Exergy Analysis of Ethylene Dichloride Cracking Unit at Abu-Kammash Chemical Complex

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Abstract :

Energy demand is hugely increasing worldwide nowadays. Chemical plants need continuous sources of energy to execute the tremendous number of manufacturing processes. On the other hand, the traditional energy sources, oil and gas, are decaying. Thus, it is needed to redesign the manufacture processes and improve their thermal efficiencies in order to save more energy**.** This research made a comparison between two design models of the thermal cracking process of Ethylene Dichloride (EDC) to produce Vinyl Chloride Monomer (VCM) at Abu-Kammash Chemical Complex. The developed design was set against the amount of heat saved. In addition, Both EDC cracking units (old and new design) were

thermodynamically analyzed in terms of the availability idea, (Exergy analysis).

Introduction:

The chemical process industries consume more than one third of the energy used by all manufacturing industries, as the energy is frequently the major costs in chemical plants. Thus, chemical engineers should be suitably aware of the generation sources, control, uses, and conservation of energy [1, 2].

Energy is hugely generated and consumed in chemical plants through the combustion of fossil fuels, natural gas and hydrocarbon oil, in fired units such as furnaces. This heat is mainly consumed in generation of steam and heating fluids prior to further processes. The combustion process produces large quantity of heat, which will be contained in the flue gas leaving the combustion chamber at high temperatures. The thermal efficiency of the fired unit will be highly reduced if this heat wasted un recovered. In terms of the thermodynamic analysis, the more heat wasted means that the more increase in the process irreversibility, and the more decrease in the availability [3-5].

The term Exergy was used for the first time by Rant in 1956, and refers to the Greek words ex (external) and ergos (work). Another term describing the same is Available Energy or simply Availability. The term Exergy also relates to Ideal Work as will be explained later, and Exergy Losses relate to Lost Work. One of the challenges in Thermodynamics compared to Mechanics is the introduction of somewhat abstract entities (or properties) describing PVT systems, such as Internal Energy, Entropy and Exergy. In addition, there are special energy functions such as Enthalpy, Helmholtz energy and Gibbs (free) energy that are important in

thermodynamic analysis but can be difficult to fully comprehend. While Enthalpy is important for flow processes (open systems) in Mechanical Engineering Thermodynamics, Helmholtz energy (to define equations of state) and Gibbs free energy (for physical and chemical equilibrium) are important in Chemical Engineering Thermodynamics [6].

In this research, the Exergy analysis (availability) will be introduced for the selected processes. This analysis considers the maximum work which can be obtained from a process and the corresponding irreversibility and lost work.

Exergy (Availability) Analysis:

The *availability* is the measure of the maximum capacity of an energy source to perform useful work as it proceeds from its initial state (T, P) to a specified final state in equilibrium with the surrounding (T_0, P_0). Thus, the maximum work that can be extracted from the energy source depends on the surrounding properties (temperature and pressure). In other words, the greater the difference between the energy reservoir and its surrounding in terms of the temperature and pressure, the greater the capacity to extract work from the system. In this case, the capacity of an energy source to perform work is also termed as *exergy* [3].

Availability in Open Systems :

The first law of thermodynamic for open systems can be written as follows when omitting the change in the kinetics and potential energies,

$$\dot{m}(h_{out} - h_{in}) = \dot{Q} + \dot{W}_s \qquad (2)$$

For the ideal process, the entropy generation of the universe equals zero. Thus, the second law of thermodynamics for the ideal open systems is expressed through these equations:

$$\dot{m}(s_{out} - s_{in}) = \frac{\dot{Q}}{T_{surr}} \qquad (3)$$

$$\dot{Q} = T_{surr}\dot{m}(s_{out} - s_{in}) \qquad (4)$$

By substituting the heat rate term from Equation (4) in Equation(2) and making the required rearrangement, we obtain:

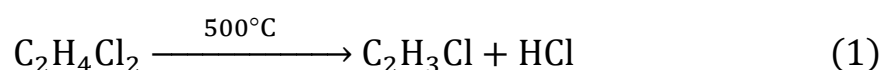$$\dot{W}^{Ideal} = \dot{m}[(h_{out} - h_{in}) - T_{surr}(s_{out} - s_{in})] \qquad (5)$$

It is worth noting that the term of *Ideal Work* is used here to express the energy either was in the form of mechanical work, (turbine, compressor, etc), or heat (heat exchanger, boilers, etc). The ideal work is the maximum work obtained from a process, or the minimum work given to a process. The ideal work, either obtained or given to a certain process, can be replaced by availability decrease or availability increase, (Δφ). This term is also called exthalpy.

$$\dot{W}^{Ideal} = \text{exthalpy} = \dot{\varphi}_{out} - \dot{\varphi}_{in}$$
$$= \dot{m}[(h_{out} - h_{in}) - T_{surr}(s_{out} - s_{in})] \qquad (6)$$

Equations (6) will be used to calculate the availability of energy for the heat exchangers utilized in the EDC cracking process.

Process Description :

The flow diagram of the (EDC) cracking process, (old design), is shown in Figure 1. The Pure EDC is pumped into the cracking furnace after being scrubbed by water. In the furnace, the EDC is preheated, evaporated, superheated and finally cracked at the high temperature of 500ºC and pressure of 27 bar to VCM and HCl [7, 8]. The thermal decomposition reaction of EDC, with conversion of 50%, is taking place as follows

$$C_2H_4Cl_2 \xrightarrow{\text{500°C}} C_2H_3Cl + HCl \qquad\qquad (1)$$

The produced gaseous mixture that leaving the furnace is sent to a quench tower where the mixture is suddenly cooled and partly condensed by a reflux stream. The quench tower head product is partly condensed in two downstream coolers before it is sent for phases separation. It is obvious that the quenching of the reaction products down from approximately 500ºC will cause the dissipation of vast quantity of heat. The process design has been developed to decrease the heat lost to the environment.
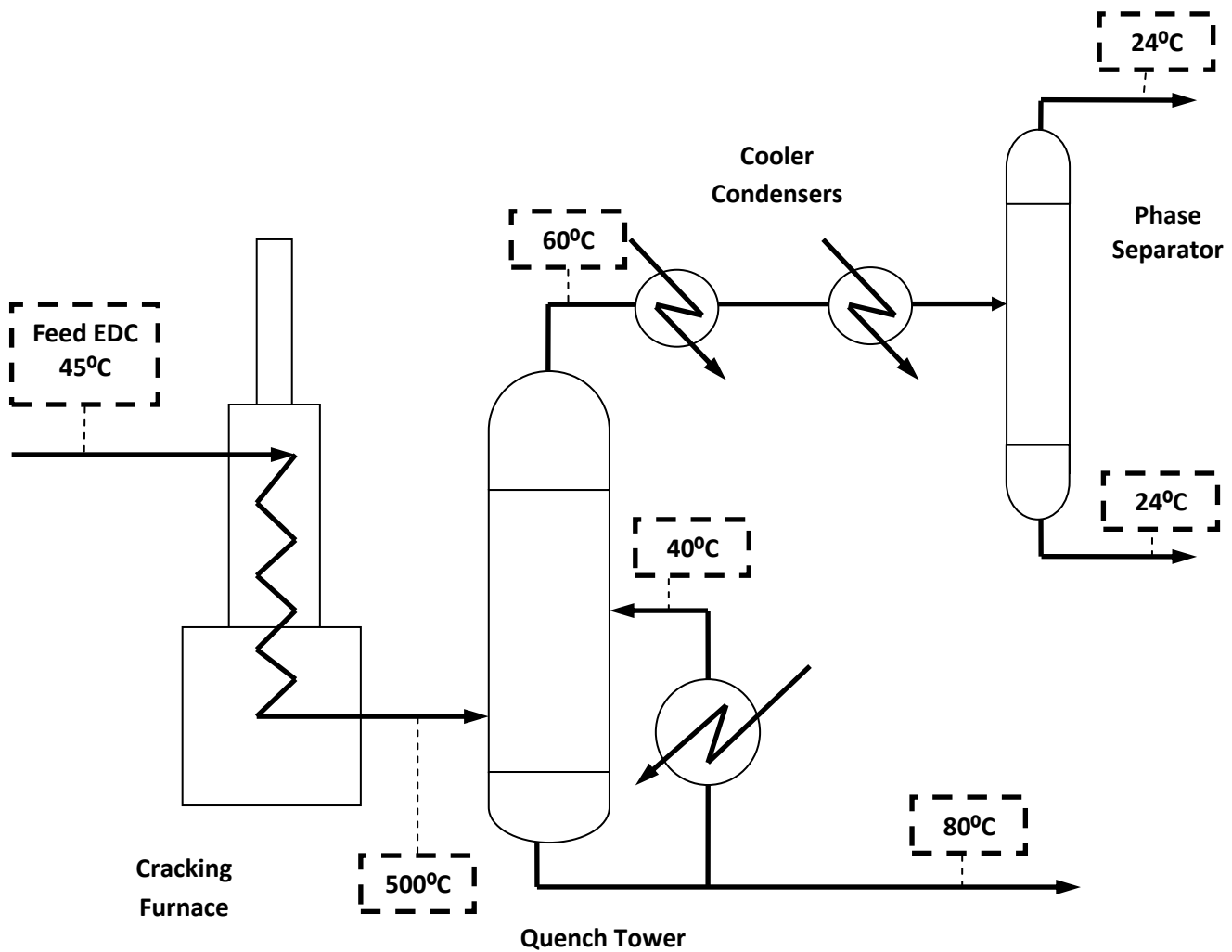
Figure 1: The Cracking unit of EDC –*Old design* [7].

Figure (2). Liquid feed EDC is heated up through two stages: first by a steam heater and secondly in the convection section of the furnace. The EDC is then evaporated and superheated to about 298ºC by recovering the heat of the reaction products leaving the furnace. The superheated EDC is

eventually cracked in the furnace to VCM and HCl. The produced mixture is cooled through the super heater and the evaporator respectively, before entering the quench tower at a temperature of 261ºC.
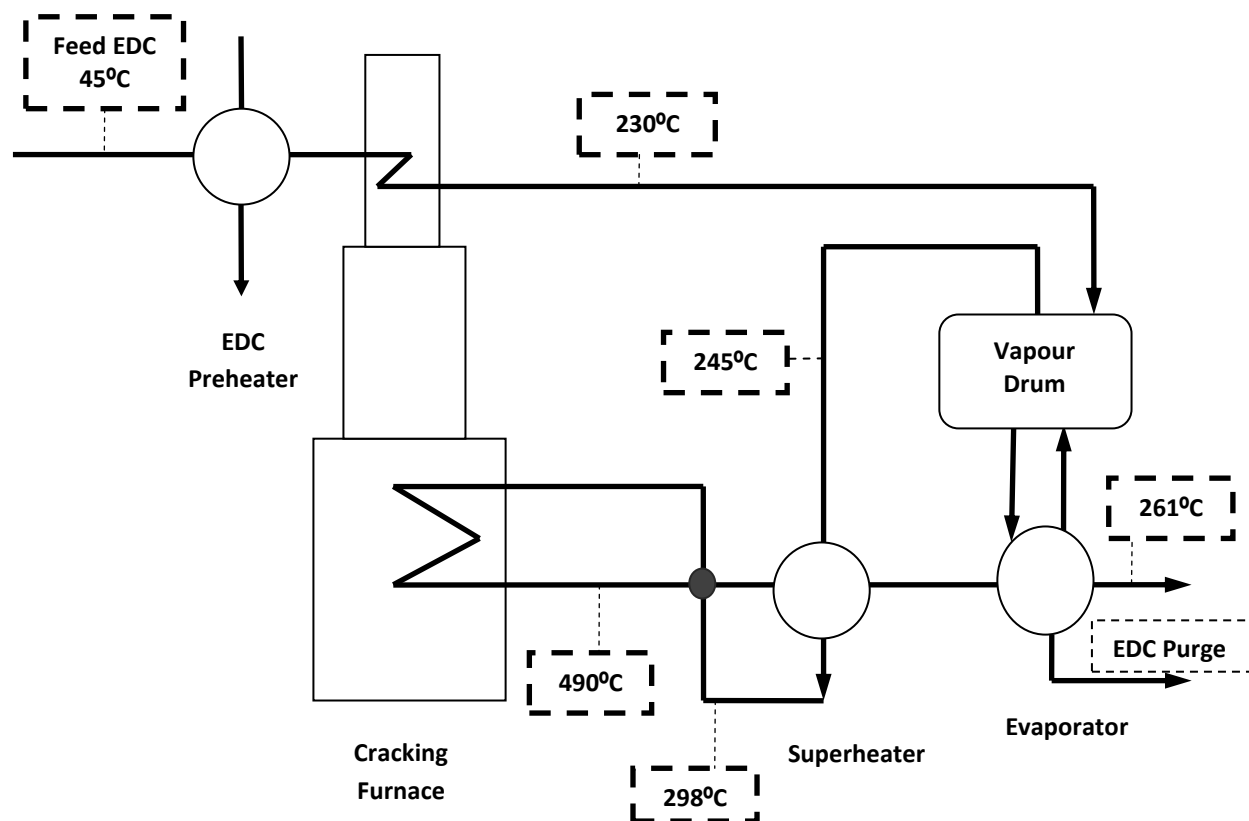

Figure 2: The Cracking unit of EDC – *new design* [8].

Furnace Exergy:

The exergy of fuels, which is used in the thermal cracking furnace can be estimated on the basis of the Lower Heating Value (LHV) of the

hydrocarbon fuel of the chemical formula C_aH_b. The relation between the (LHV) and the exergy is calculated from the equation [3]

$$\dot\phi_{Fuel} = \left(1.033 + 0.0169\frac{b}{a} - \frac{0.0698}{a}\right) \times LHV \qquad (7)$$

Where,

$$LHV = 0.947\left[(2.3(145.4 \times C\% + 620 \times H\%) - 215.6 \times H\%) \times \frac{MW}{1000}\right]$$
$$-42.5, \quad kJ/mol \qquad (8)$$

The molar enthalpy and entropy of pure substances between two temperatures at constant pressure is calculated by the equations:

$$h_2 - h_1 = \int_{T_1}^{T_2} Cp\, dT \qquad (9)$$

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{Cp}{T} dT \qquad (10)$$

The following equation is used to find the intensive enthalpy and entropy of an ideal mixture.

$$H = \sum n_i h_i \qquad (11)$$

$$S = \sum n_i s_i - R \sum n_i \ln y_i \qquad (12)$$

Exergy Efficiency(η) :

It is also called the second law efficiency. It is measures of the losses in the availability or its approach to the reversibility during the heat transfer from a hot reservoir to a cold receiver [5].

$$\eta = \frac{\text{Availability decrease from the hot stream}}{\text{Availability increase in the cold stream}}$$

$$= \frac{\left(\dot\phi_{out} - \dot\phi_{in}\right)_{\text{hot stream}}}{\left(\dot\phi_{out} - \dot\phi_{in}\right)_{\text{cold stream}}} \qquad (13)$$

The lost work is calculated through the change in the entropy of the universe by the extensive entropy differences in each stream during the process:

$$\dot{W}^{Lost} = T_{surr}\Delta S_{univ} \qquad (14)$$

$$\Delta\dot{S}_{univ} = \left(\dot{S}_{out} - \dot{S}_{in}\right)_{\text{cold stream}} + \left(\dot{S}_{out} - \dot{S}_{in}\right)_{\text{hot stream}} \qquad (15)$$

Results and Discussion:

In terms of different parameters, the results of comparison between the two processes, old and new design, are summarized in Table 1. As it was obtained from the furnace energy balance and exergy analysis, there is large save in energy, as about7.4 MW saved. Because of the increase in the reaction (1) conversion in the new design unit comparing to the old one, the development in the unit reflected in the VCM production capacity increase by about 41.6%. This was achieved with less consumption of

hydrocarbon fuel, and subsequently less CO_2 emission to atmosphere by 47%. In addition, coke formation was reduced inside the furnace because the EDC evaporation and superheating respectively took place in the heat exchangers before entering the furnace.

TABLE 1. Comparison between the two process design.

Parameter	Old Design	New Design
Used Fuel	Dodecane $C_{12}H_{26}$	Dodecane $C_{12}H_{26}$
Excess Air	100%	100%
Production Rate of VCM	62525 ton/year	88536 ton/year
Overall Conversion	50%	60%
Total Lost Work	8.0297 MW	0.5940 MW
Flow Rate of Combustion Fuel	982.25 Kg/hr	522.4 Kg/hr
Production Rate of CO_2	3044.45 Kg/hr	1619.16 Kg/hr
Coke formation in the furnace	High	Low

The results of energy balance and exergy analysis of the heater, cooler and heat exchangers used in the EDC cracking process, (both designs), are tabulated below. The cooler condenser was used in the old process, as shown in Figure 1. It is clearly seen that the cooler exergy efficiency is low and subsequently the lost work is huge. However, the heat exchanging equipment in the new process showed good to high availability efficiency. The EDC preheater benefited from about two third of the available work in the steam to heat up the pure EDC stream. Moreover, the

percentage of the recovered energy increased dramatically in the EDC superheater and evaporator respectively.

TABLE 2. Exergy Analysis of Heat Exchanging Equipment

Equipment	Ideal Work(kJ/hr)	Lost Work(kJ/hr)	Exergy Efficiency %
Cooler Condenser	-16013	13702	14.4
EDC Preheater	-1890661	685929	63.7
EDC Superheater	-1030225	242852	76.4
EDC Evaporator	-3503947	636084	81.8

Conclusion:

The thermodynamic analysis for the EDC cracking unit was made based on the availability of work. The analysis was made comparatively between two cracking units in terms of the lost work in both processes. The results have proven that there was large quantity of heat lost in the cracking process before development (old design). This waste energy was significantly reduced by installing the new unit which saved about two third of the lost work.

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