage of 18 % at the end of the inertization. For the type 2 leakage (Table 5), when the purges are carried out in 2 or 6 minutes, at the end of the inertization, the amount of oxygen inside the reactor is less than 10% molar and, as with the leakage of type 1, that indicates that, concerning the tightness of the reactor, the safety of the ethoxylation reaction is assured. On the other hand, when the purges take 10 minutes to reach the desired pressure, the amount of air leaked to the reactor increases again from the second purge. This behavior indicates that inertization is not sufficient to guarantee the safety of the ethoxylation reaction under these conditions. Thus, if the completion of each purge during inertization takes more than 20 minutes for the type 1 leakage or more than 10 minutes for the type 2 leakage, the vessel cannot be used without repairs to improve its tightness.

4.3 Air leakage to the reactor before the beginning of the ethoxylation reaction

Due to unexpected batches of ethoxylation reactions, the reaction is not started right after the inertization stage. This waiting time was analyzed for the two types of leakage studied and the results are shown in Figure 3a and 3b. For the type 1 leakage, the wait can take up to 15 minutes, from which point the amount of air inside the reactor is greater than 10%. While for the type 2 leakage, the waiting time is slightly shorter, approximately 8 minutes, so that up to 10% of the air has returned to the reactor.

The consequences of waiting to start adding ethylene oxide, as the graphs show, are the invalidation of the purge and, depending on the time, all the air may have returned to the reactor, implying serious safety issues to the ethoxylation reaction.



a) b)

Figure 3: Concentration profile in the reactor during different waiting periods before the beginning of ethoxylation reaction a) leakage type 1 and b) leakage type 2.

5. Conclusions

This work aimed to simulate the inertization of a reactor used for the ethoxylation reaction. A strategy was used to indicate the amount of air that can be leaked into a reactor depending on the leak test, which was also

modeled. This study showed the importance of effective pressure control, not only during the ethoxylation reaction but also in the steps that precede it. Still, the risks were calculated for the moment the addition of ethylene oxide begins and, depending on the tightness of the reactor, it is found that this addition needs to happen immediately after inertization.

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