Methods for Evaluating the Sustainability of Green Processes

Raymond L. Smith* and Michael A. Gonzalez
U.S. Environmental Protection Agency
Office of Research and Development
National Risk Management Research Laboratory
26 W. Martin Luther King Dr.
Cincinnati, OH 45268 USA

Abstract

A methodology, called GREENSCOPE (Gauging Reaction Effectiveness for the ENvironmental Sustainability of Chemistries with a multi-Objective Process Evaluator), is under development at the U.S. EPA’s Office of Research and Development to directly compare the sustainability of processes that employ various chemistries or technologies. Evaluations using the method answer two questions: is an alternative green (i.e., does it have a lower environmental burden) and is it sustainable? For evaluating sustainability, methods are being developed in four areas, called the four E’s: Efficiency, Environment, Energy and Economics. This paper represents the first descriptions of the evaluation methods for GREENSCOPE, including an example for the oxidation of toluene.

Keywords: Sustainability, Green Chemistry, Green Engineering, GREENSCOPE

1. Introduction

A considerable amount of research is being performed under the banners of “sustainable” and/or “green.” The development of chemistries and technologies under these banners needs to be analyzed in order to support these claims and to guide future research. In the U.S. EPA’s Office of Research and Development a methodology, called GREENSCOPE (Gauging Reaction Effectiveness for the ENvironmental Sustainability of Chemistries with a multi-Objective Process Evaluator), is under development to evaluate the sustainability of processes that employ various chemistries or technologies. Evaluations using the method answer two questions: is an alternative green (i.e., does it have a lower environmental burden) and is it sustainable? Evaluation measures, known as the four E’s, have been developed for Efficiency, Environment, Energy and Economics. A process that is better in these four areas will more likely be sustainable, although one can expect that most process evaluations will result in tradeoffs. This paper represents the first time that evaluation methods for GREENSCOPE are being defined, whereas earlier work focused on the theory and philosophy of GREENSCOPE with respect to green chemistry and engineering (Gonzalez and Smith, 2003). For those interested in computer aided process engineering, these evaluation methods represent possible objectives for optimization.

* Author to whom correspondence should be addressed: smith.raymond@epa.gov
2. Efficiency

The calculation of efficiencies for chemical reactions provides chemists with a measure of how green their reactions are (Constable et al., 2002). This is reflected in values such as conversion and selectivity, which define yields, reactor effluent product distributions, and recycle flows to make a desired quantity of product. Another measure of how green a reaction is can be obtained from the atom economy (i.e., how much mass from the feed ends up in the product). These measures, which are well known in green chemistry, are related to environmental impacts, as the product distribution defines what chemicals and amounts may leave a process. These efficiencies can be considered an initial evaluation of a process, and they represent a bridge between the lab-scale experiments of a chemist and further engineering calculations.

In this work, the selectivity has been calculated as the moles of desired products divided by the moles of reaction of the limiting reactant. In an analogous way, the atom economy for a particular product is the mass of the product divided by the mass of reactants reacted. With these definitions, the atom economy tells one about the inherent chemistry (i.e., how efficient is the reaction itself), while selectivity provides the product distribution based on all of the reactions that occur. Each of these measures is presented as a percentage.

3. Energy

Energy is a basic component of any chemical process. Its use depletes resources, creates potential environmental impacts and incorporates additional cost into a processes operations. Likewise, a less efficient process can be expected to use more energy, and so one can see that the efficiency and energy measures of sustainability are interconnected. By evaluating energy balances for alternative processes another measure of sustainability is obtained.

A target for minimizing energy use is available from pinch analysis. Linhoff and Flower (1978) describe how to determine minimum hot and cold utilities using the method of pinch analysis. For this work, the minimum hot utility is used as the best possible target, although different technologies (e.g., chemistries or process designs) could improve upon this value. Using only utilities (without networking heat exchangers) produces a worst case energy use. These best and worst cases provide limits for a scaled equation of performance,

\[
\text{Percent Score} = \left(\frac{(\text{Actual} - \text{Worst})}{(\text{Best} - \text{Worst})}\right) \times 100\% \tag{1}
\]

which is a common form for presenting results using GREENSCOPE. The key in using such a method for analyzing a process is that the best and worst case bounds are well defined. This differentiates GREENSCOPE from many other methods used to analyze green chemistry and engineering (Gonzalez and Smith, 2003).
4. Environment

To evaluate the environmental aspects of alternative chemistries or technologies GREENSCOPE employs the Waste Reduction (WAR) algorithm (Young and Cabezas, 1999). The WAR algorithm is used to determine the potential environmental impacts of releases from a process in eight impact categories: human toxicity by ingestion (HTPI) and dermal/inhalation routes (HTPE), aquatic toxicity (ATP), terrestrial toxicity (TTP), acidification (AP), photochemical oxidation (POCP), global warming (GWP) and ozone depletion (ODP). The potential impact per time out of a process, \( \dot{I} \), can be obtained as

\[
\dot{I} = \sum_i \alpha_i \left( \sum_j M_j \psi_{ij} \right)
\]  

(2)

where \( M_j \) is the mass flowrate of non-product \( j \) exiting the process, \( \psi_{ij} \) is the potential environmental impact per mass of component \( j \) for impact category \( i \), and \( \alpha_i \) is a weighting factor that can be used to combine impact categories. In this work the \( \dot{I} \) values are calculated separately for each impact category.

Similarly to the calculations for energy, best and worst case values for each impact category were developed using a best case from pinch analysis for the minimum energy consumption (with WAR impacts for energy use from Young, 2002) and a worst case where only utilities are used and all fresh feed and product streams are assumed to be dumped into the environment. These two limits are used to frame the percent scores as described in Eqn. (1).

Using WAR to analyze processes is another improvement of this method. While the potential impacts of WAR are defined as mid-point indicators (as opposed to end-point indicators which could specify the physical effects of acidification, for example), the measures for the various categories are well defined, which is a substantial improvement over arbitrary environmental or mass-based scores.

5. Economics

Finally, the economics of alternative processes are measured according to their costs. For economists this is an oversimplified view of markets, but for our engineering calculations the annualized costs are significant measures. Of course, these costs are tied into the process through efficiencies, energy and environmental impacts. The relationship between these measures is substantial, although without a positive economic performance, no process is sustainable.

The calculation of economic performance has been accomplished using methods described in Douglas (1988) as annualized profits (i.e., economic potentials). Best and worst case bounds were determined by assuming that revenues equal profits for the best case and that zero economic potential represents the worst case. The form of Eqn. (1) was then applied to obtain percent scores.
6. Oxidation of Toluene Case Study

Example calculations have been performed on a process to make benzaldehyde and co-product benzoic acid from the oxidation of toluene. A base case design was developed on a spreadsheet using hierarchical process design (Douglas, 1988). This base case design for the production of $6.4 \times 10^7$ gmoles of benzaldehyde per year, as shown in Figure 1, was not optimized. It was assumed that distillation was used for all required separations, although extraction and crystallization could have been used (Opgrande et al., 1998a,b). A selectivity to all desired products of 94% was assumed, based on the similar oxidation of ethylbenzene (Schmidt, 1978), and with the formation of byproducts as described by Opgrande et al. (1998b). Selectivity among the desired products and reaction conditions were obtained from Kantam et al. (2002), although only a reactor feed molar ratio of 0.1 of acetic acid solvent to toluene reactant was used. The purge fraction was set to 0.02, while prices were obtained from Chemical Market Reporter (2003).

![Diagram of the process for benzaldehyde and benzoic acid production. The purge stream includes acetic acid, toluene, formic acid, and benzene. The bottoms of Still 2 is composed of benzyl formate, benzyl alcohol, and benzyl acetate. The bottoms stream of Still 4 includes biphenyl and phthalic acid.](image)

Figure 1. Process for benzaldehyde and benzoic acid production. The purge stream includes acetic acid, toluene, formic acid, and benzene. The bottoms of Still 2 is composed of benzyl formate, benzyl alcohol, and benzyl acetate. The bottoms stream of Still 4 includes biphenyl and phthalic acid.
Assuming that one plans to research chemistries and technologies that could be beneficial for the efficiency, energy use, environment, and economics of the process, a number of “what-if” calculations were performed. The results provide an indication of how beneficial a new chemistry or technology could be, i.e., what are the incentives for further research in this (or in a general sense, any) area. These results are presented for this case study in Tables 1 and 2.

From the results, one can gain a greater understanding of potential increases in greenness and sustainability that a technology could create. For instance, developing a catalyst that can operate in a neat reaction has a moderate affect on energy and environmental scores. This is not surprising since a very low solvent to feed molar ratio was assumed in the base case. A more selective catalyst, assuming that biphenyl and phthalic acid are not produced, increases selectivity, energy, economic, and environmental scores. The change in the catalyst performance seems rather modest, as only two of the many byproducts are eliminated, but it allows the process to be designed without Still 4 of Figure 1. This case shows how improvements in chemistry and engineering can together produce dramatic results. Finally, if either the catalyst or reactor system can be designed to increase conversion without reducing selectivity, the affects on energy, economic, and environmental scores can be large. Increased conversion reduces recycle rates, process unit sizes, energy use and costs.

7. Conclusions

The analysis of processes with GREENSCOPE according to their efficiency, energy use, environmental impacts, and economics can be very valuable. In the case of possible green and/or sustainable research projects, a what-if analysis provides important information on the benefits of success. Once one knows what success would mean, decisions on pursuing research can be made on a much firmer basis.

Table 1. Oxidation of toluene process efficiencies, energy, and economic scores. All scores represent the percentage of the best case bound as described in Eqn. (1).

<table>
<thead>
<tr>
<th></th>
<th>Conversion</th>
<th>Selectivity</th>
<th>Atom Economy Bz-ald/Bz-acid</th>
<th>Energy</th>
<th>Economics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Case</td>
<td>13%</td>
<td>91%</td>
<td>98% / 98%</td>
<td>0%</td>
<td>12%</td>
</tr>
<tr>
<td>Neat Reaction</td>
<td>13%</td>
<td>91%</td>
<td>98% / 98%</td>
<td>13%</td>
<td>13%</td>
</tr>
<tr>
<td>Selective Catalyst</td>
<td>13%</td>
<td>93%</td>
<td>98% / 98%</td>
<td>19%</td>
<td>19%</td>
</tr>
<tr>
<td>High Conversion Reactor</td>
<td>26%</td>
<td>91%</td>
<td>98% / 98%</td>
<td>74%</td>
<td>17%</td>
</tr>
</tbody>
</table>
Table 2. Oxidation of toluene process environmental scores. All scores represent the percentage of the best case bound as described in Eqn. (1).

<table>
<thead>
<tr>
<th></th>
<th>HTPI/ TTP</th>
<th>HTPE</th>
<th>ATP</th>
<th>GWP</th>
<th>ODP</th>
<th>POCP</th>
<th>AP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Case</td>
<td>34.9%</td>
<td>0.0%</td>
<td>0.1%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>60.6%</td>
<td>0.0%</td>
</tr>
<tr>
<td>Neat Reaction</td>
<td>43.2%</td>
<td>13.5%</td>
<td>13.6%</td>
<td>13.5%</td>
<td>13.5%</td>
<td>65.1%</td>
<td>13.5%</td>
</tr>
<tr>
<td>Selective Catalyst</td>
<td>46.3%</td>
<td>18.5%</td>
<td>18.6%</td>
<td>18.5%</td>
<td>18.5%</td>
<td>66.6%</td>
<td>18.5%</td>
</tr>
<tr>
<td>High Conversion</td>
<td>80.9%</td>
<td>74.0%</td>
<td>74.2%</td>
<td>74.2%</td>
<td>74.2%</td>
<td>88.4%</td>
<td>74.2%</td>
</tr>
</tbody>
</table>

References

Constable, D.J.C., A.D. Curzons and V.L. Cunningham, 2002, Metrics to ‘Green’ Chemistry – Which are the Best?, Green Chemistry 4, 521.
Young, D.M., 2002, Personal communication.