Use of simulator for decision to reuse of industrial effluents

Case study – the use of process's condensate as make up water boiler.

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Received: December 27, 2020. Revised: March 3, 2021. Accepted: March 13, 2021. Published: March 23, 2021.

Abstract* - The need to reduce operational inefficiency because no generation of effluent encourages industries to search improvements in the procedures and technologies. However, in case that is not technically or economically feasible, the water reuse is a good option. The removal of volatile organic compounds (VOC) in liquid streams at a nitrogen fertilizer industry is carried out in a stripper that generates treated condensate that can be reused. The present work aims at the reuse of the treated condensate to produce steam and it was conducted according to methodology: collection and reconciliation of data in the industrial plant; simulation operating conditions and changed conditions for the most contaminant removal; tests in *loco* and analysis of physic-chemical parameters to assess the quality of the treated condensate. The simulation was performed in steady state for two scenarios: the first one using operating conditions with vapor pressure between 3.2 bar and 6.0 bar and a flow rate of saturated steam between 1.5 t/h 5.0 t/h; the second simulation scenery considered the removal of the D stream process of the stripper, that has a high concentration of ammonia and methanol. In the first scenario, it was observed by manipulating of the pressure to 6.0 bar and steam flow to 2.0 t/h make better the removal ammonia efficiency. For the second scenario has also greater efficiency in the removal of both ammonia and methanol. The tests in *loco* and physic-chemical analysis showed that removal of the D stream process can enable the of reuse to make up for water in boiler to produce steam of until 41 bar after additional treatment, reducing the conductivity and iron concentration. The reuse of this treated condensate provides an economic gain of approximately US$ 500 000 each year, reducing the cost with the use of demineralized water and wastewater treatment. The use of the simulator allowed studying different scenarios, to reduce the number of experimental tests in *loco* and establishing routes for reuse industrial wastewater.

Keywords— Stripper, ammonia, condensate, reuse.

I. INTRODUCTION

In recent decades the need to reduce waste generation and the use of water is encouraging industries to researcher better procedures and new technologies. Researches to reduce the use of water in industrial plants have been reported in the literature [1,2].

The Group of Clean Technology from Federal University of Bahia (TECLIM-UFBA), in their works, shows the importance of reducing the contaminants in the source as a priority to reduce the volume of wastewater generated. In its various projects in industrial plants, this has adopted preventive practices, with focus to minimize waste in all stages of the production process [3].

Despite of the action at source to be the most environmentally way recommended, some equipments with technology end of pipe is crucial for suitability of effluents in industrial operations.

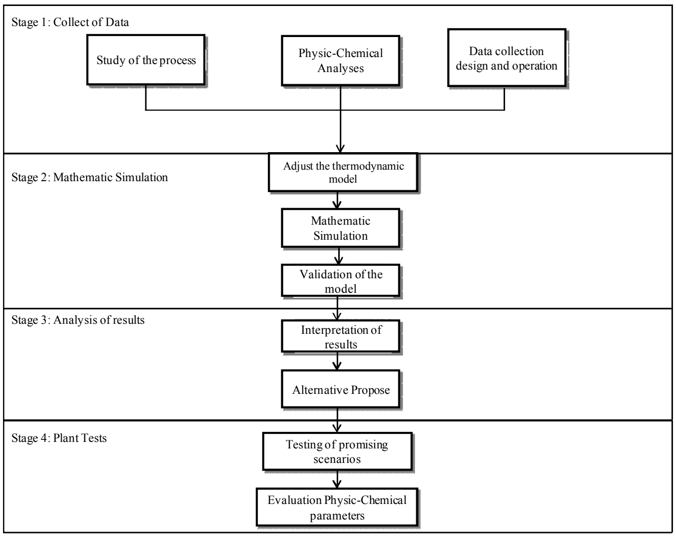
The stripping column or stripper is equipment designed to remove high levels of volatile organic compounds (VOC) in liquid streams. In the process of ammonia production this equipment is used to adapt the condensate process to the accepted environmental parameters at the operating license of the plant. This article proposes an evaluation by mathematic simulation of the factors that affect the efficiency during operation of an ammonia stripper and its validation in an industrial plant, in addition to the possibilities for reuse of the treated condensate instead to make up of water in medium pressure boilers (until 41 bar).

II. Material and Experimental Procedures

A. Simulation in Steady State

The methodology proposed for the realization of this work has four stages, as shown in *Fig. 1*. The first stage was a study of the operating conditions of the equipment and its process, through the flowcharts and engineering process and descriptive manual processes for obtaining the data needed to make the simulation.

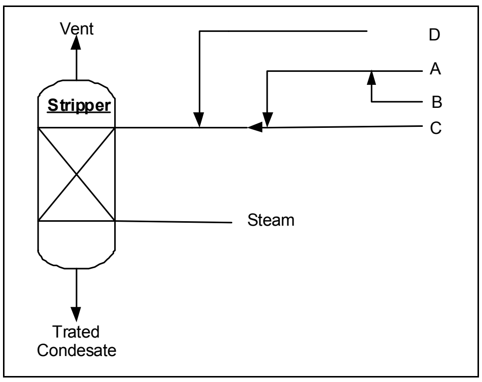
Fig. 1. Methodology used for simulation in steady state to a stripper column.



The stripper column is fed with a steam low pressure flow of 3.2 bar and another condensate process, which is composed of four streams (A, B, C and D) with different concentrations of ammonia and methanol, as shown in *Fig. 2*.

The stream A is the condensate removed in separator condensate of the compression 1st stage of ammonia synthesis gases. Since, the separator also receives the gas stream of unreacted of the synthesis process of ammonia which is recovered through a unit for reprocessing.

Fig. 2. Schematic designed of the stripper column.



The stream B is the condensate removed in separator condensate of the compression 2nd stage of ammonia synthesis gases.

As the process unit is integrated with the unity of the production of urea, it burns natural gas for generation of steam, energy and obtaining CO_2 for the production of urea. Thus, it has been condensed to generate the stream C, which is removed in the condensate separators of the CO converters to CO_2, which follows treatment in the same stripper. Finally, there is the stream D, which is the condensate generated in the compression process of CO_2.

Due to the limited information, it was necessary to carry out chemical analysis of samples of the upstream column to know the concentrations of ammonia and methanol in the feed. For feed streams of intermediate process were used the results of the water balance reconciled through the objective function proposed by [3] as shown in Table 1:

TABLE I. Relative values of flows and concentrations of column feed.

Stream	Flows and Compositions		
	Relative flow (%)	***Relative concentration of ammonia (% weight)***	***Relative concentration of methanol (% weight)***
A	6.23	0.06	7.15
B	0.02	0.01	0.00
C	76.40	99.35	7.02
D	17.35	0.58	85.83

From the obtained data, it was performed the second stage, which consisted of the simulation equipment. Thus, it was researched a thermodynamic model to represent the vapor-liquid equilibrium between the components. The model GC-EOS was applied to the two phases, due to temperature and pressure conditions of operation and the type and size of the molecules present in the streams [4]. The packed used to contact was the HyPak metal rings type with two inch.

With the aid of UNISIM ®, the simulation was performed in steady state for two scenarios: the first one using the typical operating conditions, where the variation of vapor pressure was between 3.2 bar and 6.0 bar and the flow of steam was between 1.5 t/h and 5.0 t/h.

The second simulation scenario was performed considering the removal of the D stream process, since this has a pH of approximately 7.5, indicating stabilization of ammonia in the form of their salts and high methanol concentration, then another possible treatment for this stream should be studied in order to reuse, because the unit operation is not appropriated for the removal of ammonia in this molecular form.

Both scenarios were considered an efficiency of 60% to each packed section - adjusted value to approach the simulation result with the composition of the bottom stream of the column known by physico-chemical analysis. For the scenarios mentioned was conducted the validation of the model by comparing the results obtained by simulating with the laboratory analysis of the constituents presents in the bottom stream of the column. After the simulation, in a third step, the results analysis and their interpretation were performed.

B. Test "in loco"

For knowledge of the process parameters, the test in *loco* was taken place for the scenario that corresponds to the actual conditions of operation in the process with the removal of the D stream process, due its physico-chemical characteristics. This test was conducted to evaluate the new parameters of treated condensate and new possibilities to reuse with seven hours with a steam flow rate of 2.4 t/h and pressure of 3.2 bar.

To evaluate the physical and chemical characteristics of the treated condensate were conducted analyzes of ammonia, methanol, partial alkalinity, total alkalinity, pH, conductivity, scanning of the ions (acetate, formate, nitrite, nitrate, bromide, phosphate, sulfate, lithium, sodium, fluoride, chloride, potassium, magnesium, calcium, zinc and iron) in the Chromatograph Compact IC Pro – Metrohm.

III. Results and Discussions

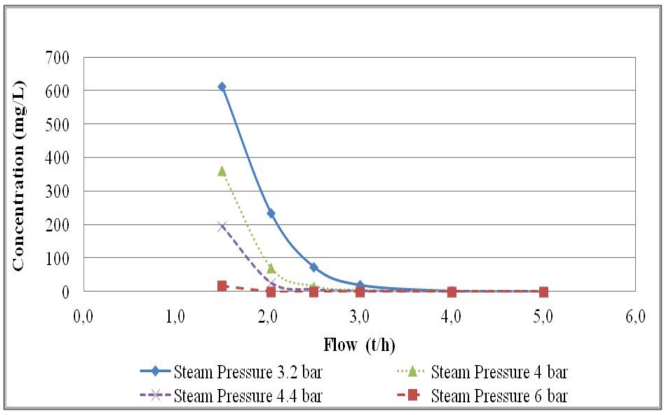
A. Mathematic Simulation in Steady State

To know the best operating conditions of this equipment, a simulation was carried out and the results achieved supported decision making in order to improve the performance of the column, i.e., the operation that promotes a higher ammonia removal within the operating limits of the equipment.

1) Scenario 1: typical operating conditions – This one shows the operating conditions in which the column receives four streams (A, B, C and D) and to promote separation is used a stream of saturated steam pressure of 3.2 bar and flow rate of 2.0 t/h.

For this scenario was performed the simulation and sensitivity analysis for the following variables: pressure and flow rate of steam. The removal of ammonia and methanol after treatment may be observed in *Fig. 3* and *Fig. 4*.

Fig. 3. Concentration of ammonia in the bottom of the stripper *versus* the steam flow.

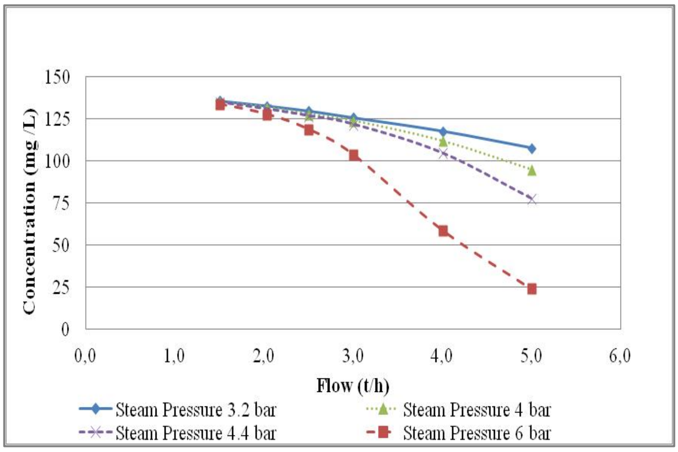


It is observed from *Fig. 3* that by the manipulation of the flow and pressure of saturated steam that feed the column, it achieves a condition of operation with greater efficiency for the removal of ammonia, for example, maintaining the flow of steam 2.0 t/h and increasing the pressure to 6.0 bar.

For the methanol is observed that the operating condition of pressure of 6.0 bar and flow rate of 5.0 t/h has a greater removal efficiency, *Fig 4*.

The percentages for removing ammonia and methanol in relation the feed to the saturated steam flow of 1.5 t/h and in the respective pressures of simulation this showed greater removal of ammonia and methanol for the condition of steam pressure greater, for example, 6.0 bar, removal of 99% ammonia and removal of 16% methanol. For saturated steam flow of 5.0 t/h, the removal percentage of ammonia and methanol are also higher to steam pressure of 6.0 bar, 100% and 85%, respectively. This ammonia and methanol removal enhanced can be attributed to the higher amount of energy provided by the higher pressures steam. However the removal of methanol is less efficient than that of ammonia.

Fig. 4. Concentration of methanol in the bottom of the stripper *versus* the steam flow.

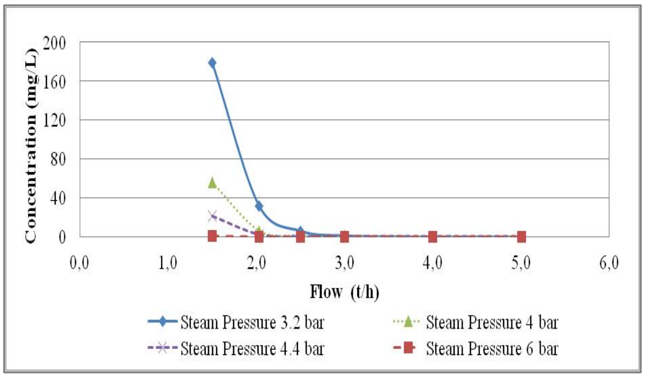


2) Scenario 2: after removal of D stream process –The D stream process has a high concentration of ammonia stabilized as salts and methanol. The presence of methanol affect the operation of the stripper, since this unit operation was not designed for this removal, despite that it was studied this possibility.

For this new scenario was performed a simulation for typical operating conditions with the removal of the D stream process of the stripper's feed and also performing a sensitivity analysis of the variables mentioned in the previous scenario. Those results can be seen in *Fig. 5* and *Fig. 6.*

It can be observed in *Fig. 5* that the removal of D process stream allows greater ammonia removal to any saturated steam pressure and it also allows to assert that to the pressure steam of 4.0 bar or 4.4 bar was achieved a removal ammonia of approximately 100% of the feed with a steam flow rate of, approximately, 2.0 t/h.

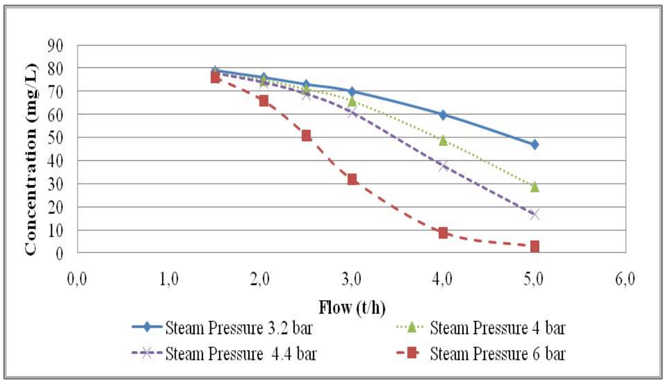
Fig. 5. Concentration of ammonia in the bottom of the stripper *versus* the steam flow after removal of the D stream process.



In *Fig. 6* it is observed significant reduction of the methanol concentration, since this is the stream that has the largest contribution of methanol to the system.

The removal of ammonia and methanol in relation to the feed without D stream process for flow of saturated steam of 1.5 t/h and pressure of 6.0 bar showed removal of 100% and 51%, respectively, indicating better quality treated condensate and less consumption of steam. For saturated steam flow of 5.0 t/h, it is observed the removal of ammonia shows it had not gain, since in the most unfavorable energetic conditions the system shows a maximum removal. In the case when the methanol has a steam pressure of 6.0 bar, it was observed removal of 98% in relation to the feed.

Fig. 6. Concentration of methanol in the bottom of the stripper *versus* the steam flow after removal of the D stream process.



The second scenario is characterized by a situation of changing in the process operating instead of the measurement end of pipe, which is normally practiced, which leads to greater energy efficiency, because for the same power consumption is achieved a higher level of separation. As this stream represents 20% of full flow of the column, then allows alternative forms of treatment, for example, by biotechnology that can provide the reuse in other places in the process.

B. *Test "in loco" - Reuse of Condensed Treated*

The simulation results to evaluate the scenario for the current situation of operation, steam flow rate 2.0 t/h and pressure of 3.2 bar, showed the removing of the D stream process provided reduction of 86% (237 mg/L to 32 mg/L) in the concentration of ammonia in the treated condensate, which is significant; and to this stream removal, the methanol content shows a reduction of 57% (132 mg/L to 76 mg/L), however this is still above the maximum allowable concentration for reuse as boiler make up water. According [6], the quality of the condensate stripper off should be 7 mg/L of ammonia and 250 mg/L of methanol and this is used for direct use or as a mixture of make up water to demineralizer. And the customers can use this condensed water after treatment as replacement boilers to produce steam of 41 bar.

As this scenario was indicated as the most promising among the two simulated scenarios, the test equipment was performed under the conditions described by removing the D stream process for seven hours, where three samples were collected for the parameters and the average concentration of ammonia and methanol, pH, conductivity, total and partial alkalinity of treated condensate were determined and the results of mean percentage reductions are shown in Table 2.

According to Table 2 shows that with the removal D stream process provides a significant quality improvement in various parameters of the condensate. The scanning ions showed just the iron concentration was not acceptable for reuse, its concentration was around 0.1 mg/L and is given less than 0.02 mg/L [8]; conductivity also presents higher than the minimum recommended for the intended reuse.

TABLE II. PARAMETERS OF QUALITY OF TREATED CONDENSATE BEFORE AND AFTER THE REMOVAL OF THE D STREAM PROCESS OF FEED STRIPPER TEST *"IN LOCO"*.

Parameters	***Before Removal the stream D***	***After Removal the stream D***	***Mean Reduction (%)***	***Maximum value for reuse in demineralisers***	***Possibility of Reuse***
Ammonia (mg/L)	101.0	22.0	78	7 mg/L[(a)]	No
Methanol (mg/L)	32.0	8.7	73	250 mg/L[(a)]	Yes
pH	9.5	9.4	2	9,5[(b)]	Yes
Conductivity (μS/cm)	647.0	179.0	72	< 5 μS/cm[(c)]	No
Part. alkalinity (mg/L)	172.4	37.2	78	-	-
Tot. alkalinity (mg/L)	400.1	139.9	65	200 mg/L[(c)]	Yes
Iron (mg/L)	0.18	<0.1	44	0.02	No

1. (a) values adopted [6], (b) values adopted [7] and (c) values adopted [8].

The subsequent treatment of this condensate in demineralizer removed the ammonia of treated condensate, but studies indicate that the presence of ammonia in the stream would not be limiting condition for reuse because ammonia and amines are components that can be used as corrosion inhibitors being added to the feedwater and condensate lines [7]. Thus, to use this effluent to produce demineralized water is necessary only additional treatment to remove iron and adjustment of conductivity.

C. Environmental and Economic Gains

An assessment was made of the economic benefits, whereas the cost of demineralized water for steam production was US$ 1.50/m³. Therefore, the operation with second scenario allows the reuse of 30 m³/h of treated condensate, which provides an annual cost reduction in your purchase for steam production of about 400 thousand dollars. Besides the gain of reuse water has also reducing the volume of effluent to be treated, that currently cost is US$ 0.36/m³, giving a reduction in the annual cost of wastewater treatement of approximately 100 thousand dollares. Totaling an annual gain in the reuse of this treated condensed on the order of 500 thousand dollars.

Economic gains are noticeable and attractive to the enterprise management system, since the cost for disposal of this effluent stream after treatment in stripper corresponds to approximately 18% of the costs. In addition, environmental benefits of reuse of condensed should be considered as reduce the water uptake of approximately 4.0% for this industrial activity. In new scenarios that indicate shortages and the rising price of this natural resource, therefore, the future impact activities that require high amounts of this feature.

IV. Concluding Remarks

The simulation scenarios with saturated vapor pressure between 3.2 bar and 6.0 bar indicate that a lower flow rate may be used (1.5 t/h) when the column operates with a higher saturated vapor pressure (6.0 bar), situation that cannot be tested and implemented, because the tower was designed to operate at atmospheric pressure.

For the test of removal of the D stream process, the results presented showed a significant reduction of the ammonia and methanol concentration, indicating that the removal of stream provides a reduction in the overload of contaminants from the column. But the limitation in respect to the concentration of ammonia in the effluent prevents its removal, indicating the necessity of studies to its treatment.

After study of the process together with the chemical analysis, it was observed the B stream process has small flow rate and methanol concentration, and high concentration of ammonia in comparison with the other streams, approximately 10%, indicating an opportunity to reuse, such as example, for measurement water in the ammonia final product, recovering the ammonia presents in the stream.

The physic-chemical analysis of treated condensate indicated that the parameters conductivity and iron content did not enable its direct reuse of this like water make up of boiler to 41 bar.

The completion of the tests in *loco* with physic-chemical analysis of treated condensate on the condition proposed in the second scenario indicates the necessity of additional treatment, but only two parameters assessed. Thus, it is suggested that the operation with the removal of the D stream process as well as additional study of the individual treatment to its reuse.

The simulator processes UNISIM ® allowed the study of scenarios, with few capital investment, and the development of effective experimental design, because only the most promising scenario was tested in the industrial plant. Thus, the combination of modeling/simulation validation in the industrial plant was efficient and environmental-economic practical consistent to study possibilities for reuse of industrial effluents. Thus, reducing the need to water uptake, cost of water treatment and wastewater treatment inside the manufacturing process.

Acknowledgment

We are grateful to the team of Engineering, Laboratory Operations and support provided by the company during the course of the activities, and the ANP for financing the research project.

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