

# Industrial and simulation analysis of the nitrogen trichloride decomposition process in electrolytic chlorine production

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## Abstract

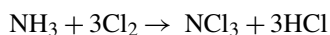
This work presents the dynamic simulation of the thermal decomposition of nitrogen trichloride (NCl<sub>3</sub>) during electrolytic chlorine (Cl<sub>2</sub>) production, using an industrial plant as a case study. NCl<sub>3</sub> is an extremely unstable and explosive compound and the decomposition process has the following main problems: changeability of the reactor temperature and loss of solvent. The results of this work will be used to establish a more efficient and safe control strategy and to analyze the loss of solvent during the dynamic period. The implemented model will also be used to study the use of a new solvent, considering that currently used solvent will be prohibited from commercial use in 2010. The process was simulated by using the commercial simulator Aspen<sup>TM</sup> and the simulations were validated with plant data. From the results of the simulation it can be concluded that the rate of decomposition depends strongly on the temperature of the reactor, which has a stronger relationship to the liquid Cl<sub>2</sub> (reflux) and gaseous Cl<sub>2</sub> flow rates which feed the system. The results also showed that the loss of solvent changes strongly during the dynamic period.

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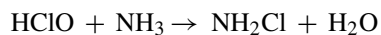
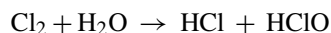
**Keywords:** Nitrogen trichloride; Decomposition; Simulation; Dynamic; Control

## 1. Introduction

The influence of impurities is frequently cited as the cause of accidents in the chemical industries. Under certain conditions (pressure, temperature and composition) where there is potential for rapid and exothermic reactions of decomposition, contamination with impurities can cause very serious accidents. Classic examples of these reactions are processes with organic nitrogen and reactive monomers, as well as some chemical processes involving inorganic material, for example, electrolytic Cl<sub>2</sub> production from aqueous solutions of NaCl or KCl. Due to the presence of ammonium (NH<sub>3</sub>) in salt, NCl<sub>3</sub>, which is an extremely unstable and explosive compound, will be present in the final Cl<sub>2</sub>, because of the following reaction:



Vogler [1], Dokter [2], Gustin [3,4] and Gerrath [5] have discussed some explosions of Cl<sub>2</sub> plants caused by high NCl<sub>3</sub> concentrations. Therefore, NH<sub>3</sub> has to be eliminated before the electrolytic process. This is carried out by injecting gaseous Cl<sub>2</sub> into the stream of the salt solution (to the electrolytic cells), thus producing nitrogen chloride (NH<sub>2</sub>Cl), which is volatile. The reactions which take place are



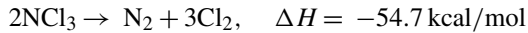
Even if the concentration of NH<sub>3</sub> is very low it will not be completely eliminated, leading to the formation of NCl<sub>3</sub>. This NCl<sub>3</sub>, produced inside the electrolytic cell, flows together with the gaseous Cl<sub>2</sub> and becomes a dangerous impurity for the liquid Cl<sub>2</sub>, once the evaporation of liquid Cl<sub>2</sub> in closed vessels increases the NCl<sub>3</sub> content. According to the report GEST 76/55 [6], 1 ppm of NH<sub>3</sub> in the salt solution to be electrolyzed is enough to result in more than 50 ppm of NCl<sub>3</sub> in the liquid Cl<sub>2</sub>, so it is strongly

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recommended that the  $\text{NCl}_3$  concentration in all parts of the plant is kept below 1000 ppm.

Considering the safety aspect, the  $\text{NCl}_3$  decomposition is a fundamental stage in the production of electrolytic  $\text{Cl}_2$ . Thus thermal decomposition, using carbon tetrachloride ( $\text{CCl}_4$ ) as solvent, is widely used in the  $\text{Cl}_2$  industries [6], mainly due to simplicity and the cost of the installation, according to the chemical reaction:



The solvent has to be miscible with  $\text{NCl}_3$  and  $\text{Cl}_2$ ; furthermore it must be inert because of the presence of  $\text{Cl}_2$ .  $\text{CCl}_4$  is the most indicated solvent because it has a low risk of additional chlorination and its bubble point is higher than that of  $\text{NCl}_3$ . However, according to the Montreal Protocol [7], the commercial use of  $\text{CCl}_4$  will be prohibited in 2010, a reason why industries are already looking for its replacement.

Because of the importance of the reactions involving  $\text{Cl}_2$ , knowledge of them is fundamental for the safety of these industries. However, detailed information about the  $\text{NCl}_3$  decomposition process during the electrolytic  $\text{Cl}_2$  production is rarely mentioned in the published literature. Therefore, this paper presents a dynamic simulation of the thermal decomposition of  $\text{NCl}_3$  during electrolytic  $\text{Cl}_2$  production, using an industrial plant in Brazil as a case study. The main problems related to the process are: the unstable temperature of the reactor (where decomposition is taking place) and the significant loss of solvent. The main purpose of this work was to identify the dynamic of the process, as it is important to establish a strategy to control the process (to make it more secure) and to analyze the loss of solvent during

the dynamic period. The implemented model will also be used to study the substitution of  $\text{CCl}_4$  and to analyze the operational faults of the system. The commercial simulator Aspen<sup>TM</sup> was used to simulate the process and the simulations were validated with data from an industrial plant.

## 2. Problem statement

The decomposition system can be described as a reactive distillation without a top condenser, with withdrawal at the bottom, and with the decomposition taking place in the reactor (see Fig. 1).

Gaseous  $\text{Cl}_2$  ( $\text{CL2-GAS}$ ) produced in the electrolyte cells and contaminated with  $\text{NCl}_3$  is fed in at the bottom of the bubble cap tray column (precooler), while liquid  $\text{Cl}_2$  ( $\text{CL2-LIQ}$ ), at approximately  $-36^\circ\text{C}$ , feeds the top as an external reflux. Gaseous  $\text{Cl}_2$  from the reactor (reboiler) is washed by liquid  $\text{Cl}_2$  to remove the  $\text{NCl}_3$  of the gaseous phase and to cool the gaseous  $\text{Cl}_2$  before compression. The  $\text{NCl}_3$  condenses and dissolves in the liquid  $\text{Cl}_2$  heading to the reactor.

The liquid holdup of the reactor mainly consists of  $\text{CCl}_4$  (more than 97%), which extracts  $\text{NCl}_3$  from the liquid  $\text{Cl}_2$  and avoids high concentrations of  $\text{NCl}_3$ . In other words, the presence of  $\text{CCl}_4$  ensures a safe and secure decomposition process, working as an inert compound during extraction and dilution. Considering the composition of the holdup,  $\text{CCl}_4$  is the main compound of the RECY stream.

Steam circulating in the jacket of the reactor is used to heat and vaporize the liquid holdup. The flow rate of the steam is specified by a feedback control.

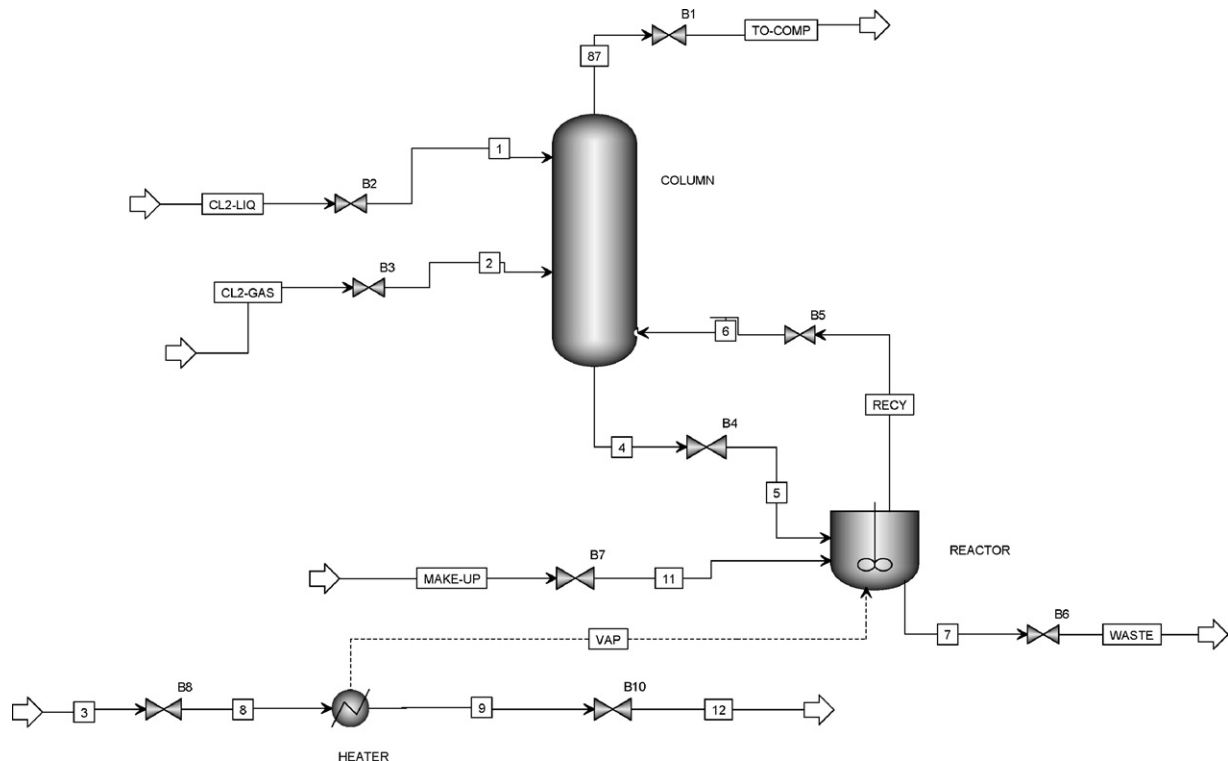


Fig. 1.  $\text{NCl}_3$  decomposition system used in the industrial plant.

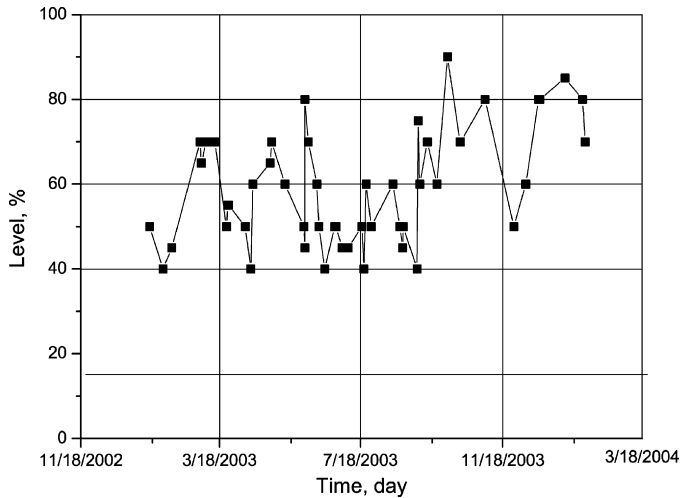


Fig. 2. Plant data of the reactor liquid level.

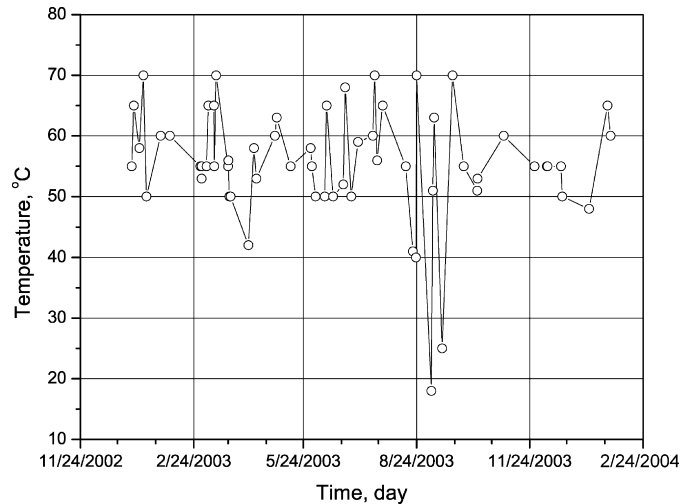


Fig. 3. Data plant for the reactor temperature.

Generally, the decomposition rate of 12.5 g/h of  $\text{NCl}_3$  per kg of  $\text{CCl}_4$  at 50 °C could be improved by increasing the reactor's temperature, which must not exceed 70 °C. On the other hand, when the temperature is lower than 40 °C the decomposition of  $\text{NCl}_3$  takes place slowly resulting in high concentrations of  $\text{NCl}_3$  in the reactor [5].

$\text{CCl}_4$  is continuously lost from the top of the pre-cooler, causing a lower level in the reactor. The make-up stream is used to replace the loss of  $\text{CCl}_4$ . The reactor level oscillates because of the loss and replacement of  $\text{CCl}_4$ , as can be observed in Fig. 2. The replacement of  $\text{CCl}_4$  is done weekly, which will be a very critical aspect once the commercial use of this compound is prohibited in order to satisfy the Montreal Protocol [7], which Brazil has also signed. Therefore the developed model will also be used, when trying to substitute  $\text{CCl}_4$ .

The waste stream is used in operations where the liquid holdup is discarded. In other words, when the system is shut down or when the solvent is being replaced.

According to the data plant, the other important problem of the system (see Fig. 1), besides the loss of solvent, is the variability of the reactor's temperature (see Fig. 3). It should be noted that the temperature of the reactor has a direct effect on the loss of solvent.

### 3. Aspen<sup>TM</sup> model

Steady-state simulations were realized using the Aspen Plus<sup>TM</sup> simulator and the results were used as initial values for the dynamic simulations, which were carried out using the Aspen Dynamics<sup>TM</sup> simulator.

The pre-cooler was simulated using the internal routine Rad-Frac of the Aspen Plus<sup>TM</sup>. The Peng–Robinson equation of state was used to represent the thermodynamics of the process: phase equilibrium and properties (particularly, enthalpy and entropy). The data for this column were: 8 stages (1st–4th stage with a diameter of 1.0 m; 5th–8th stage with a diameter of 0.5 m) and a Murphree efficiency of 70%.

The internal routine RCSTR of the Aspen Plus<sup>TM</sup> was used to simulate the reactor as a Continuous Stirred Tank Reactor (CSTR) type with the following specifications: diameter of 1.4 m and height of 2.0 m. Heat exchange with the environment and the capacitance of the reactor (metal) were considered. The industrial reactor was simulated as a CSTR due to the strong agitation in the equipment. In order to have a more realistic simulation, the stream of steam was connected to a heat exchanger, whose heat duty was transferred to the reactor. At the outlet of the heat exchanger, the stream was specified as a saturated liquid.

For the reactor simulation it was necessary to know the kinetics of the decomposition of  $\text{NCl}_3$  in the presence of  $\text{CCl}_4$ . The kinetics of the decomposition of  $\text{NCl}_3$  are widely discussed in the literature, however, most cases relate to its decomposition in water or its formation [8–10]. Only in the papers of the Chlorine Institute [1] and the Euro Chlor [5] were the kinetics of the decomposition of  $\text{NCl}_3$  in the presence of  $\text{CCl}_4$  found. According to these publications the decomposition is a first-order reaction and the rate is expressed by the following equation:

$$r = -Kx$$

where  $x$  is the mass fraction of  $\text{NCl}_3$ .

In Aspen Plus<sup>TM</sup>, the implementation of the kinetics of the reactions was carried out by the Arrhenius equation:

$$K = K_0 e^{-(E_a/RT)}$$

where  $K_0$  is a pre-exponential constant,  $E_a$  is the activation energy of the reaction,  $R$  is the universal constant of gases and  $T$  is the temperature of the mixture. Data for the constant  $K$  as a function of  $T$  were available [5] and have been used to calculate  $K_0$  and  $E_a$ . The values of  $E_a$  and  $K_0$ , respectively 1.347E05 J/mol and 5.8E19 h<sup>-1</sup>, were calculated by linear fitting of the Arrhenius equation using the polynomial fitting.

To begin the simulations, the flow rates and the compositions of the gaseous and liquid  $\text{Cl}_2$  streams were the same from the plant, as well as the rate of flow of the steam to the jacket of the reactor. However, it was very difficult to obtain the steady-state solution, which was only achieved when lower values than the

plant data of the steam flow rate were considered. This resulted in a lower value for the reactor temperature, compared to the value of the plant. Even so, this result was used as the initial value for the dynamic simulation.

The problems with convergence may have two causes: a strong interaction between the column and the reactor (because of the recycling) and the loss of the solvent at the top of the precool. The second cause, perhaps the most important one, is that for the real operational temperature of the reactor, there is a loss of solvent resulting in an imbalanced mass and energy of the system. That is probably why it was only possible to obtain the convergence for low reactor temperature values, a situation when there was no loss of solvent.

The results for the steady-state were exported to the Aspen Dynamics™ simulator. The conditions observed at the plant, especially the temperature of the reactor, were achieved by manipulating the control valves, shown in Fig. 1. Thus, the process was run (in time) by the integration (Euler implicit method) of the differential equations.

#### 4. Results and discussion

Considering Fig. 1 and according to engineering judgment, the variables that have the greatest effect on the process are: liquid and the gaseous  $\text{Cl}_2$  flow rates to the column (precooler) and the flow rate of the steam to the jacket of the reactor. The results obtained from the Aspen™ model present the dynamic behavior of the system when these variables are disturbed. All the results are for the open-loop condition. However, before continuing this study, the simulations were validated by comparing the Aspen™ results with the data from the plant, for a disturbance of the rate of flow of the steam to the jacket of the reactor.

##### 4.1. Validating the Aspen™ model—disturbance on the steam flow rate

As mentioned earlier, the conditions at the plant were achieved by manipulating the control valves. When the temperature of the reactor achieved the observed value at the plant,  $52^\circ\text{C}$ , the  $\text{NCl}_3$  content in liquid holdup was 160 ppm, while the average of this value was 150 ppm in the plant. The values of the gaseous and liquid  $\text{Cl}_2$  flow rates were the same as those observed in the plant; the same values are found for the  $\text{NCl}_3$  in the gaseous  $\text{Cl}_2$  feed. At these operating conditions, without any disturbance, the loss of  $\text{CCl}_4$  is approximately 1.5 kg/h, the reason why the level in the reactor decreases, as depicted in Fig. 4. For the column, just the top temperature, approximately  $-36^\circ\text{C}$  (the bubble point of  $\text{Cl}_2$  at that pressure), was validated.

As cited before, the loss of solvent is directly proportional to the operating temperature of the reactor and that is why the process does not achieve a steady-state. In other words, when the temperature of the reactor is increasing, it is more difficult for the process to achieve its steady-state. Furthermore, it would be necessary to have more stages in the precooler, which would involve a modification of the project.

With the substitution of the solvent, the solvent loss will depend on the bubble point of the new solvent, which will

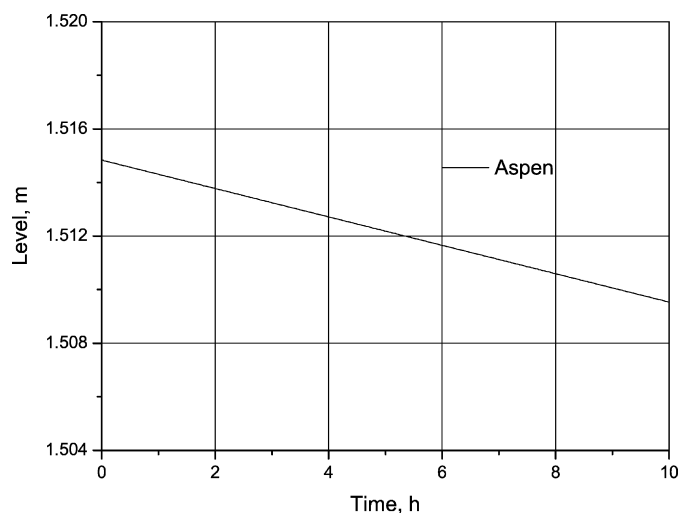


Fig. 4. Reactor liquid level without disturbance.

probably be the chloroform ( $\text{CHCl}_3$ ). In spite of similarities to  $\text{CCl}_4$ , especially with regards to the number of chlorine atoms,  $\text{CHCl}_3$  has a lower bubble point, indicating that the loss of solvent will be larger. Preliminary studies using  $\text{CHCl}_3$  to replace  $\text{CCl}_4$  proved that, at the actual value of temperature of the reactor, the loss of the solvent will be twice the present amount.

The validation was also realized based on a test, where there was a step disturbance (increase of 6%) to the rate at which steam flowed to the jacket of the reactor. According to Fig. 5, the simulated and the real data, for the temperature of the reactor, are in excellent agreement, which can be considered satisfactory for validation. In Fig. 5 it can be observed that the test at the plant was only conducted for about 4 h because of security concerns. If the test were to continue, the temperature would achieve the bubble point of  $\text{CCl}_4$  (approximately  $87^\circ\text{C}$ ) at the operational pressure of the reactor. It has to be remembered that, actually, the flow rate of steam to the jacket is the variable for controlling the process.

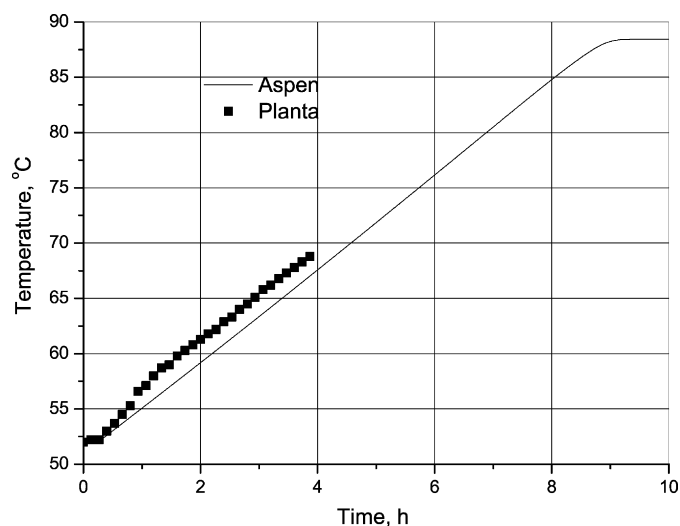


Fig. 5. Reactor temperature for a step disturbance on the steam flow rate.

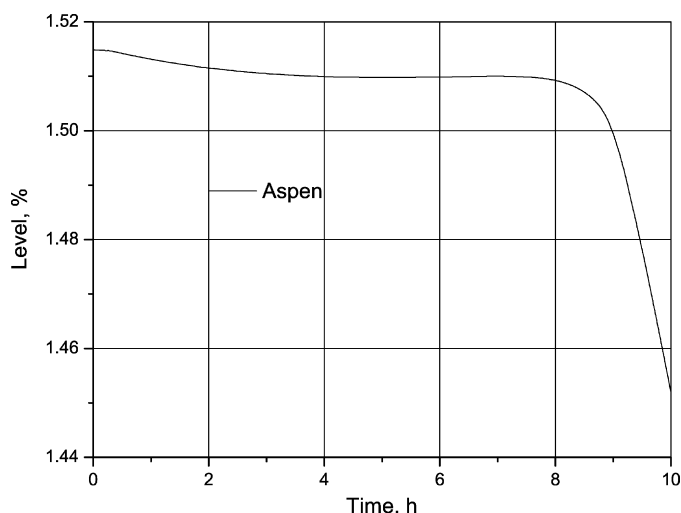


Fig. 6. Reactor liquid level for the step disturbance on the steam flow rate.

The increase in the temperature of the reactor is due to the change in the composition of the liquid holdup, due to the complete vaporization of  $\text{Cl}_2$ . So, only  $\text{CCl}_4$  remains in the reactor. It should be noted that only 4 h after the disturbance, the temperature passes the allowed limit ( $70^\circ\text{C}$ ).

In terms of control, the system presents an integrator behavior, where the observed final temperature value in Fig. 5 (result from Aspen<sup>TM</sup>) indicates the saturation of the system.

The increase in the rate of flow of steam to the jacket will cause the reactor to empty as a consequence of the complete vaporization and loss of  $\text{CCl}_4$  at the top of the column, as shown in Fig. 6. Another observation from Fig. 6 is that the lowering of the liquid level in the reactor (loss of solvent) increases rapidly when the temperature of the reactor achieves the bubble point of the solvent, approximately 9 h after the disturbance, as shown in Fig. 5.

#### 4.2. Disturbance on the liquid $\text{Cl}_2$ flow rate

Figs. 7 and 8 show the behavior of the temperature and the  $\text{NCl}_3$  content, respectively, considering a positive increase of 6% in the flow rate of the liquid  $\text{Cl}_2$ . It can be observed that the temperature and the  $\text{NCl}_3$  content are inversely related: with a decrease in the temperature (Fig. 7), the  $\text{NCl}_3$  content in the reactor increases (Fig. 8). The decrease of the temperature in the reactor is caused by the increase of the mass fraction of  $\text{Cl}_2$  in the liquid holdup of the reactor. However, the increase in  $\text{NCl}_3$  content is a result of the decrease in the decomposition rate. It has to be remembered that for a period of a little more than 1 h, the  $\text{NCl}_3$  content exceeds its recommended limit (1000 ppm).

The simulation has proved that even for small disturbances to the flow rate of the liquid  $\text{Cl}_2$ , which is also a variable used to control the process, the temperature of the reactor tends to be a minimum value. To avoid this, the actual control system increases the rate at which the steam flows to the jacket. From a dynamic point of view, the temperature has a large transient period. In other words, the temperature of the reactor, and consequently the  $\text{NCl}_3$  content, oscillates a lot, so the control system

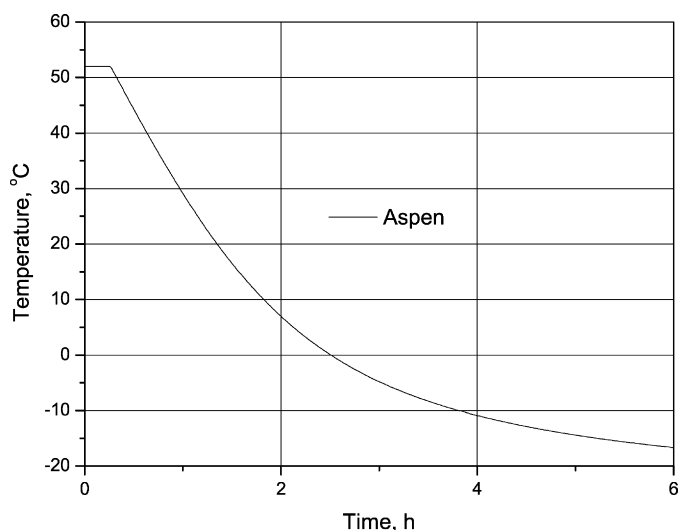


Fig. 7. Reactor temperature for a step disturbance on the liquid  $\text{Cl}_2$  flow rate.

will not allow very low temperatures to be achieved. However, according to Fig. 3, the temperature is not maintained in a secure interval.

Since the liquid  $\text{Cl}_2$  and steam flow rates are the variables used to control the process, it is interesting to analyze the effect that each one has on the dynamics. Comparing Figs. 5 and 7, it can be noticed that the liquid  $\text{Cl}_2$  flow rate presents a larger effect on the temperature than the steam flow rate. Therefore, an option for the control system is to use a stream of liquid  $\text{Cl}_2$  (not the reflux) as a manipulated variable and to set the steam flow rate to the jacket of the reactor.

#### 4.3. Disturbance on the gaseous $\text{Cl}_2$ flow rate

In contrast to the liquid  $\text{Cl}_2$  and steam flow rates, the gaseous  $\text{Cl}_2$  flow rate is not used to control the process. The change in the value of the gaseous  $\text{Cl}_2$  flow rate is due to operational problems or modifications to the plant's capacity.

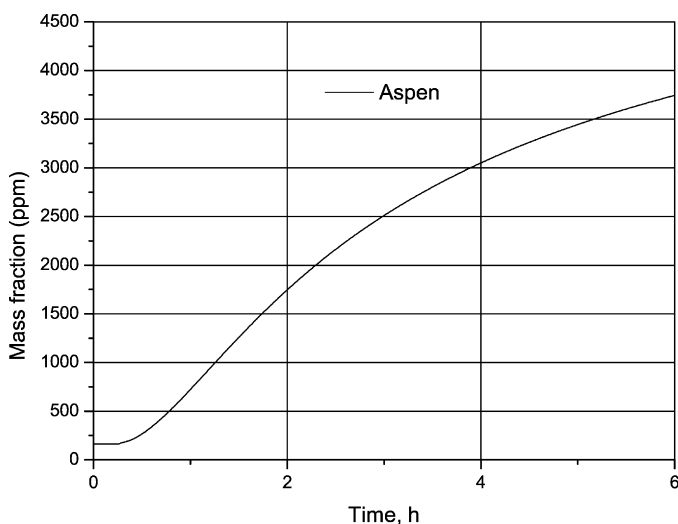


Fig. 8.  $\text{NCl}_3$  content in reactor for a step disturbance on the liquid  $\text{Cl}_2$  flow rate.

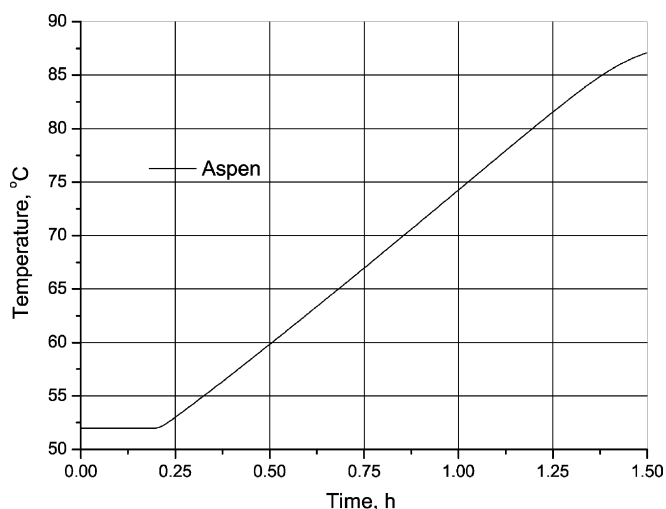


Fig. 9. Reactor temperature for a step disturbance on the gaseous  $\text{Cl}_2$  flow rate.

According to Figs. 9 and 10, for a positive increase of 6% in the gaseous  $\text{Cl}_2$  flow rate, temperature and  $\text{NCl}_3$  content presents a inverse behavior to that presented by a disturbance to the liquid  $\text{Cl}_2$  flow rate and is similar to the behavior when considering an increase in the rate at which the steam flows to the jacket of the reactor. Actually, with an increase in the gaseous  $\text{Cl}_2$  flow rate the heat duty for the reactor becomes more than sufficient to vaporize liquid that is descending; as result, the reactor temperature tends to increase and, consequently, the  $\text{NCl}_3$  content decreases. The liquid level of the reactor tends to go down, due to the loss of the solvent at the top of the column.

However, comparing Figs. 5 and 9, it should be noted that the disturbance in the gaseous  $\text{Cl}_2$  flow rate causes a smaller transient period than that caused by the disturbance to the rate of flow of the steam to the jacket of the reactor. Thus, it can be

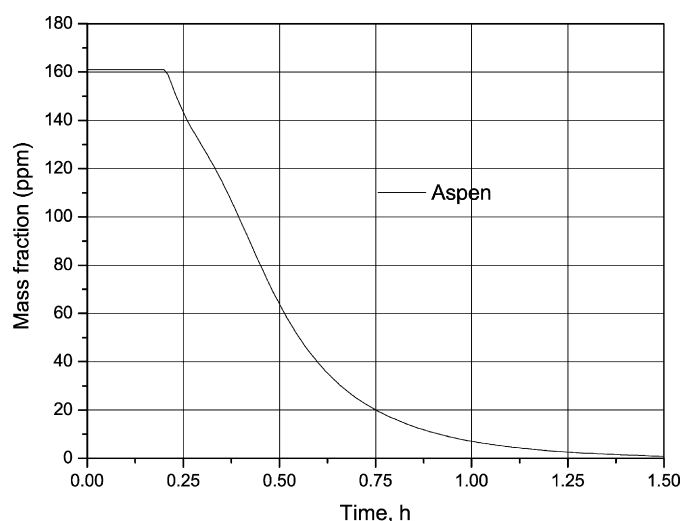


Fig. 10.  $\text{NCl}_3$  content in reactor for a step disturbance on the gaseous  $\text{Cl}_2$  flow rate.

suggested that a stream of liquid  $\text{Cl}_2$  is used to feed the reactor directly, in order to control the temperature of this equipment.

## 5. Concluding remarks

The results of the simulation are in agreement with the data from the plant, which means that the model can be used to design the new control system and to analyze the effect of the different operational conditions on the loss of solvent.

Specifically, it can be stated that: the loss of solvent is directly proportional to the operational temperature of the reactor, is strongly affected by the dynamic of the process and does not allow the system to achieve steady-state. For a smaller transient period, the loss of solvent will be faster. Another important observation is that the loss of the solvent increases rapidly when the temperature of the reactor achieves the bubble point of the solvent. The results for operation with  $\text{CHCl}_3$  and its comparison with  $\text{CCl}_4$  will be presented in another time.

The temperature and the  $\text{NCl}_3$  content (rate of decomposition) in the reactor are inversely related and both variables are extremely dependent on the liquid and gaseous  $\text{Cl}_2$  flow rates, as well as on the rate at which the steam flows to the jacket. Considering the possible variables to control the process, the liquid  $\text{Cl}_2$  flow rate has a greater influence on the temperature of the reactor and, consequently on the composition, than the flow rate of the steam (to the jacket). From the process control point of view, the system has an integrator behavior.

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## References

- [1] C.E. Vogler, Chemistry of nitrogen trichloride—a review of the literature, in: Proceedings of the Eighth Meeting of Chlorine Plant Managers, 1963.
- [2] T. Dokter, Fire and explosion hazards of chlorine-containing, *J. Hazard. Mater.* 10 (1985) 73–87.
- [3] J.L. Gustin, Influence of trace impurities on chemical reaction hazards, *J. Loss Prev. Process. Ind.* 15 (2002) 37–48.
- [4] J.L. Gustin, Safety of chlorine production and chlorination processes, *Chem. Health Safety* (2005) 5–16.
- [5] C. Gerrath, Recent developments in chlorine, Document KREBS SWISS presented at TECHNOGERMA, 2002.
- [6] GEST 76/55, Maximum Levels of Nitrogen Trichloride in Liquid Chlorine, 10th ed., Euro Chlor Publications, 2001.
- [7] Montreal Protocol, <http://www.unep.ch/ozone/pdfs/Montreal-Protocol2000.pdf>.
- [8] N.M. Rubtsov, Kinetic Mechanism and Chemical Oscillations in the Branching Chain Decomposition of Nitrogen Trichloride, *Mendeleev Communications Electronic Version* (1998).
- [9] S.W. Leung, R.L. Valentine, An unidentified chloramine decomposition product. II. A proposed formation mechanism, *Wat. Res.* 28 (1994) 1485–1495.
- [10] K. Kumar, R.W. Shinness, D.W. Margerum, Kinetics and mechanisms of the base decomposition of nitrogen trichloride in aqueous, *Inorg. Chem.* 26 (1987) 3430–3434.