Journal of Energy Research and Environmental Technology (JERET)
p-ISSN: 2394-1561; e-ISSN: 2394-157X; Volume 4, Issue 1; January-March, 2017, pp. 95-97

http://www.krishisanskriti.org/Publication.html

Green Solvents–The Promising Technology

Sara Fatima[1] and Iram Arman[2]

[1]Department of Chemical, ZHCOET Aligarh Muslim University
[2]Department of Petroleum, ZHCOET Aligarh Muslim University
E-mail: [1]fatima.sara786@gmail.com, [2]iramarman@gmail.com

Abstract—*Green Chemistry is the technological approach to prevent pollution and reduce consumption of non-renewable resources. Solvents are consumed in large quantities in many chemical syntheses, cleaning and degreasing. But traditional solvents are often toxic or chlorinated. In the US in early 1990s, solvent production was 26 MTA. Many of the top chemicals released/ disposed were solvents like MeOH, Toluene, Xylene, CS_2, MEK and CH_2Cl_2. These conventional solvents pose hazards such as flammable (chlorinated solvents), carcinogenic (chlorinated solvents, aromatics), high vapour pressure (inhalation route), narcotic (ether, chloroform), toxic (MeOH, CS_2), mutagen/teratogen (toluene), peroxides (ethers) and smog formation. These include methanol (CH_3OH), ethanol (C_2H_5OH), acetone (C_3H_6O), isopropanol (C_3H_7OH) and hexane. Methanol is flammable, toxic and damages organs. Ethanol is neurotoxic psychoactive and flammable. Acetone is volatile, flammable and may cause drowsiness/dizziness. Isopropanol is flammable and may cause dizziness. Chloroform and hexane pose air and water hazard plus persistency. Toluene is suspected of damaging the unborn child. Dichloromethane even as a short-lived halogenated substance has shown to be ozone-depleting. Hence green solvents as alternatives have been emphasized in the recent past. The criteria for the selection of these green solvents include process sustainability, environmental impact, human health and safety, regulation (waste and toxicity) and cost of manufacture.*

Keywords*: Green solvents, bioprocess aerogels, carbohydrate chemistry, biomass processing, separation process.*

1. INTRODUCTION

On what basis the solvent selectivity and assessment be decided. Cristian Capello et al, 2007, formulated two methods of solvent selectivity: EHS (Environment, Health and Safety) and LCA (Life Cycle Assessment). EHS method includes solvent properties like release potential, reaction/decomposition, flammability, explosiveness, toxicity, air and water hazard and persistence. This uses an Excel Tool which acts as database for solvent selection based on above mentioned solvent parameters. LHS method involves quantification of emissions and resource use over the whole life-cycle of solvent. This method studies solvent properties like non-renewable resource depletion as a consequence of petro-chemical solvent production, air emissions due to solvent incineration or high energy investment for solvent recycling processes. LCA involves modeling of ancillaries' consumption, energies, co-products' generation and emissions of pollutants. On EHS scale, it found formaldehyde to have high scores in acute and chronic toxicity, irritation and air hazards. Dioxane has high persistency, while formic and acetic acid both show high scores of irritation. Low overall scores were found for methyl acetate, ethanol and methanol.

2. ASSESSMENT OF CONVENTIONAL SOLVENTS

Cristian Capello et al, 2007 assessed solvents on the basis of EHS and LCA parameters. Figure 1 shows the use of tetra-hydrofuran, butyl acetate, cyclohexane, and 1–propanol is not recommendable from life cycle perspective. They cause high environmental impact during petrochemical production. Also formic acid, ethyl acetate, acetonitrile, dioxane, 1-butanol and dimethyl formamide are not also recommended due to low net calorific value. Figure 2 shows dioxane, acetonitrile, acids, formaldehyde and tetra-hydrofuran show high environmental impact.

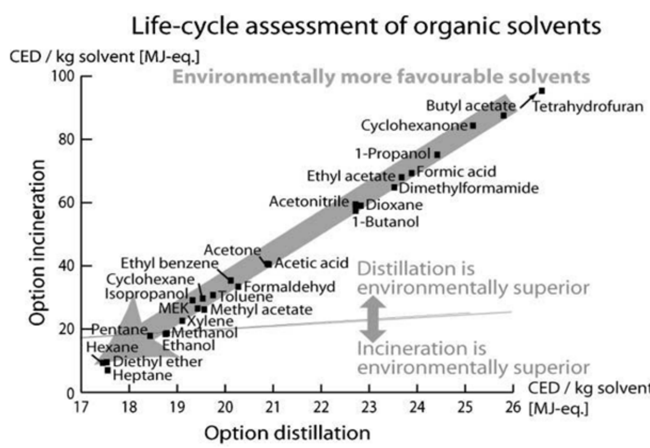

Fig. 1: Life-cycle assessment of the treatment options, incineration and distillation, for the 26 solvents (step (2) in the framework for the assessment of green solvents).

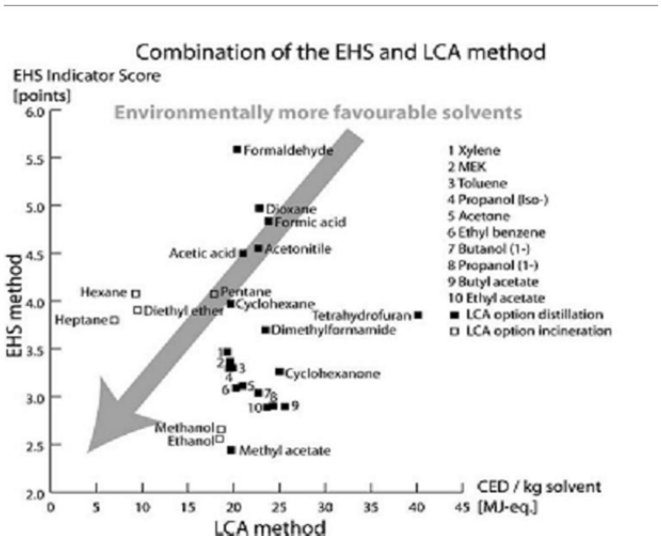

Fig. 2: Environmental assessment of the 26 organic solvents: combination of the EHS method with the LCA method.

3. APPLICATIONS OF GREEN SOLVENTS

Today green solvents find application in variety of fields like biomass synthesis, carbohydrate chemistry, biopolymer aerogels, separation processes, medicine etc. Some of these green solvents have been discussed here.

3.1 Biomass Synthesis

Lindsay Soh [5] et al, 2016, analyzed the solvents used in biomass synthesis. It states that US Department of Energy characterizes a bio-refinery by the ability to efficiently covert a broad range of biomass feedstock into commercially viable biofuels and other bio-products. These feedstock may be carbohydrate-rich (corn, sugar-cane), lingo-cellulosic (corn, switch grass) or lipid-rich (palm micro-algae). It found 1, 3 propanediol, dimethylsulfoxide, acetonitrile, tetrahydrofuran, methyl acetate, toluene, 2-methyl thf and heptane as problematic (P) solvents, while pyridine, 1, 2 dichloro-ethane and hexane as hazardous (H) solvents and listed chloroform as highly hazardous (HH) solvent. These rankings were based on Hildebrand solubility parameter, Hansen solubility parameter and Kamlet-Taft parameters. Solubility is an important selection criterion as poor solvent function can lead to low yields and increased process waste. The survey found that all chemical companies avoided chlorinated solvents–minimizing the use of dichloromethane (ozone-depleting compound) and effectively eliminating the use of chloroform and CCl_4; but the adoption of green solvents was not widespread. Water itself can be considered as an ideal green solvent; however its applicability is limited to specific chemistries. Bio-derived solvents include bio ethanol obtained from carbohydrate feedstock and lingocellulosis. Also include compounds like ethanol, furans, glycerol, hydrocarbons, carboxylic acids like lactic acid and succinic acid, aldehyde and levulinic acid and polyols like sorbitol and xylitol. Solvent selection guides should include EHS metrics like boiling point and LCA metrics like materials consumed, gross energy credit, water consumption, organic C-content, fossil fuel feedstock, photochemical ozone creation potential, global warming potential, acidification and eutrophication. Energy consumptive processes include esterification and alkylation. Furfural from lingocellulosics shows promise as a green solvent - Two promising furfural based green solvents are 2-mehyl tetrahydrofuran (2-MeTHF) and ϒ-valerolacetone (GVL).

3.2 Biopolymer Aerogels

Raman Subramanyam [3] et al, 2016, discusses about role of green solvents in Biopolymer Aerogels. These aerogels (pectin, alginate, chitosan, cellulose etc) exhibit both specific inheritance functions of bioproducts and 80-90% porosity and specific surface upto 800 m^2/g of polymer and aerogels. This amalgamation of properties makes biopolymer aerogels promising candidates for a wide variety of applications such as thermal insulation, tissue engineering and regenerative medicine, drug delivery systems, functional foods, catalysts, absorbents and sensors.

3.3 Carbohydrate Chemistry

Angeles Farran [4] et al, 2015 discusses the role of green solvents in carbohydrate chemistry. Ionic Liquids as solvents were proposed. Ionic Liquid solvents (IL)–for extraction and dissolution of carbohydrates. The solubility of ILs is a determining factor here. Such IL solvents include sorbitol, xylitol for bio-refining etc. They demonstrated a capability to act as selective solvents and catalysts for biomass processing. The recovery of carbohydrates, such as cellulose and hemicellulose from biomass is also possible by use of ILs. Most ILs are composed of a heterocyclic (pyridine or imidazole) cation and a halide organic acid or isocyanate anion. (2) Supercritical Fluids - In particular, peracetylated sorbitol and β- D-galactose are soluble under mild conditions and high pressures in $ScCO_2$. For example, peracetylated sorbitol and β- D-galactose are soluble under mild conditions and high pressures in $ScCO_2$. (3) Fluorous solvents are fluorinated alkanes, ethers and tertiary amines for use in biphasic systems. They are highly flourished and immiscible with both organic and aqueous solvents. The miscibility of flourous solvent with organic compounds is temperature dependant. At room temperature, perflourohexane forms a bilayer which becomes completely miscible at 24.8 °C while with other solvent systems; there is a variation in complete-miscibility temperature. In the field of catalysis, a lipase-catalyzed reaction in a flourous solvent showed formation of polyethylene glycol-lipase complex having higher alcoholysis activity than in conventional solvents. This alcoholysis reaction requires the addition of an organic solvent (iso-octane) miscible with flourous solvent in order to dissolve non-fluorinated substrates. (4) Deep Eutectic solvents(DES)– is a fluid that is generally composed of 2-3 safe and inexpensive compounds that form a eutectic mixture with melting point lower than either of the component. DES were first discovered by mixing metal salts like Zn, Al, Sn and Fe chlorides with quaternary ammonium salts. Green deep eutectic solvents include choline-chloride with alcohols and urea with sugars or organic acids. DES are cheaper and more environment friendly than ILs.

Table 1: Sources of Biomass to Obtain Green Solvents

Source of Biomass	Biopolymer
corn, wheat, starch crops	Starch
green plants, paper, switchgrass	Cellulose
sorghum, woody biomass	Lignin
beet molasses, shrimp shells	Chitin
sugar cane, vegetable oils, seaweed,	lipids, proteins
wood residues	polyhydroxyalkanoates

Angeles Farran [4] et al, also discussed solvents derived from fats and oils of animal sources (triglycerides) and from biomass as in Table 1. Biodiesel from rapeseed, soybean, vegetable oil etc is obtained by trans-esterification with methanol. Here, glycerol, a byproduct of biodiesel industry has been found to be a valuable green solvent. Also, Terpenes (derivatives of isoprene that are ubiquitous in the plant world) are essential oils and they can also be source of green solvents. E.g. turpentine. They are both immiscible in water and can substitute for methylene chloride or toluene.

3.4 Separation Processes

Dupont et al, 2000, discusses the use of green solvents in separation processes. This review covered the main achievements on the use of room temperature ionic liquids (RTILs) as green chemistry solvents. Molten salts, or ionic liquids, can be described as liquid compounds that display ionic-covalent crystalline structures. They include pure inorganic compounds (NaCl), organic compounds (Tetra-butyl phosphonium chloride) and eutectic mixtures of inorganic salts (such as lithium chloride/ potassium chloride) or organic-mineral combinations (tri-ethyl ammonium chloride/ copper chloride). These liquids have been widely used in electrochemical technologies as solvents for highly charged complex ions, for electronic absorption spectra, for organic synthesis and catalysis, including Ziegler-Natta reactions. In this series, PF6, ionic liquid can be viewed as a classical solvent and is suitable for L-L separation processes. The partitioning data of various organic solutes (aniline, benzene, phthalic acid etc). between PF_6 and water shows a close correlation with partition coefficients of the same solutes between 1-octanol and water. Although the distribution coefficients for the ionic liquid-water system are, in general, an order of magnitude lower than those of 1-octanol-water system, these values are suitable for practical purposes. RTILs have recently demonstrated potential for replacement of toxic VOCs as solvents. E.g. thymol blue dye. The pH of the media was adjusted by use of CO_2 and NH_3.

4. CONCLUSION

Green solvents must follow the twelve principles of green chemistry and can be broadly classified into six categories (supercritical or superheated water, liquid polymers like polypropylene glycol, switchable hydrophobicity/ hydrophilicity solvents like $C_6H_5NMe_2$, supercritical CO_2, ionic liquids like NaCl and $NaBF_4$ and solvent less conditions). Today green solvents find application in varied fields like biopolymer aerogels, medicine, carbohydrate chemistry, biomass processing, and separation processes etc. Hence green solvents is a promising technology keeping in mind the strict environmental regulations imposed in various countries in the recent past over the use of hazardous chemicals.

5. ACKNOWLEDGEMENTS

This work was a collaborative review article of two Junior Research Fellows previously working together for a project of Department of Science, India, called DST-PURSE project.

REFERENCES

[1] Andrea, Tamer., "Greener Solvents", *American Chemical Society, Green Chemistry*, November 2013, pp. 1-74.

[2] Byrne, Fergal P., Saimeng Jin., Paggiola, Giulia., Petchey, Tabitha H. M., Clark James H., Farmer, Thomas J., Hunt, Andrew J., McElroy, C. Robert and Sherwood, James, "Tools and techniques for solvent extraction : green solvents selection guide", *Sustainable Chemical Processes*, *4*, May 2016, pp. 7.

[3] Subrahmanyam, Raman., Gurikov, Pavel., Meissner, Imke., Smirnova, Irina., "Preparation of BioPolymer Aerogels using Green Solvents", *Journal of Visualized Experiments*, *113*, April 2016, pp. 1-5.

[4] Farrán, Angeles., Cai, Chao., Sandoval, Manuel., Xu, Yongmei., Liu, Jian., Hernáiz, María J. and Linhardt, Robert J., "Green solvents in Carbohydrate Chemistry: From Raw materials to Fine Chemicals", *Chemical Reviews, 115*, 2015, pp. 6811-6853.

[5] Soh, Lindsay. and Eckelman, Matthew. J., "Green Solvents in Biomass processing", *American Chemical Society, Sustainable Chemistry and Engineering, 4*, 2016, pp. 5821-5837.

[6] Henderson, Richard K., Jimenez-Gonzalez, Concepcion., Constable, David J. C., Alston, Sarah R., Inglis, Graham G. A., Fisher, Gail., Sherwood, James., Binksa, Steve P. and Curzonsf, Alan D., "Expanding GSK's solvent selection guide–embedding sustainability into solvent selection starting at medicinal chemistry.", *Royal Society of Chemistry, 13*, March 2011, pp. 854-862.

[7] Afonso, Carlos A.M. Pedro, Joao. and Crespo, G., Green Separation Processes : Fundamentals and Applications, John Wiley and Sons, 2006,pp 330-337.

[8] Capello, Cristian., Fischer Ulrich and Hungerbuhler, Kohrad, "What is green solvent? A comprehensive framework for the environmental assessment of solvents", *Royal Society of Chemistry*, March 2007, 927-934

[9] Dupont Jairton, Consorti Crestina S. and Spencer, John, "Room Temperature Molten salts: Neoteric Green solvents for chemical reactions and processes", *Journal of Brazilian Chemical Society*, 11, August 2000, pp 1-5.