

CHAPTER III

PROCEDUES

3.1 Implementing of Process Design Programs with Financial and Environmental Risk Management

The implementation of process design programs can compass a series of activities that can vary in complexity, and can be successfully implemented during various phases of the process. The proposed methodology for implementing of process design programs consists of five major steps (see Figure 3.1): design the process models, random uncertainties, establish financial and environmental risks, develop of process model, and select the model alternatives.

1. Design the process models

The process models are accomplished using the process simulator ProII to obtain mass and energy information.

2. Random uncertainties

In uncertainty conditions, the uncertainty parameters are sampled by using random function in the GAMS program and to calculate net present worth and environmental impact in each scenario.

3. Establish financial and environmental risks

This phase identifies the potential environmental impacts and net present values of the models and those values are used to set up risk curves.

4. Develop the process models

The information generated in the previous steps is used to develop a process model that served as an analysis tool to evaluate the current performance of the process and the behavior of possible pollutant source and cost reduction alternatives.

5. Select the model alternatives

The selection of the model alternatives that maximizes or minimizes the expected value of a given criterion incorporates four objectives that present the desired state of the system. That is, alternatives should seek to maximize the net present worth, minimize the environmental impact, maximize the net present worth at risk of i , and minimize the environmental impact at risk of i by using a multi-

objective optimization which allows a decision maker to emphasize each objective by different weighting factor.

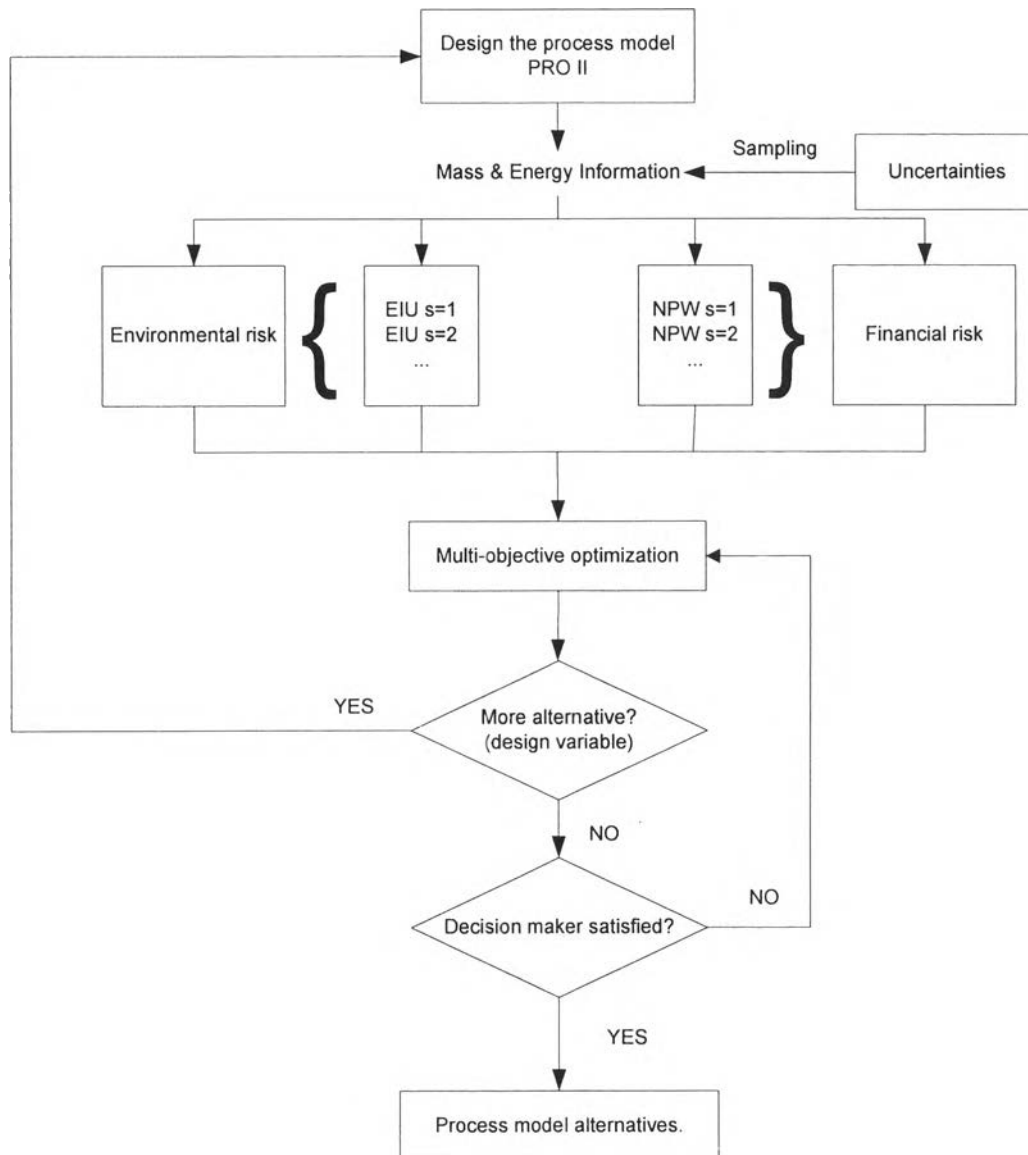


Figure 3.1 Proposed methodologies general diagram.

3.2 Case Study: the Manufacture of Vinyl Chloride Monomer Production Process

The principle operating steps used in the ethylene based balanced process for the production of vinyl chloride are shown in the reactions below and block

diagram in Figure 3.2 (Kroschwitz and Howe-Grant, 1997). Ethylene is chlorinated to EDC by the processes of oxychlorination and direct chlorination. EDC is purified in the EDC purification section and fed to the pyrolysis reactor where vinyl chloride purification section and the recovered hydrogen chloride and EDC are recycled. The main reactions involved are:



The kinetics for these reactions is described below and detailed rate expressions are given in Appendix A. Apart from the main products shown in the equations above, a variety of byproducts are produced in these reactors. Some of the more significant byproducts are hazardous substances (Kroschwitz and Howe-Grant, 1997) such as chlorinated hydrocarbons which are toxic compounds, carbon dioxide which is the cause of global warming problem, and hydrogen chloride which is corrosive.

This process is based on the PRO/II Casebook (1992) on the vinyl chloride monomer plant. The three reaction sections are integrated into a balanced process flowsheet with the separation sections (EDC purification and VCM purification) having recycling line of HCl to the oxy-chlorination, and the EDC line recovered from the VCM purification to the EDC purification section.

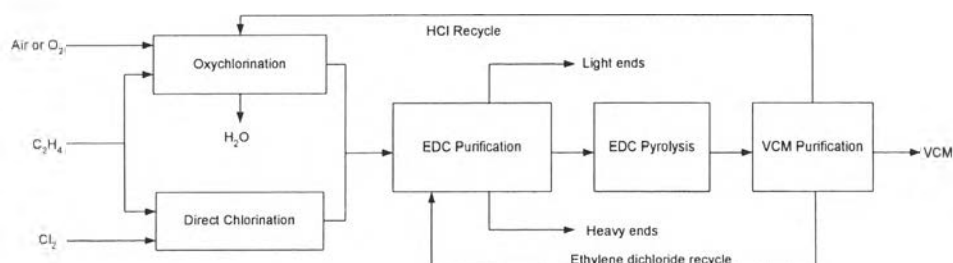


Figure 3.2 Principle steps in a balance vinyl chloride process.

3.2.1 Direct Chlorination Process (see Figure 3.3)

Direct chlorination of ethylene to EDC is conducted by mixing the gaseous reactants (CL₂F and C₂F₁ in Figure 3.3) into a volume of liquid EDC in the presence of ferric chloride catalyst. The direct chlorination reactions were modeled using kinetics from Wachi and Morikawa (1986) and presented in Appendix A. A CSTR reactor was modeled in Excel to determine consumption of reactants and production of products and transferred to ProII for a Process simulation. A slight excess of ethylene was used to maximize conversion of ethylene. The operating conditions are 60 °C and 4 atm. The product EDC is removed as a mixed phase which also contains unreacted ethylene and chlorine. Liquid EDC is recovered by condensation. Any HCl and Cl₂ remaining in the vent gas (VNT1) are removed in a caustic scrubber. The liquid EDC goes to a caustic wash vessel where dissolved chlorine and byproduct HCl are removed. From the caustic wash, EDC overflows to a decanter.

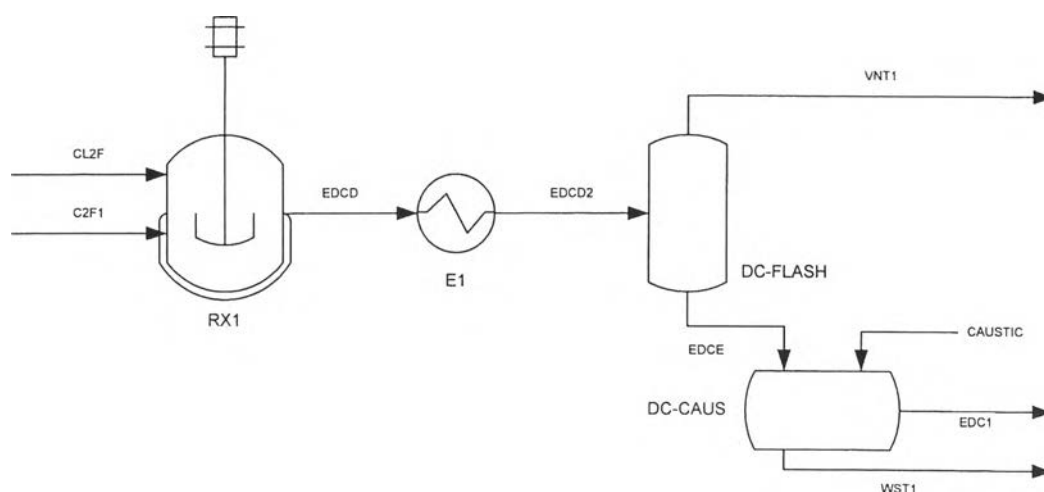


Figure 3.3 Direct chlorination process.

Simulation

The main feeds to the VCM plant are ethylene (C₂F₁) and chlorine (CL₂F) fed into a CSTR (RX1). The flow of ethylene-to-chlorine ratio in the reactor feed is 1.06. The conversion of chlorine is 100% with 99% selectivity for EDC. The product

streams (EDCD) from the reactor is passed a heat exchanger (E1) and flashed (DC-FLASH) to separate a vent stream (VNT1) and a raw product stream (EDCE). The raw product stream EDCE is washed and scrubbed to remove all of the HCl and Cl₂ (see Figure 3.3).

3.2.2 Oxychlorination Process (see Figure 3.4)

Ethylene and oxygen react with hydrogen chloride gas produced from the pyrolysis of EDC to produce EDC and water. Oxy-chlorination reaction kinetics were derived from Sai Prasad *et al*, 2001 and presented in Appendix A. The operating conditions of oxychlorination reactor is 310 °C and 4 atm. EDC is formed through a heterogeneous catalytic, cupric chloride catalyst impregnated on a porous alumina support, in PFR. The PFR reactor was modeled in Excel to determine consumption of reactants and production of products and transferred to ProII for a process simulation. EDC and other gases from the oxychlorination reactor pass through a condenser and a caustic scrubbing tower to removed unreacted HCl. The crude EDC recovered from a flash system mixed with water flows to the decanter where it combines with the direct chlorination product in Figure 3.6. Uncondensed gases pass to a venting system.

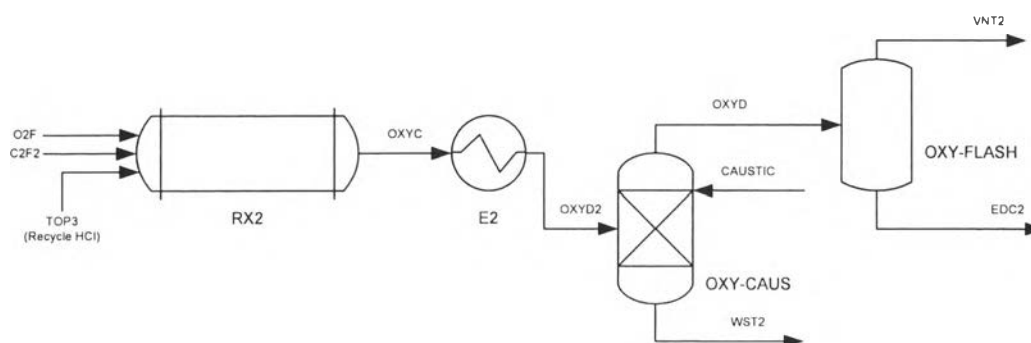


Figure 3.4 Oxychlorination process.

Simulation

The ethylene feed (C₂F₂), oxygen feed (O₂F), and HCl recycle is fed into oxychlorination reactor (RX2). The product stream (OXYC) from the reactor (RX2)

is cooled (E2) and sent to the caustic wash to remove unreacted HCl. Then, the remaining product stream is flashed to remove all non-condensables as a vent stream (VNT2) (see Figure 3.4).

3.2.3 Pyrolysis Process (see Figure 3.5)

Vinyl chloride monomer is produced by thermal cracking of EDC at temperature of 700 K, and pressure of 30 bars. The endothermic reaction was performed with respect to 108 reversible elementary reactions with 47 molecular and radical species. Pyrolysis reaction kinetics were derived from Choi *et al*, 2001 and presented in Appendix A. The pyrolysis reactions were modeled in Excel to determine consumption of reactants and production of products and transferred to ProII for a process simulation.

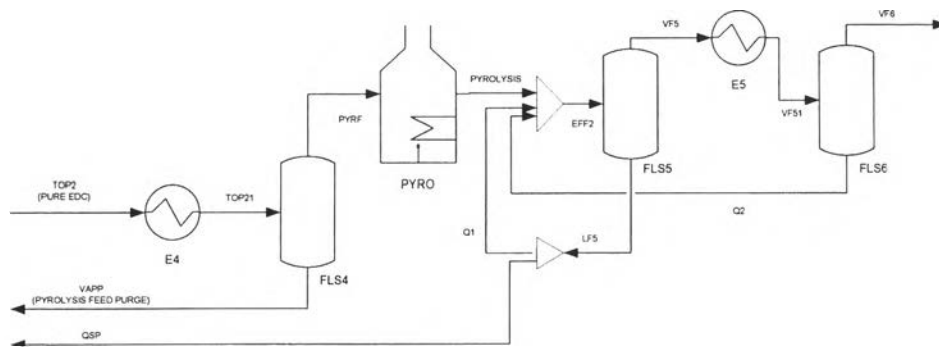


Figure 3.5 Pyrolysis process.

Simulation

The pyrolysis simulation model is shown in Figure 3.5 Pyrolysis Process. The top product (TOP2) from the heavies column (COL2) of the EDC purification section is sent to a pure EDC surge tank. The pyrolysis furnace receives its feed (PYRF) from this tank (FLS4). The feed (TOP2) is heated (E4) and flashed (FLS4) to recover a liquid stream (VAPP). The balance is a vapor stream (PYRF) which is fed to the pyrolysis reactor (PYRO). The reactor effluent (PYROLYSIS) is quenched by liquid streams (Q1 and Q2) to yield a quenched product (EFF2). This stream passes to a quench separator (FLS5). The vapor phase (VF5) is further cooled (E5) in one or more heat exchangers and flashed (FLS6) to recover a liquid stream (Q2).

3.2.4 EDC Purification Process (see Figure 3.6)

Trace quantities of impurities in the pyrolysis feed can inhibit the cracking reactions and cause fouling of the reactors. So, the combined EDC from three different sources must be purified to 99% EDC from: direct chlorination, oxychlorination, recovered, and recycled from the cracking step.

The combination of EDC from both direct chlorination and oxychlorination sections is washed with water and scrubbed with caustic to remove chlorine, HCl and other water extractable impurities such as chloral.

In two distillation columns, the crude EDC and unconverted recycle EDC from the VCM column are combined, dried, and purified. In the first (the light column), water and lower boiling point impurities (light ends) are separated as the overhead product. The bottoms product is mixed with a purge stream from the feed vaporizer and fed to the heavies column. Another purge stream from the quench system, downstream of the cracker, is also directed to the bottom of the heavies column. Pure EDC of around 99% purity is taken as the overhead product while the heavy impurities leave the column as the bottoms product (heavy ends).

The bottoms product from the heavies columns may be further processed, normally via batch distillation, to provide distilled “heavies” byproduct, mainly recovered EDC, and a residual heavy tar.

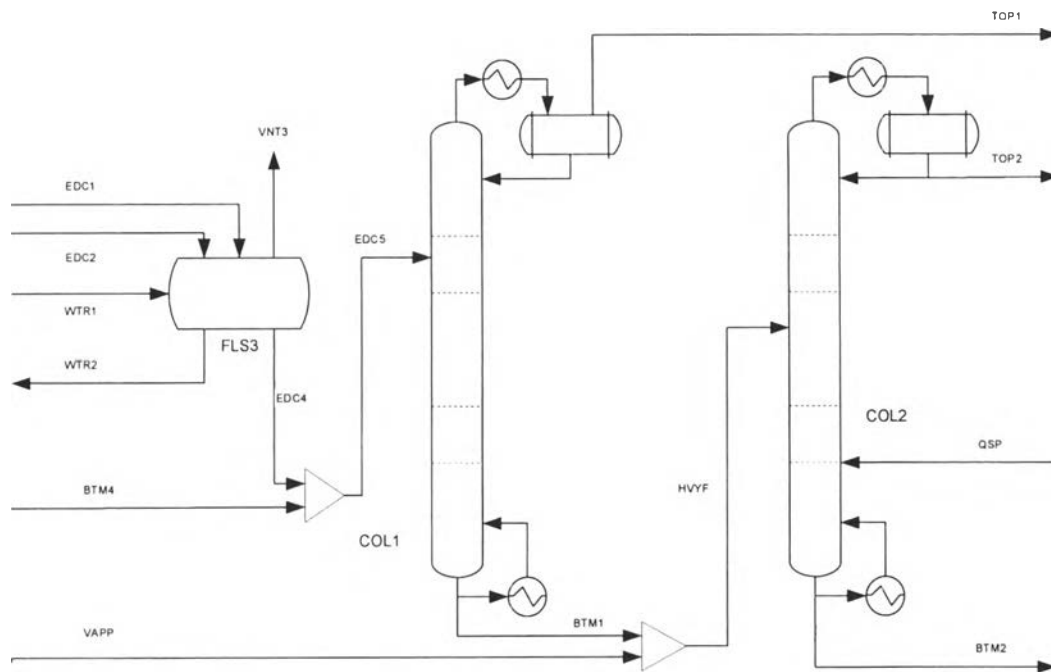


Figure 3.6 EDC purification process.

Simulation

Streams EDC1, EDC2, and WTR1 (a large excess of water) are fed into a saturator/decanter unit (FLS3). The SRK equation of state with DECANT=ON is used for thermodynamics. While the water phase is decanted as pure water, the amount of water dissolved in the hydrocarbon phase is predicted based on solubility data. The free-water decant model reduces the computational time required to solve this unit and does not impact the overall flowsheet model.

Three streams exit unit FLS3: a vent stream (VNT3), the aqueous phase (WTR2), and a crude, wet EDC stream (EDC4). This EDC stream is mixed with a recycle EDC stream (BTM4) from the bottoms of the VCM column. The combined feed (EDC5) is fed to the lights column (COL1). This column has 17 theoretical trays. The bottom product is specified to contain only 0.1% of the water entering the column (99.9% dehydration). A partial condenser is used for this column. The top vapor product (TOP1) removes most of the water and other light species with some loss of EDC. The remaining EDC and heavies (BTM1) pass on to the heavies column

(COL2). Before being fed to the heavies column, the partially dehydrated EDC is mixed with a recycle liquid purge stream (VAPP) from the pyrolysis reactor feed vaporizer. The combined feed (HVYF) goes to COL2 which has 30 theoretical trays. The stripping section of the column also receives another recycle purge stream (QSP) from the quench separator. This purge prevents collections of heavy cracking byproducts in the quench system. The specifications for COL2 are about 99.9% pure dry EDC in the top product (TOP2). The IO distillation algorithm is used to simulate the two columns in this section (see Figure 3.6).

3.2.5 VCM Purification Process (see Figure 3.7)

VCM is separated from HCl and EDC in both columns. The first is HCl column receiving mixed phase feeds containing mainly EDC, VCM, HCl, and some of other byproducts. HCl is distilled off at the top and recycled to the oxychlorinator directly. The bottom product is fed to the VCM column for final separation of the purified VCM product as the overhead. EDC is recycled to the lights column of repurification. The HCl column is operated to achieve impurity specification of less than 100 ppm VCM in the distilled and less than 5 ppm HCl in the bottoms.

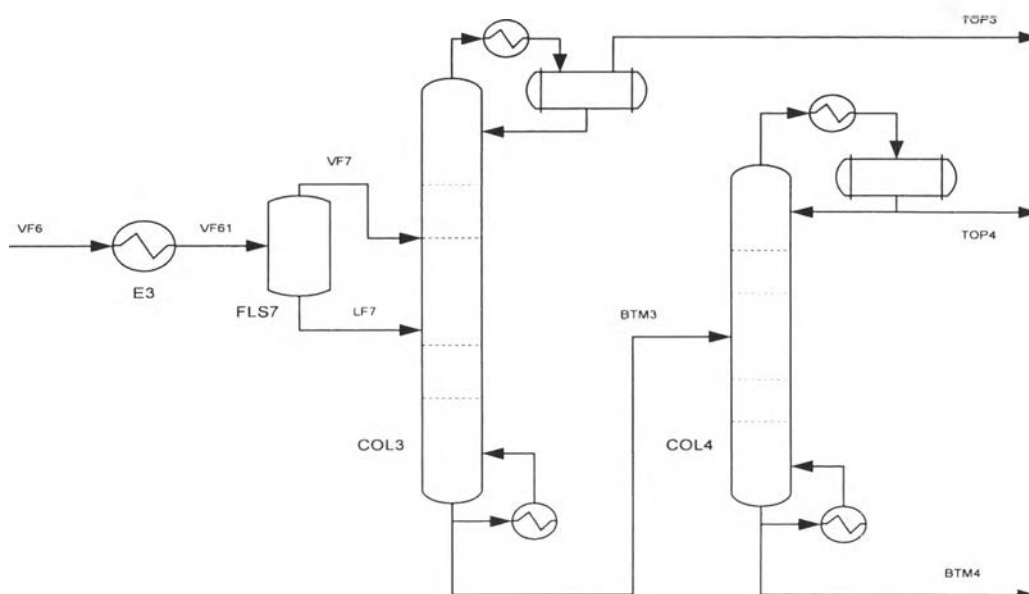


Figure 3.7 VCM purification process.

Simulation

The HCl column in this application has 42 theoretical trays, including the condenser and the reboiler. The feed to this column comes from the flash unit (FLS7) upstream of the column. The vapour (VF7) is fed to tray 18 while the liquid (LF7) is fed to tray 22. One of the control specifications is for the reflux ratio to be maintained at 1.0. The other control specification is a suitable tray temperature. In this example, the temperature of tray 34 is maintained at 73°C. Examination of the resulting column temperature profile reveals that this tray provides sufficient sensitivity to changes without sacrificing stability. A top pressure of 135 psig is maintained by using a partial condenser using refrigerant propane. The top temperature is around -31°C.

The top product (TOP3) is recycled to the oxychlorination section, while the bottoms pass on to the VCM column (COL4). The VCM column has 20 theoretical trays and a top pressure of 65 psig. The control specifications are the reflux ratio of 0.45 and tray 17 temperature of 140°C. The column converges with ease and provides a high purity (greater than 99.9%) VCM product as the distillate (TOP4). The bottoms product (BTM4) is unreacted EDC which is recycled to the EDC purification section.

Both columns successfully converge with the IO algorithm and the SRKM equation of state (see Figure 3.7).

3.3 Treatment System

Many of waste byproducts formed during the production of VCM are toxic substances which are dangerous to the environment and human health. From this reason, waste byproducts have to be treated to reduce which a treatment process cannot totally remove or eliminated. All treatment process system is shown in Figure 3.8 consisting of processes: activated carbon adsorption unit, carbon regeneration unit, incineration unit, and absorption unit for complete treatment.

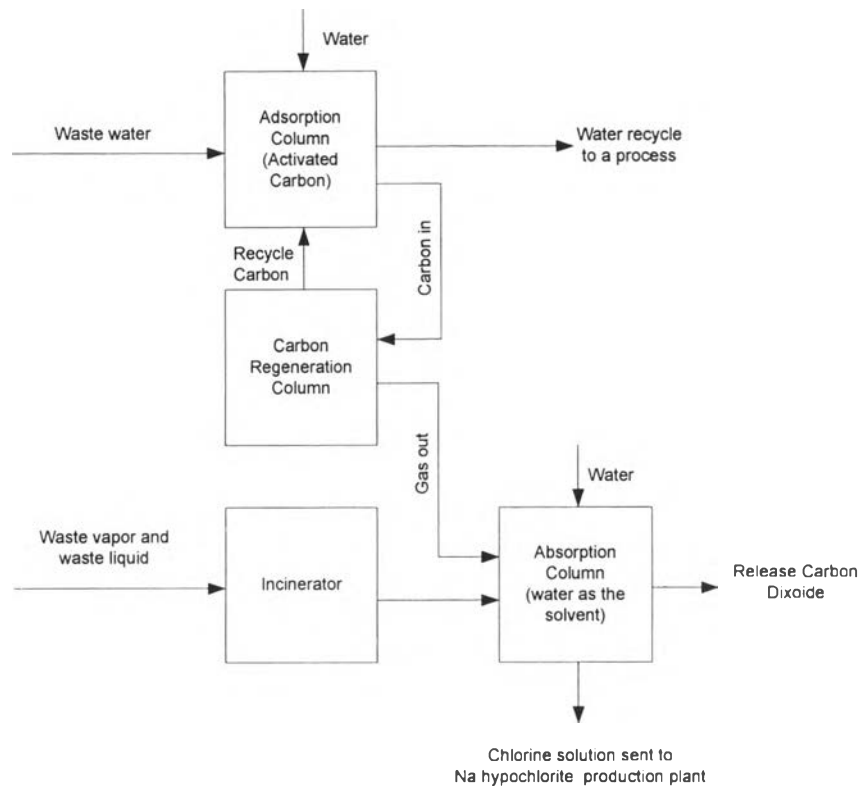


Figure 3.8 Flowsheet of treatment process system.

3.3.1 Vapor and Liquid Byproduct Treatment

Several of the waste byproducts is volatile organic compounds having a lot of methods to treat them such as condensation, adsorption, incineration, absorption, and others. In this case, a thermal incineration system is introduced to eliminate volatile organic compounds because the technology can apply for a wide variety of gas concentrations and components, and have high efficiencies to remove or treat the wastes (Hunter *et al*, 2000). If the waste gas stream is halogen or sulfur compound, acidic gases can be formed, so the incinerator system must be designed to handle the corrosion. A scrubber or absorption column following the incineration is necessary under most circumstances to remove the acid gases before the gas stream is released to the atmosphere. Therefore, absorption column is set up to remove or dissolve acid gas (HCl) and chlorine gas and release carbon dioxide to the atmosphere. Then, chlorine solution is sent to sodium hypochlorite production plant

(Kroschwitz and Howe-Grant, 1997) prepared by chlorination of NaOH, which sodium hypochlorite is by industries, laundries, and in swimming pool sanitation.

3.3.2 Water Treatment

Granular activated carbon (GAC) absorption is the choice chosen in the water treatment system because of reliable technology to remove dissolved organics, simple design and operation and low space requirements (EPA, 2000). Carbon regeneration is needed to remove or desorb pollutants from GAC by thermal means. Organic matter within the pores of the carbon is oxidized and this removed from the carbon surface. The regeneration method is multiple hearth furnaces to desorb and decompose VOC. Those off-gases are sent to absorption system later.

3.4 Uncertainty, Risk Analysis, and Probability

In uncertainty conditions, forecasting a cost, a net present worth (NPW), or an environmental impact index which uses only a point to represent the performance of a design can be severely misleading. Therefore, risk analysis can help to answer question such as: “How confidence are the design or alternative will have NPW more than?”

Uncertainty sources in analysis of this work are prices of product and raw materials, rate of interest, and product demand in each year. The estimating or forecasting uncertainty parameters is done by using random in GAMS Program of the mean and standard deviation. These values was done and shown in Appendix C.

The steps for the environmental and financial risk analysis are shown in the follow Figure 3.9

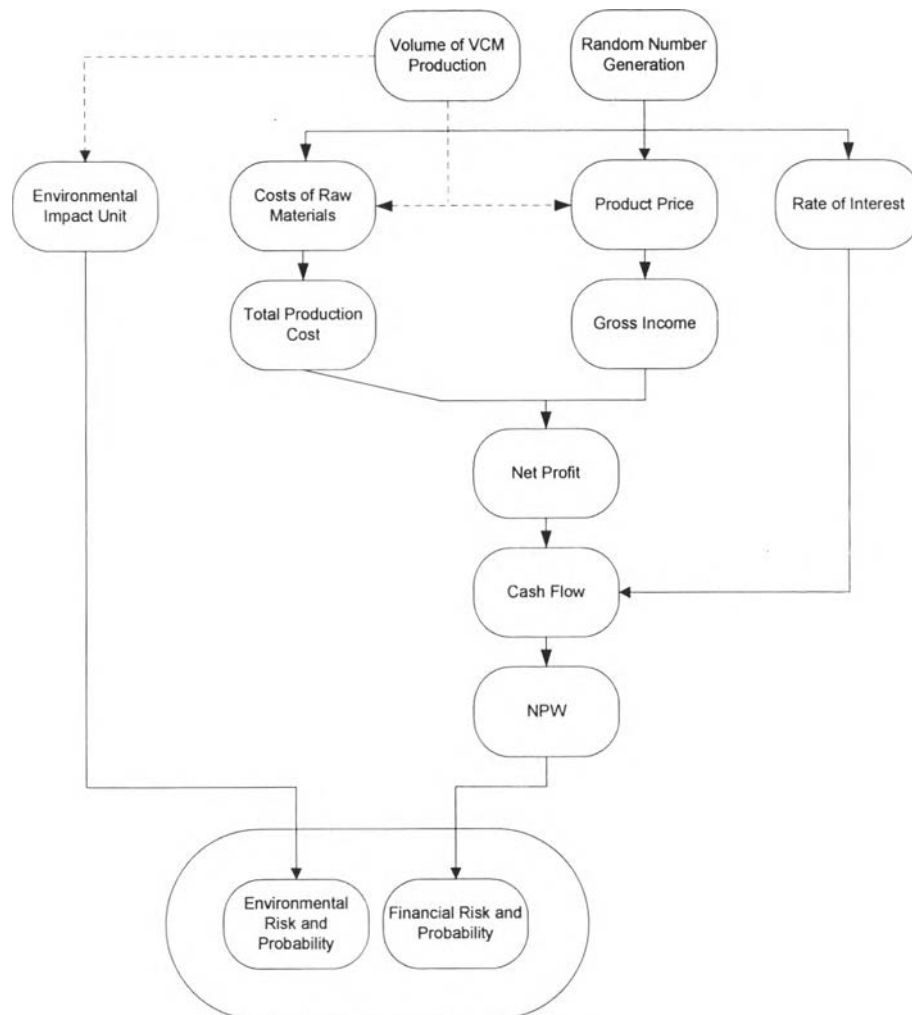


Figure 3.9 Procedure of risk analysis.

Gross income depends on raw material costs, demand of VCM in each year, and product prices. Additionally, rate of interest have an effect on cash flow and NPW. The volume of VCM production for each year is different for different years until the demand meet maximum capacity of plant, so environmental impact unit can vary because of changing of mass and energy production.