

An introduction to exergy and its evaluation using Aspen Plus

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## **Abstract**

The second law of thermodynamics describes how energy and entropy are configured in a system as well as how they are transferred through multiple systems. Exergy is a concept which is derived from the second law of thermodynamics. Exergy has been defined as “the ability to do work” or “the amount of work that can be extracted from a substance”. Due to the irreversibilities in real processes, exergy can be lost. Exergy can also be gained by receiving energy from other sources. The calculation of exergy and its losses is used in the analysis of industrial processes. Exergy analyses come in various methodologies and are used to optimize the economics and resource usage of a process or piece of equipment and to reduce its environmental impact. The use of exergy as an analysis tool has grown to a point where popular process modeling software includes it as a report option in process design models. The exergy analysis function of the modeling software Aspen Plus is demonstrated and discussed for an ethyl lactate process. Ethyl lactate is a monobasic ester that is being considered as a nontoxic replacement for petroleum-based solvents.

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# Chapter 1 - Introduction

This report will serve as an introduction to the concept of exergy for those who are familiar with thermodynamics but have not yet studied the concepts of exergy and energy availability. Exergy will be defined and the classifications of exergy in different forms of potential work will be highlighted. Example problems of exergy calculations and exergy loss calculations will be provided. Exergy analysis methods and their role in industry will be examined. The procedure for calculating exergy using Aspen Plus will be reported and exergy analyses using Aspen Plus will be demonstrated. After studying this paper, the reader will have gained a basic understanding of exergy and its usefulness in process analysis as well as the knowledge and skills to perform basic exergy analyses in Aspen Plus.

Industrial processes are essential for producing the goods and materials we use in life. These processes, however, use substantial amounts of energy and raw materials. Processes can be optimized with the aid of a strong understanding of the nature of the process. Part of this understanding is categorized as the field of thermodynamics. Thermodynamics explains how the energy of a system is a function of the configuration of parts that make up that system as well as the rules for changing that configuration. The first law of thermodynamics states that energy cannot be destroyed or created. The second law of thermodynamics, *“states that processes that occur spontaneously in one direction do not occur spontaneously in the opposite direction”* (Nevers, 2002, pg. 23). A property called entropy is a function of the second law of thermodynamics and is defined as *“the physical quantity that represents the capacity of distribution of energy over the energy levels of the individual constituent particles in the system”* (Sato, 2004, pg. 21). Entropy is useful in the analysis of processes because it takes into account the “direction” of the process as well as the energy changes. The four equations below define



entropy change in terms of irreversibility and reversibility as well as heat, work, and internal energy.

$$dS = dS_{rev} + dS_{irr} \quad (1)$$

$$dS_{rev} = \frac{dQ_{rev}}{T} \quad (2)$$

$$dS_{irr} = \frac{dQ_{irr}}{T} > 0 \quad (3)$$

$$\frac{dQ_{rev}}{T} = \frac{dU - dW_{rev}}{T} \quad (4)$$

(Sato, 2004, pg. 21-22)

$dS$  (J/K) is the change in entropy where the subscripts “rev” and “irr” refer to reversible and irreversible changes in the system respectively.  $dQ$  (J) is the amount of heat transferred into the system,  $dW$  (J) is the amount of work put into the system, and  $dU$  (J) is the change in the internal energy of the system. It is important to note that the observable properties of a system like volume, pressure, mass, and temperature are variables of the state which means that they only pertain to a system in that specific state or configuration (Sato, 2004, pg. 2). The thermodynamic functions, like entropy, which are calculated from these variables, are only concerned with the difference of the respective states and not how a change between the states was achieved.

Reversibility, irreversibility, and spontaneity are other concepts that are important to consider in the discussion of thermodynamics. Sato defines a system change as reversible if its variables proceed forward and backward at an infinitesimally small rate and both the system and surroundings remain in a state of quasi equilibrium. Reversible changes are ideal changes and are not found in nature although some processes very closely resemble an ideal change. All

changes in a process that are not reversible are termed irreversible and result in a dissipation of energy classified as either a creation of entropy or uncompensated heat (dissipated energy that can't be returned to its previous state) (Sato, 2004, pg. 21). Irreversible changes in the thermodynamic sense do not necessarily mean that the changes cannot be undone or reversed but that the reversal will require more energy than that which was obtained with the original change. This is represented in thermodynamic equations like equation (3) above with changes in entropy being required to be greater than zero. Some examples of irreversible work include stirring, friction, and heat transfer to a separate system, all which increase the system's entropy (Dincer, 2007, pg. 6-7).

Exergy is a quantity related to entropy and derived from the second law of thermodynamics. Exergy, simply put, is a concept that describes, quantitatively, how much energy can be put into useful work. A system can undergo a change that results in an energy state with more or less useful work potential than before. This change results in the loss or gain of opportunity to put energy into useful work, or, change of exergy. Calculations of a process's exergy change can be made to analyze the energy efficiency of ecosystems, industrial systems, thermo-economic systems, and the environmental impacts of a process. Environmental impact analysis is especially aided by exergy calculations since the equilibrium state to which exergy is ultimately lost is the environment surrounding the process. Exergy resembles humanity's intuitive perception of energy and its natural flow. The fact that energy is always conserved doesn't seem to be readily observed in real life. Electricity, gasoline, and natural gas are used up so that more must be purchased. Food must be consumed again and again or else an organism will expire. Hot chocolate left out on a table too long must be reheated. Ice cubes in a warm climate melt but never refreeze on their own. Calculations of exergy change mirror our

observations in real life as energy sources fall into equilibrium with their surroundings and require an additional energy input to reverse the change.

## Chapter 2 - Exergy Theory and Forms of Exergy

The term “exergy” and its official definition was coined in the 1950’s as a combination of the two words (erg) which means work and (ex-) meaning being released (Rant,1956). Before its introduction as a bona fide energy concept, exergy was considered in close relation with the affinity or free enthalpy change of an irreversible process (Sato, 2004, pg. 97). Authors tend to have cosmetic differences in their definitions of exergy. Sato calls exergy a new energy function which expresses “*the amount of available energy; its ability to be converted into other kinds of energy; and especially the capacity for doing work that we utilize with a given system of energy carriers in our normal environment on the earth*” (Sato, 2004, pg. 97). Another definition of exergy is “*the maximum amount of work obtainable when an energy carrier is brought from its initial state to a state of thermodynamic equilibrium (an inert state) with the common substances of the natural environment by means of reversible processes*” (Szargut, 1987). Another way of referring to exergy is by the name of thermodynamic availability (Seader, 2004, pg. 9S-15). If the process is made to proceed in the opposite of its spontaneous direction, exergy can then be considered the minimum amount of work required to bring a substance from its equilibrium state to the desired state.

Exergy is a state function and its maximum quantity is preserved so long as a reversible process is assumed. It defines the maximum amount of work that can be derived from a process when a substance goes from an initial energy state to a reference energy state. This reference energy state for physical exergy calculations is characterized by the values of “atmospheric” conditions (Querol, 2013, pg.10). This reference state is not arbitrary and is defined by the pressure and temperature the material will reach when it comes to a physical equilibrium with its surroundings. It is important then, when calculating exergy and its loss, to ensure the reference

state used is accurate since atmospheric conditions or the equilibrium state in the mountains of Alaska in December will be considerably different than the atmospheric conditions of the Texas Gulf Coast in August. It is important to note that there is another thermodynamic quantity called affinity which also defines the maximum amount of work energy can be transferred into. This quantity, however, requires that both initial and final states are determined for a specific instance whereas in the calculation of exergy, the final state is determined by the conditions of the surrounding environment (Sato, 2004, pg.98).

An important concept has been noted in the definitions and explanations of exergy with respect to the irreversibility or spontaneity of a process. Energy, as stated in the 1<sup>st</sup> law of thermodynamics, is always conserved but exergy, being bound by the second law of thermodynamics, can be lost or destroyed. These losses come by means of unintended energy transfer to non-targeted energy reservoirs both outside and inside the process bounds. Gundersen explains... *“Internal losses (“destruction”) are caused by irreversibilities in the process (heat transfer at  $T > 0$ , chemical reaction, mixing, unrestricted expansion, etc.); while external losses (“leakage”) are caused by exergy content in effluent streams that are not utilized (exhaust gases, purge and bleed streams, cooling water, etc.)”* (Gundersen, 2011, pg.19)

Spontaneity, as explained by Sato, is *“Any spontaneous change of substances that occurs in the natural environment advances with a decrease in exergy of the substances: this is the law of exergy decrease in spontaneous processes in analogy to the law of affinity decrease in spontaneous processes. In contrast to energy which is always conserved in any processes due to the first law of thermodynamics, exergy is exempt from the law of conservation and so is the affinity.”* (Sato, 2004, pg.99)

The exergy of a substance can generally be divided into two parts: physical/mechanical exergy and chemical exergy, with mixing exergy sometimes considered a part of either exergy division or its own exergy quantity. The physical part of exergy is comprised of a multitude of classifications including temperature, pressure, kinetic, and potential exergies. The chemical division is only chemical with the mixing and separation exergies sometimes included.

<b>Exergy</b>					
Mechanical/Physical				Chemical	
General Physical Exergy	Heat	Pressure	Electricity and Work	Mixing/Separation	Reaction

**Table 1- Classification of some exergy forms (Gunderson, 2011, pg. 8)**

Exergy is represented by different variables depending on its form and the respective author. ( $\beta$ ) often represents the specific exergy function while (B) represents the total exergy function. Sometimes exergy is expressed with the variable (A) meaning energy availability while the majority of literature and this report will represent exergy with (Ex). When assumptions are made so that exergy is only related to temperature and pressure, then exergy is a function of enthalpy, temperature, and entropy.

$$\Delta Ex = \Delta H - T_0 \Delta S \quad (5)$$

(Gunderson, 2011, pg. 8)

This equation bears a resemblance to the classic equations for Gibbs free energy or Helmholtz free energy.

$$G = H - T^*S \quad (6)$$

$$F = U - T^*S \quad (7)$$

(Sato, 2004, pg. 26)

This resemblance makes sense since these two variables represent the thermodynamic potential of a system or the amount of energy that is free from entropy restrictions and therefore able to be utilized (Sato, 2004, pg. 26). Gibbs energy, however, represents thermodynamic potential when isothermal and isobaric conditions are assumed while Helmholtz energy assumes isothermal and isometric conditions. Exergy calculations, on the other hand, forgo isobaric and isothermal assumptions to find the amount of available work between two thermodynamic states.

### **General Physical Exergy**

Physical Exergy is a function of enthalpy and entropy differences measured between an initial and final state.

$$Ex_{ph} = [h(T, P) - h(T_0, P_0)] - T_0 [S(T, P) - S(T_0, P_0)] \quad (8)$$

(Querol, 2013, pg.9)

This is the equation for the calculation of physical exergy where  $Ex_{ph}$  (J) transport per unit mass of flow where  $h, H$  (J) is the enthalpy,  $S$  (J/K) is entropy,  $P$  (Pa) is pressure,  $T$  (K) is temperature while  $h_0, T_0, P_0$  and  $S_0$  refer to those values at environmental or equilibrium conditions. As seen in the equation above, exergy change, like Gibbs free energy or Helmholtz energy, is a function of entropy. An increase in the entropy of a substance through a process causes a loss of the

available work that can be obtained from the products of that process. Entropy is the enemy of exergy and will always win due the irreversibilities of reality. Equation (8) is often used in simulation software where libraries of the entropy and enthalpy of chemicals are used to calculate the entropy and enthalpy of the process streams. Since physical exergy is a function of enthalpy and entropy it can also be calculated from the process streams. Exergy is a state function and thus any type of energy transfer that resulted in that particular state of enthalpy and entropy has already been accounted for. This is helpful when some energy forms like potential energy, kinetic energy, energy loss by friction, etc., may be hard to account for since exergy will be calculated from the beginning and final states.

### **Exergy of Heat**

Heat is one of the most familiar forms of energy that humans experience. While it is necessary for biological functions and chemical reactions, heat transfer also functions as a double edged sword since heat transfer is also one of the most consequential ways that exergy is lost or wasted. Heat exergy of a system is also called the “energy quality of heat” (Gunderson, 2011, pg. 21).

$$E_{x,heat} = Q(1 - \frac{T_0}{T}) \quad (9)$$

(Gunderson, 2011, pg. 20)

Q (J) is the heat produced or used, T (K) represents the starting temperature while  $T_0$  represents the environmental temperature. The exergy efficiency of the process can be calculated to analyze its usefulness. Heat can be divided into two parts. One part represents heat that is able



to be used for work and the other part represents heat that cannot be used for work or is wasted. This wasted heat is called “Anergy” and is defined as “*the difference in amount between energy and exergy*” (Gunderson, 2011, pg. 66), (Sato, 2004, pg. 99).

## **Exergy of Pressure**

Gas at a lower or higher pressure than that of the atmosphere has some amount of exergy. The pressure difference allows work to be done, usually in the form of an expanding volume. The exergy can be calculated as a function of pressure or even entropy assuming the vapor is an ideal gas and the change is isothermal.

$$Ex = nRT_0 \ln \left( \frac{p}{p_0} \right) = -T_0 n(s - s_0) \quad (10)$$

(Sato, 2004, pg. 101)

In this equation n represents the number of moles of gas, p (kPa) and p<sub>0</sub> represent the starting pressure and atmospheric pressure respectively, R (J/mol\*K) represents the universal gas constant, s and s<sub>0</sub> represent the entropy of the substance at the two respective pressures, and T<sub>0</sub> represents the atmospheric temperature at which the expansion occurs.

## **Exergy of Work**

Exergy is defined as the maximum work potential so that the exergy in a process is the same as the work (J) available from that process where work is represented by W.

$$E_x = -W \quad (11)$$

(Querol, 2016, pg. 26)

## Exergy of Electricity

Electricity as an energy carrier is often as close to an ideal situation as you can get.

Electricity can be transformed into multiple types of work with minimal losses in its transportation and is virtually equivalent to the energy content of work (Querol, 2016, pg. 26).

$W_e$  is electrical work.

$$E_x = -W_e \quad (12)$$

(Querol, 2016, pg. 26)

## Exergy of Mixing

Even everyday actions that seem normal can result in a loss of exergy. Mixing with no reaction, for example, results in a decrease of exergy compared to unmixed components. The exergy of mixing ideal gasses is calculated with the same equation as the exergy calculation of perfect solutions at atmospheric conditions.

$$E_{x,mixing} = \sum_i x_i T_0 R \ln(x_i) \quad (13)$$

(Sato, 2004, pg. 105)

$x_i$  is the molar fraction of the species,  $T_0$  (K) is the atmospheric temperature, and  $R$  (J/mol\*K) is the universal gas constant. The enthalpy of mixing  $h^m$  (J) is added when the mixture is not a perfect solution or ideal.

$$E_{x,mixing(non\ ideal)} = h^m + \sum_i x_i T_0 R \ln(x_i) \quad (14)$$

(Sato, 2004, pg. 105)

## Exergy of Reaction

The chemical exergy calculation is a little more complex than that of physical exergy.

Since the nature of reactions can cause the products of a process to vary depending on the conditions the reaction is subjected to there is a need to know how the reaction will terminate in order to calculate the process's exergy. Some examples of possible variations for atmospheric reference states include  $\text{O}_2$  vs  $\text{O}$ ,  $\text{Cl}^-_{(\text{aq})}$  vs  $\text{Cl}$ , and  $\text{SiO}_2$  vs  $\text{Si}$  (Dewulf, 2008, pg. 2222).

Chemical exergy is the maximum useful energy theoretically obtained by a chemical process which turns reactants to products that are in chemical equilibrium with the environment (Querol, 2013, pg. 19). It is important to note that chemical exergy applies only to the chemical process and not to the temperature or pressures surrounding the reactants and products. The physical exergy must be calculated separately or in concert with the chemical exergy but is not a part of the chemical exergy. Since there is no single equilibrium state for chemicals the final state must be determined. Thermodynamic literature generally considers chemical exergy in reference to compositions found in atmospheric air, seawater, and lithospheric solids (Sato, 2004, pg. 107). Oxygen and nitrogen, for example, are found in the atmosphere in their  $\text{O}_2$  and  $\text{N}_2$  forms, so any oxygen and nitrogen gasses freed in a chemical reaction would eventually reach their equilibrium state in the diatomic form as well. In terms of mixing exergy, atmospheric air has a composition of 21%  $\text{O}_2$  gas and 78%  $\text{N}_2$  gas. A mixture of gasses destined for the atmospheric state would have its exergy calculated by its composition in comparison with the atmospheric composition. A table of some common reference enthalpies and exergies is listed below.

Species	Specific Base Enthalpy (kJ/g-mol)	Specific Chemical Exergy (kJ/g-mol)
Ammonia (NH <sub>3</sub> )	382.585	2.478907 lny+337.861
Carbon/Graphite (C)	393.505	410.535
Carbon dioxide (CO <sub>2</sub> )	0.000	2.478907 lny+20.108
Carbon monoxide (CO)	282.964	2.478907 lny+275.224
Ethane (C <sub>2</sub> H <sub>6</sub> )	1564.080	2.478907 lny+1484.952
Hydrogen (H <sub>2</sub> )	285.851	2.478907 lny+235.153
Methane (CH <sub>4</sub> )	890.359	2.478907 lny+830.212
Nitrogen (N <sub>2</sub> )	0.000	2.478907 lny+0.693
Oxygen (O <sub>2</sub> )	0.000	2.478907 lny+3.948
Sulfur (rhombic) (S)	636.052	608.967
Sulfur dioxide (SO <sub>2</sub> )	339.155	2.478907 lny+295.736
Water (H <sub>2</sub> O)	44.001	2.478907 lny+8.595

**Table 2- Base enthalpy and chemical exergy values of selected species where y represents the mole fraction of the species. (Dincer, 2007, pg. 33)**

The chemical exergy of one substance in a mixture can be expressed with the standard molar chemical exergy given by

$$\varepsilon_i^0 = -RT_0 \ln(x_{i,0}) \quad (15)$$

(Sato, 2004, pg. 107)

where  $\varepsilon_i^0$  represents the standard molar chemical exergy of a pure species i at unit activity, R (J/mol\*K) is the universal gas constant, T<sub>0</sub> (K) is the mixture temperature, and x<sub>i,0</sub> is the molar

fraction of the species in the mixture. This equation is only valid when a chemical is in its equilibrium state and is said to be at its unit activity (unit fugacity or unit atmospheric pressure) (Sato, 2004, pg. 107). With the standard molar equilibrium at the environmental reference state, one can also calculate the chemical exergy of a component in a mixture at that state. The partial molar chemical exergy of a particular substance in a mixture can then be calculated.

$$\varepsilon_{chem,i} = \varepsilon_i^0 + RT_0 \ln(a_i) \quad (16)$$

(Sato, 2004, pg. 108)

$a_i$  is the activity of the specific species in the mixture. The exergy of the mixture at standard temperature and pressure is then found as a sum of the partial molar chemical exergy parts.

$$E_{mix} = \sum_i n_i \varepsilon_{chem,i} = \sum_i n_i \varepsilon_i^0 + RT_0 \sum_i n_i \ln(a_i) \quad (17)$$

(Sato, 2004, pg. 108)

The equation can be simplified for ideal gas and liquid mixtures.

$$E_{mix} = \sum_i x_i \varepsilon_{chem,i} = \sum_i x_i \varepsilon_i^0 + RT_0 \sum_i x_i \ln(x_i) \quad (18)$$

(Querol, 2013, pg. 23)

$x_i$  is the molar fraction of each particular species in the mixture. For a reaction where the final state is not the standard atmospheric conditions of the region, the change in exergy is equal to the affinity of the reaction.

$$\Delta E_{chem,T,p} = E_{react,T,p} - E_{prod,T,p} = A \quad (7)$$

(Sato, 2004, pg. 109)

Chemical exergy can also be expressed in terms of chemical potential ( $\mu$ ).

$$E_{chem} = \sum_i (x_i \mu_0) - \sum_i (x_i \mu) \quad (20)$$

(A.B.K., 1994, pg. 15)

Finally, the physical part of exergy is added to account for changes in temperature, pressure, and concentration so that a general expression for chemical reaction exergy is obtained.

$$\Delta E_{chem,T,p} = \Delta E_{chem,T^0,p^0}^0 + \Delta E_{phy} = A^0 + \Delta E_{phy} \quad (21)$$

(Sato, 2004, pg. 109)

$\Delta E_{rxn,T,p}$  is the exergy change for a chemical reaction that takes place at conditions other than standard state,  $\Delta E_{chem,T^0,p^0}^0$  is the exergy change or affinity at atmospheric temperature and pressure due to the chemical reaction, and  $\Delta E_{phy}$  is the exergy change due to the physical changes of the reaction like temperature and pressure changes.

If appropriate, the physical exergy equation can be expanded by adding kinetic and gravitational exergy forms. In the equation below  $V$  is the initial state velocity while  $V_0$  (m/s) is the velocity of the material at the reference state. The gravitational constant is represented by  $g$  ( $m^3/(kg*s)$ ), while  $z$  and  $z_0$  (m) is the initial state elevation and reference state elevation respectively.

$$\dots + \left( \frac{(V - V_0)^2}{2} \right) + g(z - z_0) \quad (22)$$

(Hermann, 2006)

Since exergy represents the work potential of energy, any form of energy can also be expressed as exergy as long as that energy can be turned into usefull work. The figure below lists some exergy forms along with their exergy value compared to energy or their method of calculation.

resource	exergy value or calculation method
	$\beta$ in $\text{kJ}_{\text{exergy}}/\text{kJ}_{\text{energy}}$
potential energy	$\beta = 1$
kinetic energy	$\beta = 1$
physical energy	$\text{Ex} = (h - T_0s) - (h_0 - T_0s_0)$
chemical energy	$\beta = \sim 0.8 \text{ to } 1.0$ , depending on composition
heat at temperature $T$	$\beta = 1 - T_0/T^a$
pressure of an ideal gas at $T_0$	$\text{Ex} = nRT_0 \ln (P/P_0)$
solar irradiation (whole spectrum)	$\beta = 0.9327$
nuclear energy	$\beta \approx 1$
electricity	$\beta = 1$
radiation	$\beta = 1 + (1/3)(T_0/T)^4 - (4/3)(T_0/T)$
<sup>a</sup> Note that when $T < T_0$ , $\beta$ is negative. This is because the resulting exergy flow is in the opposite direction of the energy flow.	

**Figure 1- Summary of exergy calculations for different kinds of resources, where  $\beta$  is the exergy to energy ratio (Dewulf, 2008)**

## Chapter 3 - Examples of Exergy and Exergy Loss Calculations

### Exergy of an Ideal Gas Expansion

Gunderson uses two scenarios of ideal gas expansion to show how different exergy calculations can be made (Gunderson, 2011). In both of these scenarios an ideal gas will be expanded in a reversible process. In scenario one both the inlet and outlet gas temperature is above that of the environment/equilibrium state temperature. In scenario two the inlet gas temperature is lower than that of the equilibrium state. These expansions will result in an exergy change between the initial and final states. Since exergy is independent of path, the two states can be split into two more states each where pressure and then temperature is held constant while the exergy change of the other is calculated. To do this an ideal gas and isentropic expansion are assumed so that the outlet temperature can be calculated from the inlet temperature and pressure ratio.

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}} \quad (23)$$

Scenario 1		Variable	Scenario 2	
State 1	Equilibrium State		State 1	Equilibrium State
In=523 Out=330.2	298	Temperature (K)	In=223 Out=330.2	298
5	1	Pressure (bar)	5	1
1	1	Specific Heat (kJ/kg*K)	1	1
.287	.287	R (kJ/kg*K)	.287	.287
1.4	1.4	k (c <sub>p</sub> /c <sub>v</sub> )	1.4	1.4

**Table 3- Variables used for the calculation of ideal gas expansion exergy between two states**



Exergy change resulting from the change in pressure can be calculated from the general physical exergy equation with some assumptions made to simplify it. First, the exergy equation is split into two equations, one in which temperature is held constant and one in which pressure is held constant. Exergy can then be calculated at each state.

$$Ex_{ph} = [h(T, P) - h(T_0, P_0)] - T_0 [S(T, P) - S(T_0, P_0)] \quad (8)$$

becomes

$$Ex_{temp} = [h(T, P) - h(T_0, P)] - T_0 [S(T, P) - S(T_0, P)]$$

$$Ex_{press} = [h(T_0, P) - h(T_0, P_0)] - T_0 [S(T_0, P) - S(T_0, P_0)]$$

For an ideal gas, enthalpy is a function of temperature while entropy is a function of temperature and pressure. Constant specific heat capacity is assumed for simplicity.

$$h - h_0 = C_p(T - T_0) \quad (24)$$

$$s - s_0 = C_p \ln \frac{T}{T_0} - R \ln \frac{P}{P_0} \quad (25)$$

These assumptions allow the following expressions to be derived for exergy.

$$Ex_{pres} = RT_0 \ln \left( \frac{P}{P_0} \right) \quad (26)$$

$$Ex_{temp} = c_p [T - T_0 (1 + \ln \left( \frac{T}{T_0} \right))]$$

**Scenario 1****Initial Gas Exergy**

$$Ex_{pres} = 298 \left( .287 * \ln \left( \frac{5}{1} \right) \right) = 137.65 \text{ kJ/kg} \quad (27)$$

$$Ex_{temp} = 1 * [523 - 298 * (1 + \ln \left( \frac{523}{298} \right))] = 57.38 \text{ kJ/kg}$$

**Final Gas Exergy**

$$Ex_{pres} = 298 \left( .287 * \ln \left( \frac{1}{1} \right) \right) = 0 \text{ kJ/kg} \quad (28)$$

$$Ex_{temp} = 1 * [330.2 - 298 * (1 + \ln \left( \frac{330.2}{298} \right))] = 1.62 \text{ kJ/kg}$$

The total work produced by the expander is equal to the amount of exergy lost to it.  $\dot{W}$  (kJ/time) represents work flow while  $\dot{m}$  (kg/time) represents mass flow.

$$\frac{\dot{W}}{\dot{m}} = -\Delta Ex_{Temp} - \Delta Ex_{press} = -(1.62 - 57.38) - (0 - 137.65) \quad (29)$$

$$= 55.76_{Temp} + 137.65_{press}$$

$$\underline{= 193.41 \text{ kJ/kg}} \text{ (maximum ideal work produced by the expander)}$$

## **Scenario 2**

### **Initial Gas Exergy**

$$Ex_{pres} = 298 \left( .287 * \ln \left( \frac{5}{1} \right) \right) = 137.65 \text{ kJ/kg} \quad (30)$$

$$Ex_{temp} = 1 * [223 - 298 * (1 + \ln \left( \frac{223}{298} \right))] = 11.40 \text{ kJ/kg}$$

### **Final Gas Exergy**

$$Ex_{pres} = 298 \left( .287 * \ln \left( \frac{1}{1} \right) \right) = 0 \text{ kJ/kg} \quad (31)$$

$$Ex_{temp} = 1 * [140.8 - 298 * (1 + \ln \left( \frac{140.8}{298} \right))] = 66.23 \text{ kJ/kg}$$

$$\frac{\dot{W}}{\dot{m}} = -\Delta Ex_{Temp} - \Delta Ex_{Press} = -(66.23 - 11.4) - (0 - 137.65) \quad (32)$$

$$= 54.83_{Temp} - 137.65_{Press}$$

$$= \underline{82.52 \text{ kJ/kg}} \text{ (maximum ideal work produced by the expander)}$$

It is seen that 193.41 kJ/kg of work is done by the expander when the initial temperature of the gas is above ambient but only 82.52 kJ/kg of work is done when the initial gas temperature is below ambient. In the first scenario the expander produces 55.76 kJ/kg of temperature-based exergy from the temperature change. The second scenario, however, sees temperature-based exergy being lost in the expander as the temperature grows closer to ambient conditions. The ideal nature of these scenarios assumes, of course, that all the work produced can be captured and used. A real example of an above ambient temperature expander is a turbine. Pressurized sub-ambient gasses can be used to produce extra cooling by expanding the gas streams for cooling and power.

## Calculation of Heat Exchanger Exergy

The total change in exergy for a heat exchanger can be solved from the general equation by considering the exergy for each stream individually and then solving the exergy balance across the exchanger. For this example, the pressure will be constant at atmospheric conditions. No phase change will occur in the fluid which consists of water in both hot and cold streams. Specific heats capacities are also assumed to be constant.

$$Ex_{ph} = [h(T, P) - h(T_0, p_0)] - T_0 [S(T, P) - S(T_0, P_0)] \quad (33)$$

(Querol, 2013, pg.9)

Solving for the exergy of a stream using the general equation requires the enthalpy and exergy of the material to be known for each combination of pressure and temperature as well as the environmental pressure and temperature. Process simulators like Aspen Plus also use this approach.

Stream	Pressure (Mpa)	Temperature (K)	Enthalpy (kJ/kg)	Entropy (kJ/kg*K)
Atmospheric	0.101325	298	104.29	0.3651
1 (Cold In)	0.101325	303	125.2	0.43466
2 (Cold Out)	0.101325	306	137.73	0.47584
3 (Hot In)	0.101325	323	208.79	0.70183
4 (Hot Out)	0.101325	318	187.89	0.6366

**Table 4- Water enthalpy and entropy values for the respective pressure and temperature  
(NIST, 2018)**

$$Ex_{Stream1} = [125.2 - 104.29] - 298 [.43466 - .3651] = 0.18112 \text{ (kJ/kg)} \quad (34)$$

$$Ex_{Stream2} = [137.73 - 104.29] - 298 [.47584 - .3651] = 0.43948 \text{ (kJ/kg)}$$

$$Ex_{Stream3} = [208.79 - 104.29] - 298 [.70183 - .3651] = 4.15446 \text{ (kJ/kg)}$$

$$Ex_{Stream4} = [187.89 - 104.29] - 298 [.6366 - .3651] = 2.693 \text{ (kJ/kg)}$$

The exergy change in the cold streams can be found by subtracting the outgoing cold stream exergy from the incoming cold stream exergy. The exergy change in the hot stream can be found by the same method.

$$\Delta_{Exergy\ Cold} = Ex_2 - Ex_1 = 0.43948 - 0.18112 = 0.25836 \text{ kJ/kg}$$

$$\Delta_{Exergy\ Hot} = Ex_4 - Ex_3 = 2.693 - 4.15446 = -1.46146 \text{ kJ/kg}$$

The exergy change in the cold stream represents the total amount of exergy per kg that the cold stream has obtained from the hot stream through the heat exchanger. The exergy change in the hot stream shows the amount of exergy that has been taken from the hot stream and either transferred to the cold stream or destroyed. If exergy was conserved in the same manner as energy, then the exergy change would be represented by an ideal heat transfer and the amount of exergy lost from the hot stream would equal the amount of exergy gained by the cold stream. Exergy, however, is not conserved; and, the amount of exergy lost or destroyed on a mass basis across the exchanger can be found by adding the respective changes in exergy.

$$\begin{aligned} \Delta_{Exergy\ Exchanger} &= \Delta_{Exergy\ Hot} + \Delta_{Exergy\ Cold} = 0.25836 - 1.46146 \\ &= \underline{\underline{-1.2031 \text{ kJ/kg}}} \end{aligned}$$

## Chapter 4 - Exergy Analysis Methods

Exergy is a useful tool when combined with other methods to analyze an industrial process or plant. Some benefits of including an exergy analysis in design evaluation or continuous improvement efforts are that exergy losses represent true losses of potential to generate the desired product. An exergy analysis allows you to compare how close a process comes to the ideal or theoretical state (Dincer, 2007, pg. 33).

At its most basic level exergy loss can be calculated and compared for different process alterations or equipment changes to find a design which minimizes the amount of available work lost. Exergy efficiency ( $\eta_{Ex}$ ) calculations are the next step for comparing how well potential work is conserved. After the change in exergy calculation is made, the exergy difference can be broken down into lost exergy and destroyed exergy if desired. Exergy loss often refers to waste or byproduct streams where exergy is not included in the product but is recoverable in principle while exergy destruction refers to an irrecoverable loss (Rocco, 2014). Heat released to the atmosphere from a piece of equipment, for example, might be considered destroyed exergy since there is no way to make use of it but a heated waste water stream directed to a holding pond might be considered lost exergy since it could theoretically be used to heat another part of the process.

$$\eta_{Ex} = \frac{Exergy\ Out}{Exergy\ In} = 1 - \frac{Exergy\ Lost + Exergy\ Destroyed}{Exergy\ In\ (ex.\ Fuel)} \quad (35)$$

(Gunderson, 2011, pg. 66; Rocco, 2014)

Exergy efficiency is a measure of the exergy lost or destroyed in irreversible processes. In industry exergy loss and destruction is usually calculated across a single piece of equipment or a small part of the production process. This exergy loss and destruction can be used to compare

pieces of equipment for operational efficiency, equipment cost of operations, and environmental analyses for things like waste heat (Dewulf, 2008). Figure (2) highlights some typical percentages of exergy loss and destruction found in common plant equipment.

<b>description</b>	<b>type</b>	<b>exergy destruction or exergy unrecovered in % of the fuel exergy</b>
steam generator combustion	destruction	30
steam generator heat transfer	destruction	30
turbine	destruction	3
condenser	destruction	5
pump	destruction	negligible
stack gas	loss	3
cooling water	loss	2

**Figure 2- Common exergy destruction and loss in a steam power plant (Dewulf, 2008)**

There is general agreement that exergy analysis is most effective when performed at the equipment level rather than over an entire production unit or plant. Exergy can be assigned a cost but since overall cost is comprised of multiple factors, such as construction expense, exergy sometimes only makes up a small part. Instead, exergy must be considered amongst other factors.

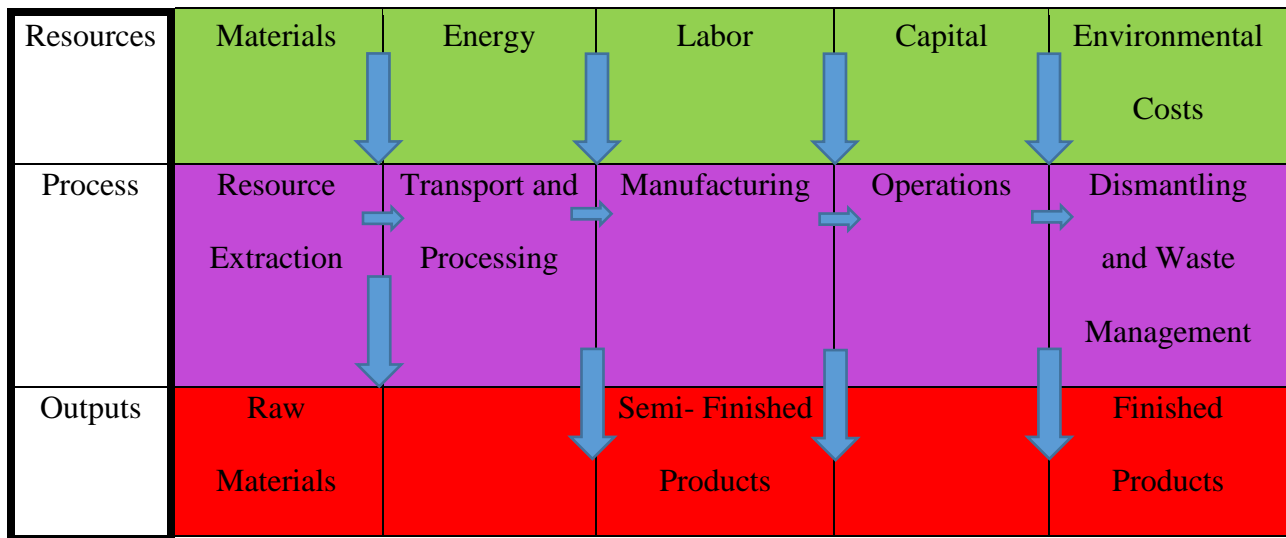
Dincer gives some guidelines for energy and exergy analyses (Dincer, 2007, pg. 33).

- Subdivide the process under consideration into workable sections
- Perform conventional mass and energy balances to find all pertinent quantities like work, temperature, and pressure.
- Decide what the environmental equilibrium/reference state will be for each section.
- Evaluate the energy and exergy values relative to the reference state.

- Select efficiency definitions and evaluate efficiencies.
- Review the results and make appropriate changes to better the energy efficiency, reliability, and economics of the process.

How one approaches the exergy analysis often depends on the primary goal of the analysis.

A monetary analysis will have a different focus due to circumstances such as capital investment than an environmental analysis. Traditional methods based their analysis on the steady-state operation of a process but failed to provide acceptable results when applied to unusual conditions like start up and shutdowns. The most rigorous exergy analysis will cover the entire lifecycle of a product/process and encompasses everything from the raw materials to the waste streams of the product. The majority of industrial analyses, however, focus on the operations phase of the process. The lifecycle analysis of a process using exergy has evolved through several iterations but is most commonly known as an exergetic life cycle assessment or ELCA (Rocco, 2014).



**Table 5- Product lifecycle map with resources and materials**

(Rocco, 2014)

One of the challenges of a life cycle analysis is expressing all inputs and outputs in the same terms. The final product cost is given by the sum of the cost of fuels, materials, energy,



operating costs, and a share of the construction and decommission phases. To express all these costs in a single format, thermoeconomics or the thermoeconomic cost theory was developed. Thermoeconomics combines second law principles with traditional cost accounting methods to express costs in terms of exergy. This is used to find the best tradeoff between capital and operating costs to minimize the economic cost of the product. There are, however, some drawbacks to this method including volatility in market considerations and resources as well as inaccuracies in environmental accounting (Rocco, 2014).

The Cumulative Exergy Consumption (CExC) and “Exergy Costing” methods were developed to address these inconsistencies so that the process could evaluate the resources, environmental impact, and energy use in the common form of exergy. All these methods were combined to form the ELCA methodology. This methodology does not, however, include monetary accounting. A comprehensive methodology called “Extended Exergy Accounting” applies the cost of the exergy related to each part of the process as part of the analysis so that both money and resources are considered (Rocco, 2014).

Fortunately, process modeling software like Aspen Plus has developed functions that calculate exergy along with their models that calculate costs, duties, and other plant functions. These features give modelers some capacity to perform a simple exergy analysis without the need for additional software or a great amount of extra time and manpower. It is important to state that Aspen Plus’s current exergy calculations are limited only to those which are a function of enthalpy and exergy of the process stream. All other types of exergy, such as chemical exergy, are not included. While this fact may render the tool a little more limited, it is also understandable given that final environmental chemical state of the main product and waste product may very well likely be several processing steps outside the industrial unit in question.

This additional functionality, however, would be very useful. Recycling waste and by-products so that they can be used as raw materials could also render a chemical exergy calculation useless since the starting and final states would be identical so that the atmospheric state would never be reached. An example of this would be a salt process where components are split and reunited again for electrolysis. Additional exergy functionality in modeling programs would need to include atmospheric states for all forms of exergy addressed in the process.

For those that need a rigorous analysis including all forms of exergy, customization of a process modeler can be performed. Querol and his team develop a VBA program which makes use of Aspen's libraries, user input, and user equations to calculate all forms of exergy.






Total Exergy	$Ex_{Total} = Ex_{Chemical} + Ex_{Physical}$
Physical Exergy	$Ex_{Physical} = h - h_0 - T_0(s - s_0)$
Component Chemical Exergy	$Ex_{Chemical}(X) = \sum n_i Ex_{Physical}(elements) + g_{formation}(X)$
Stream Chemical Exergy	$Ex_{Chemical} = \sum x_i Ex_{Chemical}$
Heat Exergy	$Ex_{heat} = \left(1 - \frac{T_0}{T}\right) \dot{Q}$

**Table 6- Exergy equations used in Querol ECLA VBA program**

After the exergies are calculated, the program will then use fixed cost and thermoeconomic costs entered by the user along with calculated exergies to prepare results and summaries of unit costs and resource use (Querol, 2013).

Abdollahi used the features of Aspen HYSYS to create user customized calculations in the modeling program rather than bringing them into a separate Excel sheet. This combines the

useful of Aspen's libraries and its customizability. A sample of the stream calculation process is given in Table 7 where exergy calculations on the right are made from two process condition states on the left. The exergy results are then totaled and evaluated. Aspen Plus's exergy calculator only calculates physical exergy.

Stream Conditions at (T,P)		
Stream at reference conditions (T <sub>0</sub> ,P <sub>0</sub> )		Physical Exergy
Ideal pure substances contained in the stream at (T <sub>0</sub> ,P <sub>0</sub> )		Chemical Exergy Phase 1
Ideal pure atmospheric species formed by a reaction for ideal pure substances in the stream at (T <sub>0</sub> ,P <sub>0</sub> )		Chemical Exergy Phase 2
Ideal pure atmospheric species at (T <sub>0</sub> , conventional partial pressure)		Chemical Exergy Phase 3
Ideal pure atmospheric species at (T <sub>0</sub> , real partial pressure)		Chemical Exergy Phase 4
		Total Stream Exergy=Σ(Physical Exergy, Chemical Exergy)

**Table 7- Aspen HYSYS exergy calculations sample procedure**

(Abdollahi, 2011)

Exergy can also be used when performing an analysis with environmental considerations. Hermman created a high-level quantification of global exergy resources (Hermann, 2006). For earth's biosphere, exergy comes from "reservoirs" in the forms of solar energy, gravitational energy, thermal energy from the earth's interior, and nuclear energy from fissionable atoms. Exergy is then redirected into secondary reservoirs like fuels. Once on earth, exergy is diminished through processes that cause loss and destruction. An example of loss is when solar energy is redirected back into space by reflection from clouds and the earth's surface. An

example of exergy destruction is when humans use fuels to power machines. Human caused exergy destruction is called anthropogenic energy destruction (Hermann, 2006).

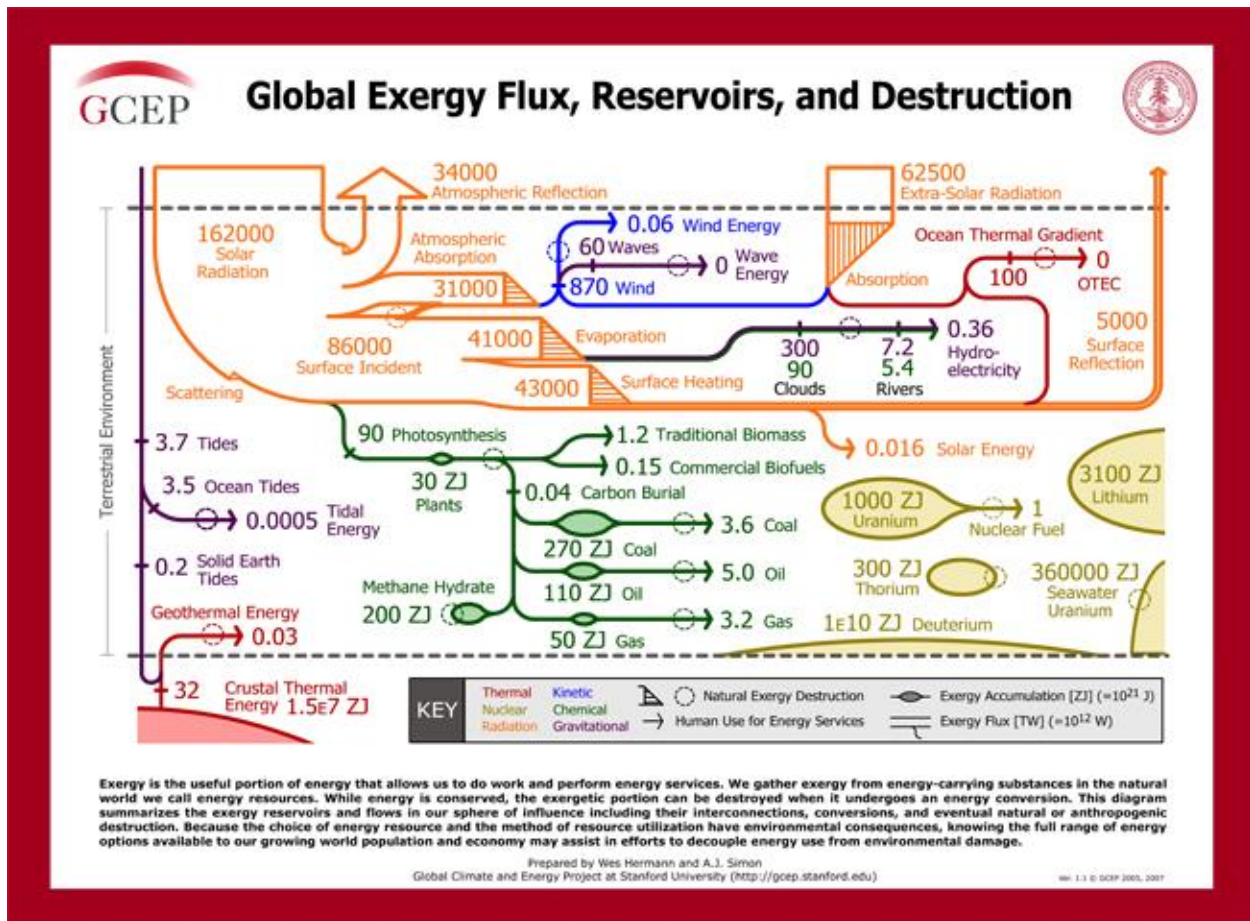


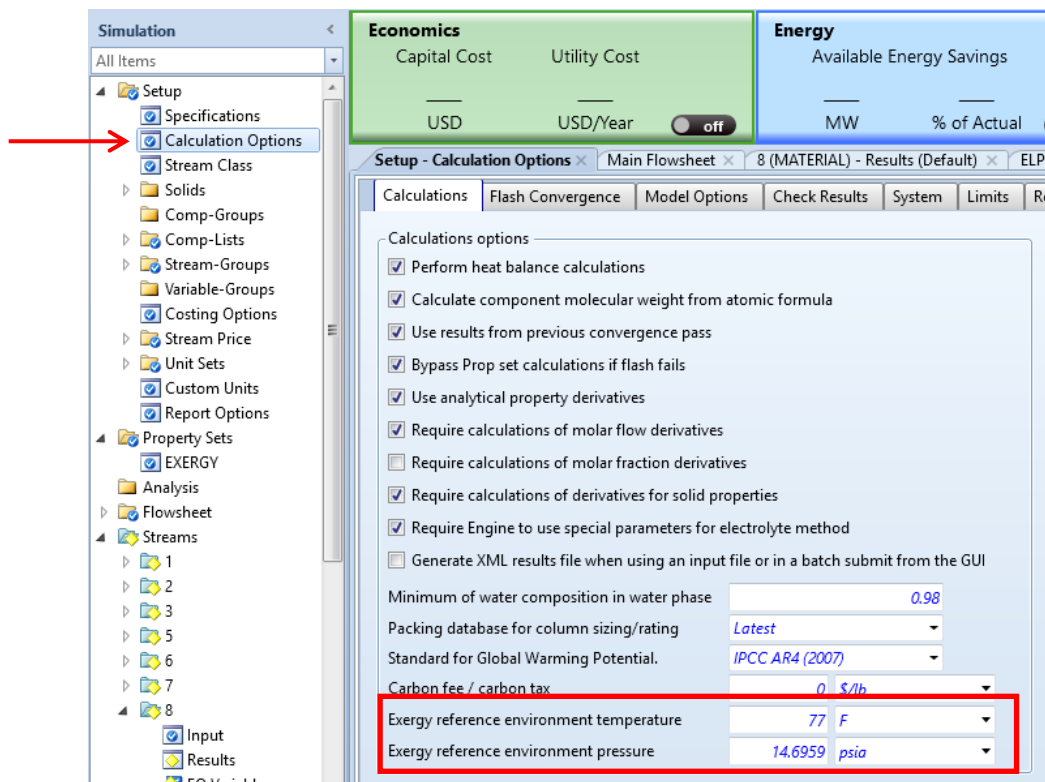
Figure 3- Exergy distribution in earth's biosphere (Hermann, 2006)

## **Chapter 5 - Aspen Plus Exergy Analysis Walkthrough and**

### **Discussion**

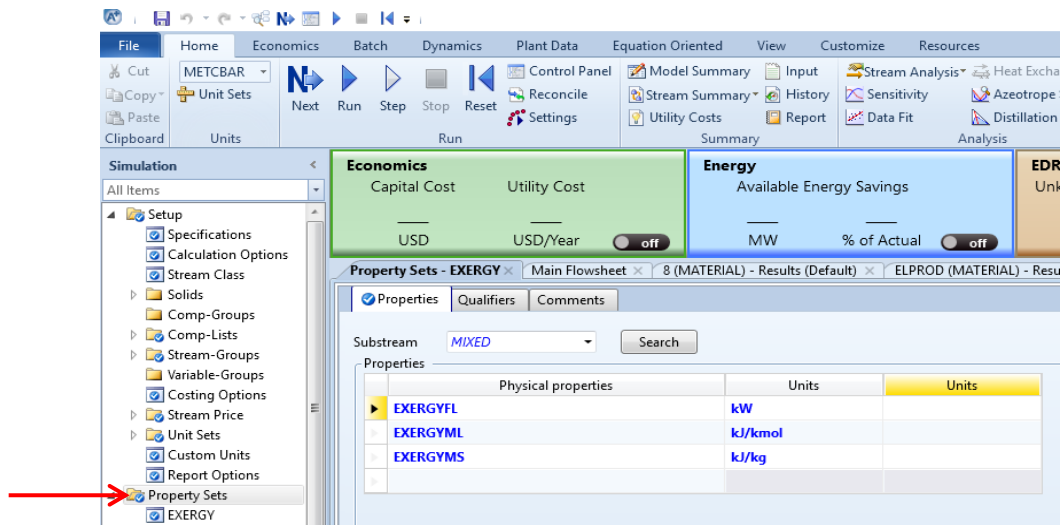
### **Walkthrough**

This walkthrough will assume that the reader has a working knowledge of Aspen Plus modeling and how to display pertinent results. This walkthrough was done on version 10 of Aspen Plus. It is best to first create the model, solve it, and troubleshoot if needed to make sure the model has a good convergent solution. Once the model has been solved and results have been reviewed for accuracy, the user will select the “Calculations Options” tab from the “Setup” folder in the “Simulation” menu on left side. On the right-hand side, click on the “Setup- Calculation Options” tab. At the bottom of this page are two fields which read “Exergy reference environment temperature” and “Exergy reference environment pressure”. These are the conditions of the atmospheric or equilibrium reference state against which the process stream state will be compared. If you choose not to do this step, the reference temperature will automatically be set at 25°C and the pressure will be set to 1 atm.



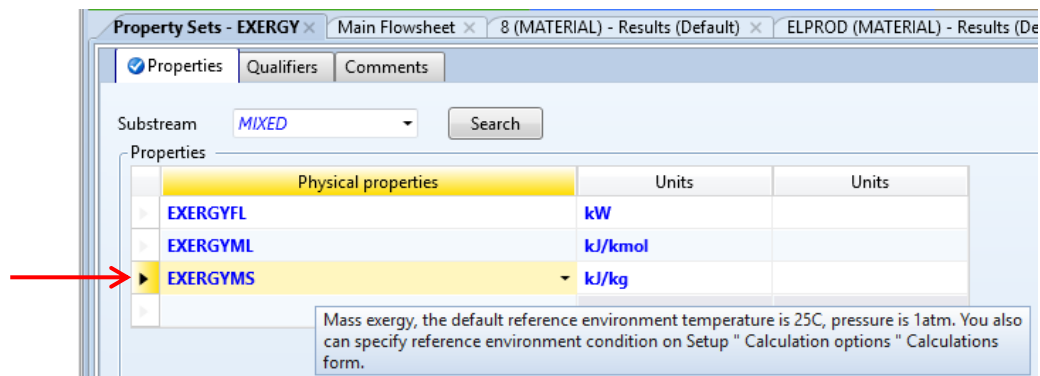
**Figure 4- Aspen simulation “Calculation Options” page**

Next, select the “Property Sets” in the “Simulation” menu on left side. Select the “properties” tab on the page on the right (if not already selected) and add a new value. Search through the options for the three exergy-related options name “EXERGYFL”, “EXERGYML”, and “EXERGYMS”. You can add any or all of them. Preferred units can be selected in the “Units” column next to the “Physical properties” column.



**Figure 5- Select exergy calculation types in the “Property Sets” folder**

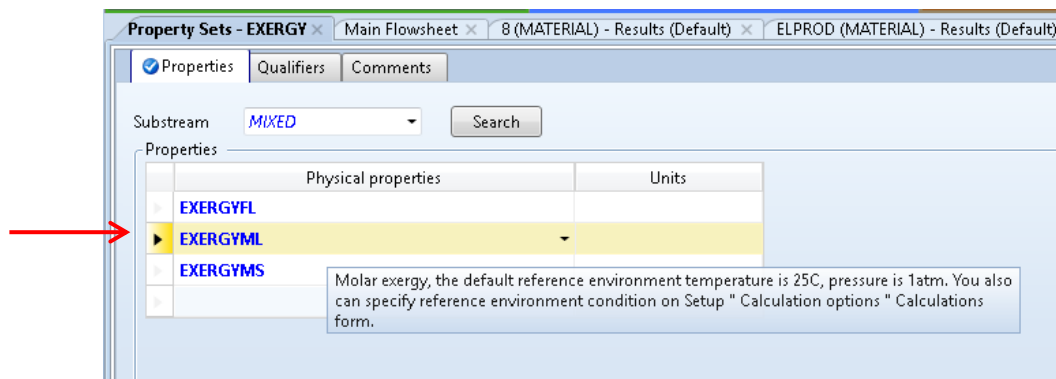
Mass exergy (EXERGYMS) will calculate the exergy value per unit mass of the process stream.



**Figure 6- Mass exergy selection, units will be in the selected exergy/unit mass**

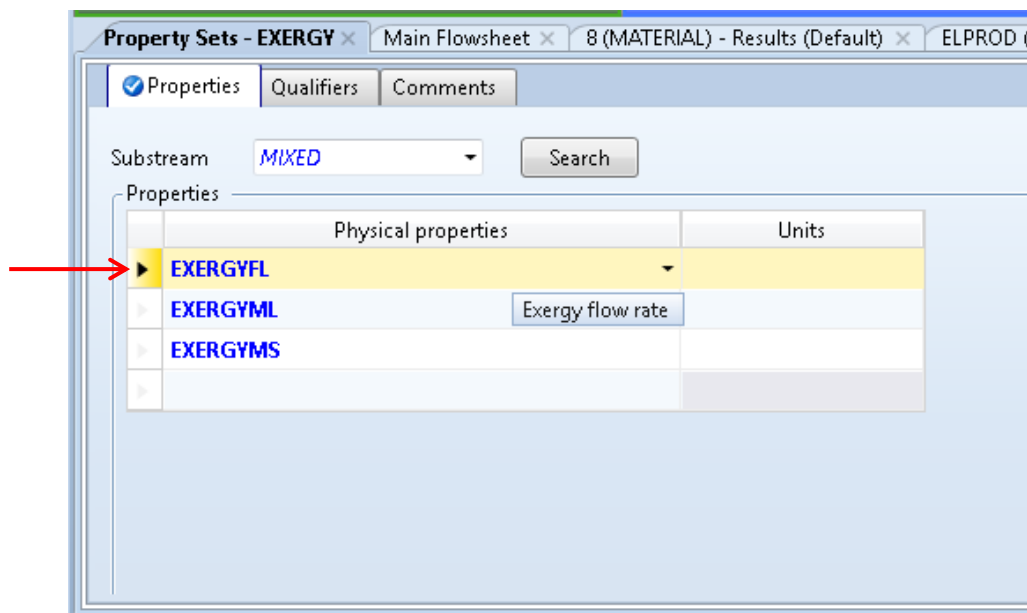
Molar exergy (EXERGYML) will calculate the exergy value per unit mole of the process stream.

Again, preferred units can be selected.



**Figure 7- Molar exergy selection, units will be in the selected exergy/ unit mole**

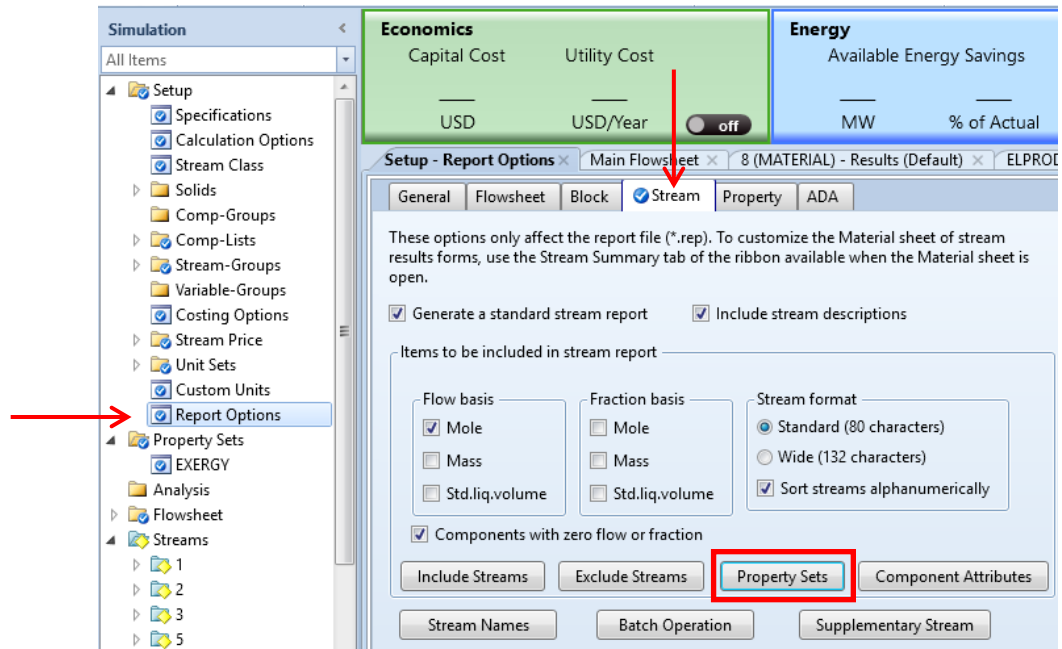
Exergy flow rate (EXERGYFL) will calculate exergy per unit time that the process stream is carrying.



**Figure 8- Exergy flow rate selection, units will be in selected exergy/unit time**

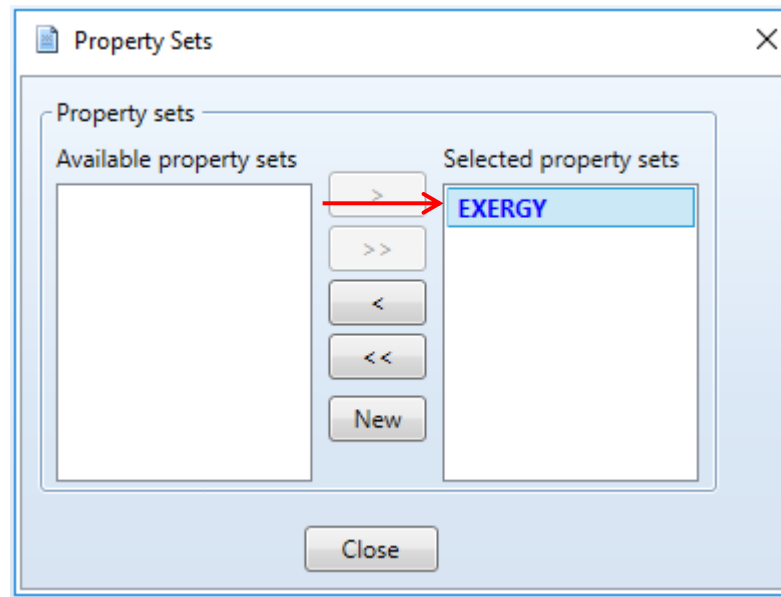
Next, select the "Report Options" tab from the "Setup" folder in the "Simulation" menu on the left. Select the "Stream" tab on the page at the right and select the "Property Sets" button towards the bottom of the page.





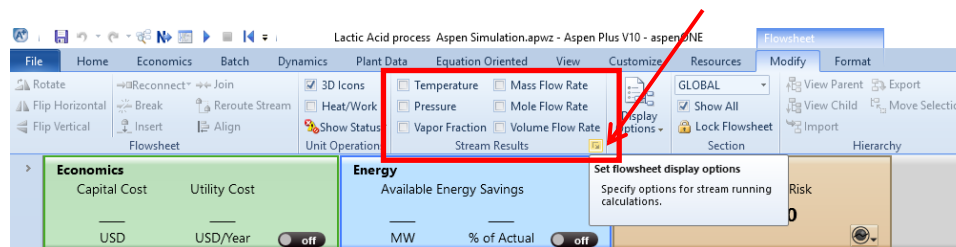
**Figure 9- Select property sets in the stream tab in the left menu report options tab**

Move the desired exergy property sets from “Available property sets” to “Selected property sets”.



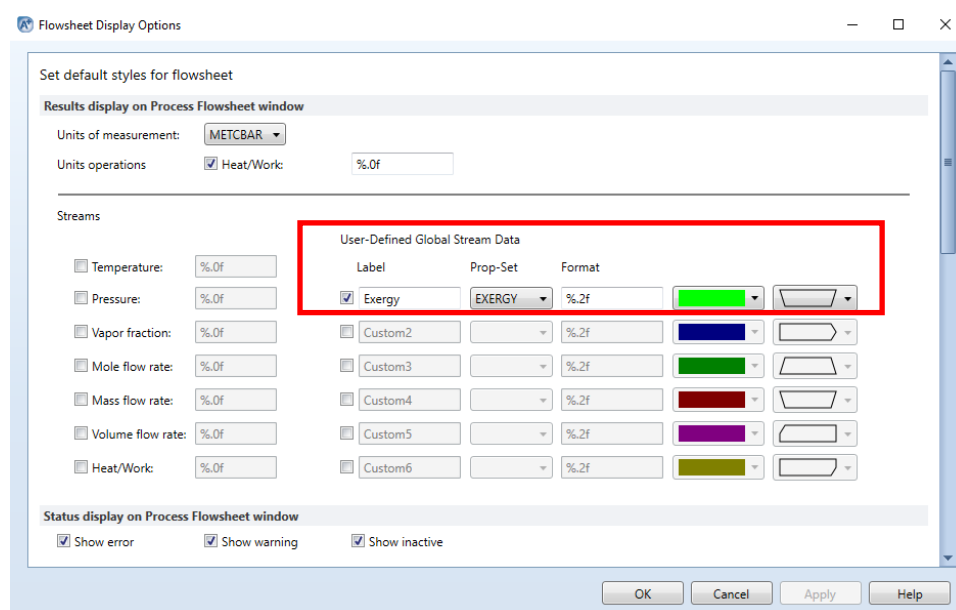
**Figure 10- Exergy as a selected property set**

In the menu options above the right page there is a section called “Stream Results”. In the bottom right hand corner of this area click the box will bring up the “Flowsheet Display Options” menu.



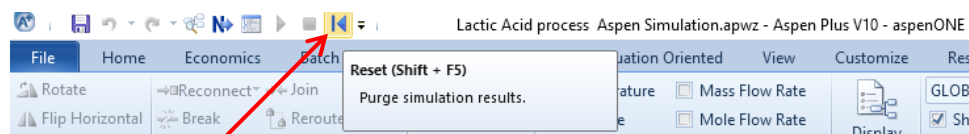
**Figure 11- Open stream results tab for display options**

In the “User-Defined Global Stream Data” section, mark a check box and then enter the label name you wish to call the option, and then select the property set “Prop-Set” you wish to have displayed on the flow sheet. Customize the display format if desired and then choose which text color and border style with which you wish to have your exergy values displayed on the worksheet. Add more property set options if desired. All three exergy property sets can be added as individual display



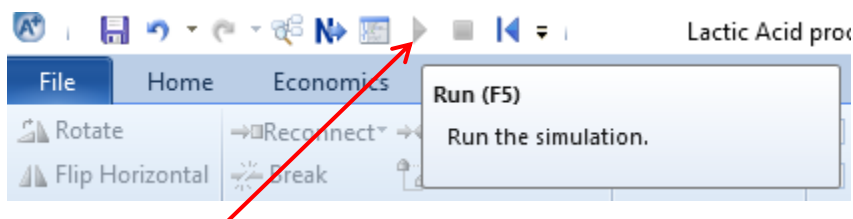
**Figure 12- Select exergy and customize display options**

Reset the simulation so it can be run with exergy calculations.



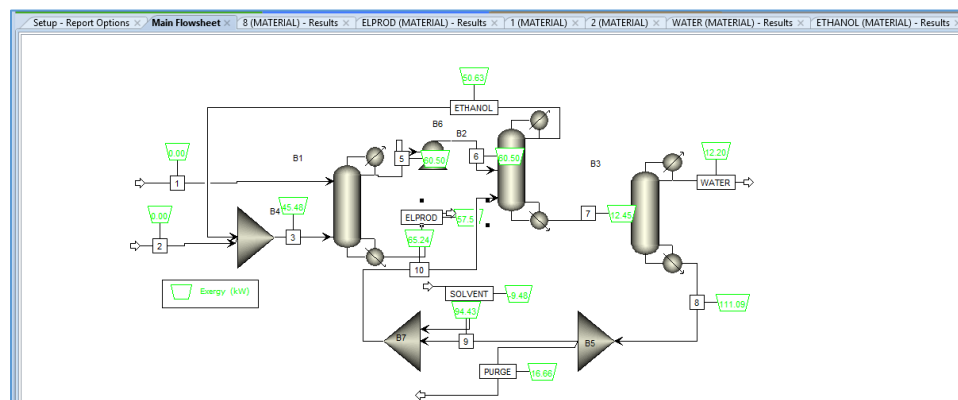
**Figure 13- Reset the simulation**

Run the simulation now including exergy calculations.



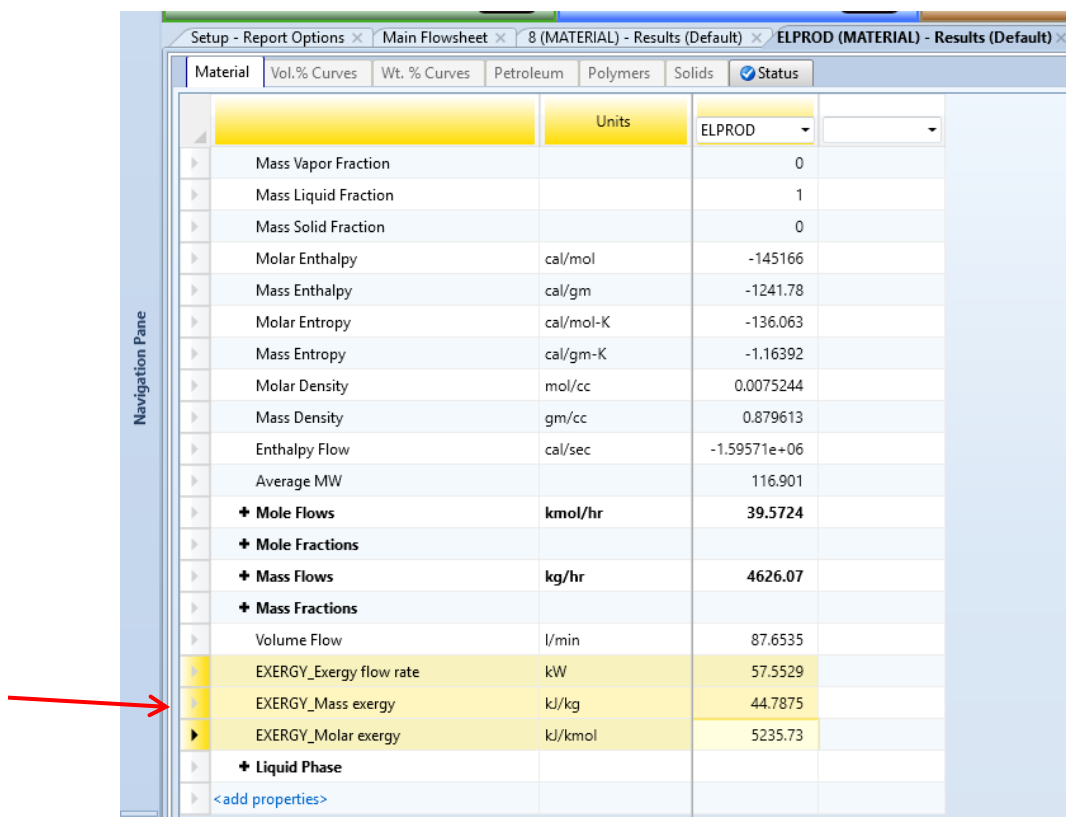
**Figure 14- Run simulation**

Select the “Main Flowsheet” tab on the page on the right if not already selected. You will see one of the boundaries and colored texts you selected associated with each part of the process stream. This will display the calculated exergy values you selected. Modifications can be made to the display results. The process can be repeated if different results are desired.



**Figure 15- Flowsheet with exergy values displayed**

Exergy values can be seen in the “(Material)-Results (Default)” tab or in individual stream results tabs.

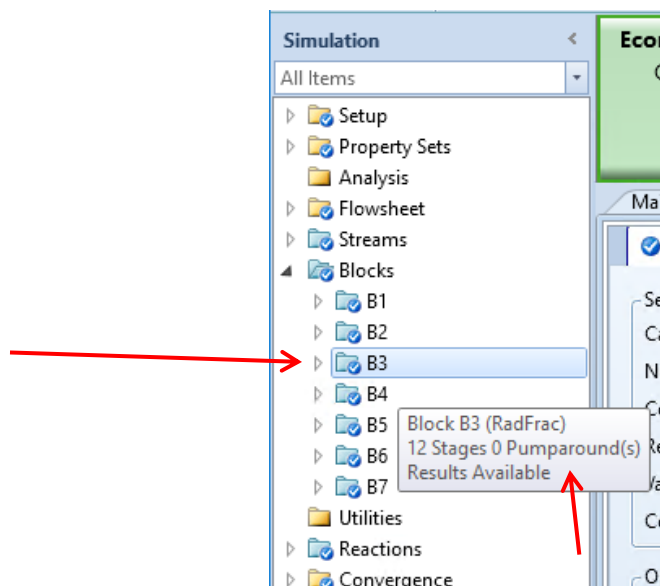


	Units	ELPROD
Mass Vapor Fraction		0
Mass Liquid Fraction		1
Mass Solid Fraction		0
Molar Enthalpy	cal/mol	-145166
Mass Enthalpy	cal/gm	-1241.78
Molar Entropy	cal/mol-K	-136.063
Mass Entropy	cal/gm-K	-1.16392
Molar Density	mol/cc	0.0075244
Mass Density	gm/cc	0.879613
Enthalpy Flow	cal/sec	-1.59571e+06
Average MW		116.901
✚ Mole Flows	kmol/hr	39.5724
✚ Mole Fractions		
✚ Mass Flows	kg/hr	4626.07
✚ Mass Fractions		
Volume Flow	l/min	87.6535
EXERGY_Exergy flow rate	kW	57.5529
EXERGY_Mass exergy	kJ/kg	44.7875
EXERGY_Molar exergy	kJ/kmol	5235.73
✚ Liquid Phase		
<add properties>		

**Figure 16- Exergy values displayed in results**

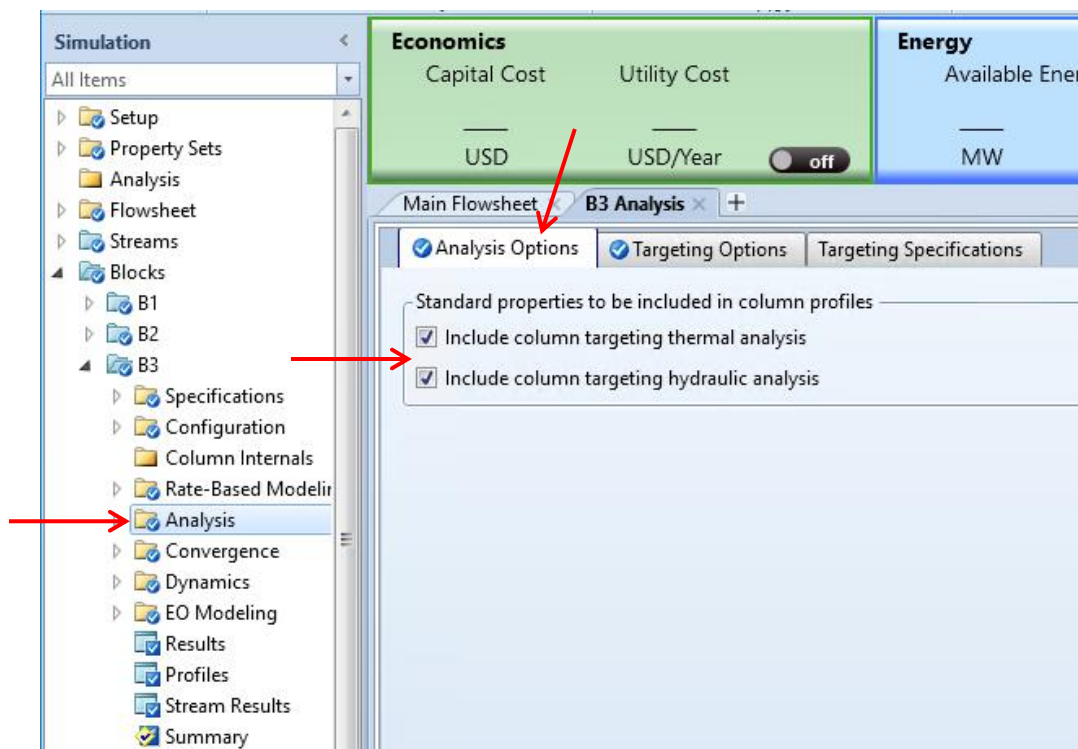
Aspen Plus has included more detailed exergy analysis capabilities in its distillation column tools. The process simulator is able to calculate exergy losses at each stage of a RadFrac column using the column targeting capabilities. This feature is able to identify irreversibilities in the column brought on by momentum loss, thermal loss, and chemical potential loss. These losses are driven by pressure, temperature, and mass transfer considerations, respectively.

With a simulation that has already converged successfully, choose the RadFrac-type column block you would like to analyze from the “Blocks” folder of the left side simulation menu.

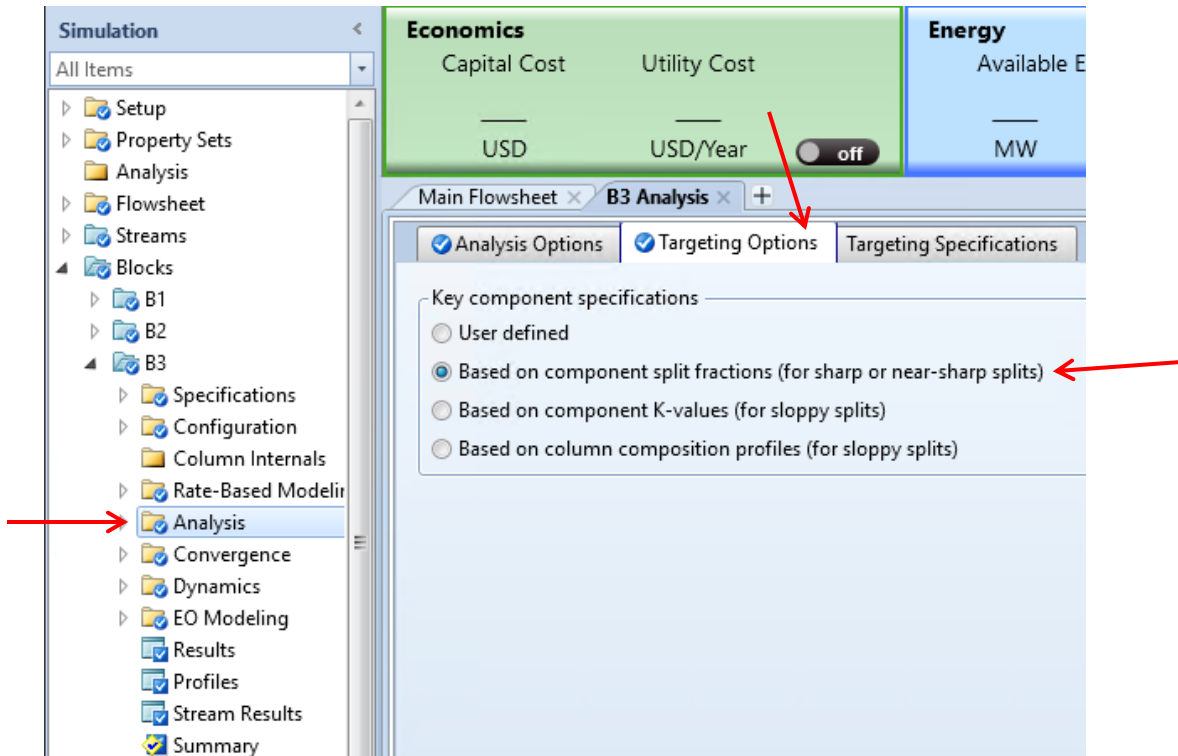


**Figure 17- RadFrac type column block selection**

Expand the RadFrac block and click on the analysis option. On the “Analysis Options” tab of the right-side page, select both the “Include column targeting thermal analysis” and “Include column targeting hydraulic analysis” options. Then select the “Targeting Options” tab and choose either “Based on component K-values (for sloppy splits)” or “Based on component split fractions (for sharp or near-sharp splits)” depending on how well split the components are in the stream.



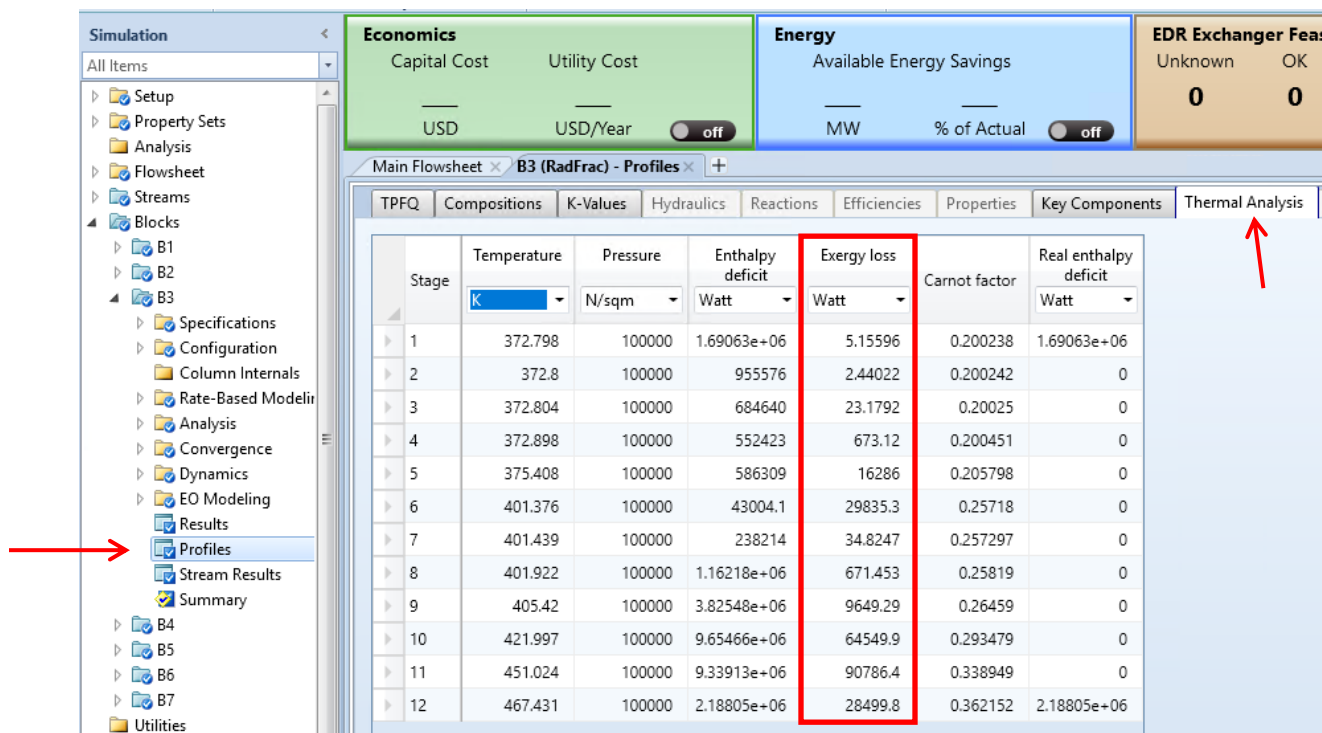
**Figure 18- Column block analysis options selection**



**Figure 19- Select the appropriate component base for targeting options**

Click on the “Profiles” option of the left side block menu to bring up profiles for the column.

Select the “Thermal Analysis” tab of the right side “B\* (RadFrac)- Profiles” tab to see the exergy loss per stage.

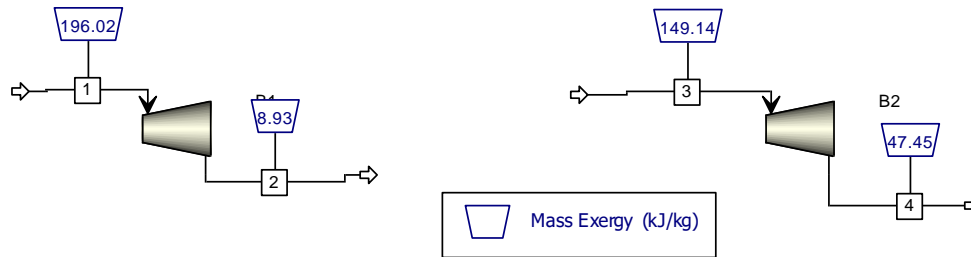


**Figure 20- Exergy loss per stage from the block "Profiles" tab**

## Discussion

As mentioned previously, exergy is often more useful when considered for individual pieces of equipment. The two scenarios previously considered for the calculation of gas expansion exergy can be modeled using a simulator. Recall that exergy is a function of enthalpy, entropy, and temperature differences at two different states, namely a specified process state and an ambient state. Aspen Plus calculates exergy and not exergy loss for its process streams so exergy differences across equipment must be calculated by the user. The flowsheet representation of the two gas expansion scenarios is shown in Figure 21. Exergy is calculated in

kJ/kg from Aspen Plus. The difference in exergy between the inlet and outlet streams of a piece of equipment is the amount of exergy lost either through process irreversibilities or its use in work.

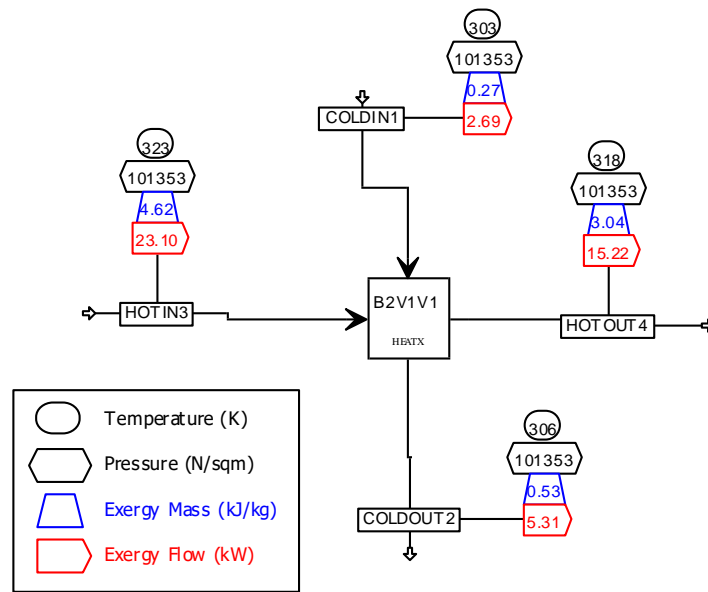


**Figure 21- Aspen Plus flowsheet models for the exergy calculation of gas expansion.**

The exergy differences for scenario 1 and scenario 2 are 187.09 kJ/kg and 101.69 kJ/kg, respectively. The 187.09 kJ/kg of exergy lost, or work produced in the first scenario is fairly close to the hand calculation value of 193.41 kJ/kg. The second scenario differs a little more with 101.69 kJ/kg compared to the 82.82 kJ/kg found in the above hand calculation. In this instance it can safely be assumed that the Aspen Plus values are more accurate as Gunderson's values were likely oversimplified by the assumption of ideal gasses, constant heat capacities regardless of temperatures, and perfect expansion. The usefulness of modeling programs lies in their ability to use stored libraries and equations to produce results that depend less on assumptions.

The heat exchanger exergy calculation shown before can also be solved in Aspen Plus. Like the hand calculation the simulation calculates exergy on a stream basis, and the overall exergy change must be calculated by hand since Aspen Plus does not total the exergy differences from all the streams together. The general exergy equation is used in both calculations. The results of the Aspen Plus calculation compared with the hand calculation are listed below.





**Figure 22- Aspen Plus heat exchanger exergy calculation**

### Aspen Plus

$$\text{Hot Stream Exergy Change} = 3.04 - 4.62 = \underline{-1.58 \text{ kJ/kg}}$$

$$\text{Cold Stream Exergy Change} = .53 - .27 = \underline{.26 \text{ kJ/kg}}$$

$$\text{Total Exergy Change} = -1.58 \text{ kJ/kg} + .26 \text{ kJ/kg} = \underline{-1.32 \text{ kJ/kg}}$$

### Hand Calculation

$$\text{Hot Stream Exergy Change} = \underline{-1.461 \text{ kJ/kg}}$$

$$\text{Cold Stream Exergy Change} = \underline{0.258 \text{ kJ/kg}}$$

$$\text{Total Exergy Change} = \underline{-1.203 \text{ kJ/kg}}$$

In comparison, the results of the two calculations have similar values. Since the same equation is used in to solve both cases, the difference in the results stem from the differences in

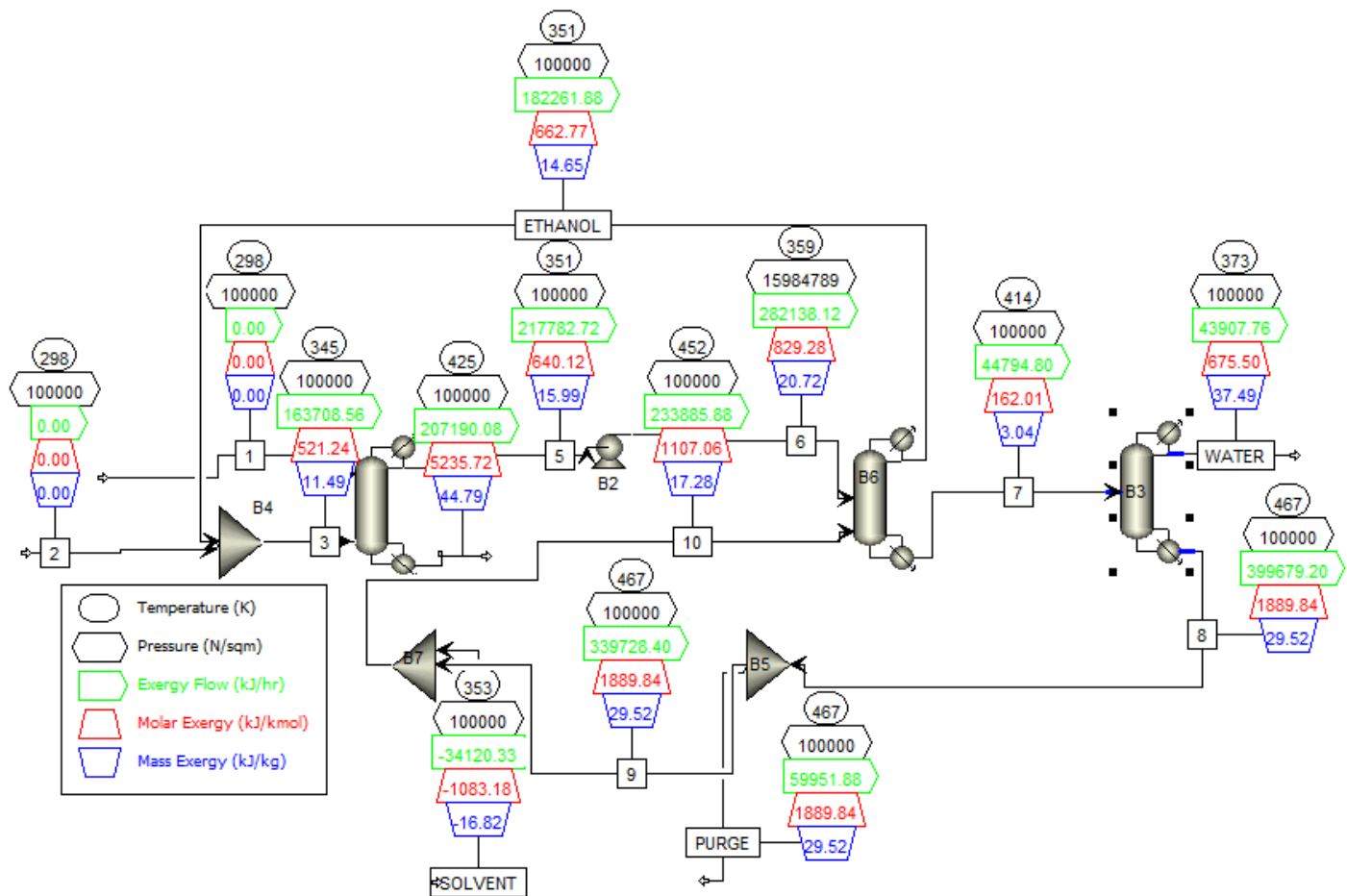
the entropy and enthalpy values used in the calculation. The enthalpy and entropy values differ because different libraries used come from different sources.

## Process Simulation

Aspen Plus can calculate exergies of all the streams in the flowsheet concurrently. The Aspen Plus model used for this discussion is a process that produces ethyl lactate from the esterification of lactic acid. Ethyl lactate can be used as a renewable industrial solvent (Budke, 2018). Exergy in Aspen Plus is a function only of enthalpy and entropy so heat, pressure, work, etc. generated or consumed by interactions are accounted for so much as they can be represented by the enthalpy and entropy of the stream. Stream exergy is calculated using the differences in the enthalpy and entropy between the process state and the environmental state.

$$Ex_{Stream} = (h_{stream} - h_{0_{stream\ at\ ambient\ T,P}}) - (T_{0_{stream\ at\ ambient\ T,P}} (s_{stream} - s_{0_{stream\ at\ ambient\ T,P}}))$$

The exergies of the streams in the model are linked to the stream identifications. A larger copy of the model and its exergies is included in Appendix A. Exergies are listed top to bottom as exergy flow, molar exergy, and mass exergy respectively. \*If the reader is the designated Aspen Plus administrator for their organization then the exergy equation Aspen Plus uses to calculate stream exergy can be found in the Aspen Plus user guide.



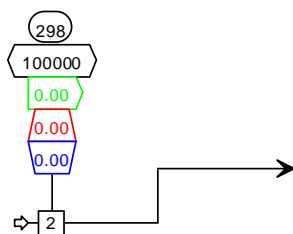
**Figure 23- Aspen exergy calculations for ethyl lactate production**

	Units	1	2	3	5	6	7	8	9	10	ELPROD	ETHANOL	PURGE	SOLVENT	WATER
Temperature	K	298	298	345	351	359	414	467	467	452	425	351	467	353	373
Pressure	N/sqm	100000	100000	100000	100000	15984789	100000	100000	100000	100000	100000	100000	100000	100000	100000
Molar exergy	J/kmol	0	0	521243	640119	829277	162013	1889837	1889837	1107062	5235718	662770	1889837	-1083185	675502
Mass exergy	J/kg	0	0	11494	15993	20719	3045	29515	29515	17275	44787	14647	29515	-16820	37487
Exergy flow rate	Watt	0	0	45475	60495	78372	12443	111022	94369	64968	57553	50628	16653	-9478	12197

**Table 8- Stream summary with exergy, temperature, and pressure**

As seen in Figure 23 the raw materials coming in by means of streams 1 and 2 show a stream with 0 exergy. This is to be expected since the material stream is at atmospheric temperature (298 K) and pressure (100 KPa). Heat, pressure change, or some sort of other exergy influx will be required to bring work potential into the stream. Often the stream receiving

this exergy will draw exergy from another stream resulting in an exergy loss from that stream. If the other stream was a product stream, this event could result in a loss of desired exergy from the product or other useful stream. Aspen Plus only calculates the exergy for each stream. It does not calculate the exergy loss across a piece of equipment that has a stream with different exergies on either side of it. Exergy loss calculations must be made manually except in the special case of the distillation column targeting tool.



**Figure 24- Process streams at atmospheric pressure and temperature have 0 exergy**

From the other streams one can see the evolution of exergy as heat and work is brought in and out of the process. From the results one can see opportunities to save exergy by reusing streams like that of the purge stream, which is wasting 59993 kJ/hr if it is not being put to use in another process. Any of the outflowing streams with exergy not connected to another process stream are theoretically losing all the exergy to the environment as they sit in tanks, are delivered to waste stream, or are treated needlessly by coolers or other exergy reducing equipment.

### Mixing

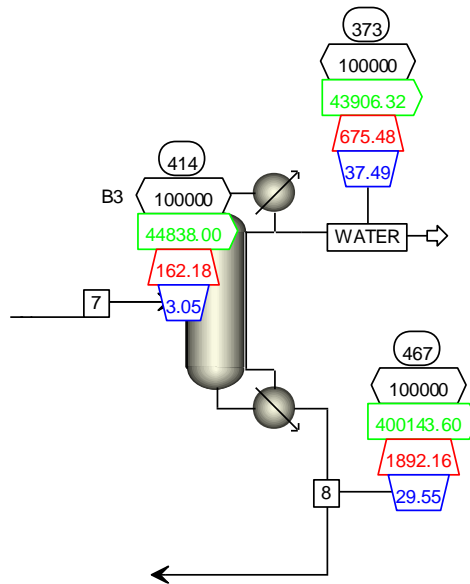
One can see that the ethanol line with 663 kJ/kg of exergy is mixed with the zero-exergy line from stream 2. The product stream, stream 3, has an exergy of 521 kJ/kg. The mixing resulted in a loss of 142 kJ/kg exergy. This loss is comprised of the temperature drop found when the ethanol stream is compared with stream 3 as well as the mixing of streams. The

decrease in exergy coincides with the increase in entropy that's expected with mixing. It can be seen at mixer B7 that the incoming solvent stream has a negative exergy value even though its temperature and pressure are above atmospheric. It is interesting to note that this is an error that occurs when Aspen Plus does not have the necessary properties stored in its libraries for one the components in the stream. This reminds us that it is important to be vigilant in model design and to make sure the calculations make sense even with professional process simulating software.

### **Pumping**

Equipment B2, the pump in this process, adds exergy to the process as seen when the exergy difference between stream 5 and stream 6 is calculated. The 67 kJ/kg increase in exergy correlates with the increase in pressure and temperature that occurs across the pump. This makes sense since increasing the temperature and pressure of the stream also increases the ability of the stream to do work. It is important to remember that while there is an increase in process exergy from the pump, there is a loss of exergy across the pump from the energy input to the process. Just as overall entropy can only increase in non-ideal scenarios, overall exergy can only decrease. Measuring this exergy loss and using it in comparisons of other equipment or operating conditions can help optimize resource use. Unfortunately, Aspen Plus does not yet have these analysis tools included except in the case of distillation.

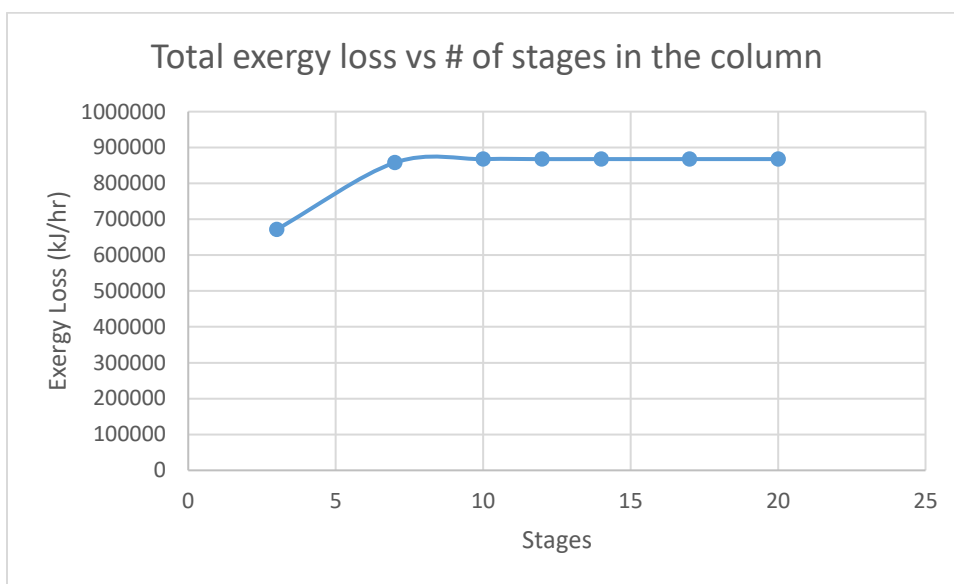
## Distillation



**Figure 25- Block B3 RadFrac type distillation column**

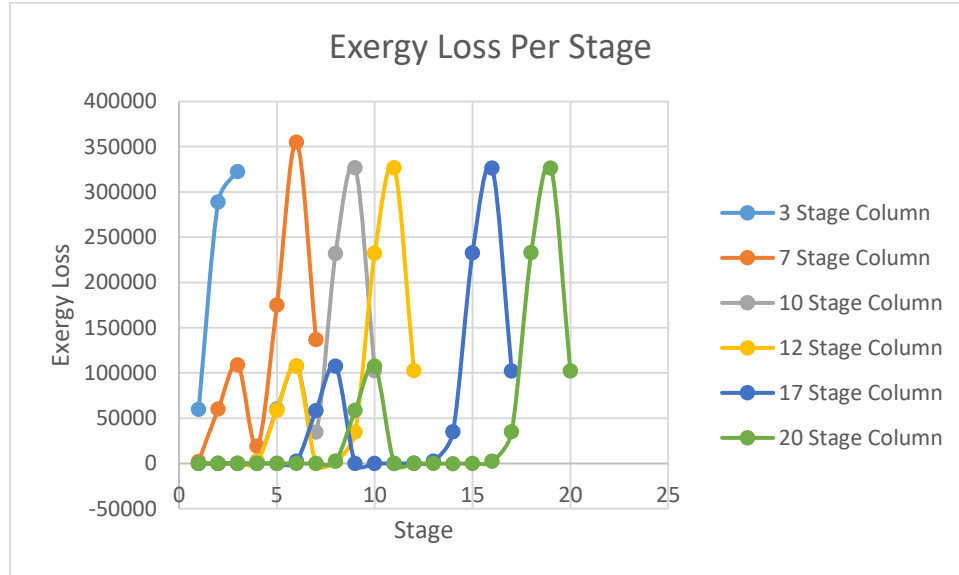
In order to find the exergy change across the column, a comparison of the exergy of the streams going into and coming out of the distillation column will be performed. Before any calculation is made, we can hypothesize what exergy changes one would expect to see take place across a distillation column. First, distillation makes use of boiling point differences between the different components of the system so we would expect heat to be added to the column which would also mean the addition of exergy. Second, distillation generally has the opposite effect of mixing where exiting streams have fewer components in greater concentrations. This would also lead to an increase in exergy. Lastly, depending on the type of distillation, there might be an exergy increase due to an increase in pressure or even a reaction. The reaction's exergy would not be captured but temperature and pressure changes resulting from the reaction would be. The total exergy gained across the distillation column B3 is 64 kJ/kg when the calculation is made.

Although there is a net gain in exergy across the distillation column that doesn't mean that the column design can't be improved to maximize exergy gains by changing the design or process conditions of the column. The RadFrac column exergy analysis in Aspen Plus gives more detail in how exergy gain is being limited in the column. In this analysis exergy loss is calculated on a per stage basis due to pressure, temperature, and mass transfer. Exergy losses from the column stages can be used to trouble shoot or debottleneck a column. Figure 26, for example, shows the total exergy lost in a column for seven different stage configurations ranging from a column with 3 stages to a column with 20 stages.



**Figure 26- Total exergy loss from all stages of the column vs the # of stages in the column**

With this plot it can be seen that an additional number of stages past 7 stages will not greatly change the overall amount of exergy loss. This could be a helpful analysis, for example, in a discussion deciding whether to minimize tray design to reduce energy/exergy losses vs adding extra trays to counter losses in separation from fouling. The graph indicates that additional trays would likely have a negligible effect on exergy loss. With the additional detail we can also get an idea of where exergy losses are occurring in the column itself.



**Figure 27- Exergy loss vs the specific stage at which its lost for several columns with a varying amount of stages**

In Figure 27 exergy loss is plotted on a per stage basis. The spikes in exergy loss in this example correlate with the stage directly below the feed and reflux inlets. This is not unexpected since the interaction between the incoming streams and the material inside the reactor likely result in a pressure drop, temperature change, and/or mass transfer change. The values can now be used to optimize distributor designs, reflux ratios, and tray or packing designs with the ultimate goal of reducing exergy loss or potential work loss in the column. As heat or mass transfer can correlate with fouling, potential high fouling areas might also be identified by high instances of exergy loss.

### **Distillation Column Exergy Analysis**

Whichever exergy analysis method is chosen, the ultimate goal is to express resources and operability in common units. One of the simplest methods of analysis is an exergy



efficiency calculation. As an example, assume that 1,274,212 kJ/kg of steam exergy is required for a distillation column to produce a distillate and bottoms stream with a combined exergy of 399,212 kJ/hr. If Aspen Plus calculates total tray exergy loss in the column at 875,000 kJ/hr., then the exergy efficiency of the column can be calculated using equation 34.

$$\eta_{Ex} = 1 - \frac{\text{Exergy Lost} + \text{Exergy Destroyed}}{\text{Exergy In (ex. Fuel)}} \quad (36)$$

$$\eta_{Ex} = 1 - \frac{875,000 \frac{\text{kJ}}{\text{hr}}}{1,274,212 \frac{\text{kJ}}{\text{hr}}} = .313 \text{ or } 31.3\% \text{ exergy efficiency}$$

If it is assumed that 450 lb. steam is used to supply heat to the column at \$8/ 100000 BTU, then a cost can be assigned on an exergy basis (United States, 2012). The cost of \$8/ 100000 BTU or 7.58E-05 \$/kJ can be applied to the exergy values previously calculated above so that distillation column can be evaluated on its performance. The cost of exergy put into the distillation column comes out to be \$96.60 per hour or \$846,370 annually if consistent operation over the course of a year is assumed. The cost of the exergy lost to the distillation column occurs at a rate of \$66.35 per hour or \$581,201 annually.

Using a process simulator's exergy calculator can aid in the analysis of multiple distillation column configurations so that the optimal configuration with the lowest costs and least amount of exergy loss can be selected. With experience, more pieces of equipment or exergy input streams can be included in the analysis so that energy sources, equipment variations, operating conditions, and a multitude of other variables can be compared for optimization. The fact that exergy is the common basis for usable work lets the optimization of scenarios be compared in common units.

While a process simulator's capability to easily calculate exergy is very helpful there is still a lot of opportunity available to improve the simulator's exergy analysis. Aspen Plus currently only calculates a stream's physical exergy, but chemical exergy could also be added to the analysis without too much effort. With Aspen Plus's considerable libraries, a final chemical state could be included in the property setup option where the exergy temperature and pressure reference are specified. Since an analysis relies on exergy loss, another simple addition to the simulation software would be an exergy loss calculation across a piece of equipment. This would allow for a quick analysis as exergy loss is calculated and compared for multiple configurations. Finally, Aspen Plus already has many analysis tools including an environmental footprint evaluation, an economic evaluation, a safety evaluation, and optimizations for solids or batch processes. With the framework for a thorough study already laid and the values required for exergy calculations often already being referenced in the aforementioned tools, the inclusion of an advanced exergy analysis would be both manageable and convenient.

## **Conclusion**

Exergy is a state property that represents the amount of usable work that can be obtained from a substance at a specific state when compared to the atmospheric state. This property is closely related to the second law of thermodynamics but whereas overall entropy can only increase in a real or irreversible process, exergy can only decrease in that same process. Exergy change can be used as a common property to compare the thermodynamics of a process and its equipment. Several methods of exergy analysis have been developed over time which use exergy to compare process and equipment arrangements both for economics and resources. The popularity of these methods has led process simulation companies to include exergy calculation abilities in their software. The exergy calculation capabilities of the process modeling program

Aspen Plus has been outlined and demonstrated in this work. While useful, the exergy calculation is confined to only that of a process stream and only physical exergy is calculated. To maximize the usefulness of an exergy analysis the simulation software should include the exergy loss and efficiency calculations of single pieces of equipment as well as an overall exergy balance. All types of exergy should be included in the analysis. Relating resources and costs to this balance would also be necessary for a higher value analysis.

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Appendix A - Figure 23 Enlarged

