SCIENTIFIC PAPER

OPTIMIZATION OF THE VINYL-MONOCHLORIDE RECOVERY PROCESS FOR THE REDUCTION OF COSTS AND ENVIRONMENTAL IMPACT

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Abstract

Reducing environmental impacts in the production processes is the focus of large industries. In the PVC production process, the loss of vinyl monochloride (VCM) through an incineration stream of inert materials is a point of attention due to emission of greenhouse gases. VCM is lost as part of the stream of uncondensed gases from the VCM recovery unit.

The optimization of the VCM recovery process was carried out by modelling the industrial system and running it using a process simulator. The unit model and simulation results have been verified through plant operating data. Sensitivity analyses were performed to identify which independent variables improved the VCM condensation rate. Based on plant operating experience, three independent variables were selected and their influence on the VCM recovery flow rate was verified: pressure, composition of the input stream and utility water flow rate. After the sensitivity analysis, the plant operating pressure was selected for optimization, resulting in the additional quarterly recovery of 7.5 tons of VCM and a reduction of more than 5 tons of natural gas fuel, that is, an annual reduction of 23 tons of fuel, which represents 53 tons of CO_{2eq}. Overall, the annual savings amount to US$15,000, US$1,060 by reducing the consumption of fuel gas alone. Therefore, by ensuring greater VCM recovery, competitiveness improves by reducing production costs, and greenhouse gas emissions are reduced due to the decrease in gas incineration.

Keywords: Vinyl monochloride, simulation, heat exchangers in series, optimal operating conditions.

Article Highlights

- The steady-state simulation of an Vinyl Chloride recovery unit made up of three condensers banks
- Use of parametric sensitivity analysis to evaluate the influence of operational parameters
- Optimizing and proposing improvements to the existing system based on parametric sensitivity
- Development of a process monitoring tool using a commercial simulator

Introduction

The environmental impacts caused by industrial processes and their contribution to climate change is one of the most important themes of our time, and developing solutions that reduce greenhouse gases (GHG) emissions is essential. At present, human society is dependent on plastics, among which is polyvinyl chloride (PVC) that uses VCM as raw material. One of the existing technologies for PVC production, and the one used in this study, is batch production, in which VCM, water, nitrogen and other products are added to the polymerization reactor. After completion of the reaction two streams result: a bottom stream composed of the PVC sludge, sent for drying, and a top stream composed of unreacted VCM and inert materials, sent to the VCM recovery unit [1], where it goes through compression and condensation processes through a series of shell and tube heat exchangers, separating the VCM from other substances. The VCM is then distilled and recycled to the reactor feed. The stream of uncondensed gases is sent to an incinerator due to the presence of chlorinated organic vapours. This optimization study concentrates on the operating conditions of the set of shell and tube heat exchangers of the VCM recovery unit.

VCM is recognized as a carcinogen for humans and animals. Recent studies have reported that even below the minimum exposure limit, workers suffered health problems [2-6]. Over the years, possible harm to health was identified, and as a result, regulations have been created to define the maximum concentration of VCM in the final product, which drove the development and improvement of technologies to guarantee maximum recovery of VCM and meet the specifications that became more restrictive [7]. According to ASTM D3749 the maximum content allowed is 1 ppm mass [8]. In terms of environmental impacts, VCM has direct and indirect impacts. There is the possibility of contamination of groundwater reservoirs from emission of chlorinated organic vapours, such as VCM, into the atmosphere, since, as they encounter rain, they become solubilized and percolate into the soil, reaching the groundwater reservoirs [9]. Halogenated solvents, particularly chloroethylene, are among the most prevalent pollutants [10]. In relation to indirect impacts, there are those due to the use of non-renewable sources of industrial utilities and of raw materials for VCM production [11,12].

Several technologies have been developed over the years to maximize VCM recovery or minimizing its emission from the recovery unit uncondensed gas stream, with varying recovery efficiencies. These technologies and its efficiencies are condensation and incineration (97%) [12], adsorption (95%) [13], absorption (99%) [14] and membrane (99.9%) [15], the latter being the most widely adopted. Combined methods, where two or more types of technologies are adopted in the same industrial process, are also used to increase the recovery efficiency of the uncondensed gas stream [12-16].

Other studies have already been carried out in similar systems in an attempt to increase the recovery efficiency of VCM. For condensation technology, sensitivity analyses were reported based on the temperature variation of cooling fluids, thermal exchange area, pressure increase and cooling fluid exchange, and only the possibilities for economic gains were highlighted [17]. Other studies evaluate the efficiency of other VCM recovery methods, where the results do not include CO_{2eq} values [12-16]. This optimization study is based on the condensation and incineration technology of an operating plant and is aimed at identifying the best system operating conditions to increase VCM recovery and, therefore, reduce both production costs and GHG emissions by using less fossil fuels in the incinerator. The actual efficiency of this system is 95.5% [18].

Process Description

In the PVC polymerization reaction, there is a surplus of VCM that is recovered from the reactors and sent to a tank at ambient conditions for subsequent treatment and use [17,18]. The recovery of the monomer from the reactors is done using vacuum, and due to the lack of tightness, air enters the system. Furthermore, nitrogen is added to the process and is recovered together with the VCM at the end of the batch, which determines the composition of the system's input stream [18].

From this tank on the VCM treatment process is undertaken. The gaseous stream leaving this tank passes through a compression unit, before entering the condensing unit, whose system pressure is maintained within an operational range of 5 kgf/cm² (g) to 7 kgf/cm² (g) by a pressure control valve, and the temperature, as a pressure-dependent variable, between 70°C and 90°C. In the condensing unit, a series of shell and tube heat exchangers carry out the VCM condensation process using different cooling fluids in the shell side. The condensed monomer is treated and subsequently used as a fraction of the polymerization reactor loads for PVC and the uncondensed remainder is sent for incineration.

As air and nitrogen are admitted, the composition varies according to natural process oscillations, and the presence of these gases has a strong effect on the MVC recovery rate.

VCM condensation system

The system studied in this work is highlighted in Figure 1 and is based on an existing industrial unit, which consists of a series of four shell and tubes heat exchangers, divided into three stages. The first has two heat exchangers operating in parallel and the others have two condensers operating in series. As the pressure is constant and controlled by an automatic control valve, the temperature range required to condense the VCM throughout the process is obtained using water, diethylene glycol and liquid VCM as cooling fluids in the 1st, 2nd and 3rd stages, respectively.

Figure 1 – VCM recovery unit heat exchange system.

Methodology

The modelling and simulation of the VCM condensation system has been undertaken using the Aspen Plus commercial simulator with the Aspen Exchanger Design and Rating (EDR) extension adopting the rigorous simulation method [19], in steady-state condition. The thermodynamic models selected and verified through literature data were Peng Robinson [20,21] and Soave Redlich Kwong [19]. The simulation results were verified by comparison to operating data from an existing industrial plant.

The selection of variables to be optimized was based on plant operational experience. From this selection, parametric sensitivity analyses were carried out using the direct method, where one variable is changed (independent variable), and the results of the other variables in the system are evaluated (dependent variables). In this study, the main dependent variable evaluated was the VCM flow sent to incineration and the independents variables selected were based on plant operating experience: pressure, composition of the input stream and utility water flow rate. Then, to correlate the VCM loss flow rate with the independent variable, regressions were developed due the simulations results that allowed these sensitivity evaluations to be undertaken.

After the sensitivity analysis, the industrial process was optimized by selecting the variables that influenced VCM recovery, and thus generating the results of this work in relation to the reduction of GHG emissions due to lower consumption of natural gas fuel in the incinerator and the economic impact of lower VCM loss.

In the end, proposals for future work were made that aim to increase the efficiency of the VCM recovery in this process stream.

Simulation set-up

The first step was the selection of the thermodynamic models, which was based on research works that evaluated similar systems and obtained good results. The models that have shown the best results are the Peng Robinson [20, 21] and Soave Redlich Kwong [17] models, and so were select to be used in the present work.

Secondly, process conditions of the system input stream were added [19]. Temperature, pressure, and flow rate were collected from online instruments of the existing industrial unit, while stream composition was determined by chromatography through the collection and analysis of five different samples.

The actual geometries of the heat exchangers were collected from the design drawings and introduced into the simulator using the Aspen Exchanger Design and Rating (EDR)® vs.11 extension and later added to Aspen Plus® vs.11, adopting the type HeatX exchanger, in Simulation mode with a rigorous method to evaluate the behaviour of the variables [19].

The heat exchanger system shown in Figure 1 was implemented in Aspen Plus ® vs. 11 according to the flowchart in Figure 2. The TC-01 A/B heat-exchanger promotes much of the VCM condensation in this system. The liquid phase (LIQ2) is accumulated in the V-01 A/B vessels. The gaseous flow (ENT-TC-02) goes to the second stage (TC-02) condenser, resulting in two output streams: a gaseous phase (inerts with some residual VCM-GAS3) and a liquid phase (LIQ6) which also returns to the V-01 A/B vessels. The gaseous phase is directed to the TC-03 (GAS3) condenser, which uses the liquid VCM (heat of vaporization) in the shell side to condense part of the VCM from the process stream. The resulting gaseous stream is sent to incineration (VENTA) and the liquid part (LIQ5) returns to the V-01A/B vessels.

Figure 2 – VCM recovery unit flowchart for process simulation.

Due to the confidentiality of the industrial plant data, the input stream process variables, flow rate, pressure and temperature are here described as ranges. The flow rate varies from 3 t/h to 10 t/h and the VCM mass concentration from 92% to 97%. The average mass composition of the five samples analysed is: VCM (92.7%), O_2 (0.5%), N_2 (5.6%), CO (0.1%), CO_2 (0.6%), H_2O (0.5%). The system pressure is maintained within an operational range of 5 kgf/cm² (g) to 7 kgf/cm² (g) by a pressure control valve, and the temperature, as a pressure-dependent variable, between 70°C and 90°C.

The design flow rates will be those adopted for the existing heat exchanger utilities. The cooling water flow rate in the range of 26 t/h to 35 t/h, the diethylene glycol flow rate from 2 t/h to 3 t/h and the VCM flow rate, as cooling fluid, from 0.2 t/h to 0.25 t/h, all operating in the shell side of the heat- exchangers.

Model and simulation verification

To verify the simulation results, comparisons were made between the simulated VCM flow rates sent to the incinerator and the actual flow rates observed at the industrial unit. For each sample of the input stream, samples of the output stream for incineration were collected and analysed, and these laboratory results were used to verify the simulation results. A total of ten simulations using the Peng Robinson and Soave Redlich Kwong models were carried out adopting the five samples and their respective process variables: conditions of both the input and utilities streams at the time of sample collection.

Once the simulation model had been verified, sensitivity evaluations were made possible and subsequently undertaken.

Parametric sensitivity analyses

For the sensitivity analyses the direct method, in which the operating parameters are varied one at a time and the effects on the system responses are analysed, was selected [17, 22, 23]. The focus was to observe the trajectory of the operating system and the behaviour of the VCM recovery flow rate as a function of each variable.

Based on operational experience, the following parameters were varied: operating pressure, feed composition and cooling water flow rate to the TC-01A/B heat exchangers. The dependent variables were temperature, composition (VCM concentration) and flow rates of the process streams, including the output stream for incineration, the focus of this work.

Adopting fictitious initial pressure values of 5kgf/cm²g, a mass composition of VCM (92.7%), O_2 (0.5%), N_2 (5.6%), CO (0.1%), CO_2 (0.6%), H_2O (0.5%) and water flow of 26t/h, the variations carried out in the simulator were: pressure: +5%, +10%, +25%, +30%, inert composition: -10%, -5%, +5%, +10%, +30% and cooling water flow: -20%, -10%, +10%, +20%.

Process optimization

After sensitivity analyses, process optimization was proposed. An effort vs. impact [24] matrix was used to select the variables based on operational experience and with the results of the VCM reduction from the optimization, it was possible to quantify the economic and environmental gains.

Economic and Environmental results

To evaluate the economic gain, Equation (1) was used. Equations (2), (3), (4) and (5) were used to calculate the amount of natural gas that was saved [25].

$$Savings(\$) = \frac{8100h}{y} \, x \; VCM \; recovery \; (t/h) \; x \; \text{Price VCM (\$/t)} + \; m_{ng} \; (t/y) \; x \; \text{natural gas price (\$/t)} \tag{1}$$

$$Q_{VMC\ combustion} = Q_{natural\ gas\ combustion} \tag{2}$$

$$(PCI * \dot{\mathrm{m}})_{VCM} = Q_{natural\ gas\ combustion} \tag{3}$$

$$Q_{natural\ gas\ combustion} = (PCI * \dot{\mathrm{m}})_{ng} \tag{4}$$

$$m_{ng} = \dot{\mathrm{m}}_{\mathrm{ng}} * \mathrm{time} \tag{5}$$

Where,

PCI- lower heating value (GJ/t of VCM) and (GJ/t of natural gas)

$\dot{\mathrm{m}}_{\mathrm{VCM}}$- mass flow rate of recovered VCM in t/h.

$\dot{\mathrm{m}}_{\mathrm{ng}}$- mass flow rate of recovered natural gas in t/h.

m_{ng} - mass natural gas in t.

Knowing the amount of natural gas (ng) that was not burned, it is possible to calculate the amount of CO_{2eq}, through Equation (6). The fuel conversion factor for CO_{2eq} is derived from the Boiler/Furnace Protocol: EPA AP-42, which indicates which constant should be used for the conversion and is obtained from the average composition of the fuel. In the case of natural gas used in the industrial plant under study, the conversion factor is 2.26 t of CO_2/t of natural gas [26].

$$CO_{2\mathrm{eq}} = m_{ng} * 2.26 \, \frac{\mathrm{t\,CO_2}}{t\ ng} \tag{6}$$

Results and discussions

Simulation

Figure 3 shows the differences between the simulation results and the actual plant data for the flow rates of VCM loss in the uncondensed gases stream for each thermodynamic model. The results had a maximum difference of 9.7% for the PR model and 10.4% for the SRK model. These deviations are considered acceptable, both because flow rate instruments have a measurement error of up to 10%, and the flow rate of VCM to be incinerated is 20 times smaller than the main process stream. Based on these results, the Peng Robinson model was selected to continue with the evaluations in this study.

Figure 3 – Deviations between the simulations results and actual plant data.

Parametric sensitivity analyses

The results of the disturbances in the independent variables chosen on the VCM flow rate to incineration are presented in Figure 4.

Figure 4 – VCM flow rate to incineration after process changes.

In Figure 4 it is possible to observe that both composition (N_2 concentration) and pressure have impacts on the VCM recovery results, while the change in water flow rate did not affect the studied variable.

a) Effects of pressure variation

Figure 4 shows an inverse relationship between the system pressure and the flow rate of VCM loss to incineration. This is because the equilibrium temperature for condensing the VCM increases with increasing pressure. Therefore, for a fixed volume (the installed equipment has a fixed capacity), the higher the pressure, the greater the difference between the temperatures of the cold and hot sides in the condenser, which improves heat exchange and, consequently, increases the amount of VCM condensed for the same process conditions of utilities and installed equipment [25].

The amount of VCM loss to incineration, in kg/h, as a function of system pressure, in kgf/cm²g, is represented by Equation (7) obtained by the data regression method with an R^2 of 0.9987.

$$\dot{m}_{VCM\ lost} = 34.959\ P^2 - 624.01\ P + 2{,}869.5 \tag{7}$$

The minimum point of the curve is described by Equations (8) and (9) and indicates the lowest flow rate of VCM loss and the corresponding system pressure. Using the minimum value of the method [27] represented by these equations, the minimum flow rate of VCM loss is 84.89 kg/h at a pressure of 8.92 kgf/cm² (g).

$$\dot{m}_{VCM\ lost} = -\frac{\Delta}{4\ a} \tag{8}$$

where $$\Delta = b^2 - 4ac \tag{9}$$

and parameters a, b and c, 34.959; 624.01 and 2,869.5, respectively, are taken from Equation (7).

b) Effects of composition variation

Of all the variables analysed, according to Figure 4, the change in composition had the greatest impact on the VCM condensation rate. This can be explained by the higher concentration of Nitrogen (inert) in the input stream, which pressurizes the system and forces the pressure control valve to open more frequently. As a result, there is a greater loss of VCM due to the drag effect, as well as greater difficulty in condensation due to the reduction in the partial pressure of the VCM in the mixture, which, by getting smaller, ends up requiring a lower temperature for phase change (equilibrium conditions). This same effect can be evidenced in Figure 3, in which samples 2, 3 and 4 showed greater deviations between the simulated values and the actual of the industrial unit.

A better understanding of the effect on the VCM partial pressure, can be shown by adopting Equation (10), Dalton's law [28].

$$p_i = y_i P \tag{10}$$

If the total pressure of the system is the sum of the partial pressures of each substance in the mixture, keeping the pressure constant (due to the pressure control valve), the greater the concentration of Nitrogen, the greater its partial pressure and the lower the pressure partial VCM in the mixture, as shown by Equation (11), in which the arrows illustrate the increasing (↑) or decreasing (↓) trends of each variable).

$$p_{N2} \uparrow + p_{O2} \downarrow + p_{CO2} \downarrow + p_{H2O} \downarrow + p_{VCM} \downarrow = (y_{N2} + y_{O2} + y_{CO2} + y_{H2O} + y_{CO} + y_{VCM})\, P \tag{11}$$

Therefore, as the system volume is constant because the installed equipment does not undergo structural changes, the lower the saturation pressure, the lower the temperature must be to condense the VCM. However, it is not possible to easily adjust the temperature of utilities in the industrial plant due to the needs of other consumers present in the distribution network of water, diethylene glycol and liquid VCM used in the shell side of TC-03, which reduces the efficiency of VCM recovery in the process stream.

The relationship between the increase in Nitrogen in the system and the flow rate of VCM loss to incineration is directly proportional, as can be seen in Figure 4 and in Equation (12), which represents the correlation of the composition (flow rate) of N_2 with the flow rate of VCM loss, with an R^2 of 1.0.

$$\dot{m}_{VCM\ lost} = 2\,x\,10^{11}\,{N_2}^4 - 4000{N_2}^3 + 3\,x\,10^9 N_2^2 - 10^8\,N_2 - 2\,x\,10^6 \tag{12}$$

To find the lowest possible values of VCM loss to incineration, the solutions of this equation would be necessary, but the equation has no real roots. Despite this, as explained previously, the smaller the amount of N_2, the higher the condensation of VCM and, so, the greater its recovery. Therefore, the Nitrogen concentration should be reduced as much as possible.

c) Effects of cooling water flow rate variation

As can be seen in Figure 4, the flow rate of cooling water in the shell side of the TC-01 A/B heat exchangers has almost no effect on the amount of condensed VCM. This can be explained by the correlation (Equation (13)) that describes the sensible heat exchange of pure liquids [25].

$$Q_{cold} = \dot{m}_{cold} cp \Delta T \tag{13}$$

For example, a 30% increase in water flow rate would provide about 30% more sensible heat, which would increase VCM recovery by only 3.11%, for the existing process conditions.

The regression of the data presented in Figure 4 led to Equation (14), which represents the correlation of the cooling water flow with the VCM loss flow rate with an R^2 of 0.9905.

$$\dot{m}_{VCM\,loss} = -3\,x\,10^{-9}\,Q^2 - 10^{-4}\,Q + 214.08 \tag{14}$$

To eliminate the loss of VCM, the water flow must be increased to 250,985.7 t/h, which in practice would not be possible since the two heat exchangers are not large enough, making it necessary to install a new one, in addition to the fact that the heat exchanger system cooling water is already fully used by other process demands.

Process optimization

Using an effort vs. impact matrix [24] and the pressure was selected as the initial variable to be optimized because it is easily manipulated and requires no initial investment.

To increase the operating pressure of the VCM recovery unit, it was first necessary to evaluate the maximum permitted working pressure conditions in order to avoid equipment ruptures and damage to installations. An analysis of equipment documentation indicated that the pressure could be safely increased by up to 14% in relation to the current operating value. To evaluate the possible gains from this change, an additional simulation was undertaken with the new proposed pressure condition.

Then, after the pressure change, a new simulation was carried out to optimize the system based on the composition: 20% reduction in Nitrogen in the input stream, also based on the effects of the inerts in this system.

Simulation results for the pressure value adjustment

Simulations were performed for the five feed compositions and their respective flow rates for the pressure set 14% above the present operating condition. The results of the flow rate of VCM sent to incineration evaluated with the new pressure compared to the present plant data are shown in Table 1.

Table 1: Comparison of VCM loss before and after pressure adjustment.

Table 1 shows that the pressure adjustment of 14% is not enough to increase the recovery efficiency of the VCM of all samples, indicating that the amount of inerts in the process stream has a strong effect on the dependent variable, as can be seen in the results of samples 2, 3 and 4. Therefore, the higher concentration of inerts affects the equilibrium pressure of VCM and, consequently, reduces its condensation rate compensating in some amount the effect of pressure increase. However, based on operating experience, it was expected that the increase of pressure would reduce the loss of VCM to a certain extent, as the control valve would both reduce the frequency of openings (depressurization), thus reducing the drag effect, and result in a VCM partial pressure higher than the present value, thus improving heat exchange. Besides, carrying out this change in the industrial plant is easy and does not require any investment.

Simulation results for the composition value adjustment

After the pressure change, simulation was carried out to optimize the system based on a 20% reduction in Nitrogen in the input stream, also based on the effects of the inerts in this system, and the results of the sensitivity analysis are represented in Table 2.

The proposal to reduce 20% of N_2 flow is based on the risk of VCM emission to the atmosphere, because this Nitrogen will be sent to a safety vent, and by increasing the amount of N_2, the greater the probability of dragging more VCM [18].

Table 2: Results of the amount of VCM loss vs. reduction of N_2 in the input stream.

$$^{*}Reduction\ \dot{m}_{VCM\ loss} = Present\ m_{VCM\ loss} - (m_{VCM\ loss}\ \text{after less 20\% of}\ N_2) \quad (15)$$

Economic and Environmental analysis

Pressure adjustment

Pressure adjustment was implemented in the plant through a test plan. After three months, the financial and environmental results were evaluated based on the internal VCM indicator used to produce PVC, these values being presented in Table 3.

Table 3: Results of the reduced amount of VCM loss over 3 months.

It can be observed that the increase in the VCM recovery rate occurred consistently throughout the three-month period with a reduction of around 5 t in the consumption of natural gas in the incinerator. As the process is not constant, variations in the concentrations of substances in the process mean that the amount of VCM loss is not constant. As a premise for calculating the amount of VCM loss over the period, the difference between the average flow rate of VCM loss (t/h) in the previous year and the average rate of VCM loss during three-month period was considered.

To evaluate the economic gain, Equation (1) was used. Equations (2), (3), (4) and (5) were used to calculate the amount of natural gas that was saved [25]. Knowing the amount of natural gas (ng) that was not burned, it was also possible to calculate the amount of CO_{2eq}, through Equation (6).

Thus, from Table 3, US$ 3,435 could be saved over the three-month period due to lower consumption of natural gas and VCM loss, since the recovered VCM is recycled. In one year, savings would reach almost US$ 15,000/y, US$ 1,060 only from the reduction in fuel gas consumption. Based on the average recovery value of VCM during the three-month period, it would be possible to reduce CO_{2eq} emissions by up to 53 t/y.

Composition adjustment

Based on the average reduction of 82.6 kg/h (Table 2), the savings are calculated by the Equation (1), using the Equations (2-5). Besides this, due the environmental analysis (Equation (6)), it would be possible to reduce 1,080 t/y of CO_{2eq} emissions and generate savings of up to US$ 300,000/y (Equation (1)).

Further improvements would require investments and therefore a technical and economic evaluation study is recommended to evaluate the most adequate solution between changing to a technology with better efficiency or carrying out structural changes to reduce the concentration of Nitrogen in the input stream.

Concluding remarks

The selection of optimal operating conditions for a VCM recovery process has been undertaken through the systematic application of computer simulations and economic analyses. The unit models and plant simulation were verified against actual plant operating data and the maximum error between the actual and simulated VCM compositions was around 9.7%, which is considered adequate due to the accuracy of the plant instruments and considering the simulation objectives.

A sensitivity analysis was carried out to identify the set of parameters that affected the loss of VCM and among the selected variables, both the operating pressure and the composition of the feed were those that most affected the VCM loss for incineration. However, when carrying out a stress impact analysis it became clear that manipulating the composition of the feed is not as easy as adjusting the setpoint of the PSVs of the vessels and the pressure control valve. Therefore, the plant pressure was increased by 14%, which made it possible to reduce by 7.5 t the VCM loss and reduce consumption 5t of natural gas, which represents savings of US$3,435. Annually there is the possibility of reducing CO_{2eq} emissions by 53 t from 23 t of fuel saved, which represents US$ 15,000.

Despite the financial and environmental savings, there was no significant increase in the recovery efficiency of the VCM when compared to the theoretical efficiency of the system (97%) [12].

For future work, in relation to other technologies that have better VCM recovery efficiency [12-16], it is recommended that a technical and economic evaluation study be carried out to verify whether changing the technology would make sense for the this industrial unit, or whether the solution of changing the composition of the input stream by reducing the concentration of inerts would be more appropriate, as preliminary results showed that a reduction of 20% in N_2 would allow to increase the recovery efficiency of VCM with the reduction of 1,080 t/y of CO_{2eq} emissions and annual savings of up to US$300,000.

Another achievement of this work was the development of the simulation strategy, which made it possible to create a procedure that helps the unit operational team in making more assertive decisions, as well as enabling the identification of process deviations more quickly, which guarantees better competitiveness since it lowers the correction time.

Nomenclature

cp - Heat capacity

CO - Carbon monoxide

CO_2 - Carbon dioxide

CO_{2eq} - Carbon dioxide equivalent

DEG- Diethylene glycol

EDR - Exchanger Design and Rating

GHG - Greenhouse gases

H_2O - Water

$\dot{m}_{cold}$ - Mass flow rate of the cold product in t/h.

m_{ng} - Mass natural gas in t.

$\dot{m}_{ng}$- Mass flow rate of recovered natural gas in t/h.

$\dot{m}_{VCM}$- Mass flow rate of recovered VCM in t/h.

$\dot{m}_{VCM\ loss}$ - Mass flow rate of vinyl chloride loss in t/h.

N_2 - Nitrogen

O_2 – Oxygen

P - Pressure in the system

p_{CO2} - Carbon dioxide partial pressure

PCI- Lower heating value (GJ/t of VCM) and (GJ/t of natural gas)

p_{H2O} - Water partial pressure

p_i - Partial pressure of a component i in a mixture

p_{N2}- Nitrogen partial pressure

p_{VCM} - Vinyl chloride partial pressure

p_{O2} - Oxygen partial pressure

ppm - Part per million

PR- Peng Robinson

PSV´s - Pressures relief valves

PVC - Polyvinyl chloride

Q- Total Heat

Q_{cold} – Cold heat

R^2 - Correlation factor

SRK- Soave Redlich Kwong

TC-01 A/B- First heat exchange of the system

TC-02- Second heat exchange of the system

TC-03- Third heat exchange of the system

VCM - Vinyl chloride

y_{CO} - Carbon monoxide composition in the mixture

y_{CO2} - Carbon dioxide composition in the mixture

y_{H2O} - Water composition in the mixture

y_{N2} - Nitrogen composition in the mixture

y_{O2} - Oxygen composition in the mixture

y_{VCM} - Vinyl chloride composition in the mixture

y_i - Component i in a gaseous mixture

ΔT- Delta temperature

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Figure Caption

Figure 1 – VCM recovery unit heat exchange system.

Figure 2 – VCM recovery unit flowchart for process simulation.

Figure 3 – Deviations between the simulations results and actual plant data.

Figure 4 – VCM flow rate to incineration after process changes.

Tables

Table 1: Comparison of VCM loss before and after pressure adjustment.

Samples	Present VCM loss (kg/h)	VCM loss after 14% increase in Pressure (kg/h)	Variation (%)
1	174.0	173.2	**-0.5%**
2	574.3	612.1	**6.6%**
3	478.4	503.4	**5.2%**
4	636.4	697.1	**9.5%**
5	99.9	94.3	**-5.6%**

Table 2: Results of the amount of VCM loss vs. reduction of N_2 in the input stream.

Samples	Present VCM loss (kg/h)	Simulation results VCM loss (kg/h)	-20% of N_2-VCM loss (kg/h)	Reduction of VCM loss (kg/h)*	% Reduction
1	178.2	176.1	115.8	62.4	34.2
2	336.7	355.0	229.0	107.7	35.2
3	389.1	418.0	311.3	77.8	25.5
			Average	82.6	

Table 3: Results of the reduced amount of VCM loss over 3 months.

Month	VCM reduction (t)	NG reduction (t)	Total Savings (US$)
1	2.3	1.54	1,047
2	3.2	2.17	1,472
3	2.0	1.35	916
TOTAL	**7.5**	**5.06**	**3,435**

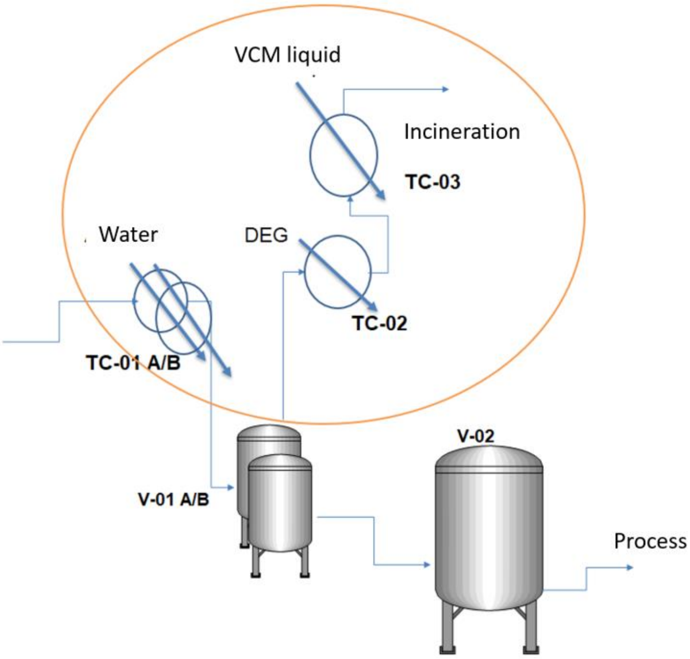
VCM liquid
Incineration
TC-03
Water
DEG
TC-02
TC-01 A/B
V-01 A/B
V-02
Process

Figure 1

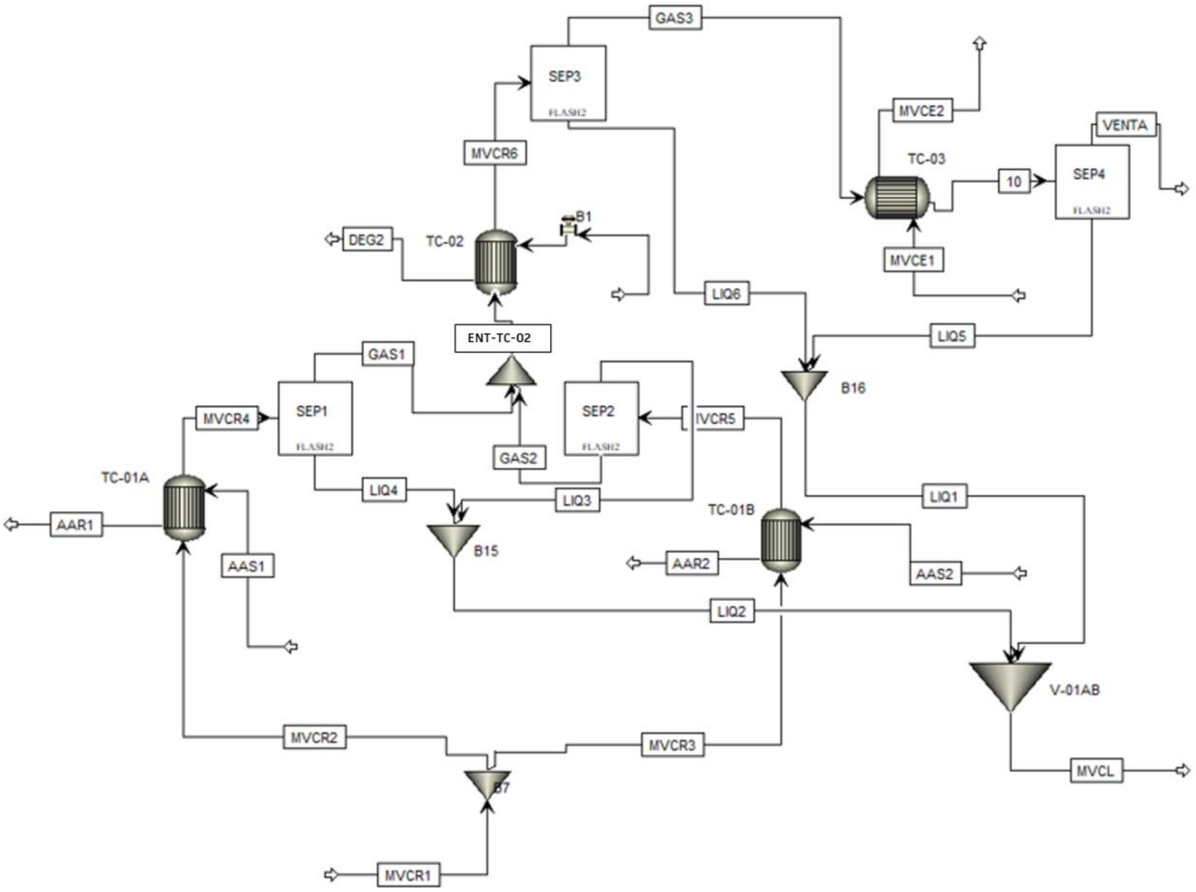
GAS3
SEP3
FLASH2
MVCE2
VENTA
TC-03
10
SEP4
FLASH2
MVCR6
B1
DEG2
TC-02
MVCE1
LIQ6
ENT-TC-02
LIQ5
GAS1
SEP1
FLASH2
SEP2
FLASH2
IVCR5
B16
MVCR4
TC-01A
GAS2
LIQ4
LIQ3
LIQ1
TC-01B
AAR1
AAS1
B15
AAR2
AAS2
LIQ2
V-01AB
MVCR2
MVCR3
B7
MVCL
MVCR1

Figure 2

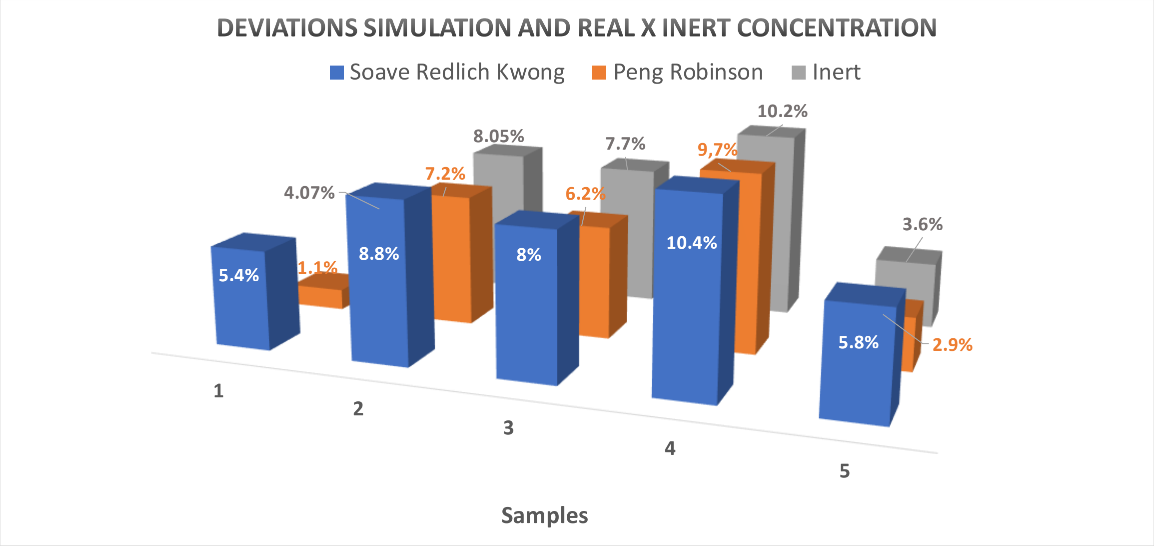
DEVIATIONS SIMULATION AND REAL X INERT CONCENTRATION
Soave Redlich Kwong
Peng Robinson
Inert
5.4%
1.1%
4.07%
8.8%
7.2%
8.05%
8%
6.2%
7.7%
10.4%
9,7%
10.2%
5.8%
2.9%
3.6%
1
2
3
4
5
Samples

Figure 3

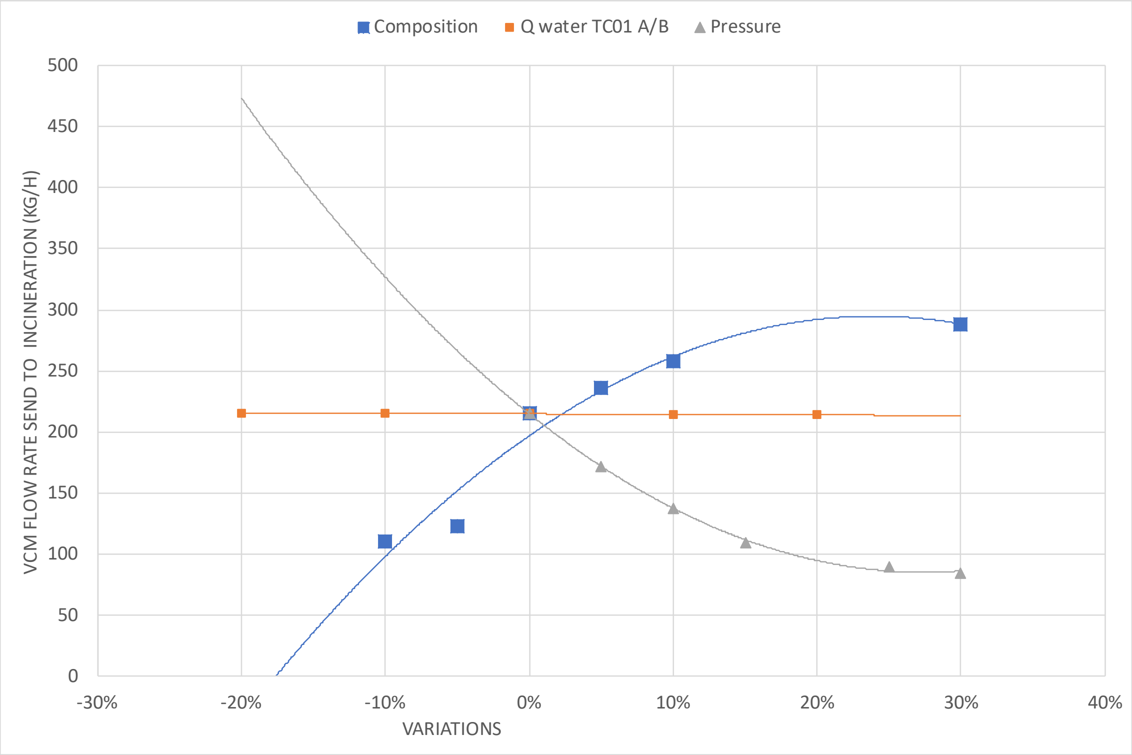
■ Composition
■ Q water TC01 A/B
▲ Pressure
VCM FLOW RATE SEND TO INCINERATION (KG/H)
500
450
400
350
300
250
200
150
100
50
0
-30%
-20%
-10%
0%
10%
20%
30%
40%
VARIATIONS

Figure 4