Evaluating the Greenness of Green Chemistry via Traditional and Thermodynamic Life Cycle Assessment

Yi Zhang, Bhavik R. Bakshi, and Endalkachew Sahle-Demessie
zhang.468@osu.edu
bakshi.2@osu.edu
Sahle-Demessie.Endalkachew@epamail.epa.gov

Abstract

Developments in Green Chemistry are expected to result in novel approaches that are more environmentally benign than traditional methods. Much of the research in green chemistry focuses on replacing toxic and hazardous substances such as solvents, catalysts and reaction media by alternatives that are non-toxic or reduce emissions. Unfortunately, most new developments in green chemistry are not evaluated for their "greenness" via a systematic analysis of their environmental impact during their life cycle. Consequently, it is likely that many techniques that are claimed to be green may not really have a smaller environmental impact over their life cycle. Although LCA is a well developed approach, it is still best suited for evaluating mature technologies for which life cycle inventory data are available. Such data are very difficult to find for emerging technologies. This paper presents one of the first LCAs to compare green versus traditional chemistries. A traditional LCA is performed with data reported by chemists. This approach is not convenient because information about emissions and impact is rarely available from the laboratory scale processes. A novel thermodynamic approach that does not rely on information about emissions and their impact is also used. This approach relies on input-side information, which is usually more readily available, and seems to be well correlated with emissions and their impact.

This paper takes Ionic Liquids (IL's) as examples, two kinds of promising applications of ionic liquid are analyzed to compare it with traditional methods or traditional solvents. Ionic liquids are organic salts whose melting point is normally below about 100°C. Recent research about IL's and their applications is booming, partly because they are considered to be 'green solvents'. This impression of environmental friendliness is due to their extremely low vapor pressure, which makes them good substitutes to traditional industrial solvents, most of which are Volatile Organic Compounds (VOCs). Replacement would prevent the emission of VOCs, a major source of environmental pollution. One of applications of Ionic Liquids is to be used as solvents in hydrogenation reaction.

Although Ionic liquids seem like a promising solution in organic chemistry, there are still several issues that need to be explored for confirming their "greenness". It is critical to collect environmental, health data before encouraging the use of IL's as alternatives for organic solvents, as well as perform their Life Cycle Assessment to study the environmental impacts throughout a product's broader life cycle to ensure that the environmental impact is not just being shifted to other stages of the life cycle.

The two examples of IL's applications are hydrogenation of benzene to form cyclohexane and Diels-Alder Reaction. 1-methyl-3-butyl-imidazolium tetrafluoroborate ([Bmim][BF_4]) is selected as a typical Ionic Liquid. Hydrogenation is an important catalytic method in synthetic organic chemistry both on the laboratory and the production scale. The classical hydrogenation catalysts are heterogeneous catalysts. However, homogeneous

hydrogenation catalysts in liquid phase have attracted considerable interest recently, and Ionic Liquids are good alternative reaction mediums. The methods evaluated include the traditional industrial process, and newer green chemistries based on ionic liquids and water solvents. Besides the advantage that Ionic Liquids have no (or negligible) vapor pressure, they have some other benign properties: Ionic liquids provide a polar, non-nucleophilic environment which can stabilize the homogeneous hydrogenation catalyst and increase catalyst lifetime; comparing with water, which is also considered as one of "Green Solvents", Ionic liquids can dissolve more hydrogen, which leads to a higher reaction rate.

Diels-Alder reaction is also an important and widely used reaction in organic synthesis, and in the chemical industry. The rate enhancement of this reaction can be achieved by using ionic liquids, water, and 5M lithium perchlorate–diethyl ether mixtures (5M LPDE). In this paper, the reaction of cyclopentadiene and ethyl acrylate is selected as an example to compare the efficiency of [Bmim][BF_4], water and LPDE. The reaction produce two kinds of molecules: *endo* and *exo*, and we take *endo* molecule as product.

A "cradle to gate" Life Cycle Assessment is performed to compare alternatives in each example. LCA inventories are from public database. The inventory data are converted to environmental impact by the method of Eco-Indicator 99. Three overall comparison results are shown in the following tables.

Table 1. Overall Comparison of Solvents (per kg)

Units / solvents	DALY	PDF*m2*yr	MJ surplus
[Bmim][BF4]	3.1E-03	1.0E+02	1.6E-03
5M LPDE	1.8E-03	5.7E+01	1.4E-03
H2O	6.3E-10	1.9E-05	5.5E-07
Diethyl Ether	1.8E-03	6.4E+01	1.1E-03
Benzene	3.3E-03	1.4E+02	4.4E-02
Acetone	5.03E-03	1.78E+02	1.91E-04

Table 1 is comparison of solvents, including [Bmim][BF4], water and some organic solvents. It shows that water is always the best, the Diels-Alder reaction candidate 5M LPDE is better than [Bmim][BF_4], but [Bmim][BF_4] is not worse than the other three organic solvents.

Table 2. Overall Comparison of Three Scenarios for Cyclohexane Production (/kg)

Units / scenarios	DALY	PDF*m2*yr	MJ surplus
Industrial	3.4E-03	1.4E+02	4.1E-02
H2O	5.7E-03	2.1E+02	4.6E-02
[Bmim][BF4]	1.3E-02	4.5E+02	5.0E-02

Table 2 shows the results of cyclohexane production. [Bmim][BF_4] scenario is the worst scenario, water is the second, and industrial scenario is the best. We can conclude no solvents are usually better than solvents. Although water is very environmental benign, and homogeneous catalyst system may achieve higher yield and higher efficiency, solvent systems need separation after the reaction phase, and separation needs organic solvent to extract, which makes the solvent system impracticable.

Table 3 shows the results of Diels-Alder reaction. The results are close for the three solvents because all the reaction conditions are the same for the three solvents, but it still tells us the 5M LPDE is the best, then is [Bmim][BF_4], and the worst is water.

It is interesting to compare the results of water and [Bmim][BF_4] in the two examples. For cyclohexane, [Bmim][BF_4] case is worse than water, however, for Diels-Alder reaction, [Bmim][BF_4] case is better than water. This is because two different issues dominate the results in these two examples. Ionic Liquids are complicated compounds, and a long life chain is required to synthesis them, so large amount of pollutions are produced during this process. It makes IL's are much worse than water, which is shown in the table 1. Since the solvents issue dominate the environmental impacts, cyclohexane production in [Bmim][BF_4] is worse than water. However, yields dominate the results of Diels-Alder reaction, the sequence of yields from high to low is 5M LPDE, [Bmim][BF_4] and water. The more material loss results in more environmental impacts. It worth to be notified that yield of cyclohexane in [Bmim][BF_4] is also higher than in water, but it is not so significant.

Table 3. Overall Comparison of three solvents for Diels-Alder Reaction

Units / Solvents	DALY	PDF*m2*yr	MJ surplus
[Bmim][BF4]	2.1E-02	7.4E+02	1.2E-02
5M LPDE	1.9E-02	6.8E+02	1.2E-02
H2O	2.2E-02	7.5E+02	1.3E-02

Thermodynamic Life Cycle Assessment is also applied to the cyclohexane production example. The method is similar to Life Cycle Assessment, but it calculates total input exergy (useful energy) instead of pollutions and environmental impacts. Two values are calculated to compare different cyclohexane production methods, one is Industrial Cumulative Exergy Consumption (ICEC), and the other is Ecological Cumulative Exergy Consumption (ECEC). ICEC only considers the exergy in industrial scale, but ECEC also includes ecological products and ecological services, for example, rain and wind. ECEC is constituted of four parts: Nonrenewable energy (NR), Renewable energy (REN), Impact of pollution (IP), and Human resources (HR). Data is given in Table 4.

Table4. Thermodynamic LCA of Cyclohexane Production

	ICEC	NR	REN	IP	HR	ECEC
Industrial	7.38E+08	5.71E+12	8.85E+09	8.29E+10	6.11E+11	6.42E+12
H2O	8.48E+08	6.29E+12	3.64E+11	9.33E+10	6.87E+11	7.44E+12
[Bmim][BF4]	9.00E+09	3.23E+13	3.53E+11	5.22E+11	7.14E+12	4.03E+13

In this analysis, [Bmim][BF_4] is still the worst scenario, then the water scenario, and the industrial process is the best, except that water scenario consumes more renewable energy than [Bmim][BF_4] scenario. This is consistent with environmental LCA, which means if a process consumes more exergy, it may have more environmental impacts. So when information about emission and impact is hard to get, we can try to roughly estimate them by considering how much exergy is consumed in the input side.

From these comparisons, it seems IL's are not bad solvents, especially compared with other organic solvents. Although it needs a long life chain to synthesize, it has lower vapor pressure. So in the situation solvents are essential, and IL give a higher efficiency than organics, choosing IL may reduce the VOC emissions. But this is only valid if it is easy to separate IL from product. Diels-Alder reaction is such a case; on the contrary, cyclohexane production is not. Industrial cyclohexane process is mature, and it needs not solvents, furthermore the separation is quite easy due to the very high yield. So using IL, or even water, can only cause more trouble, especially in the separation phase. In a word, manufacture of cyclohexane via "green" solvents may not be environmentally preferable. Chemistries where IL's may outperform traditional processes from a life cycle point of view will be further discussed.