

ON THE EXERGY DETERMINATION FOR PETROLEUM FRACTIONS AND SEPARATION PROCESSES EFFICIENCY

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***Abstract.** Petroleum separation processes are intensive in energy use. However, only a very small fraction of their input energy is required for separation. Due to this significant magnitude difference as well as to the unknown molecular structure of the involved streams, the calculation of specific exergy and exergy efficiency is a delicate topic that involves significant uncertainties. Comparison and explanation of several different ways to perform exergy evaluation of separation processes of petroleum fractions are conducted. The indication of advantages and disadvantages of each formulation is presented. The chemical and physical exergy calculation for petroleum and its fractions are covered. An application is performed and the results are discussed.*

Keywords: Distillation, Exergy, Exergy analysis, Petroleum, Separation Process

1. INTRODUCTION

The exergy analysis has been applied to separation processes to evaluate their thermodynamic efficiency by several research groups: Dinçer and Erkan (1986) applied exergy analysis to a petroleum refinery and reported an overall availability efficiency of 5.9%; Rivero (2002) conducted an exergy analysis to optimize a 150,000 barrels per day (bpd) refinery; specific analysis of distillation processes were evaluated by Rivero and Urquiza (2004), Rivero et al. (2004), Al-Muslim and Dinçer (2005) and Khoa et al. (2010). The approach used to calculate the exergy efficiency have significant influence in these analyses once that different approaches rely on different properties and each property have a different error magnitude. Many methods have been proposed to estimate the basic properties of hydrocarbons from the knowledge of the boiling point and specific gravity or molecular weight. Nearly all of these correlations are empirical in nature and carry a substantial error. The exergy evaluation of separation processes intends to evaluate the fraction of consumed exergy incorporated into the products. Since consumed exergy is usually a small fraction (~1%) of the load and products in petroleum separation units, the errors present in exergy calculation are enough to derail exergy efficiency of petroleum separation processes. Different methods for calculation of separation processes exergy efficiency are evaluated and compared. The methods used to calculate the exergy of petroleum and its fractions (unknown molecular structure) are also presented.

2. EXERGY

To account for the variable quality of different disordered energy forms in the analysis of thermal and chemical plants, a universal standard of quality is needed. The most natural and convenient standard is the maximum work which can be obtained from a given form of energy using the environmental parameters as the reference state. This standard is called exergy, Kotas (1985). The exergy is usually divided in two terms indicating the nature of work capacity: physical and chemical.

3. CHEMICAL EXERGY CALCULATION

The chemical exergy of a substance is defined as the maximum work that can be obtained taking it to chemical equilibrium with its environment. In order to achieve this chemical equilibrium the substance should react with species present in the environment to produce substances also present in the environment. The environment substances enter and exit the reaction at their environmental concentration. Thus, the chemical exergy is given by Eq.(1) applied to the necessary reaction. In this equation the total pressure and temperature are constants and equal to environment values, usually 1 atm and 25^o C. Note that the chemical exergy of a substance already present in the environment is evaluated by the difference in its partial pressure (concentration). It affects the entropy term for ideal gases and enthalpy and entropy for real substances.

$$b_{\text{Chemical}} = [h - h_0 - T_0(s - s_0)]_{T_0, P_0} \quad (1)$$

Although it is impossible to estimate a standard environment for all regions, standard environment compositions were developed by several researchers. One of the most widespread was that developed by Szargut et al. (1988). Thus, the reactions necessary to take a given substance to equilibrium with the standard environment were calculated for a long list of molecules and are known as standard chemical exergy (the standard chemical exergy considers that the evaluated substance is at 1 atm). Alternatively, the chemical exergy can be provided by Eq.(2) for fuels not present in the standard environment, with complex composition. In order to calculate the factor φ it is necessary to know the elementary composition of the given fuel, see Eq.(3), provided in Kotas (1985). In this equation x represent mass fraction. The error present in Eq.(3) is 0,38%. Similar equations for specific fuels can be found in Szargut at al. (1988) and Rivero et al. (1999). Note that Eq.(2) and Eq.(3) are similar to the application of Eq.(1) to a reaction. The *LHV* (low heating value) represents the enthalpy variation while the φ takes into account entropy variation. Stepanov (1995) compared several formulations used to calculate the chemical exergy of fuels with unknown structures, and observed a 4% of deviation among the methods. Several correlations can be found to correlate a fossil fuel elemental composition to its *LHV* as in Channiwala and Parikh (2002).

$$b_{Chemical} = \varphi \cdot LHV \quad (2)$$

$$\varphi = 1.0401 + 0.1728 \frac{x_H}{x_C} + 0.0432 \frac{x_O}{x_C} + 0.2169 \frac{x_S}{x_C} \left(1 - 2.0628 \frac{x_H}{x_C} \right) \quad (3)$$

3.1 Chemical exergy for crude oil and its fractions

In order to apply Eq. (2) and Eq. (3) the elementary composition of the crude oil/crude fractions is required. Since only the light ends molecular composition are known, and an elemental analysis of the heavy fractions is problematic from cost and logistic points of view, the elementary composition of heavy fractions is obtained by application of correlations. The correlations are usually based on distillation curves and some bulk properties such as density or API grade, usually provided for hydrocarbon mixtures in industrial applications.

The standard methods to obtain the distillation curves are: ASTM D86, ASTM 1160, ASTM 2887, and ASTM 2892 (TBP). The distillation points can be converted into a polynomial curve so it can cover the whole evaporation range (0% to 100% of volume). Then, any cut temperature can be defined and, since a large number of cuts can be used, the normal boiling point temperature, T_b , can be estimated as the average between initial boiling point and end boiling point for each cut, Riazi (2005).

An estimation of the specific gravity (*SG*) of the cuts can be obtained by considering the Watson factor, K_w , Watson et al. (1935), constant for all cuts and equal to the value obtained for the crude oil, see Eq.(4). K_w intends to classify the type of hydrocarbons in petroleum mixtures based on the content of (PNA) paraffinic, aromatic, and naphthenic content.

$$K_w = \frac{(1.8 \cdot T_{b[K]})^{1/3}}{SG_{15.5[^\circ C]}} \quad (4)$$

By considering the Watson factor of the bulk feed constant it is possible to calculate the specific gravity of each cut using the respective normal boiling temperature, T_b . Other interesting correlations for *SG* estimation can be found in Albahri (2012).

The carbon to hydrogen ratio, *CH*, is defined as the total weight of carbon atoms to the total weight of hydrogen atoms. It is evaluated by Riazi and Daubert (1986) using *SG* and T_b as in Eq.(5). This equation is valid in a C20-C50 range and has an absolute average deviation of 2%.

$$CH = 8.7743 \cdot 10^{-10} \left[\exp(7.176 \cdot 10^{-3} \cdot T_b + 30.06242 \cdot SG - 7.35 \cdot 10^{-3} \cdot T_b \cdot SG) \right] \cdot T_b^{-0.98445} \cdot SG^{-1.82753} \quad (5)$$

The sulfur, nitrogen and metals content can be given together with the distillation curves for each cut analyzed. Conversely, typical sulfur curves can be provided as function of aromatic content of cut given (PNA analysis) or as function of parameters used to correlate PNA as in Riazi et al. (1999). A typical nitrogen content curve relating the nitrogen content of crude to the content of its fractions as function of T_b is given in Baird (1981). These correlations on one hand avoid laboratory work on the other hand increase the error present in the elementary composition. This work considers a petroleum composed by hydrogen and carbon only.

It is important to stress that the molecular composition of fractions higher than C5 are unknown. Most simulation software use hypothetical/Pseudo-components to represent the real components. These hypothetical/Pseudo-components are calculated as function of distillation curves so that their bulk properties values represent the real components bulk values. The elementary composition can be evaluated for the whole cut or for each hypothetical/Pseudo components of a cut. In the latter approach the chemical exergy is calculated for each hypothetical/Pseudo component i and the chemical exergy of the whole cut can be calculated as in Rivero et al. (2004), by Eq.(6). The composition used to calculate the chemical exergy is usually correlated from T_b and SG such as in Eq. (5). Thus, the calculation of chemical exergy for each pseudo-component and for the whole stream using Eq.(6) is more accurate than the direct use of the whole stream composition, since T_b for each pseudo-components is obtained from a much smaller temperature range.

$$b_{\text{Chemical_Cut}} = \sum x_i b_{\text{Chemical } i}^{\text{Standard}} + RT_0 \sum x_i \ln x_i \gamma_i \quad (6)$$

The activity coefficient (γ) influence was evaluated by Rivero et al.(1999) using Scatchard-Hildebrand model. It was observed that the use of activity coefficient equals to 1 provides a negligible error of 0.0052% in chemical exergy.

4. PHYSICAL EXERGY CALCULATION

The physical exergy of a substance is defined as the maximum work that can be obtained from taking it to physical equilibrium with the environment. In order to achieve this physical equilibrium the substance is brought to the same temperature and pressure of the environment while the composition remains constant, as indicated in Eq.(7).

$$b_{\text{Physical}} = [h - h_0 - T_0(s - s_0)]_{\text{composition}} \quad (7)$$

The enthalpy and entropy of real substances, which are not well represented by ideal gas model, are calculated by using residual properties and departure functions and an adequate equation of state (EOS) or activity model. When several components are present proper mixing rules should be applied.

4.1 Physical exergy for crude oil and its fractions

Since the molecular composition is not known for crude oil and its fractions, the critical temperature (T_c) and pressure (P_c) have to be calculated using empirical correlations such as the API recommended Eq.(8) and Eq.(9), Riazi (2005). These equations are indicated for C5-C50 with a 0.4% and 5.8% absolute average deviation (AAD) respectively.

$$T_c = 35.9413 \cdot \left[\exp(-6.9 \cdot 10^{-4} \cdot T_b - 1.4442 \cdot SG + 4.91 \cdot 10^{-4} \cdot T_b \cdot SG) \right] \cdot T_b^{0.7293} \cdot SG^{1.2771} \quad (8)$$

$$P_c = 6.9575 \cdot \left[\exp(-1.35 \cdot 10^{-2} \cdot T_b - 0.3129 \cdot SG + 9.174 \cdot 10^{-3} \cdot T_b \cdot SG) \right] \cdot T_b^{0.6791} \cdot SG^{-0.6807} \quad (9)$$

The acentric factor (ω) can be calculated by Eq.(10), Lee and Kesler (1975), for C5-C20, and Eq.(11), Kesler and Lee (1976) for fraction higher than C20. In these two equations $T_{br} = T_b/T_c$. The parameters, T_c , P_c and ω allow the use of generalized EOS.

$$\omega = \frac{-\frac{\ln P_c}{1.01325} - 5.92714 + 6.09648 + 1.28862 \cdot \ln T_{br} - 0.169347 \cdot T_{br}^6}{15.2518 - \frac{15.6875}{T_{br}} - 13.4721 \cdot \ln T_{br} + 0.43577 \cdot T_{br}^6} \quad (10)$$

$$\omega = -7.904 + 0.1352K_w - 0.007465K_w^2 + 8.359T_{br} + \frac{1.408 - 0.01063K_w}{T_{br}} \quad (11)$$

Besides Lee-Kesler method, several other methods can be used to correlate the critical properties. Hemptinne and Béhar (2006) listed: Riazi (1998), Twu (1984), Cavett (1964) and Winn (1952). The estimation of acentric factor, critical temperature and pressure can be correlated using a cubic EOS coupled with group contribution such as in Avauillé et al. (2001).

5. EXERGY EFFICIENCY OF SEPARATION PROCESSES

The aim of a separation process is to obtain separated fractions of a given mixture. For this purpose the mixture is heated, cooled and or have its pressure reduced or increased in order to achieve an equilibrium state so that the mixture can be separated in its fractions. Thus, from an exergy analysis point of view the main product of a separation process considering mixture and its fractions in equilibrium is the increase achieved in chemical exergy due to the difference in the partial pressure of the components, i.e. the logarithmic term in Eq.(12).

$$b_{Chemical} = \sum_i x_i \cdot b_{Chemical_i}^{Standard} + RT_0 \sum_i x_i \cdot \ln \left(\gamma_i \cdot \frac{P_i}{P} \right) \quad (12)$$

This work proposes to evaluate four methodologies for the calculation of the exergy efficiency of separation processes. A case study of a vacuum distillation tower is used to illustrate the main advantage and disadvantage of each approach.

5.1 Exergy efficiency of separation processes 1

According to Kotas (1985) the exergy efficiency (rational efficiency) of a separation process is calculated as in Eq.(13). In this equation B_p is the exergy of the products, B_M is the exergy of the mixture and B_C is the exergy consumed for separation. The efficiency value given by Eq. (13) is usually smaller than 10% Kotas (1985).

$$\eta_b = \frac{\sum_i B_{Pi} - B_M}{B_C} \quad (13)$$

In real crude oil separation units the exergy of products and mixture (load) has a magnitude hundred times higher than the magnitude of consumed exergy. Thus, the efficiency provided by Eq.(13) can lead to incorrect results since the AAD presented for the used equations have the same magnitude of the consumed exergy, B_C , see Tab.1.

Table 1. Absolute average deviation (AAD) in used equations.

Equation	AAD	Author
(3)	0.38%	Kotas (1985)
(5)	2%	Riazi (2005)
(8)	0.4%	Riazi (2005)
(9)	5.8%	Riazi (2005)
LHV estimation	1.4%	Channiwala (2002)

5.2 Exergy efficiency of separation processes 2

Another alternative to perform the exergy calculation for the products and mixture is by direct using $H-T_0S$. This simplification is possible since the molecular composition of the mixture does not change during the physical separation process. Thus, products and mixture reference states can be canceled. See e.g. Fig.1, for a simplified separation process. Equation (14) shows the total (chemical and physical) exergy calculation by taking each molecular structure from its temperature and partial pressure to the components that the molecular structure will form in the reference environment in its temperature and partial pressure.

All the environment terms (*env.*) are canceled resulting in a difference of enthalpies and entropies of the in process molecules. These differences are due to temperature, pressure and composition differences between separation input and output. It is worth noting that if the output and input pressure and temperature are the same the only difference will be in concentration. Relative properties (enthalpy and entropy) can be used in Eq. (14) since for physical separation processes the reference is always canceled. By using Eq. (14) the efficiency of separation process can be given as in Eq.(15).

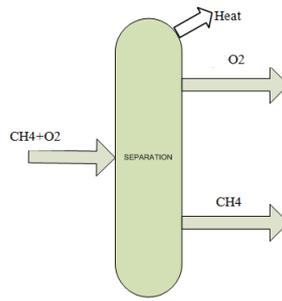


Figure 1. A simple separation process.

$$\sum_i B_{Pi} - B_M = \left[\left(H_{CH_4}^{out} + 2H_{O_2}^{env.} - H_{CO_2}^{env.} - 2H_{H_2O}^{env.} \right) + H_{O_2}^{out} - T_0 \cdot \left(S_{CH_4}^{out} + S_{O_2}^{env.} - S_{CO_2}^{env.} - 2S_{H_2O}^{env.} \right) - T_0 \cdot S_{O_2}^{out} \right]_P - \left[\left(H_{CH_4}^{in} + 2H_{O_2}^{env.} - H_{CO_2}^{env.} - 2H_{H_2O}^{env.} \right) + H_{O_2}^{in} - T_0 \cdot \left(S_{CH_4}^{in} + S_{O_2}^{env.} - S_{CO_2}^{env.} - 2S_{H_2O}^{env.} \right) - T_0 \cdot S_{O_2}^{in} \right]_M = H_{CH_4}^{out} - T_0 \cdot S_{CH_4}^{out} + H_{O_2}^{out} - T_0 \cdot S_{O_2}^{out} - \left[\left(H_{CH_4}^{in} - T_0 \cdot S_{CH_4}^{in} \right) + \left(H_{O_2}^{in} - T_0 \cdot S_{O_2}^{in} \right) \right] \quad (14)$$

$$n_b = \frac{\sum_i (H_{Pi} - T_0 \cdot S_{Pi}) - (H_M - T_0 \cdot S_M)}{B_C} \quad (15)$$

5.3 Exergy efficiency of separation processes 3

The exergy balance, Eq.(16), can be used to replace the products-mixture exergy difference for the difference between consumed (B_C) and destroyed exergies (B_D) providing Eq.(17). Note that the destroyed exergy can be calculated using Gouy-Stodola relation: $B_D = T_0 \cdot S_g$, that requires absolute entropies only. In Eq.(17) only entropy generation and the exergy of utilities (fuels, steam, electricity, heat, etc) consumed for separation are required. This approach avoids the huge magnitude difference of feed and products in relation to the consumed exergy.

$$\sum_i B_{Pi} - B_M = +B_C - B_D \quad (16)$$

$$\eta_b = 1 - \frac{B_D}{B_C} \quad (17)$$

5.4 Exergy efficiency of separation processes 4

In cases that the separation occurs by condensation, heat is removed from control volume and due to the lower temperature, the total exergy of the products are smaller than the total exergy of the mixture. It would provide a negative efficiency. Another cases may also provide negative efficiency values: heat removed from the products, very high pressure drop, etc. In these cases the exergy increment obtained by separation is overcome by the exergy destroyed by cooling and pressure drop. In these cases Eq.(18) should be applied. The information provided by Eq. (18) is different from the information provided by Eq.(13), Eq.(15) or Eq. (17). The former indicates the quantity of exergy destroyed in relation to total exergy input while the others provide the amount of consumed exergy used to enhance the load.

$$\eta_b = \frac{\sum B_{OUT}}{\sum B_{IN}} \quad (18)$$

6. CASE STUDY

The following example consist in a vacuum distillation of a heavy crude oil (16.5°API) used to separate the vacuum residue from lighter fractions so that these fractions can be easily transported. The True Boiling Point curve (TBP) for the crude and products can be seen in Fig.2. The BK10 EOS was used as indicated in Carlson (1996), for non-polar including pseudo and real components in vacuum.

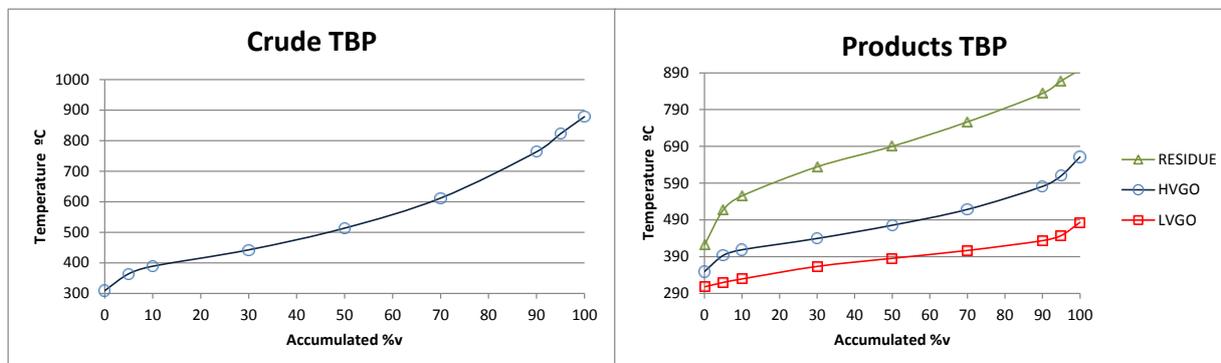


Figure 2. a) Crude oil TBP, b) Products TBP

The energy requirements of the vacuum tower shown in Fig. 3 can be seen in Tab.2. The minus (-) signal represents heat leaving the tower. The temperature in which heat gets into the tower is 434,85°C (stage temperature). Although the heat rejected by the pumparounds (PA1 e PA2) and cooler are at temperatures above environment, it is considered to be reject at environmental temperature (25 °C) once that its exergy is destroyed without any useful product been generated. It means that all the exergy present in these heat fluxes was destroyed due to entropy generation (external irreversibility).

Table 2. Vacuum tower energy requirements

Electricity Requirement	kW	Heat Requirement	kW
P1	0.48	PA1	-5,399.64 (@ 25°C)
P2	7.87	PA2	-23,446.08 (@ 25°C)
P3	29.55	Cooler	-6,554.39 (@ 25°C)
P4	23.70	Furnace	28,331.35 (@ 434,85°C)

Table 3. Vacuum tower basic thermodynamic properties

Stream	Description	m(kg/s)	T(K)	P(kPa)	h(kJ/kg)	h ₀ (kJ/kg)	s(kJ/kgK)	s ₀ (kJ/kgK)	b _{tot} (MJ/kg)	B(MW)	H-T ₀ S(MW)
1	Crude	60.64	610.41	14.00	-1,205.70	-1,953.90	3.93	2.06	45.81	2,777.60	-144.12
2	Steam	2.52	477.15	413.69	-13,083.00	-15,857.00	7.17	0.37	0.80	2.00	-38.36
3	Fuel	1.00	729.72	303.98	-859.24	-1,606.30	4.42	2.19	44.72	44.53	-2.17
4	Air	26.009	298.15	101.33	-0.28	-0.28	6.59	6.59	0.00	0.12	-51.10
5	Exh. gas	27.00	727.90	101.33	-1,081.10	-2,747.48	7.80	6.41	1.27	34.39	-91.97
6	Off-gas 1	2.52	338.71	8.00	-13,339.00	-15,962.00	1.87	1.62	2.63	6.64	-35.04
7	Off-gas 2	2.52	303.15	8.00	-15,939.00	-15,962.00	1.66	1.62	0.10	0.25	-41.43
8	Off-gas 3	2.52	302.99	158.00	-15,939.00	-15,962.00	1.65	1.62	0.10	0.25	-41.43
9	LVGO 1	8.46	409.35	8.27	-1,750.10	-1,968.20	2.43	1.77	46.80	396.06	-20.93
10	LVGO 2	8.46	406.30	616.22	-1,749.20	-1,968.20	2.41	1.77	46.81	396.12	-20.88
11	HVGO 1	29.17	576.33	8.80	-1,315.20	-1,955.10	3.50	1.96	46.23	1,348.47	-68.82
12	HVGO 2	29.17	576.05	616.75	-1,314.20	-1,955.10	3.50	1.96	46.23	1,348.50	-68.78
13	Residue 1	23.00	733.03	9.33	-860.27	-1,947.60	4.43	2.19	45.06	1,036.54	-50.20
14	Residue 2	23.00	729.63	617.28	-859.24	-1,947.60	4.42	2.19	45.06	1,036.67	-50.07

It is worth noting that the entropy and enthalpy at reference state (h_0 and s_0) shown in Tab. 3 were calculated using the same stream composition. The enthalpies provided by most of commercial software are the formation enthalpies, although the entropies are usually the relative ones. Thus, energy balance in reaction processes such as combustion, FCC, hydrotreatment, hydrogen generation, etc., can be accomplished while entropy balance cannot.

Table.3 also provides the total exergy, b_{tot} , obtained by summing physical, Eq.(7), and chemical, Eq.(6), exergies. The values of chemical exergy were calculated considering only hydrogen and carbon as in Eq.(5).

The exergy efficiency for the control volume delimited by the dashed line in Fig.3 using Eq.(13) is 11.49%. The value obtained by using Eq.(15) is 7.86%, by Eq.(17) is 7.50%, while the efficiency obtained by Eq.(18) is 98.45%. These values are summarized in Tab. 5. The heat exergy was calculated according to Eq.(19).

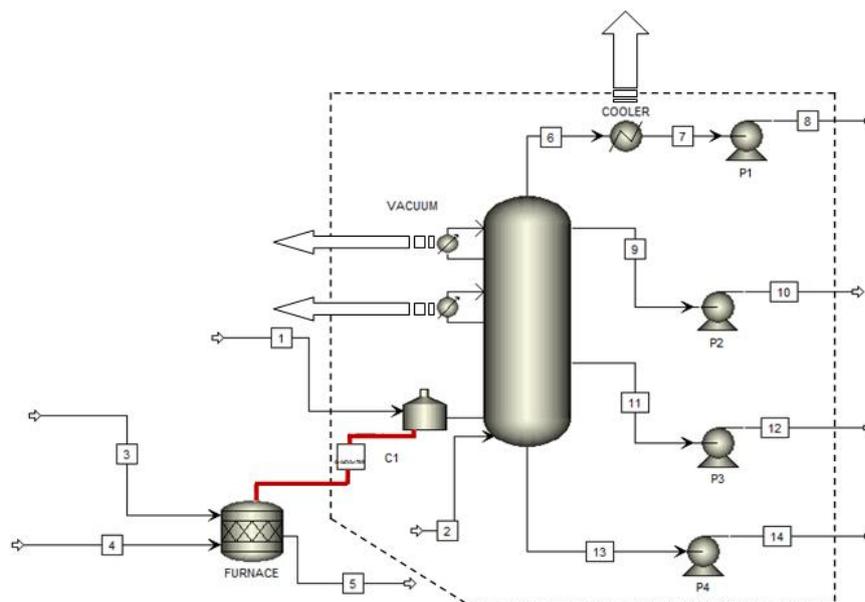


Figure 3. Crude oil vacuum distillation

$$B_{Q_{FURNANCE}} = Q \cdot \left(1 - \frac{T_0}{T_{In}} \right) \quad (19)$$

Table 5. Efficiency values and error sources

Equation/ Method	Value	Error sources
(13) method 1	11.49%	ϕ , LHV, h and s for all streams
(15) method 2	7.86%	h and s for hydrocarbons streams
(17) method 3	7.50%	s for all streams
(18) method 4	98.49%	ϕ , LHV, h and s for all streams

The method 3 is the most accurate method since it depends only on the absolute entropies of the substances. Note that as the used commercial software does not provide the absolute entropies, thus combustion process was taken out of control volume. The entropy variation due to mass input and output are calculated using relative entropies (the references are canceled) while the entropy due to heat exchange is calculated using the values in Tab.2 and $S = Q/T$.

The method 2 is also accurate but in addition to entropy it also depends on the enthalpies. This methods allows the use of relative entropies and enthalpies since, for separation processes, the reference is always canceled, see Eq.(14). Note that this method allows the inclusion of combustion process in the control volume. In this case instead of the heat exergy input a fuel exergy input should be used and the efficiency of the whole system would decrease strongly from 7.86% to 2.97% once that the combustion irreversibilities would be accounted.

The method 1 is the less accurate since it depends on ϕ , LHV, h and s for all streams. Besides it has these properties calculated for both: hydrocarbon streams and input heat, these streams have a huge magnitude difference. This method also allows the inclusion of combustion process into the control volume. In this case the efficiency would decrease from 11.49% to 4,34%.

The method 4 provides different information. Instead of quantify the consumed exergy transformed into products as in methods 1, 2 and 3, it provides an idea of the destroyed exergy in comparison with the whole exergy input, 98,49% means that only a small fraction of the total input exergy is destroyed.

7. CONCLUSION

Due to the magnitude difference between the feed and products in relation to the consumed exergy as well as to the unknown molecular structure of the involved streams the exergy and exergy efficiency calculation is a delicate topic that involves significant uncertainties. Several methods, depending on different properties, to calculated exergy efficiency were evaluated. The most accurate method is method 3 since it depends only on the entropies of the streams, and properly quantifies the function of a separation process. If the used software does not provide the values of absolute entropy all the reactions have to be performed outside the control volume such as in the given example. If in addition to

separation process the combustion process analysis is required method 2 is indicated instead. Method 1 is not indicated unless the molecular structure of the streams is well defined. For applications in which the exergy of the products are smaller than the exergy of the mixture method 4 should be applied, this last method however does not provide the information about the separation quality, been used as an indication of destroyed exergy only.

8. ACKNOWLEDGEMENTS

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