

Vinyl Acetate from ethylene, acetic acid and oxygen Industrial Plant Simulation.

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ABSTRACT

The production of vinyl acetate monomer (VAM) represents one of the largest industries with a growth estimate of a near 2.7% per year starting in 2008. In recent times, thanks to different studies and the importance of said product, one process has been developed based on the reaction of ethylene, acetic acid, and oxygen using a Pd/Au catalyst. In this work, a detailed study was made based on a simulation of the process using the Aspen Plus v2006 program and establishing the correct operation conditions. The simulated process involves, from the preparation of the raw materials until the dehydration of the monomer. The restrictions set for the simulation corresponds to the VAM composition restriction in the extractive distillation column using glycerol.

INTRODUCTION

Vinyl acetate is a colorless, flammable liquid that also has a characteristic smell that can quickly become irritating. This monomer is used principally in the production of polyvinyl acetate (PVAc) and other vinyl acetate co-polymers. Polyvinyl acetate is a precursor of polyvinilc alcohol and polyvinyl acetate resins (PVA). Vinyl acetate is also copolymerized as a minor raw material for vinyl chloride and ethylene to form commercial polymers and acrylic fibers.¹

Vinyl acetate is completely soluble in organic liquids but not in water. At 20° C a saturated solution of the monomer in water can contain between 2-2.4% of vinyl acetate, while a saturated water solution in vinyl acetate contains 1% of water. At 50°C the solubility of the monomer in water increases in 0.1% in regards to 20°C, while the solubility of water in vinyl acetate doubles at 50°C

The most important reaction of vinyl acetate is the polymerization by free radicals which is fast and exothermic. Due to the fact that the vinyl acetate is an Esther, it presents the reactive properties of said group. Keeping in mind that the corresponding chain of alcohols is unsaturated, the compound presents some differences in regards to the Esther group. The speed of hydrolysis of the vinyl acetate is 1,000 times greater than its saturated analogous in a alkaline medium, and it was researched that its speed of hydrolysis is significantly lower at a p.H. of 4.4.

¹ Kirk-Othmer, (1978), Vol 23, pp 817.

VAM PRODUCTION PROCESS

The first available process for the synthesis of vinyl acetate was the acetoxylation of acetylene in gaseous form over a zinc acetate catalyst supported on carbon. This process consisted in the reaction of acetylene with acetic anhydride in a catalyzed medium and high temperature to form diethylidene diacetate. This product passed through a cracking tower which in result gave as products acetic acid and vinyl acetate.² This type of reaction had a high production percentage (92-98%), but due to the increasing value of acetylene, new technologies and methodologies needed to be research in the 60's.

The process was modified until acetoxylation in a gaseous phase of ethylene over palladium and gold catalyst supported on silica gel was capable. The catalyst used potassium acetate to help the reaction in a temperature range of 423 – 463 K and a pressure range of 600 to 1,000 kPa. This is how ethylene acetoxylation with oxygen, acetic acid and Pd as a catalyst was developed. This process consists of two parts: a process in a homogeneous liquid phase that is used to produce 25% of the production of vinyl acetate, and another heterogeneous gaseous phase process used to produce the last 75% of the product.

The synthesis of vinyl acetate from ethylene, acetic acid and oxygen over a Palladium catalyst is a very important industrial process, but its selectivity is affected by the production of CO₂ due to the combustion of the ethylene. Various factors affect the synthesis of vinyl acetate, like for example, the dispersion of Pd, partial pressures from the reactives that are the catalyst additives (near 80% if it is Pd/SiO₂ and greater to 94% if it is Pd-Au/SiO₂) and contact time. The investigation done by Han, H. F., et al. (2004) shows that the ethylene is the principal cause for the production of CO₂ due to the fact that combustion kinetic does not change if the acetic acid is taken out of the medium.³

The process that involves ethylene, acetic acid, oxygen over a Pd catalyst medium proves to be the best option to develop. This is evident because for the last thirty years it has been applied in the industry. In the U.S.A. alone, the production of ethylene is around 11.533×10^3 tons per year, which more than 30% is used on the production of vinyl acetate.

Production Process using Ethylene, Acetic Acid and Oxygen.

The process is centered on the reaction between ethylene, oxygen and acetic acid in order to produce vinyl acetate and water. There is a second unwanted reaction in the process based on the ethylene oxidation to produce water and carbon dioxide. The gaseous effluents from the reactor are cooled trying to have a partial condensation of the stream. Next, the gas is separated from the liquids in a phase separator. The gas is washed with acetic acid from a recycle stream. This helps to recover the vinyl acetate in the absorber. Afterwards, there is a process to eliminate the CO₂ from the gas phase and recycle it back in to the reactor the Ethylene is necessary.

The liquids that come out from the separator and the acetic acid used in the washing process enter an azeotropic distillation tower. In this part of the process, the main objective is to separate the acetic acid (bottoms) from the water and vinyl acetate mixture (distillate). The distillate enters to a decantation process in which its organic product (mainly vinyl acetate) divides into a reflux stream that heads back to the distillation column

² Kirk-Othmer, Concise encyclopedia of Chemical Technology, John Wiley & Sons, 1985 (USA), pp. 1227.

³ Han, Y.F., et al, Kinetics of ethylene combustion in the synthesis of vinyl acetate over Pd/SiO₂ catalyst, Journal of Catalyst, Vol. 224, 2004, pp. 60-68.

and another stream that enters a separation train process where the proper concentration level of vinyl acetate is achieved to comply with the wanted specifications. The aqueous stream from the decanter is discarded.

A portion of the bottoms stream from the distillation column (mainly acetic acid) is used in the washing process in the absorber, while the other portion of the bottom stream is mixed with pure acetic acid from the feed streams to later enter to an evaporation process. The gaseous acetic acid obtained is mixed with the recycle gas, oxygen and ethylene to form the feed to the reactor.

For a detail analysis, the process has been divided in to three parts: reaction, distillation and dehydration. It is shown in figure 1.

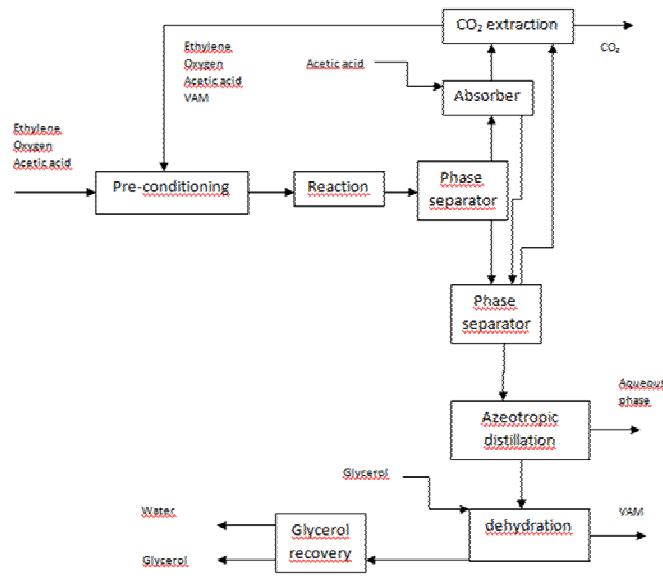
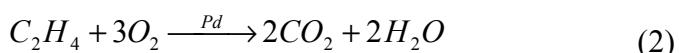
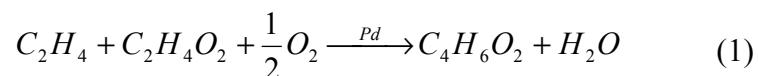


Figure 1. VAM production process flow diagram.

Reaction system

The reaction that produces the vinyl acetate takes place in a P.B.R. reactor where a gaseous mixture of ethylene, acetic acid, and air (with small presence of CO₂ and water from the recycle streams) are fed to the reactor. To obtain an annual production of 5,000 tons (amount determined for the Colombian market) of vinyl acetate, 2,197.3 mol per minute with a molar composition of 0.5 of ethylene, 0.07 of oxygen, 0.15 acetic acid and 0.263 of nitrogen have to be fed. An excess of ethylene over acetic acid (3:1) must be guaranteed. The concentration of oxygen must be kept below 8 % molar because at higher concentrations it breaches the explosive limit of the mixture.

The reactions that take place are:



These reactions are highly exothermic and the standard heat of reaction for the first reaction is 42.1 Kcal per mol of vinyl acetate, while the heat of reaction for the second reaction is -316Kcal per mol of ethylene.

The heat of reaction is removed by generating vapor in the shell section of the tubes. This vapor is used in other part of the process. This is the same for the reaction catalyzed by palladium and gold supported by silica.

The temperature must be below 200°C because at this temperature the catalyst suffers irreversible mechanical damages. The catalyst is activated with a temperature over 140° C. This allows to take an inferior operation limit temperature of 150°C.

The recommended operation pressure is between 8 and 10 atm (Dimian y Bildea, 2008) because higher pressures favor the productivity, but affect negatively the selectivity due to the adsorption of the ethylene in to the active sites of the catalyst benefiting the unwanted combustion reaction.

The rate law for this reaction (1) is given by:

$$r_{VA} = k_1 p_{Et}^{\alpha_1} p_{Ox}^{\beta_1} \quad (3)$$

Where p_{Et} is the partial pressure of the ethylene and p_{Ox} is the partial pressure of the oxygen:

$$k_1 = A_1 \exp(E_1/(RT)) \quad (4)$$

The values of the activation energy E_1 depend on the operation temperature. At temperatures between 120° C and 140° C (1st region) activation energies of 40 kJ/mol can be obtained keeping in mind a dependency of Arrhenius law. At temperatures between 140° C and 160° C (2nd region) the mean activation energy is 15 kJ/mol, there for reaction rates higher than those of the first region can be observed. This is the same for α_1 , which values are 0.38, 0.35, and 0.35 for temperatures of 120° C, 140° C, and 160° C respectively. From this observation comes the preference for temperatures over 140° C in the process.

The values of β_1 reported are 0.20, 0.20, 0.21 for temperatures of 120° C, 140° C and 160° C respectively. A molar relation of ethylene/acid higher than 3 is used.

The reaction rates were reported like TOF (turnover frequency). This type of data indicates the number of reactions or catalytic cycles done by a unit of the activated center by unit of time (molVA/(molPd seg)):

$$r \left(\frac{\text{molVA}}{\text{KgCat}} \right) = \text{TOF} \frac{w_{Pd} D}{PM_{Pd}} \quad (5)$$

Were w_{Pd} is the fraction of palladium in the catalyst (0.01), D is the palladium dispersion coefficient (with which the fraction of atoms of active palladium can be calculated) and PM_{Pd} is the molecular weight of Pd in kg/mol. The value of D is reported with a value of 0.4 by Han et al. (2005), the value of A_1 calculated with the data reported by Han et al., (2005) is of 9.7×10^{-3} molVA/(kgCat seg) (For partial pressures expressed in kPa).

For reaction (2) the same authors report a similar rate reaction law (Han et al., 2004):

$$r_{CO_2} = k_2 p_{Et}^{\alpha_2} p_{Ox}^{\beta_2} \quad (6)$$

$$k_2 = A_2 \exp(E_2/(RT)) \quad (7)$$

α_2 was determined with values of -0.27, -0.31 and -0.27 for temperatures of 140° C, 160° C and 180° C respectively. Besides this, an increase of 50% of the production of CO₂ was observed when the temperature increased from 140°C to 160°C. The values found for β_2 were 0.88, 0.82, 0.89 for temperatures of 140°C, 160°C and 180°C respectively. The activation energy E_2 obtained from data was 21 kJ/mol (higher than the activation

energy of reaction (1) which is 15 kJ/mol). No dependency was observed by the partial pressure of the acetic acid in the rate law. This confirms that the production of CO₂ is due basically to the oxidation of the ethylene.

The value of A₂ calculated taking in to account the data reported by Han et al., (2004) resulted in a value of 5.13 x 10⁻⁴ molVA/(kgCat seg). (For partial pressures expressed in kPa).

VAM distillation and dehydration.

It is based on the outlet homogeneous gaseous reactor stream in which the high temperature and pressure guarantee its state, favoring the reaction conditions. This shows that through manipulating factors like temperature and pressure, it's possible to generate changes that allow the separation of the components, principally vinyl acetate. The effluent reactor stream is composed by 45,9% mol of ethylene, 6,7% of water, 5,7% of VAM, 5,4% of oxygen, 1% of Carbon Dioxide, 12,5% of Acetic Acid y 34,3% of Nitrogen.

The general description of this system consists of an effluent reactor stream that is cooled with cooling water with the objective of generating two phases: the gaseous phase which contains principally oxygen, ethylene, carbon dioxide, and ethane when the feed of ethylene is not pure. The second phase consists of a liquid phase that contains principally vinyl acetate, water and acetic acid. The vapor phase passes to a compressor while the liquid phase passes to an azeotropic distillation column. The gas stream passes from the compressor to an adsorption column with the objective of extracting the remaining vinyl acetate, while the liquid stream exits the azeotropic distillation column in the form of distillates which later on are condensed to form two liquid phases in a decanter. The heavier of the two phases is recycled back in to the distillation column and the other passes on to the purification process to obtain the vinyl acetate, while the other is mainly water. The bottoms stream is fed back to the absorption tower. With these conditions, the column gets to generate three currents: the bottoms which are mainly acetic acid, the distillate which is composed by two immiscible phases that allow the separation of the VAM and the water. This is the most important process due to its difficulty to separate (water-VAM mixture). The liquid bottoms of the separator are mixed with the liquid stream of the separator so it can head later on to a distillation column.

On the other hand, the nearly free vinyl acetate gaseous stream goes to a carbon dioxide extraction unit in order to take out most of this component out of the stream. The stream that had the CO₂ extracted is divided in to a purge and a recirculation stream that mixes with the other portion of the stream that had no CO₂ extracted. This stream will be used to exchange heat with the outlet stream of the reactor and to serve as a base feed stream for the reactor, taking in to account that this streams is added through other feed streams that are needed for the reaction.

PROCESS SIMULATION

The development of this work began with a bibliographic compilation form which the optimum VAM production process and its conditions were established. Starting from said process, a simulation was done with the ASPEN PLUS v.2006 program from where a total process material and energy balance were established. Also, the final purity of the product and the possible modifications that allow a production of a greater quality and lower operation cost were determined.

Defined Properties

To determine the models that would be applied in the simulation, an analysis of two articles were used as strating points. These article were “*Don’t gamble with physical properties for simulations*” and the article about thermodinamics of Galen J. Suppes. Thanks to the information found in the text of Alexandre D. Dimian [1], it was deterimed that the model that best fitted the property’s description was the SR-Polar model because it takes into account the interaccion between gaseous components.

This choice was supported by the fact of the liquid phase is mainly composed by vinyl acetate (apolar), water (polar), acetic acid (polar), and supposing that there are interaction parameters due to the fact that these are known compounds. Finally, the NRTL and UNIQUAC models and all their variations were taken into consideration in order to get precision with these types of components, but after researching the Alexandre D. Dimian book, the NRTL-HOC model was chosen.

Reaction

Figure 2 illustrates the preparation of the raw material simulation and reaction flow diagram.

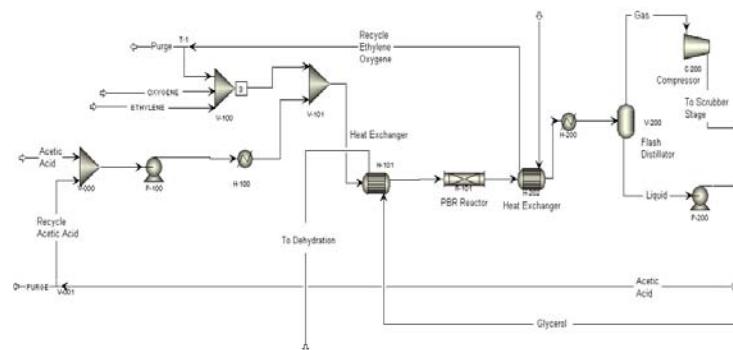


Figure 2 Reaction simulation flow diagram.

To design the reactor, it was established that it had to be done isothermally trying to prevent the sections that exceed 200°C which in turns lowers the catalyst activity. To control the temperature effect, the use of an inert gas was applied, in this case nitrogen. Besides this, the reactors are designed to achieve a low conversion of acetic acid by each pass (between 15 to 38% of acetic acid, and 8 to 10% of ethylene). It has to be taken in to account that activation energy of the unwanted reaction is greater than the activation energy of the wanted reaction, so at higher temperature the selectivity will be affected.

The reactor is a tube and shell reactor with a tube diameter of 3.7 cm, which have inside the catalyst. The calculations took in to account a refrigerant at a constant temperature of 5 degrees ($^{\circ}\text{C}$) below the inlet temperature of the reactives and afterwards, through Aspen Plus v.2006, the simulation was made using saturated water in co-current through the shell at 418K and vapor was produced at 4 atm. The simulation complies with the specification of the reactor's design.

The global heat transfer coefficient calculated by Dimian y Bildea, (2008), was used ($0.2\text{KW/m}^2\text{K}$). Likewise, the physical properties of the catalyst are the ones reported in the US Patent No. 5808136: a bulk density of 0.5 kg/L , partial size of 5 mm and a porous volume of 0.8 L/kg . Thanks to this data, an empty fraction of 0.4 , and a catalyst solid density of 0.833 kg/L were calculated. The operation inlet temperature for the reactor was 150°C .

Using all of the information, a 0.6 m/s rate was obtained which implies the use of 234 tubes and a pressure drop of 7.28% (and outlet pressure of 7.83 bar), achieving the needed conversion of acetic acid (35%). The previously mentioned parameters are suggested in this report. A reactor length of 6.01m was calculated taking in to account the data. The calculations were made always keeping in mind the volume in liters of the reactor. The volume per tube is 6.46 Lt, and the total reactor volume is 1,513 Lt.

VAM distillation

Figure 3 illustrates the distillation simulation flow diagram of the vinyl acetate monomer.

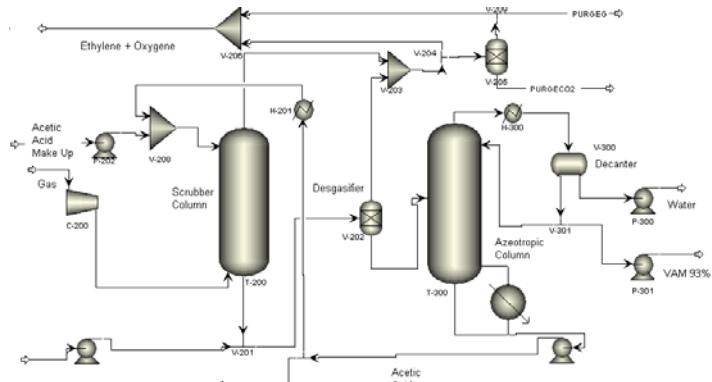


Figure 3. VAM distillation simulation flow diagram.

For the gas phase obtained from the first flash unit, a 20 stage VAM absorption tower was defined. It is in the range with what was found in the literature for two the scenarios mentioned earlier. Finally, the same analysis was conducted keeping in mind the stream temperature, although the final separation showed the same behavior as seen in the acid stream.

Finally in the carbon dioxide extraction stage, the most important factor that was taken in to account was the concentration of the absorbing agent because this stream is recycled to the reactor. It was necessary keeping a constant CO₂ concentration because it is fundamental, if not, possibly the selectivity and production could be affected. To do this, it is imperative to have a control over the concentration in this stage, so that the concentrate of the absorbing agent increases as the internal acidity increases. At an industrial level, the absorbing agents for carbon dioxide commonly used are amine solution (due to their basic characteristic) or Potassium carbonates (due to their affinity)

The liquid phase begins its separation using an azeotropic distillation column. For design purposes, the effect of the temperature over the quantity of VAM in the desired stream was researched and tested with a sensitivity analysis and was found that any effect was observed in temperature range of 0 to 1000 K. A similar situation occurs with the acid concentration in the distillate stream when the temperature is varied. On the other hand, based on the effect of the number of stages over the acid concentration in the distillate stream, it was found that a total of 23 stages is the optimum because it reaches a flow of 0.57 Kmol/h, lower than 0.85 that is generated with a larger number of stages. Finally, the effect of the recirculation flow over the vinyl acetate produced was studied and no difference was found when it was varied, so it was kept at 74.55 kmol/h for the VAM on the distillate stream.

The decanter is the unit in which one has to be more careful due the fact that is in this unit that the two phases are generated: organic and aqueous phases. Keeping in mind the temperature, and supposing that when the temperature rises the amount of vinyl acetate varies in the outlet stream, this had no effect. Therefore the

decanter's inner temperature was varied with the objective of finding the optimum temperature that can generate the two phases. This temperature was found to be 150 f and a pressure of 1 atm.

It was established that the process conditions were going to be 1 atm and a temperature slightly lower than 150 f.

Dehydration

Figure 4 illustrates the VAM dehydration simulation flow diagram.

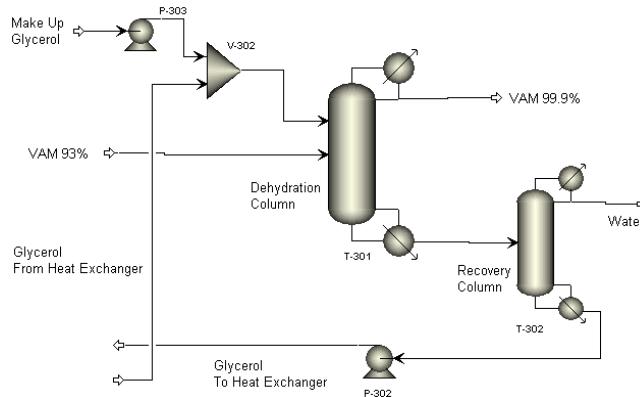


Figure 4: VAM dehydration simulation flow diagram.

The dehydration of the VAM via extractive distillation consists of adding a solvent (Glycerol) to the VAM-water mixture. This mixture is impossible to separate by normal distillation methods; it was necessary to alternate the relative volatility of the components allowing the separation. Therefore a dehydration column was design with 20 stages.

This dehydration column receives a stream of 93% pure VAM and a stream of glycerol composed of pure and recycled glycerol. This leads to a stream of 99% percent pure VAM. This stage is extremely important because when the humidity is retrieve from the product, it results in a better quality product and decreases the risk associated with the storage of the final product.

ENERGY INTEGRATION

Energy integration was used with the objective of using the energy provided by the streams with high temperature that need to be cooled or condensed so they can heat or vaporize the cold streams.

The analysis of the energy integration for the production process of vinyl acetate was done with Aspen Hx-Net program. The streams presented in the table below were analyzed. The condensers and reheaters from the distillation columns weren't taken in to account in this analysis because it was considered that their energetic requirements were going to be covered with the utilities intrinsic into the process.

Table 1. Stream to analyze

Inlet Streams	Outlet Streams	Destination	Effect
33	34	Mixer	Heating
35	32	Reactor	Heating

37	2	Vaporizer	Cooling
6	7	Absorber	Cooling
10	11	Separator	Cooling

Using the information of the streams and that of the Aspen Hx-Net program, a composite curve graph was made.

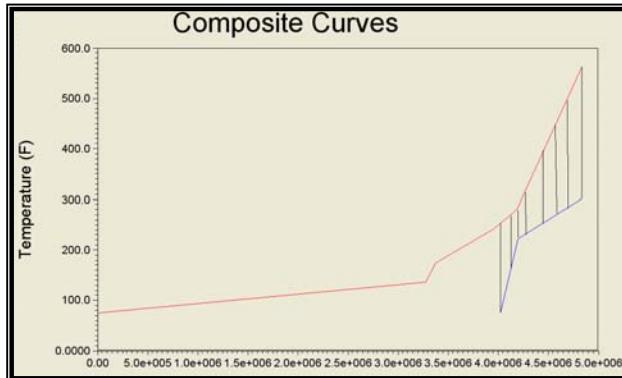


Figure 5 Composite curve

A preliminary analysis of the graph reveals that the process has an uncommon energy integration case; this case is known as threshold. This type of scenario consists of only a small portion of the energy is going to be covered by other streams and the rest of the energy requirements have to be met with outside utilities.

The Δt_{min} used in this analysis was of 10° C because it is the minimum standard for said analysis. In the composite curve graph it is illustrated the portion where stream interaction can take place.

Using the Aspen Hx-Net program it was possible to simulate the most optimum designs for the energy integration for the vinyl acetate process using cooling water as a refrigerant as a utility. After analyzing the options given by the program, a scenario was chosen due to its low consumption of energy. Its operation cost is lower than the rest. Taking these criteria in to account, it is clear that investment capital is higher but thanks to the low operation cost and low energy consumption represents a quick capital return.

Table 2. Process streams used in the analysis of the heat integration.

	Inlet Temp.	Outlet Temp.
Cooling water	20	25
High pressure vapor	250	249

Table 3. Heat integration result analysis

Design 1	Cost index (\$)	Energy and Units
Heating (value/s)	5.96E-06	Heating (kj/h)
Cooling(value/s)	2.51E-04	Cooling (kj/h)
Operation (value/s)	2.57E-04	# units
Capital	2.243.005.036	# of shells
Total value/s	2.55E-03	Total area

Table 3 (continued). Heat integration result analysis

design 1	HEN		Cost index (\$)
Heating(valor/s)	8.576.125.868	Heating value/h	2.14E-02
Cooling (valor/s)	4.255.681.722	Cooling value/h	9.04E-01
Operation(valor/s)	9	Operation value/h	9.26E-01
Capital	13		
Total value/s	4.088.872.109		
Total energy used (KW)	1.184.516.069	total	1.85E+00

CONCLUSIONS

With a thorough bibliographic revision it was possible to determine that the optimum process to produce VAM was the acetoxilation of ethylene using acetic acid and a palladium/gold catalyst. Said process was divided in to three: the reaction, the separation system and the VAM dehydration. In regards to the reaction it was evident that the temperature would determine the life of the catalyst and the selectivity of the process, even more so in this case which presents two parallel reactions.

Based on the separation system, it was evident the need to separate the liquid phase from the gaseous phase with the objective of purifying the final product and to recycle some raw material that did not react and are very expensive. To choose the most adequate properties was fundamental in order to observe and establish the correct separation characteristics of the components based on their immiscibility and azeotropic points through the simulation.

Finally the existence of an azeotropic point and immiscibility between water and vinyl acetate made it necessary to add and dehydration stage which consisted in a extraction column using glycerol as an extracting agent. Thanks to its polar properties, Glycerol allows the water to be extracted from the VAM

The analysis in regards with the total process production of VAM, it was necessary to determine the best way to use the energy in the process so it could be used to exchange with other streams and by doing this cutting back on energy expenses.

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