

Enthalpy of formation as part of energy efficiency analyses – case: olefin plant

Mari Tuomaala*, Henrik Holmberg, Heidi Auvinen
Helsinki University of Technology, Department of Energy Technology
P.O. Box 4400, FI-02015 TKK, Finland
mari.tuomaala@tkk.fi

Energy efficiency studies are normally carried out using the *specific energy consumption*, *SEC*, which describes the ratio between the total energy used and a useful output of the process, usually measured in physical units such as tons of product (for example GJ/t) (EC, 2008). The total energy used is the difference between the energy inputs and the energy outputs. In industrial processes the total energy used normally covers fuel, electricity and steam.

Steam cracking of hydrocarbons to form light olefins is one of the most energy-intensive processes in the chemical industry. The reaction is highly endothermic (energy-absorbing). The total cracking energy requirement and the energy absorbed into the products can be predicted to a certain extent with simulation software such as SPYRO (Spyro, 2008). In the calculation of the specific energy consumption, however, the amount of energy absorbed into the products and by-products is not considered.

The paper demonstrates the creation of a more precise energy balance for an endothermic process. The method involves calculating the reaction energy by defining *the enthalpy of formation* for the material streams. The approach enables the conversion energy requirement of the process to be calculated without special software. It also allows one to calculate how much energy is bound in the products and by-products in the chemical cracking reactions. This can be used to develop the life cycle analyses further as the absorbed energy and the bound CO₂ will be known. The approach is applicable to almost all industrial processes involving chemical reactions and to almost any balance region.

1. Energy efficiency monitoring

Energy efficiency issues have become more important in recent years. The main driving forces have been the threats of diminishing fossil fuel resources and climate change. These concerns are exerting pressure to lower energy consumption and emissions. These trends also facilitate the development of new processes and ways to value products. A way forward would be indicate the energy consumed in chemical reactions versus the total energy used in manufacturing.

1.1. Energy efficiency indicators in industry

Energy efficiency in industry is most often monitored using the specific energy consumption (SEC), which describes the ratio between the total energy used and a useful output of the process. It is usually measured in physical units such as tons of product (GJ/t) (EC, 2008):

$$SEC = \frac{\text{energy used}}{\text{products produced}} \quad (1)$$

Usually, all energy is converted into primary energy. For an industrial process that consumes fuel, electricity and steam (assuming the efficiency of electricity production is 40% and the efficiency in steam generation is 85%) the SEC is written as (EC 2008, modified)

$$SEC = \frac{E_{f,in} + \frac{100}{40} E_{e,in} + \frac{100}{85} E_{s,in}}{\text{products produced}} \approx \frac{E_{f,in} + 2.5 E_{e,in} + 1.2 E_{s,in}}{\text{products produced}} \quad (2)$$

SEC indicates a value for energy consumption per unit of production. The figure is most commonly used to monitor the energy use of a process over time. The SEC is often further processed into a dimensionless energy efficiency index (EC, 2008):

$$EEI = \frac{SEC_{ref}}{SEC} \quad (3)$$

The energy efficiency index (EEI) compares the actual specific energy consumption to a reference consumption. The benchmark is usually obtained from the plant's historical data. It can also be some other reference, such as a BAT (best available technique) value.

1.2. The scope of the study

Energy efficiency is calculated by taking into account the energy flows from and to the process (Eq. 1). The approach can be used to monitor energy efficiency in processes where no chemical reactions occur, e.g. paper drying in the paper industry. The situation becomes different as endothermic chemical reactions take place and a part of the energy input is consumed in the conversion process.

In this paper, a more complete energy balance is created for an olefin production unit by defining the enthalpy of formation for the material streams. The study evaluates the new information gained by using such an approach. A balance is created for an entire chemical process. The case plant is Borealis Polymers Oy's olefin production unit in Porvoo, Finland. At the case plant, the SEC is calculated using Eq. 2 with some modifications in the efficiency terms.

2. The case study

2.1. The process and the case plant

Lower olefins, i.e. ethylene, propylene and butadiene, are mainly produced by thermal cracking in the presence of steam. The endothermic reaction is called cracking or pyrolysis.

The name refers to the decomposition of a compound by heating. Olefins can be produced from a variety of raw materials. Typical raw materials are naphtha, gas oil, butane, ethane and propane. The raw materials of the case plant consist of eight different hydrocarbon fractions. Steam cracking of hydrocarbons to form light olefins is one of the most energy-intensive processes in the chemical industry.

The manufacture of olefins (ethylene, propylene and butadiene) comprises several process steps. Steam cracking is the first step (Figure 1). In steam cracking, the hydrocarbon raw material and the dilution steam are preheated before entering the furnace. Preheating occurs in the furnace convection section. The temperature of the furnace is 500-680 °C and the cracking temperature inside the coil is up to 850 °C. The cracking reaction is endothermic. After leaving the furnace, the product is cooled down quickly. This is to avoid secondary reactions and the formation of undesired by-products. After cracking, the gas is led to purification and separation sections. The process by-products include hydrogen-rich gas, pyrolysis gasoline and pyrolysis fuel oil.

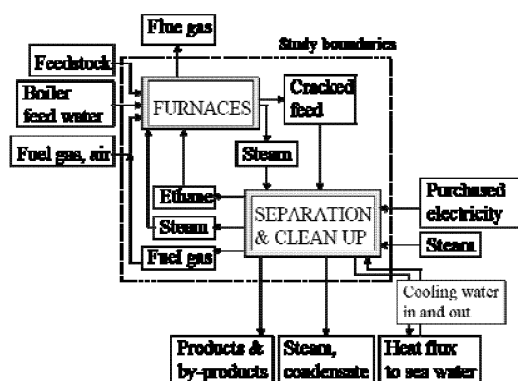


Figure 1. An olefin production flow chart (Auvinen, 2008).

2.2. Calculation of reaction energy

The creation of an energy balance using the enthalpy of formation of the material streams is challenging: most of the streams are complex mixtures and their composition varies as a function of time. In addition, their exact composition is often unknown, so average and estimated values must be used.

Energy that is absorbed or released to convert the raw-materials into products and by-products is called the reaction energy. That is calculated as (Lampinen, 1996):

$$\Delta h = h_{\text{products}} - h_{\text{reactants}} \quad (4)$$

where Δh is the amount of heat released ($\Delta h < 0$) or absorbed ($\Delta h > 0$) in a chemical reaction, h_{products} is the enthalpy of the products and $h_{\text{reactants}}$ is the enthalpy of the reactants.

In combustion, the enthalpy is negative as the reaction is exothermic. The enthalpy for a compound under given conditions in Eq. 1 is calculated as (Lampinen, 1997):

$$h(T_1, p_1) \equiv \Delta H_f(T_0, p_0) + \int_{T_0}^{T_1} c_p(T, p_0) dT + \int_{p_0}^{p_1} \left[v(T_1, p) - T_1 \left(\frac{\partial v}{\partial T} \right)_{T=T_1} \right] dp \quad (5)$$

where T is temperature, p is pressure, c_p is specific heat, v is specific volume and $\Delta H_f(T_0, p_0)$ is the standard enthalpy change of formation as follows (Lampinen, 1997):



$$\Delta H_f(T_0, p_0) \equiv h_{A_nB_m}(T_0, p_0) = h_{A_nB_m} - (nh_A + mh_B) \quad (7)$$

$$h_{A_nB_m} = \Delta H_f(T_0, p_0) + (nh_A + mh_B) \quad (8)$$

Chemical properties for the different compounds are listed e.g. in the Chemical Properties Handbook (Yaws, 1999).

2.3. The energy balance calculations

The energy balance of the process can be written as:

$$E_{w+s} + E_e + E_f = E_{mf} + E_c + E_l \quad (9)$$

where E_{w+s} is energy from water and steam, E_e is energy from electricity and E_f is energy from combustion of fuels, E_{mf} is energy absorbed into the material flow (i.e. the reaction energy that is needed to carry out a chemical reaction) and E_c is cooling energy (energy to sea water). E_l covers various energy losses and differences caused by simplified calculation methods and inaccurate data. The schematic presentation of the energy balance calculations is presented in Figure 2.

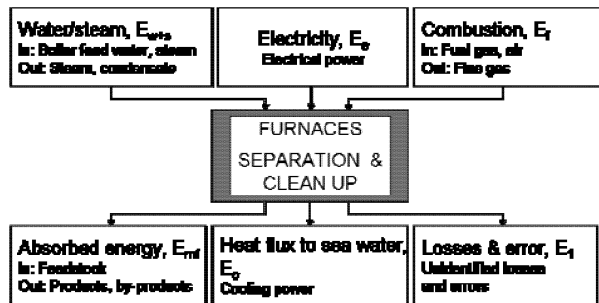


Figure 2. The energy inputs and outputs of the process (Auvinen, 2008)

Water and steam enthalpies are taken from tables and diagrams. Electricity consumption data and the heat flux into the sea water are obtained from the plant personnel. The energy contents of feedstock, products, fuel gas, air of combustion and flue gases are calculated at the standard state using Eq. 5. All gaseous components were treated as an ideal gas, in

which case the enthalpy is independent of the pressure. The impact of temperature was taken into account. Its affect was found to be rather small.

2.4. Results of the case study

2.4.1. The specific energy consumption

The energy efficiency evaluation (Eq. 1) is based on measured energy consumption. The monitoring covers energy inputs, i.e. electricity, steam and water, less energy outputs, i.e. condensate and heat flux into sea water. A trend of the SEC can be drawn based on plant data (Figure 3). Factors affecting the SEC include the capacity utilisation rate, feedstock composition and new installations.

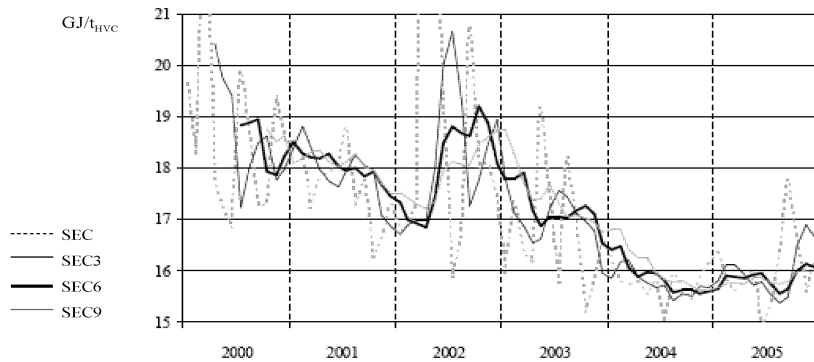


Figure 3: Specific energy consumption (SEC) based on monthly values of the case plant during 2000...2005 with the floating averages from the previous 3 months (SEC3), 6 months (SEC6) and 9 months (SEC 9)(Auvinen, 2008).

2.4.2. Results from the traditional SEC calculation approach

Figure 4a presents the input data of the SEC (Eq. 2 with some modifications in the efficiency terms). The data represents the situation in 2004. The “Total process energy use” covers all energy inputs, i.e. fuels, electricity and steam. Conversion into primary energy, i.e. the effect of the Eq. 2 efficiency factors, is indicated separately as “Primary energy +8%”. The traditional way of creating an energy balance contains information on the “Heat flux into sea water”. The principles of the calculation are presented in Figure 2. Note that in Figure 4a, E_{w+s} and E_f represent differences in stream inputs and outputs according to the Figure 2.

2.4.3. Results covering the reaction energy

Figure 4b presents the additional information that is gained by calculating the enthalpy of formation of the material streams. The approach enables the amount of energy absorbed into the products to be identified and the amount of losses (E_l in Eq. 9) to be determined. Note that in Figure 4b, E_{w+s} and E_f represent the differences in stream inputs and outputs according to the Figure 2.

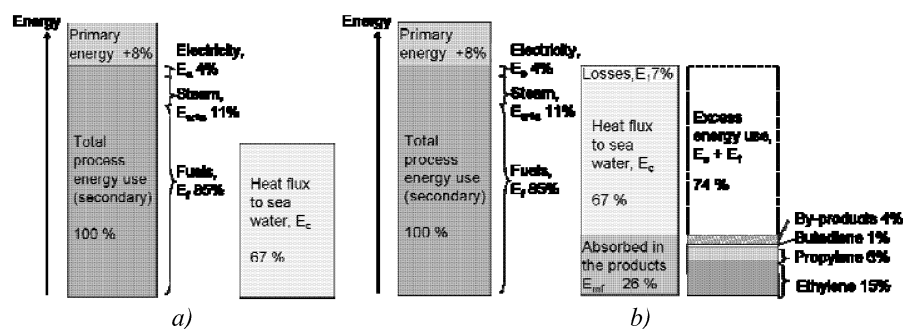


Figure 4. a) Information available in the traditional energy efficiency measurement, SEC, in the year 2004, b) Energy consumption and its division into energy absorbed into products, heat flux into sea water and losses in the year 2004 (Auvinen, 2008).

3. Conclusions

Typically, the energy efficiency is calculated by taking into account the energy flows from and to the process (Eq. 1). This approach is applicable to processes where no chemical reactions occur. The paper presents a new approach to constitute a more complete energy balance for a process with endothermic chemical reactions. This new approach takes into account the chemical energy of the material streams by calculating the enthalpy of formation of the substances. Based on the presented approach, new information is gained to support the energy efficiency evaluation: 1) the calculated reaction energy represents the theoretical minimum energy requirement of the process. Knowledge of the minimum energy requirement can be used as an additional indicator explaining the SEC behaviour (Figure 3). 2) The approach also allows the energy required to convert each product and by-product to be calculated. That is used to allocate the total energy use and the related CO₂ emissions to the products and by-products. 3) The approach indicates the share of energy that is bound in the products and by-products. This information can complement the life cycle analyses.

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