How sonochemistry contributes to green chemistry?

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Ultrasonics Sonochemistry

Special Issue "Fundamentals and Applications of Sonochemistry: ESS-15"

How Sonochemistry Contributes to Green Chemistry?

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Abstract:
Based on the analyses of papers from the literature, and especially those published in *Ultrasonics Sonochemistry* journal, the contribution of sonochemistry to green chemistry area has been discussed here. Important reminders and insights on the good practices and considerations have been made to understand and demonstrate how sonochemistry can continue to efficiently contribute to green chemistry area in the further studies.

Keywords: Sonochemistry; Ultrasound; Green Chemistry; Innovation; Green Engineering.

Sonochemistry and green chemistry: an expanding research topic in the literature

The *Ultrasonic Sonochemistry* journal has recently reported some heated discussions and comments about the green chemistry aspect of ultrasound. In the letter entitled "*Misinterpretation of green chemistry"* published by Swapnil L. Fegade and Jason P. Trembly, they pointed out the misuse of the terms "green" and "sustainable" in the scientific literature.[1] They proposed to educate readers on the importance of reactant and product toxicity information used in a "green reaction". Pedro Cintas brought a response to this latter paper and some personal comments that I totally share, in his article entitled "*Ultrasound and Green Chemistry – Further comments"*.[2] Indeed, a considerable criticism and scepticism are necessary to appreciate the "greenness" of a reaction. In reality, it is essential to reason on the overall process, from raw materials to products, including the costs of eliminating or recycling wastes (work-up protocols have to be taken into account!).

In this occasion, the Editor-in-Chief associated to regional Editors of *Ultrasonics Sonochemistry* reminded that the use of the terms "green" and "sustainable" reported in a manuscript has to be supported by a justification provided in the manuscript itself and also in the cover letter to the Editor accompanying the submission.[1] Interestingly, despite the increasing number of publications in the journal from 2000 to now, the proportion of papers in link with green chemistry and eco-friendly processes based on ultrasound has continuously increased from 4.8% in 2000 to 33.3% in 2016 (Figure 1). It is in link with the evolution of researches, institutional funding and projects,[3–5] involving more and more sustainable processes since the proposition of the twelve principles by Paul T. Anastas and John C. Warner in 1998.[6] Soon after the publication of these twelve principles, Jean-Louis Luche quickly made the connection between green chemistry and sonochemistry. In his paper of 1999 co-written with Pedro Cintas ("*Green chemistry: the sonochemical approach*"),[7] he highlighted the main advantages of sonochemistry: (a) the possibility to change the course of a reaction to reach new selectivities *via* sonochemical switching; (b) the improvement of rates (energy savings), yields, and selectivities (reduced wastes); (c) the possibility to use non-classical reagents or reagents obtained under unusual conditions, even aqueous media (safety, energy savings). More recently, Timothy J. Mason discussed the "green link" between chemistry, physics and engineering provided by sonochemistry, through industrial scale examples from the fields of environmental protection and process technology.[8]

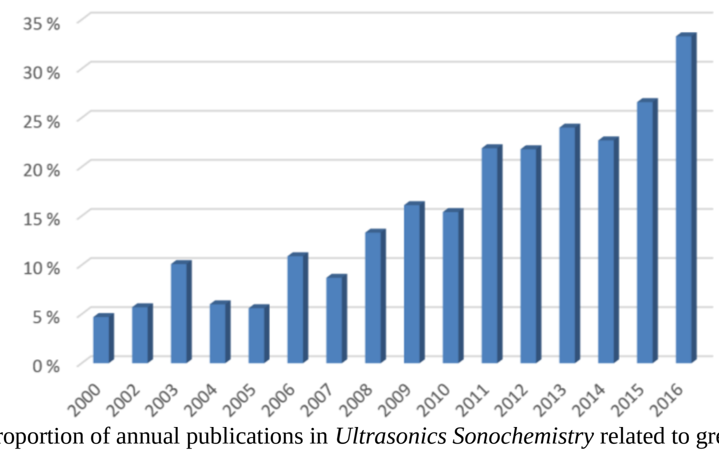

Figure 1: Evolution of the proportion of annual publications in *Ultrasonics Sonochemistry* related to green chemistry and eco-friendly processes (title, abstract, keywords and manuscript). Data from ScienceDirect website (January, 2017).

Even if the mechanisms studies are not always reported in the literature, many applications of ultrasound represent innovative and attractive advances, as a green chemistry point of view. Indeed, green chemistry is based on five basic concepts: (i) prevention, (ii) better use of the raw material, (iii) better waste management, (iv) energy savings, and (v) use of solvent compatible with the environment.[6,9] When the experimental conditions are optimized, the use of ultrasound is, in the majority of cases, in favor of the twelve principles of green chemistry. With better yields and selectivities, reduced reaction times, new reactivity, use of water as solvent, increasing or optimization of the reactivity in the presence of catalysts, the sonochemical reactions are often greener than those performed under silent conditions.[10]

Green chemistry and sonochemistry are both multidisciplinary, and the eco-friendly processes based on ultrasound have been reported in many areas such as sonocatalysis, organic chemistry, preparation of materials, polymer chemistry, biomass conversion, extraction, electrochemistry, enzymatic catalysis, environmental remediation, etc.[11] From 2000, almost 900 papers have simultaneously included the “ultrasound/sonochemistry” and “green/eco-friendly/sustainable chemistry” concepts, in different scientific fields (Figure 2) such as chemistry and chemical engineering (around 49 % of all the papers), medicine and pharmacology (16 %), material sciences (10 %), physics (9 %), biochemistry and molecular biology (7 %), environmental science (5 %) and agricultural science (3 %).

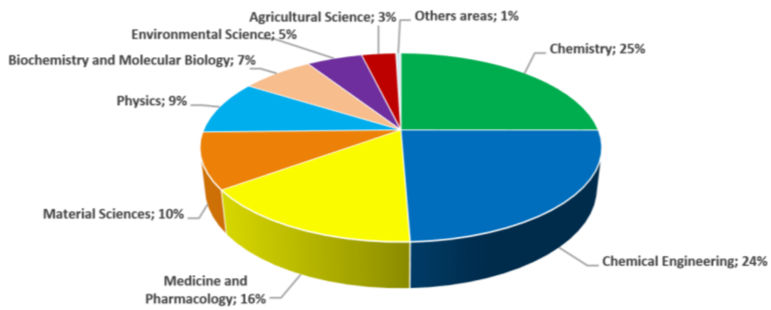

Figure 2: Proportion of manuscript involving “ultrasound/sonochemistry” and “green/eco-friendly/sustainable chemistry” concepts in relation to the scientific fields to which the study refers (from 2000). Data from Scopus website (January, 2017).

As indicated in Figure 3, the majority of these works are published in *Ultrasonics Sonochemistry* (10.8%), meaning that for the scientific community, this journal is recognized as a reference and an automatic reflex to publish this kind of work. In addition, the studies published in *Ultrasonics Sonochemistry* are more and more cited in the scientific literature (2444 citations in 2008 to almost 9000 in 2016), increasing the impact factor from (2.80 in 2008 until 4.56 now). Note that it is also important to publish in other journals of chemistry with more general audience to increase the visibility of the sonochemical community and communicate on the opportunities provided by sonochemistry in terms of green chemistry towards all the researchers.

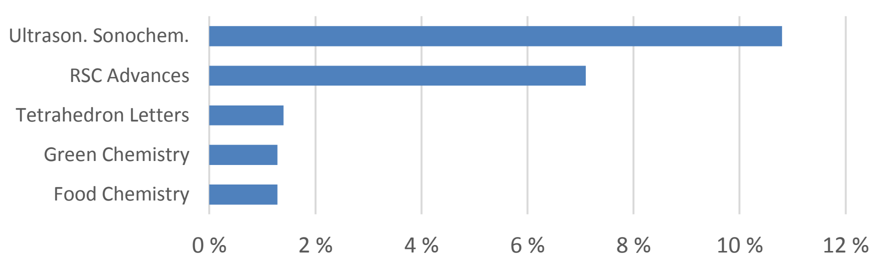

Figure 3: Proportion of manuscripts involving “ultrasound/sonochemistry” and “green/eco-friendly/sustainable chemistry” concepts in relation to the scientific international peer-reviewed journals where the study was published (from 2000). Data from Scopus website (January, 2017).

Sonochemistry in link with green chemistry is studied everywhere around the word (Figure 4), with important communities in Asia (see the Asia-Oceania Sonochemical Society, AOSS), in America (especially USA and Brazil) and in Europe (see the European Society of Sonochemistry, ESS).[12] Obviously, this distribution by country should be analyzed more finely, since it does not take into account the size and the number of research centers in each country. But in resume, the Figure 4 shows that the activity is strong in this area all around the globe, and international collaborations are important with a great potential.

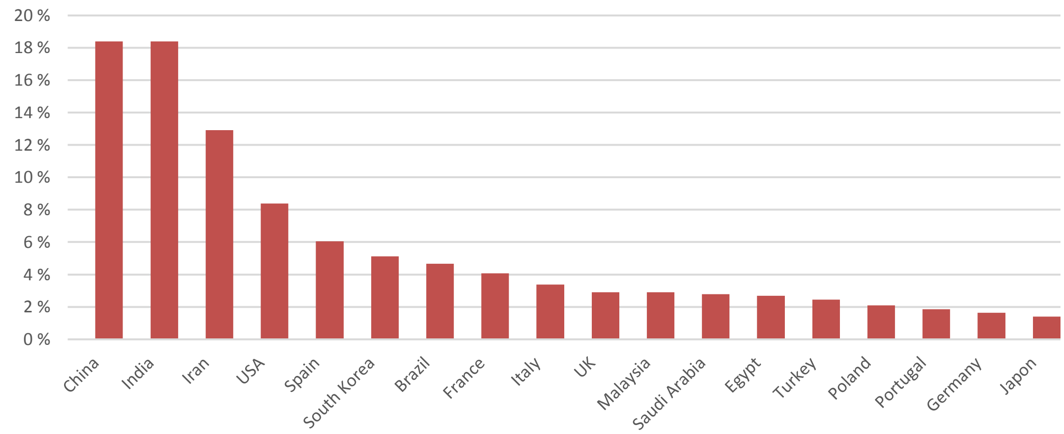

Figure 4: Proportion of manuscript involving "ultrasound/sonochemistry" and "green/eco-friendly/sustainable chemistry" concepts in relation to the country where the study was conducted (from 2000). Data from Scopus website (January, 2017).

The good use of ultrasound in green chemistry area:

Even if the number of publications in the area is impressively increasing, some precautions should be taken. Not all these studies clearly demonstrated the advantages, in terms of green chemistry, to use power ultrasound. Here, I would like to convince all the chemists that sonochemistry and the use of ultrasound are not just a *simple mixing tool*. It is more than a cleaning bath that is placed somewhere at the bottom of the laboratory. Giancarlo Cravotto and Pedro Cintas used the term "*distinctive chemistry*" to speak about sonochemistry, making the connection between *cavitational chemistry* and *mechanochemistry,* or in other words between *chemical (formation of radical species) and physical effects (mechanical force) of sonochemistry*.[13] Hydrodynamic cavitation also presents some eco-friendly advantages, often being more energy-efficient, easier to generate and less sensitive to the geometry of the reactors.[14] It was efficiently used, for examples, in the preparation of biodiesel by the transesterification of soybean oil,[15] in food processing for processing large volumes of liquid media,[16] or in environmental remediation for blue-green algae removal[17] and degradation of pesticides.[18]

One of the current limitation of sonochemistry is the problem of reproducibility. The rigorous characterization of sonochemical parameters is crucial to understand the associated chemistry and facilitate the comparison between each study reported in the literature. It is important to remind here that all the sonochemical parameters and experimental conditions have to be rigorously reported in the experimental part of publications (frequency, electric and acoustic powers, ultrasonic intensity, radical production, shape and geometry of the used reactors, etc).[11] In addition, a systematic comparison with corresponding silent conditions (blank reaction) is required to clearly highlight the ultrasonic effects. It seems logical, but unfortunately, it is not the case every time in published works. A discussion on the green chemistry aspect of the process developed under ultrasound is also required, associated with the calculations, if possible, of a maximum of green metrics (E-factor, process mass intensity, energy consumption, etc).[19–21] The overall process is to take into account from the used reagents, the consumed energy, the efficiency of the reaction and the produced waste.

In 2003, Paul T. Anastas and Julie B. Zimmerman developed the twelve principles of green engineering to outline what would make a greener chemical process or product for scale-up at an industrial level.[22] All process steps (such as steps of purification and separation) and the afterlife of products (life cycle analysis, for example) are considered through these twelve complementary principles.[23] Thus, it is also important to link the developed sonochemical processes to the green engineering concept, since the use of ultrasound at an industrial level in chemistry is clearly dependent on (i) the scale-up, (ii) the energy consumption and (iii) the design of equipment. Two strategies should be led in parallel: (1) the need of innovation on sonoreactors and transducers (design, optimization, etc); (2) the need for sonochemists to systematically report an estimation of the dissipated ultrasonic power and energy costs, even if these data could also depend on reactor type and configuration. As an industrial point of view, the overall energy consumption of a sonochemical process is essential. For example, the Sonoxide process for the treatment of water in cooling towers will be developed through the combination of ultrasound and electromagnetic radiation.[24] In addition to the advantages of the process in terms of algae elimination and limitation of the limescale formation, this system presents environmental strengths such as its low energy consumption, the elimination of the need for water softening or biocidal chemicals, and a large reduction in the requirement for make-up water in the cooling system.[25] Cravotto *et al.* estimated the overall energy consumption for a new pilot flow reactor for ultrasound irradiation, and showed how calculated the total energy consumption in the case of biodiesel synthesis, taking into account the sum of (i) the energy to heat the oil, (ii) the energy to heat methanol and (iii) the energy to sonicate the mixture for a defined time.[26]

The choice of the reactors and the irradiation mode can greatly influence the reactivity under ultrasound. For example, the more systematic use of tubular sonoreactors, with diameter and length of the tube optimized for ensuring the proper transfer of energy, should be encouraged since it represents an excellent approach to consider an industrial transposition by continuous flow irradiation. In addition, the walls of the tube become the ultrasound emission surface, that is why the cavitation is mainly focused in the center of the tube, limiting the risk of corrosion and facilitating equipment maintenance.[27–29] The development of continuous and circulating processes with an ultrasonic chamber is also encouraged. In this latter case, the irradiated volume and the irradiation time are two important parameters to consider.[30] Several applications for extraction of natural products were developed through continuous flow, showing advantages in terms of reduced time and improvement of the quality of extracted compounds.[31] For example, Chemat *et al.* reported the extraction of lipids from fresh microalgae cells in the absence of solvent through a sustainable and scaling-up approach.[32] The process allowed the reduction of extraction time and volume of solvent, and the possibility to work on 10, 20 and even 200 kg equivalent dry microalgae per hour. In addition, the quality of fatty acids is preserved through the sonochemical process.

Microfluidics could also represent an innovative solution in term of green chemistry, with the use of small quantities of reagents and solvents, and hence less waste, a precise control of reaction conditions, integration of functionality for process intensification, safer and often faster protocols, reliable scale-up, and possibility of performing multiphase reactions.[33] For example, Tandiono *et al.* reported the use of bubbles confined within a narrow channel of polydimethylsiloxane-based microfluidic devices and studied the formation of $HO^{\bullet}$ radical species and sonoluminescence.[34] In this case, the chemical reactions are closely confined to gas–liquid interfaces that allow for spatial control of sonochemical reactions in lab-on-a-chip devices, leading to better yield.

Vocabulary analysis as example: the words used show the craze

The last chapter of the recent book entitled "*Sonochemistry – New opportunities for green chemistry"* (essentially dedicated to students and new users of ultrasound)[11] reports the interviews of several sonochemists from around the world, asking them "*How sonochemistry contributes to green chemistry?*". The goal was to invite them to share their personal opinion on this subject in order to better understand the enthusiasm generated for green applications of ultrasound. The vocabulary analysis of this representative sample of sonochemists working in the field (not an exhaustive list of course!) allowed to classify the different terms used in several categories: (a) words related to sonochemistry (*e.g*. "*frequency*", "*cavitation*", words about the different "*sonochemical effects*", etc); (b) words related to green chemistry (*e.g.* "*12 principles*", "*catalysis*", use of "*biomass*", "*safer processes*", "*energy*" consideration, "*environmental issues*", "*water*", etc); (c) words related to the scale-up and industrial development of sonochemistry (*e.g.* "*processes*", "*scale-up*", "*energy*", etc) and (d) words related to new uses and applications developed under ultrasound in terms of green chemistry in "*organic chemistry*", "*extraction*", "*food processing*", "*materials*", "*catalysis*", "*biomass*" and "*fuels*", "*solvents*", "*electrochemistry*", "*waste treatment*", etc. This word analysis shows that sonochemists are multidisciplinary with different various applications associated to new and innovative results for green chemistry. A word is common to all the interviews: "*mechanisms*". The study of mechanisms in terms of sonochemical theory, development of sonochemical process but also in terms of reactivity for the different applications is crucial to better understand, when it is possible, how the things work. Once again, it is essential to show that sonochemistry is not just a *mixing* or *magic tool*! As Robert Mettin wrote in the book, sonochemistry is "*still a grey box, not totally black*", but with many mechanisms to discover.[11]

The semantics used by these researchers is also revealing with widely used words such as "*sustainable*", "*new*", "*important*", "*high*", "*safer*", "*attractive*", "*better*", "*specific*", "*future*", "*benefits*", etc, or specific sentences found in the interviews such as: "*green reaction pathways*", "*huge overall environmental and economic impact*", "*sonochemistry among the elite of green chemical methods*", "*original procedures*", "*great potential*", "*emerging applications*", "*tremendous opportunity*", "*innovative*", "*superior features*", "*great promise*", etc. In resume, combining green chemistry and sonochemistry is a very attractive research field and the associated scientific community is extremely enthusiastic. This is at the origin of the increase in the contribution of sonochemistry in the green chemistry area (publications, patents, conferences, applications, etc).

Conclusions and outlook:

As described in the bibliometric study or the vocabulary analysis reported in this paper, sonochemistry contributes more and more in green chemistry area. One explication is the similarity between the principles of green chemistry/engineering and the benefits brought by ultrasound in chemistry (change of reactivity, improvement of yields and selectivity, reduction of reaction time, energy consumption and waste production, use of water as solvent instead of organic solvents, activation of catalysts, etc). These advantages in terms of environment and efficiency lead more and more chemists to develop new applications based on ultrasound, and more and more sonochemists to apply sonochemistry in different research fields. Here are reported the recent trends involving power ultrasound and corresponding opportunities for green chemistry:

(1) **Sonocatalysis and organic sonochemistry:** Many reviews have covered the entire scale of applications of ultrasound in this area for the synthesis of fused heterocycles, oxidation reactions, hydrogenations, heterogeneous catalytic processes, etc.[35–37] In organic and/or catalytic reactions, the effects of ultrasound on the reactivity and performance, often under mild conditions, lead to serious advantages in term of green chemistry. Here, we can specifically highlight the reactions performed in water or biphasic aqueous systems under ultrasound that represent a great potential for further development. Catalytic procedures in water assisted by ultrasound and/or hydrodynamic cavitation are environmentally friendly with milder conditions, shorter reaction times and higher yields. In addition, cavitation phenomenon generates mechanical and chemical effects leading to the cleaning of catalyst surface and the formation of free reactive radicals by sonolysis of water.[38,39] The research on multiphasic systems and the identification of corresponding green impacts are encouraged. For example, Aljbour *et al.* reported the use of a capillary microreactor to carry out a multiphase reaction for the benzyl chloride hydrolysis.[40] Under ultrasound (28 kHz), higher conversions were obtained compared to silent conditions, through the better internal circulation within the multiphase slugs.

(2) **Sonochemical preparation of materials:** The radical and mechanical effects of ultrasound (sonochemistry, related to cavitational chemistry) have been widely investigated for the preparation of catalysts or specific materials: modification of solids (delamination and exfoliation of brittle and layered solids, aggregation of metal or ceramic powders, cleaning/depassivation of the surface, etc), synthesis of nanostructured solids (reduction of nucleation periods and better control of crystal size, more nanostructured particles, better distribution of size, better colloidal properties, etc.) and polymers/ biopolymers.[41,42] From the green chemistry point of view, the use of ultrasound is interesting not only to reduce the time of preparation, amount of solvents and change the size, the distribution and structure of the particles, but also to provide to these catalytic materials new properties and reactivities, often showing better results than classically prepared catalysts.[43,44]

(3) **Polymer chemistry:** Sonochemistry can be involved in the polymer formation,[45] the depolymerization or selective cleavage of polymers, and the formation of polymer composites.[46] Interestingly, recent examples proposed the polymerization under heterogeneous conditions to form insoluble polymer products, by a gelation.[45,47] In this case, ultrasound drives sol–gel transition by favoring intermolecular

hydrogen bonding between aggregates, which immobilized the solvent. For the depolymerization processes, Gogate and Prajapat recently described the different factors affecting the polymer degradation: ultrasound intensity, solvent vapor pressure and viscosity, temperature, solution concentration, initial polymer molecular weight and the chemical structure of the polymer, selection of operating and geometric parameters of sonochemical reactors.[48]

(4) **Lignocellulosic biomass conversion:** Ultrasound provides a severe physico-chemical environment for the recalcitrant, multicomponent and heterogeneous lignocellulosic biomass, that is difficult to obtain with other engineering methods. The introduction of ultrasonic energy plays a positive influence essentially on the biofuels production or for the pretreatment and extraction of biomass.[49, 50] The major advantages to use ultrasound are the reduction of processing time for similar results, the operation at lower temperature and the need of lower amounts of reactants (*i.e.,* enzyme).[51] The possible production of high-value chemicals from this non-edible biomass is also a growing subject of research.[52]

(5) **Sonochemical extraction:** The sonochemical extraction, called UAE (Ultrasound-Assisted Extraction), is becoming a real clean and green extraction technology.[53] Indeed, the use of ultrasound in this area allows in many cases to (1) enhance extraction yield; (2) enhance aqueous extraction processes without organic solvents; (3) provide the opportunity to use alternative and eco-compatible solvents by improving their extraction performance and (4) enhance extraction of heat-sensitive components under conditions that would otherwise have low or unacceptable yield.[54] The use of ultrasound is attractive extraction technology for various molecules and biomaterials,[55] including polysaccharides,[56] essential oils,[57] proteins and peptides,[58] fine chemicals (dyes and pigments),[59] bioactive molecules of commercial importance[60] and metals.[61,62]

(6) **Fundamental studies:** The fundamental studies on sonochemistry, cavitation and effects of ultrasound are essential to better understand and know the systems (hot-spot theory,[63,64], plasma theory,[65,66] electrical theories,[67,68] supercritical water theory [69] and other complementary fundamental considerations[70–72]). This exciting research of the mysteries around sonochemistry is also important for the sonochemists' community for the future discussions, debates, proofs of concept and the scientific emulation of the field.

(7) **Combinations of innovative technologies**: The combination of ultrasound with other innovative technologies starts to bring some interesting synergetic effects. The recent examples of ultrasound/ionic liquids,[73] ultrasound/microwave,[74] ultrasound/electrochemistry[75] and ultrasound/enzymes[76] couplings showed promising improvements and represent a great potential in term of innovation. In all these cases, it is crucial to separately compare silent, coupled and non-coupled conditions in order to highlight the synergetic effects of the combination. The synergies brought by these combinations open the door to many new applications in green chemistry where the contribution of ultrasound becomes essential, although many studies on the larger scale development of these combined technologies will be necessary.

(8) **Scale-up and industrial applications:** The progress of sonochemistry in green chemistry is dependent upon the possibility of scaling up the excellent laboratory results for industrial use.[2] The development of sonochemical application at larger scale is now a (the!) crucial challenge for sonochemists to reproduce the exciting results obtained at lab into continuous or large-scale processes.[8] A series of commercially available ultrasonic reactors can be directly adapted for scale-up,[77,78] giant probe system using a large bar of steel as horn found different applications in processing and catalysis,[79] and tubular reactors,[8] microfluidic systems [80] and hydrodynamic cavitation based processes [33] have already provided interesting results in continuous flow. It is essential to develop green processes based on sonochemistry at a larger scale to benefit from this contribution of ultrasound and open the doors to industrial applications.

Acknowledgements

The author gratefully acknowledges C. Argirusis, M. Ashokkumar, F. Chemat, P. Cintas, J. C. Colmenares, G. Cravotto, M. Draye, A. Gedanken, P. R. Gogate, H. Harada, G. A. Heropoulos, J.-Y. Hihn, N. H. Ince, T. J. Mason, R. Mettin, U. Neis, S. I. Nikitenko, S. Manickam, T. Van Gerven for their contribution in this debate.[11]

References

[1] S. L. Fegade, J. P. Trembly, Misinterpretation of green chemistry, Ultrason. Sonochem. (2015) online, DOI:10.1016/j.ultsonch.2015.04.007.
[2] P. Cintas, Ultrasound and green chemistry – Further comments, Ultrason. Sonochem. 28 (2016) 257–258.
[3] I. T. Horváth, P. T. Anastas, *Chem. Rev.* **2007**, *107*, 2169–2173.
[4] P. J. Dunn, *Chem. Soc. Rev.* **2012**, *41*, 1452–1461.
[5] K. J. M. Matus, X. Xiao, J. B. Zimmerman, *J. Clean. Prod.* **2012**, *32*, 193–203.
[6] P. T. Anastas, J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, Oxford, 1998, 11–54.
[7] P. Cintas, J.-L. Luche, Green chemistry. The sonochemical approach, Green Chem. 1 (1999) 115–125.
[8] T. J. Mason, Sonochemistry and the environment – Providing a "green" link between chemistry, physics and engineering, Ultrason. Sonochem. 14 (2007) 476–483.
[9] P. T. Anastas, N. Eghbali, Green Chemistry: Principles and Practice, Chem. Soc. Rev. 39 (2010) 301–312.
[10] M. Sillanää, T.-D. Pham, R. A. Shrestha, Ultrasound technology in Green Chemistry, SpringerBriefs in Green Chemistry for Sustainability, 2011.
[11] G. Chatel, Sonochemistry – New opportunities for green chemistry, Word Scientific Publishing Europe Ltd: London, UK, 2017, 188 p.
[12] Website of the European Society of Sonochemistry: http://www.europeansocietyofsonochemistry.eu/
[13] G. Cravotto, P. Cintas, Harnessing mechanochemical effects with ultrasound-induced reactions, Chem. Sci. 3 (2012) 95–307.
[14] V.S. Moholkar, P. Senthil Kumar, A.B. Pandit, Hydrodynamic cavitation for sonochemical effects, Ultrason. Sonochem. 6 (1999) 53–65.
[15] J. Ji, J. Wang, Y. Li, Y. Yu, Z. Xu, Preparation of biodiesel with the help of ultrasonic and hydrodynamic cavitation, Ultrasonics 44 (2006) e411–e414.
[16] M. Ashokkumar, R. Rink, S. Shestakov, Hydrodynamic cavitation – an alternative to ultrasonic food processing, Electronic Journal "Technical Acoustics", 9 (2011) 1–10.
[17] R. K. Joshi, P.R. Gogate, Removal of blue-green algae using the hybrid method of hydrodynamic cavitation and ozonation, J. Hazard. Mater. 235–236 (2012) 152–158.
[18] R. K. Joshi, P.R. Gogate, Degradation of dichlorvos using hydrodynamic cavitation based treatment strategies, Ultrason. Sonochem. 19 (2012) 532–539.
[19] D. J. C. Constable, A. D. Curzons, V. L. Cunningham, Metrics to 'green' chemistry – which are the best? Green Chem. 4 (2002) 521–527.
[20] J. Andraos, Unification of reaction metrics for green chemistry: applications to reaction analysis, Org. Process Res. Dev. 9 (2005) 149–163.
[21] A. Lapkin, D. Constable, Green chemistry metrics: measuring and monitoring sustainable processes, Wiley-Blackwell, 2008,
[22] P. T. Anastas, J. B. Zimmerman, Peer Reviewed: Design Through the 12 Principles of Green Engineering, Env. Sci. Technol. 37 (2003) 94A-101A.
[23] P. T. Anastas, J. B. Zimmerman, Sustainability Science and Engineering Defining Principle, Elsevier, Amsterdam, 2006, 11–32.
[24] E. Cordemans De Meulenaer, B. Hannecart, M.-F. Lepeltier, Y. Canivet, Method and device for treating a liquid medium,World Patent WO 98/01394 (1998).
[25] T. J. Mason, Large scale sonochemical processing: aspiration and actuality, Ultrason. Sonochem. 7 (2000) 145–149.
[26] P.Cintas, S. Mantegna, E. Calcio Gaudino, G. Cravotto, A new pilot flow reactor for high-intensity ultrasound irradiation. Application to the synthesis of biodiesel, Ultrason. Sonochem. 17 (2010) 985–989.
[27] L. H. Thompson, L. K. Doraiswamy, Sonochemistry: science and engineering, Ind. Eng. Chem. Res. 28 (1999) 1215–1249.
[28] T. J. Mason, Industrial sonochemistry: potential and practicality, Ultrasonics 30 (1992) 192–196.
[29] V. S. Sutkar, P. R. Gogate, Design aspects of sonochemical reactors: Techniques for understanding cavitational activity distribution and effect of operating parameters, Chem. Eng. J. 155 (2009) 26–36.
[30] E. C. Gaudino, D. Carnaroglia, L. Boffa, G. Cravotto, E. M. Moreira, M. A.G. Nunes, V. L. Dressler, E. M. M. Flores, Efficient H_2O_2/CH_3COOH oxidative desulfurization/denitrification of liquid fuels in sonochemical flow-reactors, Ultrason. Sonochem. 21 (2014) 283–288.
[31] T. J. Mason, F. Chemat, M. Vinatoru, The extraction of natural products using ultrasound or microwaves, Cur. Org. Chem. 15 (2011) 237–247.

[32] F. Adam, M. Abert-Vian, G. Peltier, F. Chemat, ‘‘Solvent-free’’ ultrasound-assisted extraction of lipids from fresh microalgae cells: A green, clean and scalable process, Biores. Technol. 114 (2012) 457–465.
[33] D. F. Rivas, P. Cintas, H. J. G. E. Gardeniers, Merging microfluidics and sonochemistry: towards greener and more efficient micro-sono-reactors, Chem. Commun. 48 (2012) 10935–10947.
[34] Tandiono, S.-W. Ohl, D. S. W. Ow, E. Klaseboer, V. V. Wong, R. Dumke, C.-D. Ohl, Sonochemistry and sonoluminescence in microfluidics, PNAS 108 (2011) 5996–5998.
[35] T. Mason, Ultrasound in synthetic organic chemistry, Chem. Soc. Rev. 26 (1997) 443–451.
[36] J.-L. Luche, Synthetic Organic Sonochemistry, Plenum Press, New York, 1998.
[37] M. Draye, J. Estager, E. Naffrechoux, J.-M. Lévêque, Organic sonochemistry, In: Ultrasound and Microwaves: Recent Advances in Organic Chemistry (Eds.: J. P. Bazureau, M. Draye), Research Signpost, 2011, 1–34.
[38] G. Cravotto, E. Borretto, M. Oliverio, A. Procopio, A. Penoni, Organic reactions in water or biphasic aqueous systems under sonochemical conditions. A review on catalytic effects, Catal. Commun. 63 (2015) 2–9.
[39] A. Tuulmets, S. Salmar, J. Järv, Sonochemistry in wáter organic solutions, Novinka Books: 2010, 54 p.
[40] S. Aljbour, T. Tagawa, H. Yamada, Ultrasound-assisted capillary microreactor for aqueous–organic multiphase reactions, J. Indus. Eng. Chem. 15 (2009) 829–834.
[41] K. Suslick, G. J. Prince, Applications of ultrasound to materials chemistry, Annu. Rev. Mater. Sci. 29 (1999) 295–326.
[42] H. Xu, B. W. Zeiger, K. Suslick, Sonochemical synthesis of nanomaterials, Chem. Soc. Rev.42 (2013) 2555–2567.
[43] A. Gedanken, Using sonochemistry for the fabrication of nanomaterials, Ultrason. Sonochem. 11 (2004) 47–55.
[44] J. C. Colmenares Q., Ultrasound and Photochemical Procedures for Nanocatalysts Preparation: Application in Photocatalytic Biomass Valorization, J. Nanosci. Nanotechnol. 13 (2013) 4787–4798.
[45] G. Cravotto, P. Cintas, Harnessing mechanochemical effects with ultrasound-induced reactions, Chem. Sci. 3 (2012) 295–307.
[46] B. M. Teo, F. Grieser, M. Ashokkumar, Applications of ultrasound to polymer synthesis, In: Handbook on Applications of Ultrasound: Sonochemistry for Sustainability (Eds.: D. Chen, S. K. Sharma, A. Mudhoo), CRC Press, Taylor & Francis Group, Boca Raton, FL, USA, 2011, 475–500.
[47] G. Cravotto, P. Cintas, Molecular self-assembly and patterning induced by sound waves. The case of gelation, Chem. Soc. Rev. 38 (2009) 2684–2697.
[48] P. R. Gogate, A. L. Prajapat, Depolymerization using sonochemical reactors: A critical review, Ultrason. Sonochem. 27 (2015) 480–494.
[49] J. Luo, Z. Fang, R. L. Smith Jr, Ultrasound-enhanced conversion of biomass to biofuels. Prog. Energy Combust. Sci. 41 (2014) 56–93.
[50] P. Cintas, S. Mantegna, E. C. Gaudino, G. Cravotto, A new pilot flow reactor for high-intensity ultrasound irradiation. Application to the synthesis of biodiesel, Ultrason. Sonochem. 17 (2010) 985–989.
[51] P. B. Subhedar, P. R. Gogate, Intensification of enzymatic hydrolysis of lignocellulose using ultrasound for efficient bioethanol production: A review, Ind. Eng. Chem. Res. 52 (2013) 11816–11828.
[52] G. Chatel, K. De Oliveira Vigier, F. Jérôme, Sonochemistry: What potential for conversion of lignocellulosic biomass into platform chemicals? ChemSusChem 7 (2014) 2774–2787.
[53] F. Chemat, M. Abert Vian, G. Cravotto, Green Extraction of Natural Products: Concept and Principles, Int. J. Mol. Sci. 13 (2012) 8615–8627.
[54] B. K. Tiwari, Trends Ultrasound: A clean, green extraction technology, Tr. Anal. Chem. 71 (2015) 100–109.
[55] S. R. Shirsath, S. H. Sonawane, P. R. Gogate, Intensification of extraction of natural products using ultrasonic irradiations—a review of current status, Chem. Eng. Process. 53 (2012) 10–23.
[56] C. Chen, L.-J. You, A. M. Abbasi, X. Fu, R. H. Liu, ptimization for ultrasound extraction of polysaccharides from mulberry fruits with antioxidant and hyperglycemic activity in vitro, Carbohydr. Polym. 130 (2015) 122–132.
[57] A.-G. Sicaire, M. A. Vian, F. Fine, P. Carré, S. Tostain, F. Chemat, Ultrasound induced green solvent extraction of oil from oleaginous seeds, Ultrason. Sonochem. 31 (2016) 319–329.
[58] S. U. Kadam, B. K. Tiwari, C. Alvarez, C. P. O'Donnell, Ultrasound applications for the extraction, identification and delivery of food proteins and bioactive peptides, Trends Food Sci. Technol. 46 (2015) 60–67.
[59] M. Yolmeh, M. B. Habini Najafi, R. Farhoosh, Optimisation of ultrasound-assisted extraction of natural pigment from annatto seeds by response surface methodology (RSM), Food Chem. 155 (2014) 319–324.
[60] F. J. Barba, Z. Zhu, M. Koubaa, A. S. Sant'Ana, V. Orlien, Green alternative methods for the extraction of antioxidant bioactive compounds from winery wastes and by-products: A review, Trends Food Sci. Technol. 49 (2016) 96–109.
[61] B. Pesic, T. Zhou, Application of ultrasound in extractive metallurgy: sonochemical extraction of nickel, Metall. Trans. B 23 (1992) 13–22.
[62] V. C. D. Peronico, J. L. Raposo Jr., Ultrasound-assisted extraction for the determination of Cu, Mn, Ca, and Mg in alternative oilseed crops using flame atomic absorption spectrometry, Food Chem. 196 (2016) 1287–1292.

[63] M. E. Fitzgerald, V. Griffing, J. Sullivan, Chemical effects of ultrasonics – “Hot spot” chemistry, J. Chem. Phys. 25 (1956) 926–933.
[64] K. S. Suslick, D. A. Hammerton, R. E. Cline, Sonochemical hot spot, J. Am. Chem. Soc. 108 (1986) 5641–5642.
[65] F. Lepoint-Mullie, T. Lepoint, R. Avni, Nature of the “extreme conditions” in single sonoluminescing bubbles, J. Phys. Chem. 100 (1996) 12138–12141.
[66] S. I. Nikitenko, R. Pflieger, Toward a new paradigm for sonochemistry: Short review on nonequilibrium plasma observations by means of MBSL spectroscopy in aqueous solutions, Ultrason. Sonochem. (2016) online, doi:10.1016/j.ultsonch.2016.02.003.
[67] Y. I. Frenkel, Electrical phenomena connected with cavitation caused by ultrasonic oscillations in a liquid, Russ. J. Phys. Chem. 14 (1940) 305–308.
[68] M. A. Margulis, Sonoluminescence and sonochemical reactions in cavitation fields. A review, Ultrasonics 23 (1985) 157–169.
[69] I. Hua, R. H. Hoechemer, M.R. Hoffmann, Sonolytic hydrolysis of *p*-nitrophenyl acetate: the role of supercritical water, J. Phys. Chem. 99 (1995) 2335–2342.
[70] T. J. Mason, Some neglected or rejected paths in sonochemistry – A very personal view, Ultrason. Sonochem. 25 (2015) 89–93.
[71] R. Behrends, M. K. Cowman, F. Eggers, E. M. Eyring, U. Kaatze, J. Majewski, S. Petrucci, K.-H. Richmann, M. Riech, Ultrasonic relaxation and fast chemical kinetics of some carbohydrate aqueous solutions, J. Am. Chem. Soc. 119 (1997) 2182–2186.
[72] W. Lauterborn, W. Hentschel, Cavitation bubble dynamics studied by high speed photography and holography: part one, Ultrasonics 23 (1985) 260–268.
[73] G. Chatel, D. R. MacFarlane, Ionic liquids and ultrasound in combination: synergies and challenges, Chem. Soc. Rev. 7 (2014) 8132–8149.
[74] G. Cravotto, P. Cintas, The combined use of microwaves and ultrasound: improved tools in process chemistry and organic synthesis, Chem. Eur. J. 2007, 13, 1902–1909.
[75] B. Pollet, Power Ultrasound in Electrochemistry: From Versatile Laboratory Tool to Engineering Solution, Wiley-VCH, Beinheim, 2012, 364 p.
[76] B. Kwiatkowska, J. Bennnett, J. Akunna, G. M. Walker, D. H. Bremner,
Biotechnol. Adv. 2011, 29, 768–780.
[77] T. J. Mason, D. Peters, Practical Sonochemistry. Power Ultrasound: Uses and Applications, Ellis Horwood, Chichester, 2002.
[78] T. Mason and J. Lorimer, Applied Sonochemistry: Uses of Power Ultrasound in Chemistry and Processing, Wiley-VCH, Beinheim, 2002.
[79] J. P. Russell, M. Smith, *Advances in Sonochemistry* (Ed.: T. J. Mason), JAI Press, London, 1999, Vol. 5, 279–302.
[80] S. Hübner, S. Kressirer, D. Kralisch, C. Bludszuweit-Philipp, K. Lukow, I. Jänich, A. Schilling, H. Hieronymus, C. Liebner, K. Jähnisch, Ultrasound and microstructures—A promising combination?, ChemSusChem 5 (2012) 279–288.