[1b] - Calculating Metrics for Acetic Acid Production

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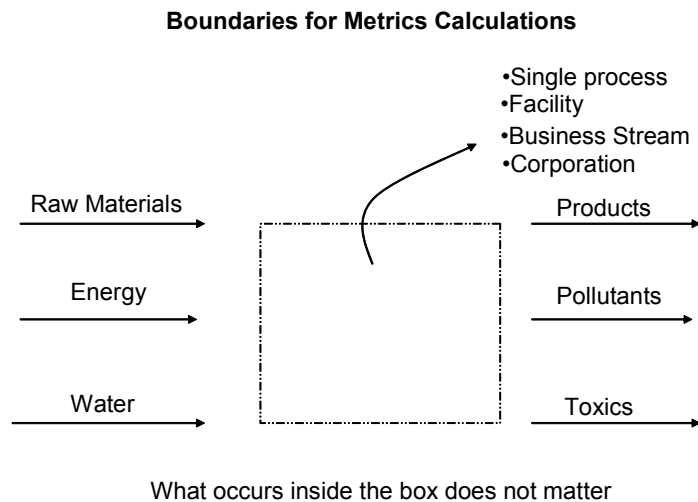*Phone: (314) 409-9068*
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Abstract:

In order to effective use sustainability metrics for assessing current performance, for setting goals or for measuring progress, the engineer must know the details of decision rules and how such a calculation is actual done. This paper uses a step-by-step process to demonstrate extraction of data from flow sheets, cost sheets, pricing information and publicly available reports to calculate metrics for a real acetic acid process. The calculation presented can be used as an instructional tool as well. Improvement of industrial processes in light of sustainable development is very challenging and requires a balance of safety, reliability, economics, quality, and an acceptable impact on the environment and society. Techniques such as total cost and benefit assessment, limited life cycle inventory and analysis, as well as eco-efficiency and sustainability metrics are creating a new view of plant design and product development.

Introduction

Industry, in particular the chemical industry, has developed and tested a variety of decision tools, e.g., metrics. The extension of the tools to other industries and eventually to academia and government is highly dependent upon simplifying the understanding, standardization and application of the tools.

The calculation allows the computation of five basic metrics: material use, water use, energy use, toxics emitted, land use and overall pollutants emitted. Further, it allows and facilitates the computation of complementary metrics, examples of which are greenhouse gases, eutrophication materials, acidification materials, ozone creating or depleting materials. It also facilitates the estimation of the net present value of costs of unrealized environmental impacts, including but not limited to, toxicity to plants and animals, depletion of natural resources and benefits to society of use of resources, such as land and raw materials. Metrics for more than fifty chemical process/product combinations were reported by Schwarz, *et. al*. (Ref. 1 & 2; see also Ref. 3).

Boundaries for Metrics Calculations

•Single process
•Facility
•Business Stream
•Corporation

Raw Materials

Energy

Water

Products

Pollutants

Toxics

What occurs inside the box does not matter

Figure 1. Simplified view used for metrics calculation.

Metrics can be calculated for a single process, a facility, a lifecycle stream from raw material to final product or for an entire corporation.

Calculating sustainability metrics for an acetic acid process.

An overall view of the acetic acid process is shown here and will be used to demonstrate calculation of metrics from available data in publications and patents. Information was taken from published sources (Ref. 1, 2 , 4, 5, 6, 7).
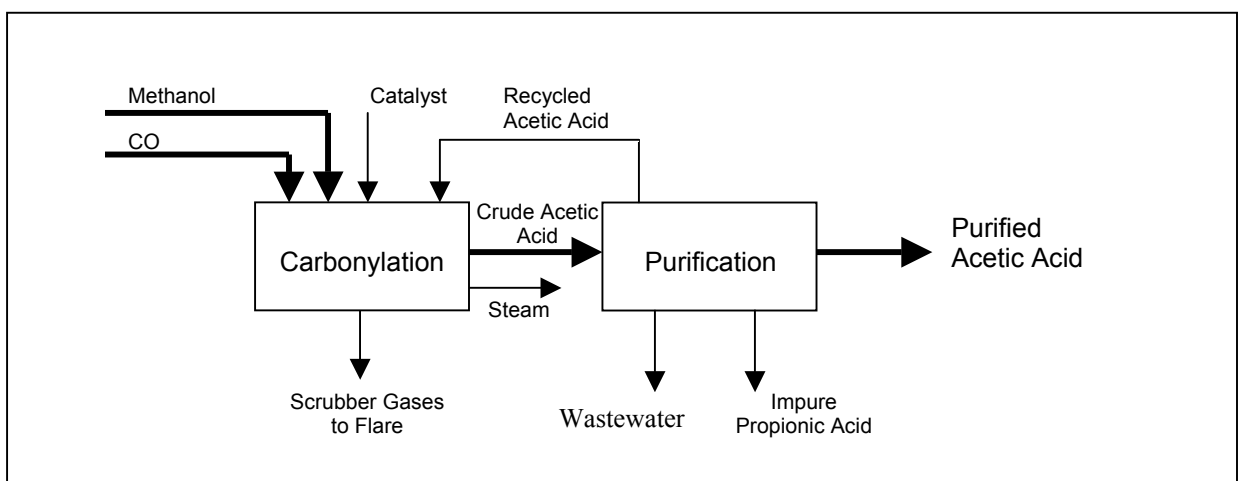
Figure 2. Acetic Acid production from methanol via low-pressure carbonylation with homogeneous rhodium catalyst.

Methanol is reacted with carbon monoxide in the presence of a homogenous rhodium catalyst and a methyl iodide promoter at temperatures in excess of 350°F and pressures greater than 450 psig. The reaction takes place in the liquid phase. The methanol is almost completely converted, approximately 99% selectivity to acetic acid. The reactor effluent is flashed to separate the reaction products from the unvaporized rhodium catalyst. Overall yield of acetic acid from methanol is 98%; and from carbon monoxide is 91%. In 1992, this process accounted for greater than 50% of the world's acetic acid capacity. The carbonylation reactor operates at about 400 psig and 350°F. Propionic acid is the major liquid by-product; trace quantities of higher carboxylic acids are also formed. In a water gas shift reaction, carbon monoxide (CO) and water react to form carbon dioxide and hydrogen. Yields based on CO exceed 90%. A large portion of the unreacted CO is lost in the vent gas intended to remove hydrogen and carbon dioxide formed in the water gas shift reaction form the system.

Design Bases
Reactor conditions:
Total Pressure > 450 psig
CO partial pressure, psig 200
Temperature: > 350° F
Catalyst composition 350 ppm Rh, 19 wt% ~ 15 wt% H_2O
Methanol conversion: ~100%
CO conversion: 92%
Selectivity of methanol to acetic acid, 99%
Allowance for plant losses 1% of product
Overall plant yield based on methanol: 98%
Overall plant yield based on CO: 91%

Catalyst Preparation and Regeneration
The catalyst mixture was prepared directly in the carbonylation reactor (the in situ procedure) or in separate catalyst reactors. Commercial plants prefer the latter procedure to ensure proper dissolving and complexing. The rhodium component fed to the catalyst dissolver consists of a mixture of fresh makeup RhI3 and spent catalyst. Catalyst preparation involves heating the spent catalyst solution (plus methanol) to 300°F. The pressure in the reactor is reduced, and the vapors are vented downstream. The reactor is cooled to room temperature agitation to precipitate out the rhodium component. The clear liquid on top of the precipitate is siphoned off and passed to the surge drum. A makeup RhI_3 catalyst is added to the reclaimed catalyst precipitate.

Carbonylation
The carbonylation reaction between methanol (technical grade) and CO (98% purity) is carried out at >350°F and >450 psig in a reactor. The heat of reaction is removed by circulation of the reaction product through an exchanger.

A heater is provided for plant startup. The overall reaction occurring in the reactor is as follows:

$$CH3OH\ (l) + CO\ (g) \rightarrow CH3COOH\ (l)$$
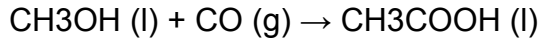
Estimated ΔH_{298} = -33 kcal/gmol methanol (exothermic). Small amounts of carbon dioxide and hydrogen are produced by a water gas shift reaction. Minor amounts of formic acid and propionic acid are also formed. Unreacted gases (mostly CO, nitrogen, and carbon dioxide) are vented through a gas cooler and vent gas scrubber. The liquid crude product stream from the reactor is flashed to 65 psig and 166°C (330°F) in a flash drum. The flashed vapors, containing acetic acid, water, methyl iodide, formic acid, and propionic acid, are sent to the purification section of the plant. The unvaporized liquid, which contains the rhodium catalyst, is returned to the carbonylation reactor. A small portion of the recycled catalyst stream (about 2%) is returned to the catalyst preparation section for regeneration. A recycled acetic acid stream from downstream product purification is stripped by reboiling before being returned to the carbonylation reactor via a surge drum.
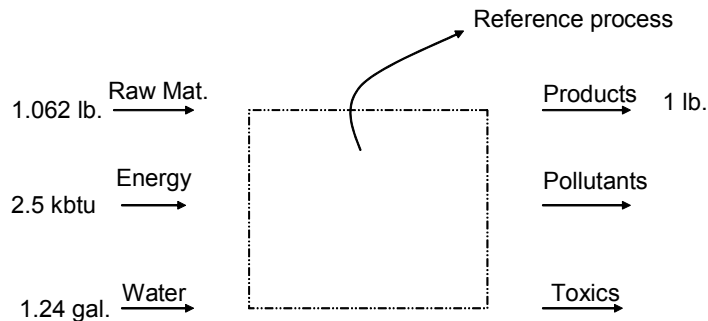
Purification
The crude product vapor stream from flash drum is distilled in a series of columns. Methyl iodide, methyl acetate, part of the water, part of the acetic acid, and a trace of unreacted methanol are separated from the crude acetic acid product stream in a crude fractionating column. The crude acetic acid is dehydrated and excess water in the system is purged. The dehydrated crude acetic acid is redistilled in refining column. Refined acetic acid leaves the column as a side steam at two plates below the top plate flows to storage. The net overhead of the column, containing mainly acetic acid and small amounts of residual water, formic acid, and methyl iodide, is recycled to the carbonylation reactor via a stripper. The bottoms from refining column, containing acetic acid and propionic acid, are stripped to reduce the acetic acid content. Bottoms from the stripper leave the column as a crude propionic acid byproduct, which could be recovered or could be a waste.

Raw Material Use

Carbon Monoxide	$0.00237 per scf	7.0628 scf
Rhodium	$0.0215 per mg	0.068 mg
Methanol	$0.382 per gal	0.082 gal

This translates into 1.062 lb of raw material per pound of product.

Acetic Acid Metrics Calculations

Reference process

1.062 lb. ——Raw Mat.——→

Products ——→ 1 lb.

2.5 kbtu ——Energy——→

Pollutants ——→

1.24 gal. ——Water——→

Toxics ——→

Figure 3. Simplified Process Flow Data

Material Metric

The metric for materials intensity is expressed as the mass of raw materials less the mass of the product, per unit of output. The numerator is measured in or converted to pounds and the denominator is measured in physical terms (pounds of product) or financial terms (dollar revenue or value-added). The material metric is expressed as the mass of raw material waste, rather than the mass of total materials consumed, as the metric was originally defined, in order to obtain a materials metric that is stackable along supply chains. Using total materials consumed would result in 'double-counting' the mass of products that become raw materials in a down-stream process. The material metric is calculated on a dry basis. However, water and air are included in the metric when hydrogen or oxygen molecules form water or air are raw materials and become a part of the molecular make-up of the product. When this occurs, the stoichiometric requirement of oxygen or water is used in the metric calculation.

The material metric for this case is: (1.062 – 1) / 1.0 = 0.062

Energy Metric

For energy intensity, the basic metric is energy consumed from all sources (numerator, measured in or converted to Btus) per unit of manufactured output or service delivery (denominator, measured in physical or financial terms). For calculation of the product metrics, purchased electricity is assumed and the energy conversion for electricity usage includes a factor to account for the

average losses incurred in the generation and transmission of electricity in the United States (0.31).

The energy metric for this case is 2.5 kbtu per pound.

Water Use Metric
The water metric developed for the product metrics is "water rendered unavailable for beneficial use, expressed as gallons per unit of output." The metric includes: water present in waste streams that must be treated because of chemical contamination, contact cooling water, water vapor that is vented to the atmosphere, water lost to deep-well injection and seven percent of non-contact cooling water. Severn percent is the factor used to account for water lost from a cooling tower due to evaporation and misting from wind.

The water metric for this case is 1.24 gallons per pound of product.

Waste Streams
A summary of the waste streams generated is: impure propionic acid, 1107 lb./hr.; Unreacted carbon monoxide, inert gases, and methanol 5541 lb./hr. Scrubbed gases are sent to a flare. The general waste treatment facilities handle the excess water, even though it contains some methyl iodide and acetic acid. The impure propionic acid is used as fuel in this case. Alternatively, the crude propionic acid could be further purified and sold, but the small amounts produced will likely make this economically unattractive.

The pollutant metric is less than 0.000001 pound per pound of product.

Uses for Calculations

Metrics calculated in the fashion above can be used to evaluate the impact of defined improvements in energy use. For example, five levels of energy requirements were established in Schwarz, *et.al.* and are described below.

Base Case Energy that is produced by the process, such as steam produced from the heat of reaction, is credited, but not other types of heat integration, heat pumps or other systems designed for energy savings included in the Reference Case.
Reference Case This includes improvements for energy efficiency such as heat exchanger networks and other systems for energy savings. It serves as a reference value, and is based on published process information.
Optimum Heat Integration Additional improvements to the base process are achieved through heat integration. It may include heat exchanger networks, heat pumps, or changes in process conditions. Basic aspects of the process (feedstocks used, the type of reaction and catalyst used, and separation processes) do not change.
Process Redesign This involves process redesign for energy efficiency and is based on the same reaction chemistry, but can reflect process changes such as changes in feedstock (e.g. pure oxygen instead of air), improved catalysts, different process configurations, or alternate separation techniques.
Theoretical Energy Requirement The theoretical energy is calculated for the reaction used in the base case, based on 100 percent conversion and 100 percent selectivity to the product.

Table 1. Practical Minimum Energy Levels

Calculating energy use for each process improvement level then yields energy metrics as shown below (details are provided in Schwarz, *et.al.* 2002)

	Base Process	Improvements to the Base Process		Process Redesign	Theoretical Energy
Electricity Requirement	103	103	103	148	
Hot Utility Requirement	1,555	1,555	1,529	1,391	
Hot Utility Credit	-363	-363	-363	-401	
Net Power & Hot Utility Requirements	1,295	1,295	1,269	1,138	
Fuel Energy for Electricity Generation	333	333	333	476	
Fuel Energy for Steam/Dowtherm	2,692	2,692	2,650	2,275	
Total Fuel Energy Required	3,024	3,024	2,982	2,751	
Fuel Energy Generated	-572	-572	-572	-632	
Net Fuel Energy Consumed	2,452	2,452	2,411	2,120	-867
Energy Metric, kbtu per pound	**2.5**	**2.5**	**2.4**	**2.1**	**-0.86**
Raw Material Energy Consumed in Process	1,173	1,173	1,173	1,173	867
Total Energy Consumed in Process	3,625	3,625	3,584	3,293	0
Total Energy Consumed in Feedstock Production	35,239	35,239	35,239	35,239	0
Total Energy Consumed in Product Chain	38,864	38,864	38,823	38,532	0

Table 2. Acetic Acid Energy Use & Metrics for Process Improvements

Base Process: From methanol via low-pressure carbonylation with homogeneous rhodium catalyst.
**Reference Case**: Only minor improvements are added to the base process.
Optimum Heat Integration: One process stream heat exchanger is added to the base process.
Process Redesign: From methanol via low-pressure carbonylation with heterogeneous rhodium catalyst.
Theoretical Energy Requirement with 100% conversion of methanol and carbon monoxide and 100% selectivity to acetic acid. The Gibbs free energy for the ideal reaction is –534 BTU/lb acetic acid.

Another use for metrics is to evaluate the impact of energy optimization efforts on other measures of sustainability. In this case, relative material use, water use and greenhouse gases are illustrated for the maleic anhydride process. Maleic anhydride is chosen because it provides an excellent example of how redesign of a process with a highly exothermic process can yield improved energy results, but at the cost of higher material use.
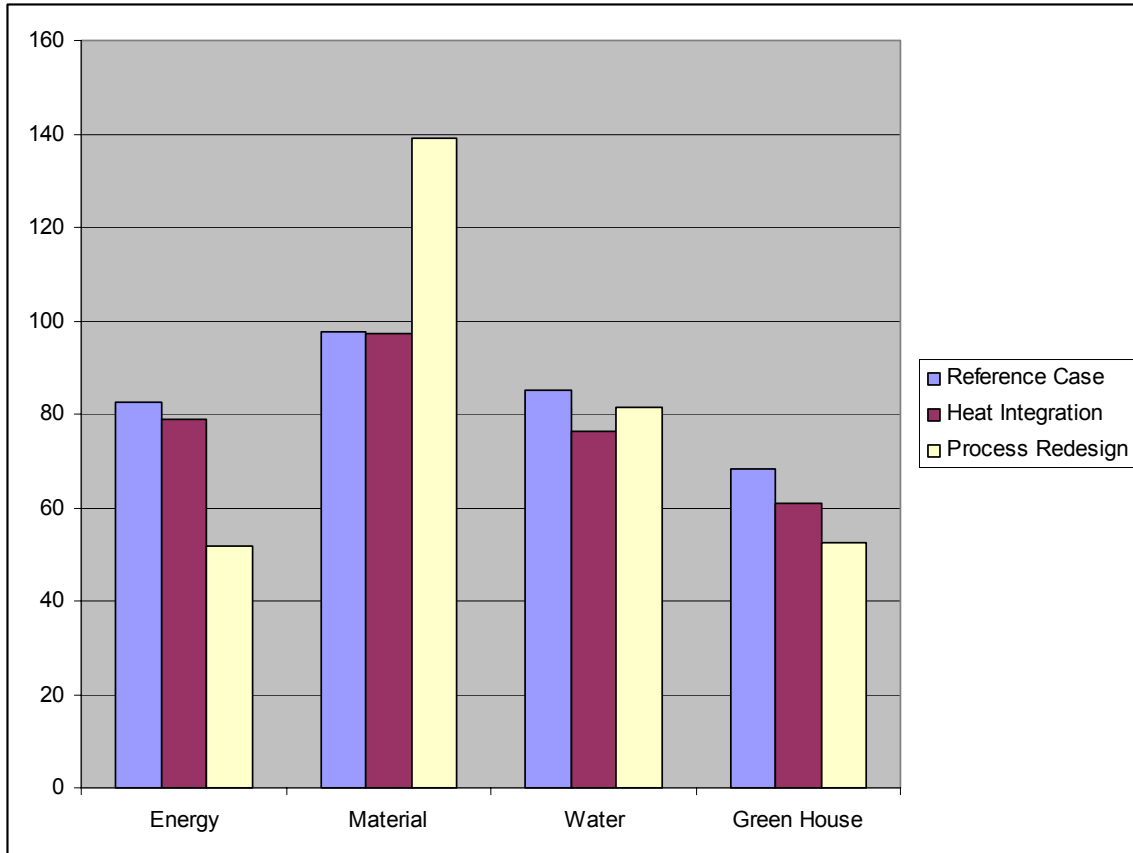
Figure 4. Relative Sustainability Metrics for Maleic Anhydride - shown as percent of base process (Base = 100). Metrics calculated per Dollar Value Added.

Figure 4 shows how the sustainability metrics for energy intensity, material intensity, water consumption and greenhouse gases vary with the energy optimization levels for maleic anhydride. As expected, the levels show reductions in greenhouse gases and water consumption with reductions in energy intensity. The metrics for Level 3, however, indicate that the improvements in the energy metric for this process design come at the expense of an increase in material intensity. This factor must be weighed in the evaluation of any process redesign.

Conclusions

1. Sustainability metrics and practical minimum energy levels used together can be particularly valuable management tools, both for targeting the products for which the most benefit can be achieved by reducing energy intensity and for evaluating the range of alternatives available to accomplish the goal of improved energy efficiency.

2. Using a simple, but well defined set of heuristics, can yield results for which products can be easily compared.

3. Metrics can be calculated from internal or external data if a logical set of heuristics is chosen.

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