Energetic and Environmental Evaluation of Titanium Dioxide Nanoparticles

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***Abstract*—The methods of energy, exergy, and life cycle analysis are applied to a new nanomanufacturing process producing 40 nm titanium dioxide particles. The use of identical boundaries for each analysis allows for direct comparison of the results from each method. It was found that the thermodynamic methods identify spray hydrolysis as a significant sink in the process and life cycle analysis shows it to be the largest source of greenhouse gas emissions. Despite this agreement, there are some discrepancies between methods, and exergy analysis appears to give additional information that energy analysis overlooks. Of course the optimal method for a given application depends on the intended goals of the analysis.**

***Index Terms*—Exergy, Improvement Analysis, Titanium Dioxide Nanoparticles**

I. Introduction

THE goal of this research is to compare common methods of process improvement analysis in their application to chemical processes. In this paper we have applied energy and exergy analysis as well as a gate-to-gate life cycle assessment (LCA) to a new process for manufacturing titanium dioxide (TiO_2) nanoparticles from raw ilmenite ore. Each of these methods reveals opportunities to improve the process. Most studies in the literature that use thermodynamic methods for evaluation focus on a single approach [1]-[3]. As a result it is unclear if these methods are complementary or substitutable. Furthermore, the ability of various methods to reveal improvement opportunities in a process life cycle has received relatively little attention.

The major contributions of this work are threefold: we propose a unique model for calculating the exergy of nanoparticles, we apply thermodynamic and life cycle analyses to a nanomanufacturing process, and we provide a direct comparison and discussion of the relative merits of energy, exergy, and life cycle analysis. This comparison is applied directly to the TiO_2 nanomanufacturing process considered, but also gives insight into more general advantages and shortcomings of the analysis methods.

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II. Background

A. Thermodynamic Analysis

Of the many ways to evaluate performance in a process or a piece of equipment, much attention is given to efficiency. Classically, efficiency is defined as a simple ratio of outputs to inputs. Within first law energy analysis, this ratio is usually defined in terms of enthalpy [4].

$$Energetic\ Efficiency = \eta_{EN} = \frac{\Delta H_{outputs}}{\Delta H_{inputs}} \tag{1}$$

For material streams, enthalpy is calculated as

$$Enthalpy = \Delta H = nC_p \Delta T \tag{2}$$

We can also use first law analysis to calculate energy losses in a process or process unit as the difference between the enthalpy leaving and entering.

A common criticism of first law analysis is that it does not take into account the quality of energy sources. While 1 Joule of sunlight may have the same energy content as 1 Joule of electricity or gasoline, we know intuitively that electricity and gasoline are more useful for doing work than sunlight. To combat this problem, second law analysis calculates the potential for doing useful work and uses that as the basis for evaluation. Exergy is defined as the amount of useful work that can be obtained from a material stream by bringing it to equilibrium with its surroundings. For every type of gradient with the surroundings there is a different type of exergy. For this paper we will ignore potential, kinetic, and nuclear exergy and instead focus on physical and chemical exergy. Physical exergy can be calculated as [5]:

$$Physical\ Exergy = b_{ph} = h_{ph} - T_0 s_{ph} \tag{3}$$

Ignoring pressure effects and assuming the heat capacity is constant with temperature, thermal exergy is expressed as:

$$Thermal\ Exergy = b_{th} = C_p\ \ T - T_0 - T_0 \ln\frac{T}{T_0} \tag{4}$$

Chemical exergy can be thought of as the work obtainable by exploiting concentration gradients between the material stream of interest and the surroundings. The standard chemical exergy of a compound can be calculated as [5]:

$$Chemical\ Exergy = b_{ch}^{\circ} = \Delta_f G^{\circ} + \quad n_{el} b_{chel}^{\circ} \tag{5}$$

Where $\Delta_f G°$ is the Gibbs' standard free energy of formation for the compound, n_{el} is the number of moles of each element per unit of compound, and $b_{el}°$ is the standard chemical exergy of the elements found in the compound. Values of $\Delta_f G°$ can be

Table I. Explanation of Symbols and Units

Symbol	Quantity	SI Units
$b°$	Standard Molar Exergy	kJ/mol
C_p	Heat Capacity	kJ/mol K
e	Volume Dilation	-
f	Surface Weighting Factor	-
$\Delta_f G°$	Standard Gibbs' Free Energy of Formation	kJ/mol
h	Molar Enthalpy	kJ/mol
ΔH	Enthalpy	kJ
I	Irreversibility Rate	kJ/hr
M	Molar Mass	kg/mol
n	Molar Flow Rate	mol/hr
q	Surface-to-Volume Ratio	cm^2/cm^3
T	Temperature	K
T_0	Reference Temperature	K
γ_{xi}	Surface Energy	J/m^2
η_{EN}	Energetic Efficiency	-
η_{EX}	Exergetic Efficiency	-
η_{TR}	Intrinsic Efficiency	-
ρ_x	Density	g/cm^3

found in the literature and in thermodynamic handbooks for most compounds [6]-[7]. Standard values of $b_{el}°$ have been calculated for each element according to its standard reaction of formation and can be found in [5]. The chemical exergy of organic fuels is typically very close to its heating value.

The difference between the exergetic inputs and outputs to a process is termed the irreversibility rate, I, of the process [8].

$$\sum \Delta \dot{b}_{IN} = \sum \Delta \dot{b}_{IN} + \dot{I} \tag{6}$$

The irreversibility rate represents the sum of exergy destruction and loss in the process. It can be used to identify the largest exergy sinks in a process.

Simple exergetic efficiency can also be calculated as the ratio of the exergies of the outputs to that of the inputs:

$$Exergetic\ Efficiency = \eta_{EX} = \frac{\sum \Delta \dot{b}_{OUT}}{\sum \Delta \dot{b}_{IN}} \tag{7}$$

Previous authors have compared first law energy analysis unfavorably to exergy analysis when considering processes with fuel or energy products such as power plants, fuel cells, or alternative energy sources [9]-[10]. The current study tests this hypothesis for a material intensive process producing a product with little or no value as a fuel.

Also of interest in the literature is the issue of transiting exergy, or material flows that travel into and out of a given unit without participating. Examples of transiting flows are reactants that are not converted to products, or reactants run in excess to ensure full conversion of other reactants. These flows artificially inflate the efficiency of the unit. By excluding them we can get a more accurate picture of the exergetic efficiency, called the intrinsic efficiency [1]:

$$Intrinsic\ Efficiency = \eta_{TR} = \frac{\sum \Delta \dot{b}_{OUT} - \sum \Delta \dot{b}_{TR}}{\sum \Delta \dot{b}_{IN} - \sum \Delta \dot{b}_{TR}} \tag{8}$$

The intrinsic efficiency will always be less than or equal to the simple exergetic efficiency, the quantities being equal in the limit that no transiting exergy is present and all of the entering materials participate in the operation of the process unit.

B. Life Cycle Analysis

Life cycle analysis, also referred to as life cycle assessment, is a method for evaluating a product that takes into account the production chain not only for the product but also for everything else that contributes directly or indirectly to the product. Often when a process is "improved" the problems are simply shifted to another area of the life cycle. The hope is that by defining your boundaries carefully you can prevent this type of oversight.

As defined by ISO 14000, life cycle analysis has four distinct parts. The first involves defining the goal and scope of your analysis. This includes defining the functional unit for the product being made and clearly defining the boundaries your analysis will cover. The second step is the life cycle inventory in which the system is modeled, and all flows into, out of, and within your system are defined. This includes not only the material and energy requirements for your process, but also the emissions and waste products.

The third step is impact assessment. In this step all the emissions from the inventory are categorized according to their potential impacts in one or more of the established impact categories. Typical categories include global warming potential, acidification potential, ozone depletion potential, and human toxicity potential. Characterization factors are used to convert the amount of emissions to standard emission equivalents. For instance, the standard emission for global warming is carbon dioxide. Methane has a global warming potential of four times that of carbon dioxide per unit mass. Thus, the characterization factor relating methane to carbon dioxide for global warming potential is four. In order to compare impacts across categories, impacts are typically normalized against the estimated total emissions for that category in the country or even the world.

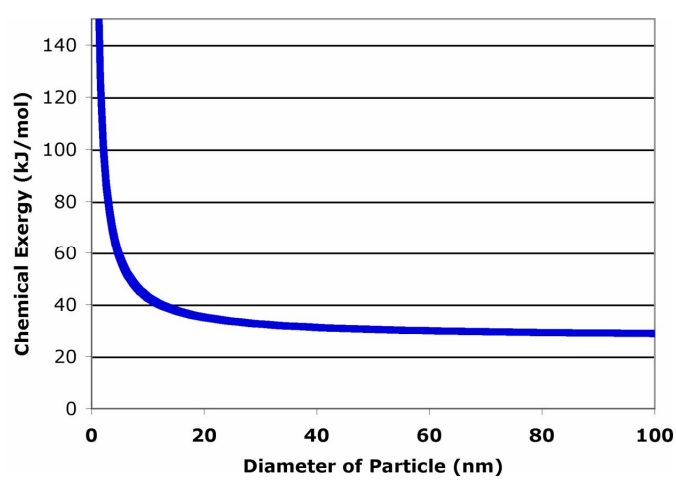

Fig. 1. Chemical exergy of anatase titanium dioxide nanoparticles as a function of particle diameter.

The final step is interpretation. This step sometimes involves weighting of the impact categories according to human preferences to achieve a single "impact score" that can be compared relatively to alternative products or processes.

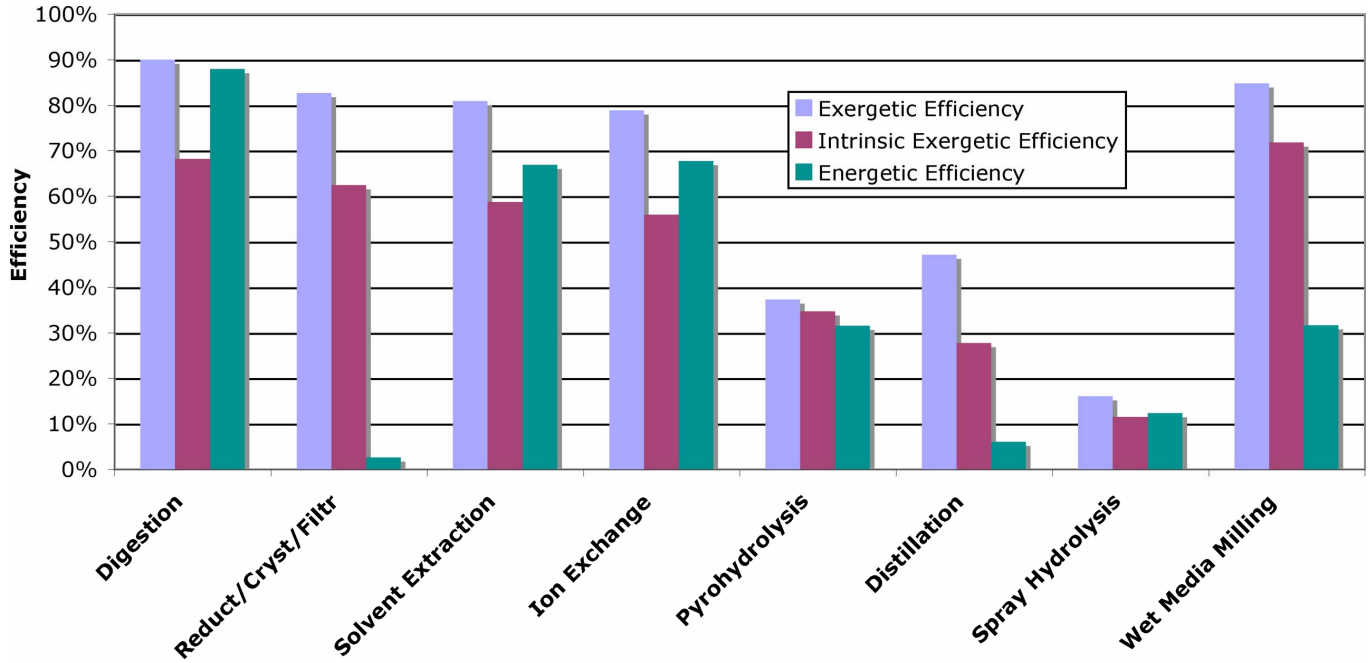

Fig. 2. Comparison of thermodynamic efficiencies. The simple exergetic efficiency is shown in blue, the intrinsic exergetic efficiency which ignores transiting flows is shown in red, and the simple energetic effiency is in green.

Interpretation is when we must step back and decide what the results we get actually mean. The decisions we make in earlier steps of the analysis influence what we can learn from our results.

A. *Titanium Dioxide Nanoparticle Manufacture*

Titanium dioxide has been commercially produced for use as a white pigment since the early twentieth century. Currently, two mature processes exist for its production, namely the chloride process and the sulphate process. The chloride process is better suited for processing naturally occurring rutile phase TiO_2 deposits, while the sulphate process is preferred for processing ilmenite ore. Typical rutile phase pigment grade TiO_2 particles produced from these established processes are on the order of 250 nm to 1 μm in diameter. However, recent demand for smaller particles for use in sunscreens and for catalytic applications has opened up a market for 20-50 nm anatase phase particles.

The Altair hydrochloride process for TiO_2 production is similar to the sulphate process in that it uses a strong acid to digest raw ilmenite ore. The sulphate process uses sulfuric acid, while the hydrochloride process uses hydrochloric acid. Following the digestion, several separation steps remove the residual iron from the ore and the excess HCl from the titanium rich solution. The Altair process also incorporates a spray hydrolysis step using a methane powered spray-drying unit, which allows for further control over the size and phase of the particles produced. Another advantage of the hydrochloride process is the near complete recycling of the acid through pyrohydrolysis with no chloride containing byproducts leaving the process boundaries.

B. *Exergy Model of Nanoparticles*

As particles get smaller, surface activity becomes more energetically relevant. A free energy model exists in the literature for the deviation from bulk behavior of nanosized particles [11]:

$$G_x^o = \Delta_f G_x^o + \frac{M}{\rho_x}(1-e)\left[q\sum f_i \gamma_{xi}\right] \tag{9}$$

Where M is the molar mass, ρ_x is the density, e is the induced volume dilation, q is the surface-to-volume ratio, f_i is the shape weighting factor based on area of the crystal faces, and γ_{xi} is the surface energy for each face. More information can be found about these parameters in [11]-[12]. Combining (9) with (5), we get an expression for the chemical exergy of nanoparticles.

$$B_x = \Delta_f G_x^o + \sum_{el} n_{el} b_{chel}^o + \frac{M}{\rho_x}(1-e)\left[q\sum f_i \gamma_{xi}\right] \tag{10}$$

This model is applied to anatase titanium dioxide nanoparticles up to 100 nm in diameter in Fig. 1. Large deviations in the chemical exergy occur in particles 20 nm and smaller. As the particles get larger, the chemical exergy approaches that of bulk titanium dioxide.

III. Results

For the current analysis, the Altair TiO_2 hydrochloride process was broken up into eight main process units and about 30 major flows. Fuel input to each unit was calculated from process information available in the literature and patents from Altair [13]-[19]. Any missing fuel inputs were estimated from these publications or from other sources considering similar units. The compositions and physicochemical properties of the major flows were also taken from these publications or estimated when necessary.

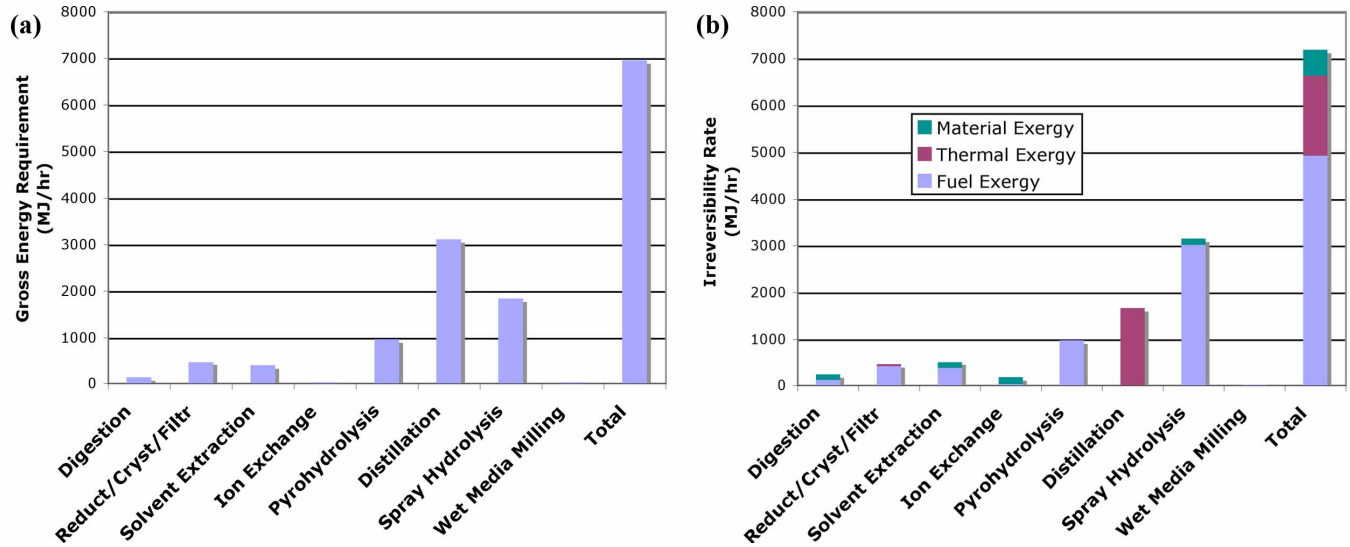

Fig. 3. (a) Gross first law energy requirements for each process unit, (b) second law irreversibility rates for each unit, representing the sum of exergy losses and destructions.

A. *Energy Analysis*

The enthalpy of all streams in the process was calculated using a reference temperature of 273.15 K according to (2). This reference temperature was chosen for convenience in comparing energy and exergy of streams at temperatures below ambient. Once the enthalpy was calculated for each stream, the energy loss and energetic efficiency were calculated for each of the units.

The energy requirement can be found in Fig. 3a and the energetic efficiency is displayed graphically in Fig. 2. The largest energy loss occurs in the distillation unit with a value of 4515.96 MJ/hr, which represents nearly half the energy loss in the overall process. Also noteworthy are the large energy losses associated with spray hydrolysis, pyrohydrolysis, and the unit comprising reduction of the slurry and crystallization and filtration of solid $FeCl_2$.

Not surprisingly, the same four units exhibit the lowest energetic efficiencies in the process. The results for crystallization are not significant as they result from operation at low temperatures necessary to precipitate out the $FeCl_2$, so the enthalpy of exiting streams is very low. This situation is better suited for exergy analysis and will be discussed in the next section. The results for distillation are more interesting and will also be discussed in more depth below.

B. *Exergy Analysis*

The material, fuel, and thermal exergy of all streams were calculated according to (3)-(5). The material exergy of TiO_2 nanoparticles was calculated using our proposed model shown in Fig. #. This new model is crucial to the success of our exergy analysis as it allows us to calculate the irreversibility rate and exergetic efficiency for the later units in our process.

Irreversibility rates were calculated using (6) and are displayed in Fig. 3b. This is the amount of exergy lost or destroyed in this step of the process. Spray hydrolysis has the largest irreversibility rate at 3153.64 MJ/hr. Most of the total irreversibilities in the process are losses of fuel exergy. This seems logical because the fuels in the process are consumed within our boundaries. The exception is the irreversibility rate in the distillation unit, which depends on high-pressure steam to separate the recycled HCl from the excess water it is transported with. The thermal exergy of the steam dominates the exergy loss in the distillation column. Material exergy irreversibilities make up a small amount of the total in the process. These losses are due mainly to exergies of mixing.

From our current analysis it is not clear what portion of the irreversibility rate, if any, would be avoidable in an ideal situation. At present, both avoidable and unavoidable irreversibilities are included in this rate.

Simple exergetic efficiency of each unit was calculated using (7). The transiting exergy and the intrinsic exergetic efficiency were calculated according to (8). Both the simple exergetic efficiency and the intrinsic efficiency can be found in Fig. 2. It should be noted that, by definition, the intrinsic efficiency is less than or equal to the simple efficiency for every unit. These values will approach one another in the limit that transiting exergy goes to zero, as described in [3]. The digestion, reduction/crystallization/filtration, and solvent extraction units have the largest transiting exergy flows due to the large excess of hydrochloric acid and water passing through these units.

C. *Life Cycle Analysis*

The goal of our life cycle analysis was to keep the boundaries of the analyses consistent so a gate-to-gate analysis was performed. The functional unit was the same as that in the previous analyses, namely the production of 97 kg of TiO_2 product per hour. The gross energy consumption in each step of the process and for the entire process was calculated, but the emissions associated with the supply chain of material and energy flows originating outside the process boundaries were not included in the current analysis.

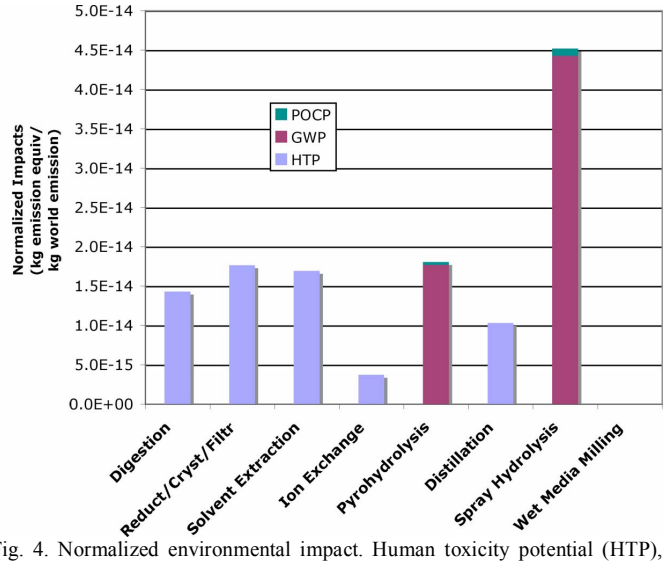

Fig. 4. Normalized environmental impact. Human toxicity potential (HTP), global warming potential (GWP), and photochemical oxidation potential (POCP).

A fugitive emission rate of 1% by mass of the volatile organics in each flow stream was assumed. This assumption may not be realistic, but it was necessary due to lack of data concerning fugitive emissions in the process. It was also assumed that all carbon dioxide produced from the combustion of methane in the hydrolysis units was emitted to the atmosphere.

Although there are many ongoing studies concerning the toxicity of TiO_2 nanoparticles to the environment and humans, we have excluded any possible adverse effects of the particles from this analysis. In the future when the impacts of nanoparticles are more certain we will incorporate this information.

In light of these assumptions, the results from our gate-to-gate life cycle analysis should only be considered qualitatively. Despite these limitations, there is still insight to be gained.

Environmental impact indicators for each unit were calculated using Leiden University's database of problem oriented approach characterization factors. The results were then normalized by the world emission rates for the year 2000 also given in Leiden University's database. The normalized environmental indicators can be found in Fig. 4. Due to our assumption of 1% emission rate of volatile organics, all units using hydrochloric acid have an impact on human toxicity potential. Predictably, the large amounts of carbon dioxide emitted from the combustion of methane in the hydrolysis units represents the largest contribution to global warming potential in the process.

IV. Discussion

This discussion will focus on each method from the standpoint of improvement analysis and compare the results. The energy and exergy analyses performed direct our attention toward the largest thermodynamic losses in the process, while the life cycle analysis emphasizes the environmental impacts of emissions. It is neither necessary nor probable that these methods will be in agreement on where improvement efforts should be dispatched.

From the above energy analysis, it is clear that the distillation unit represents the greatest sink of energy, as the gross energy requirement is greatest and the energy efficiency is the lowest for this unit (with the exception of the reduction and crystallization unit for reasons previously discussed). This would suggest that improvement of the process should start in the distillation unit.

Energy losses are also significant in the spray hydrolysis and pyrohydrolysis units. These two reaction units form the foundation of the process. Spray hydrolysis produces titanium dioxide in a form readily processed into nanoparticles and the pyrohydrolysis enables most of the hydrochloric acid to be regenerated and recycled back to the digestion unit. The methane burned in these two units to drive off the water from the reaction products is a considerable energy investment and reducing the amount of methane required even a small amount would greatly improve the total energy consumption in the process.

Exergy analysis offers a different view by allowing us to break flows down into material, fuel, and thermal exergy. By including entropy effects, exergy gives information about how much usable work the stream can provide. This is most apparent when comparing energy and exergy results for the distillation unit. As we saw in the first law analysis, the energy content of the high-pressure steam supplied for distillation is greater than that for the methane used in spray hydrolysis. However, the irreversibility rate in the spray hydrolysis unit is greater than that of the distillation unit because the fuel exergy of methane required exceeds the thermal exergy of the lower quality steam. Therefore exergy analysis gives some insight into quality of resources and directs improvement efforts toward spray hydrolysis as the primary target.

Another advantage that exergy analysis affords is it allows us to evaluate streams that have little or no enthalpy. Streams at low temperatures have insignificant enthalpy values, but these streams may still be relevant or even very important to the process. Material exergy allows us to analyze these flows where energy analysis does not.

The goal of life cycle analysis is minimizing both gross energy requirements and harmful emissions. From our results it is obvious that the methane and the carbon dioxide released from its combustion present the largest threat to global warming in our process. If our goal is to reduce the carbon footprint of the process then we should concentrate on reducing the amount of methane required, or try to capture the emitted carbon dioxide and use one or more strategies to convert or sequester it.

The life cycle analysis also identifies the hydrochloric acid in the process as a potential hazard to human health. This risk is perhaps greatest for industrial workers that work on or around these units. If not in place already, precautions should be taken to reduce any human exposure to the acid, and that includes prevention of emissions to the area surrounding the plant.

To summarize, all three methods give us similar results in that they all direct us to improve spray hydrolysis. However, the energy analysis identifies distillation as the top priority, while exergy analysis disagrees, mostly due to the lower energy quality of high-pressure steam. Life cycle analysis

shows spray hydrolysis to have the largest impact on global warming potential, but the suggested improvements would be much different from the thermodynamic methods. End of pipe solutions could be used to reduce carbon dioxide emissions or the use of different heat sources could be evaluated. In addition life cycle analysis encourages the careful isolation of all streams carrying hydrochloric acid. This would never be revealed by a thermodynamic method.

In conclusion, exergy analysis appears to yield all the information of a first law energy analysis along with information about quality of resources. However, depending on the initial goals of the evaluation any one of these methods might be optimal. If you want a quick look at the energy flows and efficiencies, energy analysis might be enough. If you have more time and want a deeper thermodynamic understanding, you should use exergy analysis. And finally if your goals are to reduce the environmental impacts of your process, life cycle analysis is the best choice.

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